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REVIEW PAPER

Microaeration for hydrogen sulfide removal during anaerobic treatment: a review

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Abstract High sulfide concentrations in biogas are a major problem associated with the anaerobic treatment of sulfate-rich substrates. It causes the corrosion of concrete and steel, compromises the functions of cogeneration units, produces the emissions of unpleasant odors, and is toxic to humans. Microaeration, i.e. the dosing of small amounts of air (oxygen) into an anaerobic digester, is a highly efficient, simple and economically feasible technique for hydrogen sulfide removal from biogas. Due to microaeration, sulfide is oxidized to elemental sulfur by the action of sulfide oxidizing bacteria. This process takes place directly in the digester. This paper reviews the most important aspects and recent developments of microaeration technology. It describes the basic principles (microbiology, chemistry) of microaeration and the key technological factors influencing microaeration. Other aspects such as process economy, mathematical modelling and control strategies are discussed as well. Besides its advantages, the limitations of microaeration such as partial oxidation of soluble substrate, clogging the walls and pipes with elemental sulfur or toxicity to methanogens are pointed out as well. An integrated mathematical model describing microaeration has not been developed so far and remains an important research gap.

Keywords Anaerobic digestion · Biogas · Elemental sulfur · Hydrogen sulfide removal · Microaeration · Sulfide oxidizing bacteria

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Abbreviations

ABR	Anaerobic baffled reactor
BTF	Biotrickling filter
CSTR	Continuous stirred tank reactor
DO	Dissolved oxygen
EGSB	Expanded granular sludge bed
FBR	Fluidized bed reactor
IC	Internal circuit reactor
MDU	Microaerobic desulfurization unit
ORP	Oxidation–reduction potential
PID	Proportional-integral-derivative
SCADA	Supervisory control and data acquisition
SOB	Sulfide-oxidizing bacteria
SOU	Sulfide-oxidizing unit

SRB	Sulfate-reducing bacteria
TN	Total nitrogen
UAF	Up-flow anaerobic filter
UASB	Up-flow anaerobic sludge blanket reactor
VFA	Volatile fatty acid

1 Introduction

Under anaerobic conditions, dissimilatory sulfate-reducing bacteria (SRB) use sulfate as the terminal electron acceptor for the degradation of organic compounds while producing hydrogen sulfide (H_2S). H_2S ends up in both the liquid effluent and biogas formed through the anaerobic digestion of organic material. High concentrations of hydrogen sulfide in biogas reduce its quality, since it causes corrosion of concrete and steel, compromises the functions of cogeneration units, produces emissions of unpleasant odors, is toxic to humans and generates emissions of sulfur dioxide during combustion. In addition, the presence of sulfide in the liquid phase causes corrosion of water transport systems and the accumulation of inert material in the sludge (e.g. metal sulfides). Moreover, sulfide is toxic to methanogens (already at concentrations above 50 mg L^{-1}) and may cause the inhibition of anaerobic processes (Buisman et al. 1990a; Hao et al. 1996; Hulshoff Pol et al. 1998; Khanal and Huang 2003b; Stucki et al. 1993; Zhou et al. 2007). For all of these reasons, the production of sulfide is a major problem associated with the anaerobic treatment of sulfate-rich wastewater and organic wastes.

Available methods for sulfide removal from biogas can be classified into physico-chemical and biological methods, as summarized in Table 1. Many commercial technologies are available on the market, such as SulfaTreat® (solid scavenger, iron sponge technology), SOXSIA® (sulfur oxidation and siloxane adsorption), THIOPAQ® (physical–chemical absorption with biological regeneration), DMT Sulfurex® (water scrubber), Sulfur-rite® (iron sponge technology), and Media-G2® (iron sponge technology).

Operation at high temperature and pressure, as well as the need for additional equipment and chemicals, make physico-chemical methods energetically demanding and expensive (Appels et al. 2008). In contrast, biological methods based on the biochemical oxidation of sulfide to sulfate, thiosulfate and elemental sulfur involve lower operational costs with lower or no need for chemical addition (Buisman et al. 1989; Syed et al. 2006). Biological removal of H_2S from biogas in closed anaerobic reactor (or digester) requires an electron acceptor. Therefore, a small amount of pure oxygen or air must be provided into the reactors for biological desulfurization.

Among the biological desulfurization methods, microaeration has recently gained growing attention. With microaeration, most authors refer to controlled dosing of small amount of air/oxygen into the liquid or gaseous phase of anaerobic digesters (Fig. 1). This method is reliable, simple and economically efficient. However, it has also some potential drawbacks such as partial oxidation of soluble substrate or clogging the walls and pipes with elemental sulfur which are discussed later in this manuscript. This contribution reviews the important aspects of biological removal of sulfide during anaerobic treatment. Particular attention is paid both to the basic principles of sulfide oxidation (microbiology, chemistry) and the technological factors influencing this process. The need for further developments of microaeration, such as mathematical modeling, is discussed as well. Furthermore, the challenges and advantages of biological oxidation of sulfide are described, including economic considerations.

2 Terminology

The action of dosing small quantities of air into the bioreactor is referred to by different terms in literature, such as "microaeration" (Duangmanee et al. 2007; Jenicek et al. 2008, 2010, 2013; 2014; Krayzelova et al. 2014a; Tang et al. 2004; Tartakovsky et al. 2011), "limited aeration" (Zhou et al. 2007; Zitomer and Shrout 2000), "aeration" (Bekmezci et al. 2011; Ikbal et al. 2003; Lohwacharin and Annachhatre 2010), "microoxygenation" (Díaz and Fdz-Polanco 2012; Díaz et al. 2011a, b; Fdz-Polanco et al. 2009; Ramos et al. 2012; Ramos and Fdz-Polanco 2013, 2014; Ramos et al. 2013, 2014b, c), "oxygenation" (Khanal and Huang 2003a, b; 2006; Khanal et al. 2003) or "moderate oxygenation" (van der Zee et al. 2007).

Table 1 The summary of physico-chemical and biological desulfurization methods others than microaeration

Physico-chemical methods	Reagent	Parameters	Situation	Additional comments	References
Precipitation	Iron chloride solution		Small scale anaerobic digester	For liquid sulfide	Kapdi et al. (2005)
					Petersson and Wellinger (2009)
Scrubbing	Sodium hydroxide	High pressure drop (high contact surface), long residence times	Lab-scale two-stage co-current contactor (scrubber)	For gaseous H_2S	Couvert et al. (2008)
				Large volume contactors	
Physical absorption	Water	Pressurizing of biogas	Counter-current packed column	High water consumpion	Kapdi et al. (2005)
				For simultaneous removal of H_2S and CO_2	Wellinger and Lindberg (1999)
Chemical absorption	Iron-chelated solutions	Room temperature Low gas pressure 1.2–2.2 bar	Lab-scale counter-current gas–liquid contactor	For gaseous H_2S	Horikawa et al. (2004)
	Sodium hydroxide			For gaseous H_2S	Petersson and Wellinger (2009)
				For very large gas volumes or high H_2S concentrations	
Chemical "dry" adsorption	Iron oxides, iron sponge	Temperature 25 °C Pressure less than 2 kPa	Lab-scale upward or downward flow gas–solid contactors (semi-batch)	For gaseous H_2S	Kohl and Nielsen (1997)
				limited regeneration ($1\times - 2\times$)	McKinsey Zicari (2003)
		Temperature 40 °C	Usually two reaction beds	Capacity 1000 Nm^3 gas h^{-1}	Petersson and Wellinger (2009)
		Atmospheric pressure		Limited regeneration	Wellinger and Lindberg (1999)
	Activated carbon (AC)	Temperature 50–70 °C Pressure 7–8 bar 300 mg H_2S per 1 g of AC	Usually two vessels for continuous system	For gaseous H_2S Limited regeneration Impregnation of AC needed	Bandosz (2002) Wellinger and Lindberg (1999)
Biological methods	**Electron acceptor**	**Dominant microorganisms**	**Situation**	**Additional comments**	**References**
Biochemical oxidation	Oxygen (pure O_2 or air)	SOB such as *Thiobacillus* sp., *Sulfolobus* sp.	Digester	For gaseous and liquid H_2S	Petersson and Wellinger (2009)
		SOB such as *Thiobacillus* sp., *Sulfolobus* sp.	Trickling filter with packing material	For gaseous H_2S	Petersson and Wellinger (2009)
		Thiobacillus sp.	Biological filter (combination of water scrubbing and biological oxidation)	For gaseous H_2S	Wellinger and Lindberg (1999)
		Thiobacillus sp.	Lab-scale fixed-film bioreactors	For gaseous and liquid H_2S	Gadre (1989)
					Jensen and Webb (1995)
	Nitrite		Lab-scale batch bioreactor	For liquid sulfide	Mahmood et al. (2007)
	Nitrite	Chemolitotrophic enrichment culture	Lab-scale batch bioreactor	For liquid sulfide	Cardoso et al. (2006)
		Pure culture of *Thiomicrospira* sp. *CVO*	Lab-scale batch and continuous bioreactor	For liquid sulfide	Gadekar et al. (2006)

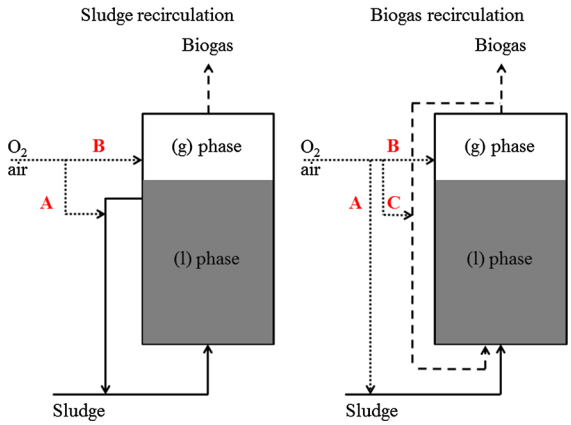

Fig. 1 The scheme of possible application of microaeration in anaerobic digesters with biogas and sludge recirculation: *A* dosage in the liquid phase, *B* dosage in the gas phase, *C* dosage in the biogas recirculation

The terms "microaeration" or "microoxygenation" reflect (in most cases) the gas used. I.e. when air is dosed into the anaerobic reactor, the process has been called "microaeration", and when pure oxygen is used, the term "microoxygenation" has been applied. However, this has not been a strict rule and not all authors follow it.

Besides, it should be noted that the terms "microaerobic" (Díaz and Fdz-Polanco 2012; Díaz et al. 2011a, b; Ramos et al. 2012, 2014b, c; Ramos and Fdz-Polanco 2013, 2014) or "microaerophilic" (Fdz-Polanco et al. 2009; Chu et al. 2005) are also applied to denote the reactor conditions (bulk liquid oxygen concentrations) as such, and at the same time referring to the act of oxygen dosage as "microoxygenation".

When referring to microaeration, the amount of oxygen is crucial. Several terms have been used when referring to the action of dosing oxygen to a culture. Authors were using the term "aeration/oxygenation" if the dose of oxygen was as high as 102–218 L O_2 L^{-1} feed (Bekmezci et al. 2011). For the amount of oxygen between 2.6 and 6.4 L O_2 L^{-1} feed (Lohwacharin and Annachhatre 2010) or 5.1 (Zhou et al. 2007), the authors used prefix "limited". Prefix "micro" was used when the amount of oxygen was 0.03–1.27 L O_2 L^{-1} feed (Díaz and Fdz-Polanco 2012; Díaz et al. 2010, 2011a, b; Fdz-Polanco et al. 2009; Jenicek et al. 2014; Krayzelova et al. 2014a; Rodriguez et al. 2012). However, van der Zee et al. (2007) used the prefix "moderate" for 0.74–0.94 L O_2 L^{-1} feed.

In this paper, the process of biological oxidation of sulfide is called "microaeration" if air was used for the oxidation of sulfide and "microoxygenation" if pure oxygen was used instead. As for the amount of air/oxygen dosed, we follow the criteria shown in Fig. 2. The term "microaerophilic" is used only to refer to microorganisms.

The concentration of dissolved oxygen (DO) is not a good control parameter for the microaeration process since the formation of elemental sulfur or sulfate proceeds at DO concentrations below 0.1 mg L^{-1}, which is the lowest detection limit of commonly available oxygen electrodes (Janssen et al. 1995). The oxidation–reduction potential (ORP) could make up a better control parameter to characterize microaerobic systems. However, a wide range of ORP values have been reported during microaeration: lower than −460 mV (Duangmanee et al. 2007); −320 to −270 mV (Nghiem et al. 2014); −265 mV (Khanal and Huang 2003b, 2006; Khanal et al. 2003); −230 to −180 mV (Khanal and Huang 2003a); 0 to −200 mV (Kobayashi et al. 2012); and higher than −150 mV (Xu et al. 2012). This large variation is probably caused by the uniqueness of each system and its operational conditions. Moreover, it is often not clear whether the results are expressed as ORP_H (with hydrogen electrode as reference) or as ORP_{Ag} (with argent chloride electrode as reference).

3 Principles of microaeration

To understand the effect of oxygen dosage, it is necessary to understand the nature of both biological and chemical oxidation of sulfide. The most important bioconversions involved in aerobic sulfide removal are (Buisman et al. 1990b; Chen and Morris 1972; Janssen et al. 1995; Kuenen 1975):

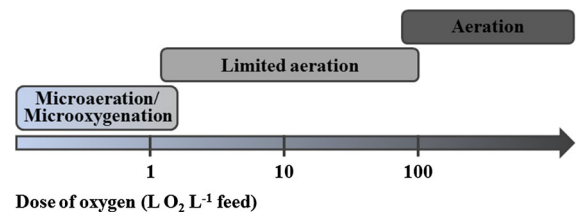

Fig. 2 The terminology for air/oxygen dosing based on the amount of oxygen dosed

$$2HS^- + O_2 \rightarrow 2S^0 + 2OH^- \quad \Delta G^\circ = -169.35\ \text{KJ mol}^{-1} \tag{1}$$

$$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2H^+ \quad \Delta G^\circ = -732.58\ \text{KJ mol}^{-1} \tag{2}$$

$$2HS^- + 2O_2 \rightarrow S_2O_3^{2-} + H_2O \quad \Delta G^\circ = -387.35\ \text{KJ mol}^{-1} \tag{3}$$

The biological removal of hydrogen sulfide (H_2S) is based on the biochemical oxidation of sulfide to elemental sulfur (S^0) or/and sulfate (SO_4^{2-}). Some authors (Díaz et al. 2011b; van den Ende and van Gemerden 1993) have also reported the production of thiosulfate ($S_2O_3^{2-}$). Sulfide serves as the electron donor while oxygen serves as the terminal electron acceptor. Under oxygen limiting (microaerobic) conditions, at oxygen concentrations below 0.1 mg L^{-1}, sulfur is the major end-product of the sulfide oxidation (Eq. 1), with a partial oxidation to thiosulfate (van den Ende and van Gemerden 1993). Sulfate is formed under sulfide limiting conditions and implies higher oxygen consumption per mole of sulfide (Eq. 2). Chemical oxidation of sulfide, resulting in the formation of mainly thiosulfate (Eq. 3) (Janssen et al. 1995) becomes important when biological activity of sulfide oxidizing bacteria is limited. This is the case especially in bioreactors highly loaded with sulfide. In such cases when oxygen is not consumed fast enough by sulfide oxidizing bacteria, the chemical oxidation of sulfide to thiosulfate becomes significant. From the economical point of view, sulfur formation is preferred, since it can potentially be recovered. Besides, the lower amount of oxygen needed for the oxidation to sulfur compared to sulfate implies lower energy consumption.

The formation of sulfur and sulfate can be controlled by the amount of oxygen supplied (Janssen et al. 1995). Theoretically, 0.5 mol O_2/mol S^{2-} is necessary for the oxidation of sulfide to elemental sulfur (Eq. 1). According to Janssen et al. (1995) a maximal sulfur production of 73 ± 10 % occurred at an O_2/S^{2-} consumption ratio in the range of 0.6–1.0 (mol L^{-1} h^{-1})/(mol L^{-1} h^{-1}) with 0.7 as the optimum. According to Alcántara et al. (2004), sulfur-producing steady states were achieved at O_2/S^{2-} ratio ranging from 0.5 to 1.5. The maximum elemental sulfur formation (85 % of the total influent sulfur) occurred at the ratio of 0.5. When the ratio was increased up to 2, sulfide was completely oxidized to sulfate. At O_2/S^{2-} as low as 0.15 mol/mol, the activity of sulfide-oxidizing severely decreased. According to the authors, it was probably related to an oxygen limitation in the culture which promoted sulfide accumulation in the reactor (Alcántara et al. 2004). At the ratios between 0.25 and 0.35 thiosulfate was detected in the culture. On the other hand, Díaz et al. (2011a) observed an increase in $S_2O_3^{2-}$ concentration when increasing oxygen rate from 9.3 to 14.1 L day^{-1}. This indicated a slight overdose of oxygen.

Munz et al. (2009) observed that in some cases, there is less than 0.5 mol O_2/mol S^{2-} necessary for successful oxidation of sulfide to elemental sulfur. Authors observed 91, 87, and 85 % of sulfide being converted to elemental sulfur at O_2/S^{2-} ratio of 0.015, 0.005, and 0.03 mol/mol, respectively. Also, they observed a strong effect of pH on the sulfide oxidation. The maximum elemental sulfur production decreased with increasing pH (from 85–91 to 53–59 % at pH 8 and 9, respectively).

According to Klok et al. (2013) biological oxidation of sulfide significantly depends on the concentration of sulfide. Sulfide oxidizing activity increased at sulfide concentrations from 0 to 0.15 mmoL L^{-1}. At concentrations from 0.3 to 1.0 mmoL L^{-1}, biological activity gradually decreased and increased again at sulfide concentrations from 1.0 to 5.0 mmoL L^{-1}. This was most likely the result of bacteria adaptation to high sulfide concentrations. Buisman et al. (1990a) observed that the contribution of chemical oxidation of sulfide was larger when sulfur loading rate increased.

4 Microorganisms involved in microaeration

Sulfide-oxidizing bacteria (SOB) are the main group involved in sulfide oxidation under microaerobic conditions. In general, SOB are photoautotrophs or chemolithotrophs. Photoautotrophs use CO_2 as the terminal electron acceptor while chemolithotrophs use oxygen (aerobic species) or nitrate and nitrite (anaerobic species). As microaeration always takes place in dark anaerobic fermenters, photoautotrophs cannot be involved in the process. Also, present paper focus on the dosing of limited amount of air or oxygen into an anaerobic reactor, therefore, chemolithotrophs using

nitrite or nitrate as an electron acceptor will not be discussed.

In terms of energy and carbon sources, SOB can be classified into four groups: (1) obligate chemolithotrophs, (2) facultative chemolithotrophs, (3) chemolithoheterotrophs, and (4) chemoorganoheterotrophs (Tang et al. 2009). Obligate chemolithotrophs need CO_2 as carbon source and an inorganic energy source. All known *Thiomicrospira* sp., many *Thiobacillus* sp., and at least one *Sulfolobus* sp. belong to this category (Kuenen and Veldkamp 1973; Matin 1978). Facultative chemolithotrophs can grow either chemolithoautotrophically with an inorganic energy source and CO_2 as carbon source, or heterotrophically with organic compounds as carbon and energy source. Some *Thiobacilli* sp., certain *Beggiatoa, Thiosphaera pantotropha*, and *Paracoccus denitrificans* are typical examples of facultative chemolithotrophic SOB (Friedrich and Mitrenga 1981; Nelson and Jannasch 1983). Chemolithoheterotrophs such as a few *Thiobacillus* sp. and some *Beggiatoa* strains generate energy from oxidation of reduced sulfur compounds. Chemoorganoheterotrophs can oxidize reduced sulfur compounds without deriving energy from them. *Thiobacterium*, *Thiothrix*, and some *Beggiatoa* sp. belong to this last group (Larkin and Strohl 1983).

As far as pH and temperature are concerned, the requirements of various SOB species are diverse. Growth at pH values in the range 1–9 and temperatures ranging from 4 to 90 °C have been reported (Tang et al. 2009). The majority of known chemolithotrophic SOB are mesophilic, *Thiobacillus* being the only genera encompassing both mesophilic and thermophilic environments. Other important thermophilic genera are *Sulfolobus* and *Thermothrix*.

The most cited species of SOB found for the oxidation of sulfide was *Thiobacillus* sp. (Alcántara et al. 2004; Annachhatre and Suktrakoolvait 2001; Maestre et al. 2010; Ravichandra et al. 2006) of *Hydrogenophilaceae* family (Luo et al. 2011), specifically *Thiobacillus denitrificans* (Krishnakumar et al. 2005; Lee and Sublette 1993; Ma et al. 2006; Ongcharit et al. 1990), *Thiobacillus nivellus* (Myung Cha et al. 1999), *Thiobacillus baregensis* (Vannini et al. 2008), *Thiobacillus thiooxidans* (Takano et al. 1997) and *Thiobacillus thioparus* (Vlasceanu et al. 1997). SOB of *Halothiobacillaceae* family were observed by Vannini et al. (2008) (*Halothiobacillus neapolitanus*) and Luo et al. (2011). Other SOB found to participate on the oxidation of sulfide were of genus *Thiomicrospira* (Gadekar et al. 2006), *Thiomonas* (Ng et al. 2004), *Thiothrix* (Cytryn et al. 2005; Maestre et al. 2010) with the specific species of *Thiothrix nivea* (Prescott et al. 2002), *Sulfurimonas* with the specific species of *Sulfurimonas denitrificans* (Maestre et al. 2010), and *Acidithiobacillus* with the specific species of *Acidithiobacillus thiooxidans* (Lee et al. 2006).

4.1 SOB found in anaerobic reactors subjected to microaeration

Most of SOB found in microaerobic reactors for biogas production belong to phylum *Proteobacteria* or, exceptionally to phylum *Actinobacteria*. *Halothiobacillus* sp., *Acidithiobacillus* sp., and *Sulfuricurvum* sp. were the most frequently cited species (Table 2). SOB were found almost exclusively in the headspace of the reactors or in the gas–liquid interphase suggesting that sulfide oxidation took place there.

Tang et al. (2004) observed a shift in the archaea population as the consequence of the introduction of microaeration. The size of *Methanosarcina* sp. population was reduced, while the size of *Methanoculleus* sp. population increased. In contrast, Ramos et al. (2014c) did not observe any particular impact on any of the archaeal populations while changing from anaerobic to microaerobic environment.

5 Technological and physical factors influencing microaeration

5.1 Oxygen dosing point and mixing method

5.1.1 Air dosing point

Number of authors compared the efficiency of microaeration when air is dosed into the headspace or into the liquid phase of anaerobic digesters (Fig. 1). When dosed into the headspace, oxygen can directly react with gaseous hydrogen sulfide and, therefore, the amount of air needed per given amount of hydrogen sulfide is minimized (Díaz et al. 2011b; Ramos et al. 2012). This is important, because dosing lower amount of air induce lower contamination of biogas by nitrogen. On the other hand, when air is overdosed in order to assure complete H_2S removal, the excess

Table 2 Sulfide oxidizing bacteria found in anaerobic reactors subjected to microaeration

Genus	Phylum	Location	Aeration gas	References
Acidithiobacillus thiooxidans	*Proteobacteria*	Bottom of biotrickling filter	Air	de Arespacochaga et al. (2014)
Arcobacter, Sulfuricurvum	*ε-Proteobacteria*	Headspace, liquid interphase	O_2	Ramos et al. (2014a)
Acidithiobacillus	*γ-Proteobacteria*			
Acinetobacter	*γ-Proteobacteria*	Headspace		
Rhodococcus	*Actinobacteria*			
Acinetobacter, Arcobacter, Sulfuricurvum	*Proteobacteria*	Microaerobic desulfurization unit	O_2	Ramos et al. (2013)
Halothiobacillus neapolitanus, Sulfurimonas denitrificans	*Proteobacteria*	Headspace	Air	Kobayashi et al. (2012)
Halothiobacillus, Thiofaba	*γ-Proteobacteria*	Headspace	O_2	Rodriguez et al. (2012)
Acidithiobacillus thiooxidans, Arcobacter mytili, Halothiobacillus neapolitanus, Thiomonas, Thiobacillus, Sulfuricurvum kujiense	*Proteobacteria*	Headspace (reactor with sludge recirculation)	O_2	Díaz et al. (2011b)
Halothiobacillus kellyi		Headspace (reactor with biogas recirculation)		
Arcobacter mytili				

oxygen will contaminate biogas (Díaz et al. 2010, 2011b).

When air is dosed into the sludge, the intense contact between oxygen and the liquid phase will facilitates non-specific oxidation of degradable organic compounds, i.e. some losses of oxygen. This will increase the necessary air dosage and, hence, the contamination of biogas by nitrogen. Potentially, certain part of organic load can be oxidized along with sulfide, but the decrease of methane yield due to this oxidation is usually negligible (Krayzelova et al. 2014a).

Dosing air into the liquid phase also causes the decrease of sulfide concentration in the liquid phase (Díaz et al. 2011b; Krayzelova et al. 2014a; van der Zee et al. 2007; Zhou et al. 2007). However, this decrease is usually only about 20–30 % (Krayzelova et al. 2014a) and cannot explain the large decrease in H_2S concentration in biogas. This implies that majority of H_2S oxidation takes place in the head space even if air is dosed into the liquid phase. Besides H_2S removal from biogas, the decrease of sulfide concentration in the liquid has the additional positive effect of decreasing sulfide toxicity towards methanogens.

5.1.2 Mixing method

The contact between oxygen and liquid phase is also intensified in digesters mixed by biogas recirculation. Analogically to dosing air into the liquid phase, this will increase the consumption of oxygen due to the reaction with organic compounds. Again, sulfide concentration in the liquid phase is decreased due to the intensified contact between oxygen and the liquid phase (Díaz et al. 2011a, b; Fdz-Polanco et al. 2009).

5.2 The location of sulfide oxidation and sulfur accumulation

For a proper design of microaeration, it is important to find out where the oxidation of sulfide occurs, i.e. whether it takes place in the biofilm covering the wall of the gas phase or in the liquid phase. Results from numerous microbial analyses (Table 2) revealed that SOB populations grow mainly on the walls of the headspace (Díaz et al. 2011b; Kobayashi et al. 2012; Ramos et al. 2014b; Rodriguez et al. 2012) or on the gas–liquid interphase Ramos et al. (2014b) suggesting that biological oxidation of sulfide takes place there.

The intensity of microaerobic processes strongly depended on the available surface area in the headspace. Ramos et al. (2014a) operated a pilot reactor with variable size of headspace to investigate where the process of biogas desulfurization predominantly took place. In this study, oxygen was injected into the liquid phase. Hydrogen sulfide was entirely removed from the biogas when the digester had 25 L headspace and little or no H_2S removal was observed when the size of headspace was minimized to almost 0 L. Moreover, the deposition of elemental sulfur in the headspace could represent a clear indication that the oxidation takes place there (Ramos et al. 2012). Kobayashi et al. (2012) observed the accumulation of microbial mats, containing elemental sulfur as the dominant component, on the inner walls of a reactor headspace including ceiling, wall, net, and catwalk. Also Ramos et al. (2014b) and Rodriguez et al. (2012) observed the elemental sulfur accumulation all over the walls of the headspace. This indicates that the headspace of a bioreactor may act as a "biofilter", where SOB can grow on all available surfaces. The sulfur mats also serve as additional support material where new microbial mats develop. Furthermore, scanning electron microscopy revealed that these sulfur mats were formed mostly by upward filaments (perpendicular to the gas–liquid interphase) creating a support with large specific surface. This may help SOB in the competition for oxygen (Kobayashi et al. 2012).

In contrast, Díaz et al. (2011b) observed only partial accumulation of elemental sulfur in the top of headspace and on the walls while Díaz et al. (2011b) and Ramos et al. (2014c) did not observe any accumulation of elemental sulfur in the headspace. These authors suggested that the elemental sulfur formed in their reactors has most probably fallen into the liquid effluent. However, this suggestion could not be proved and it remains unclear why sulfur deposition on headspace walls was not observed in these cases.

According to Krayzelova et al. (2014a), only 10 % of the produced elemental sulfur remained in the headspace of a UASB reactor, while 33 % left the reactor with the liquid effluent. In this case, the small headspace of UASB-type reactors was probably responsible for the modest depositions of sulfur in the headspace. Large range of elemental sulfur concentrations detected in the effluent samples was also observed by van der Zee et al. (2007).

Additionally, sulfur deposition in the headspace was not reported when oxygen was sparged in fine bubbles into the bioreactors (Khanal and Huang 2003a, 2006; Zitomer and Shrout 1998, 2000), thus increasing oxygen transfer to the bulk liquid phase. Under such condition, sulfide oxidation seemed to take place only in the liquid phase. Under this condition a significant consumption of oxygen for aerobic oxidation of organic matter was observed and SOB were found in the sulfur mats formed in headspace walls. This may indicate that oxidation of organic matter outcompeted the development of SOB in the liquid phase (Khanal and Huang 2006; Zitomer and Shrout 2000). The problems associated with elemental sulfur deposition on reactor walls and pipes will be discussed further.

5.3 Oxygen flow rate and biogas residence time in headspace

In general, bioreactors treating materials with low COD/S ratios, such as wastewater from brewery, sugar or paper industries (Table 3), produce large amounts of hydrogen sulfide. As a result of low COD/S ratios, these wastewater streams have been shown to require higher amounts of oxygen per volume of biogas (Zhou et al. 2007), in comparison to sewage sludge, agricultural wastes or manure. Normally, oxygen dosage (or equivalent air) between 0.3 and 3 % of produced biogas in the bioreactor is enough to achieve efficient biogas desulfurization (Table 3). However, oxygen rate of up to 12 % may be necessary if both gaseous and dissolved sulfide must be removed.

The residence time of biogas in the headspace is a key factor affecting sulfide removal efficiency, when providing oxygen/air injection into the headspace. Typically, removal efficiencies over 97 % were obtained with residence times over 5 h (Table 3). Schneider et al. (2002) found 88 % removal efficiency with a residence time of 2.5 h while it was lower than 40 % under 1.25 h. When the headspace was suppressed totally, the concentration of hydrogen sulfide in biogas produced with microaerobic treatment was similar to that found in unaerated digesters (Ramos et al. 2014a).

5.4 Removal of gaseous and dissolved sulfide and influence of pH

At pH around 7, at which anaerobic digestion typically occurs, $HS^-_{(d)}$ and $H_2S_{(d)}$ are the predominant sulfide species in the liquid phase [$pK_{a1} = 6.9$, Migdisov et al. (2002)]. The concentration of $H_2S_{(d)}$ increases when pH declines. Simultaneously, H_2S distributes between gas and liquid phases (dimensionless Henry's constant $H = c_G/c_L = 0.5$). Then, the value of pH influences sulfide distribution between liquid and gas phases and it is of particular importance when only $H_2S_{(g)}$ is removed by microaeration (i.e. by aerating the headspace). Assuming a constant amount of sulfur reduced by sulfidogenesis within the bioreactor, a lower pH results in a higher proportion of $H_2S_{(d)}$, a higher amount of $H_2S_{(g)}$ in the biogas to maintain the Henry's equilibrium and, consequently, requires a larger oxygen/air rate for efficient H_2S removal.

In those processes where sulfide removal occurs in the headspace, dissolved sulfide can be removed by increasing the contact between gas and liquid phases or by decreasing pH (to promote H_2S stripping). However, the required oxygen rate to remove both gaseous and dissolved sulfide species depends on the pH and the $Q_{biogas}/Q_{effluent}$ ratio (m^3 of biogas per m^3 of liquid effluent) in the bioreactor as shown in Fig. 3. Hence, at pH 7, the rate of oxygen needed to remove both gaseous and dissolved sulfide in digestion processes is lower than 1.3 times the rate necessary to remove exclusively gaseous sulfide with $Q_{biogas}/Q_{effluent}$ ratios larger than 15. This was confirmed by switching from sludge to biogas recirculation (Díaz et al. 2011a, b; Fdz-Polanco et al. 2009) at pH close to 7 and $Q_{biogas}/Q_{effluent} = 18$. By contrast, processes with $Q_{biogas}/Q_{effluent}$ ratios below 5, such as industrial wastewater treatment (Krayzelova et al. 2014a; Rodriguez et al. 2012), would require a much higher rate of oxygen to remove dissolved sulfide than it is needed for biogas desulfurization only, and this effect is larger when pH increases. Consequently, at high pH or low $Q_{biogas}/Q_{effluent}$, removing dissolved sulfide may affect the profitability whether by raising the costs of pure oxygen supply or by excessive biogas dilution by nitrogen if air is used. This negative effect on the costs can be partially neutralized if severe inhibition on digestion is prevented under microaerobic conditions, because a large increase in methane productivity was observed (Khanal and Huang 2006; Zitomer and Shrout 1998) in this case.

5.5 Reactor configurations

Over the years, microaeration has been tested in several different reactor configurations (Table 3). Reported configurations can be divided within two categories; a first one where oxygen/air is directly supplied into the reactor where the whole anaerobic digestion takes place, and, secondly, those configurations which comprise a chamber or separate unit where microaeration is performed.

5.5.1 Microaeration directly inside anaerobic digesters

Within the first category, microaerobic H_2S removal has been traditionally used in digesters treating agricultural wastes in Germany because of the simplicity of its application and the convenience for biogas exploitation (Schneider et al. 2002). However, the most reported and successful application, including full-scale operation, is the digestion of sludge from WWTP under microaerobic conditions. In fully-mixed sludge digesters (10 L–2100 m^3), microaeration can remove H_2S from biogas (2500–34,000 ppm_v) with efficiency higher than 97 % (Díaz et al. 2010; Fdz-Polanco et al. 2009; Jenicek et al. 2008, 2010, 2014; Ramos and Fdz-Polanco 2014). The lower efficiency found on full-scale microaerobic CSTR treating agricultural wastes, between 68 and 88 % (Kobayashi et al. 2012; Schneider et al. 2002), is probably the consequence of the low biogas residence time in the headspace in comparison to sludge digesters (see Sect. 5.3).

Recent research has broadened the usage of direct supply of oxygen to up-flow anaerobic sludge blanket (UASB) reactors, expanded granular sludge bed (EGSB) reactors, fluidized bed reactors (FBR) for the treatment of industrial wastewaters; particularly those from the brewery, sugar and paper industries that commonly present elevated sulfur load. The unaerated treatment of the wastewater of such industries resulted in a biogas with concentrations of H_2S higher than 20,000 ppm_v and up to 67,000 ppm_v, which was removed with efficiencies between 70 and 82 % under microaerobic conditions (Krayzelova et al. 2014a;

Table 3 The overview of anaerobic reactors where the use of microaeration has been reported

Reactor (volume in L)	OLR (g_{COD} L^{-1} day^{-1})	Feed (COD:S ratio)	Reactive (dosing point)	Reactive flow rate	O_2:biogas ratio (%)	O_2:$H_2S_{(g)}$ ratio (mol mol^{-1})
Fully-mixed digester (10)	2	Sludge (40)	Air (liquid)	1.6 L day^{-1}	1.7–9.2	1.3–7.4
UASB (3)	8	Synthetic brewery ww (95)	Air (liquid)	1 L day^{-1}	2.5	3.9
Fully-mixed digester (70)	2.3	Sludge (72)	O_2 (liquid)	ORP controlled (−320 to −270 mV)	n.a.	n.a.
Fully-mixed digester (7000)	1.5–2.2 g_{VS} L^{-1} day^{-1}	Sludge (–)	92–98 % O_2 (headspace or liquid)	5–34 Lm^{-3} day^{-1}	1	0.9–2
Fully-mixed digester (250)	1–1.9 g_{VS} L^{-1} day^{-1}	Sludge (–)	O_2 (headspace or sludge rec.)	1.8–19 L_{biogas} m^{-3}	0.33–0.5	1
Fully-mixed digester (250)	1.4–2.9 g_{VS} L^{-1} day^{-1}	Sludge (–)	O_2 (sludge rec.)	4.4–6.2 Lm^{-3} day^{-1}	0.44–0.62	1.9–2.8
Fully-mixed digester (338,000)	40–66 g_{manure} L^{-1} day^{-1}	Cow manure (–)	Air (headspace)	1 % of biogas rate	~1	1.8–4.4
Fully-mixed digester (265)	n.a.	Sludge (–)	O_2 (liquid)	0.16–0.46 LL_{feed}^{-1}	0.9–2.5	2.5–7
EGSB (4)	0.5–3.1	Synthetic vinasse (12)	O_2 (liquid)	0.37 L day^{-1}	4.7	1.7
Fully-mixed digester (250)	1.8–3.4	Sludge (48–93)	O_2 (headspace)	0.97 L day^{-1}	0.6–12	2–3.4
Fully-mixed digester (250)	2.4–4.7	Sludge (96–188)	O_2 (headspace or sludge rec.)	0.25 LL_{feed}^{-1}	1.4	1
Fully-mixed digester (250)	1.9–4	Sludge (143–310)	O_2 (sludge rec.)	0.25 LL $_{feed}^{-1}$	1.2–1.5	1–1.4
Fully-mixed digester (250)	1.9–4	Sludge (137–296)	Air (sludge rec.)	1.27 LL $_{feed}^{-1}$	1.2–1.5	1–1.4
Fully-mixed digester (2 × 1,500,000)	3.5	Sludge (–)	Air (sludge rec.)	n.a.	1.1	3.7
Fully-mixed digester (2,100,000)	3.5	Sludge (–)	Air (sludge rec.)	n.a.	2.9	5.5
Fully-mixed digester (250)	1.9–4.5	Sludge (152–369)	O_2 (headspace or sludge rec.)	2.6–4.8 L day^{-1}	1.3–2.4	0.7–1.3
Fully-mixed digester (11)	3.5	Sludge (–)	Air (sludge rec.)	1.1 L day^{-1}	2.1	n.a.
CSTR + SOU (92 + 1)	1.2	Sludge (690)	O_2 (liquid)	7.2 L day^{-1}	3	10–14
UASB (11)	2.8–12	Sulfite pulp mill ww. (45–60)	Air (liquid)	45–90 L day^{-1}	n.a.	n.a.
FBR (1.7)	3.5	Synthetic vinasse (144)	Air (liquid)	1.2–1.5 L day^{-1}	n.a.	440–560
UAF + SOU (4.5 + 2)	0.53–2.3 g_{TOC} L^{-1} day^{-1}	Synthetic ww. (9)	O_2 (liquid)	ORP controlled (−275 to −265 mV)	n.a.	n.a.
Fully-mixed digester (5)	1–8 g_{TS} L^{-1} day^{-1}	Synthetic waste (69)	Air	7.5 % of evolved gas	1–2.1	n.a.
Fully-mixed digester	n.a.	Agricultural waste (–)	Air (headspace)	n.a.	0.3–0.4	1.3–1.7

Gas residence time in headspace (h)	$H_2S_{(g)}$ conc. without microaeration (ppmv)	$H_2S_{(g)}$ removal efficiency (%)	$H_2S_{(d)} + HS^-_{(d)}$ removal efficiency (%)	Residual O_2 in biogas (%)	References
n.a.	13,000	≥99	68	n.a.	Jenicek et al. (2014)
n.a.	67,000	73	15	<0.1	Krayzelova et al. (2014a, b)
n.a.	6000	≥99	n.a.	1–1.8	Nghiem et al. (2014)

Table 3 continued

Gas residence time in headspace (h)	$H_2S_{(g)}$ conc. without microaeration (ppmv)	$H_2S_{(g)}$ removal efficiency (%)	$H_2S_{(d)} + HS^-_{(d)}$ removal efficiency (%)	Residual O_2 in biogas (%)	References
10	2500–4900	99	≈0	<0.1	(Ramos et al. 2014b)
8	3300–5000	99	n.a.	<0.1	Ramos and Fdz-Polanco (2014)
6	3400	90	≈0	<0.03	Ramos and Fdz-Polanco (2013)
1.4	2000–4000	68	n.a.	n.a.	Kobayashi et al. (2012)
7.6–0.2	3500	0–99	n.a.	1–2	Ramos et al. (2012)
2.4	25,000	72	40	4.1	Rodriguez et al. (2012), Lopes (2010)
7.1–8.6	3300–34,000	≥97	67–96	0.2–1	Díaz et al. (2011a)
6.3	13,000	≥98	88 (biogas recirculation)	0.6	Díaz et al. (2011b)
6.6	12,000	97.5	≈0	1–1.4	Díaz et al. (2010)
5.3	10,000	>99	≈ 0	1–1.4	Díaz et al. (2010)
n.a.	3300	99	n.a.	n.a.	Jenicek et al. (2010)
n.a.	5600	99	n.a.	n.a.	Jenicek et al. (2010)
5–8	9000–10,000	>99	≈0 (sludge recirculation)	0.3–4.8	Fdz-Polanco et al. (2009)
n.a.	34	92	n.a.	n.a.	Jenicek et al. (2008)
n.a.	1800–2600	>99	94	0.4–0.7	Duangmanee et al. (2007)
n.a.	5000–23,000	–	20–30	n.a.	Zhou et al. (2007)
n.a.	0.71 mg-S day^{-1}	>82	>52	n.a.	van der Zee et al. (2007)
n.a.	78,000	>99	99	n.a.	Khanal and Huang (2006)
n.a.	680	99	n.a.	n.a.	Ikbal et al. (2003)
2.5	2500	88	n.a.	n.a.	Schneider et al. (2002)

UASB up-flow anaerobic sludge blanket, *EGSB* expanded granular sludge blanket, *CSTR* continuous stirred tank reactor, *FBR* fluidized bed reactor, *SOU* sulfide oxidizing unit, *UAF* up-flow anaerobic filter, *n.a.* not available

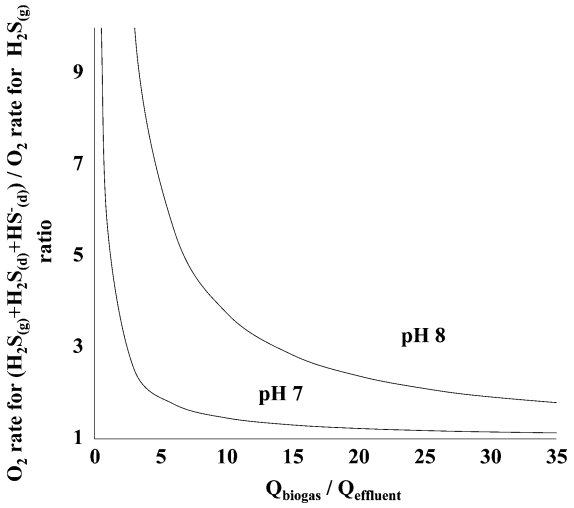

Fig. 3 Theoretical oxygen rate requirements for the microaerobic removal according to Eq. 1 assuming sulfide distribution obeys Henry's equilibrium. Oxygen rate to remove gaseous sulfide only is 1

Rodriguez et al. 2012; van der Zee et al. 2007; Zhou et al. 2007). Furthermore, microaeration can increase the performance of the organic matter removal as a result of the reduction of sulfide inhibition to methanogens (Rodriguez et al. 2012; Zhou et al. 2007). An innovative approach of microaeration is the application of water electrolysis within UASB reactors so that O_2 is produced directly in the reactor; H_2S can be removed and the production of H_2 and the electrical current significantly enhanced anaerobic digestion (Tartakovsky et al. 2011).

A novel, recently reported, configuration is the application of membranes as a tool to provide required microaeration for sulfur oxidation. Membranes were already conceived many years ago as a way to provide bubble-less aeration in fermentation processes (Cote et al. 1988). However, only scarce reports are available where membranes are used as a way to provide aeration with the objective of sulfide oxidation. In principle, membranes could be used to transfer oxygen to the headspace or to the liquid phase of an anaerobic reactor. This would be accomplished by providing the flow of oxygen or air on one side of the membrane, and exposing the other side to the biogas in the headspace or the liquid phase of the reactor. Alvarez (2014) studied the use of silicon tubing as a way to provide microaeration to the headspace of an anaerobic reactor. Mass transfer coefficients for the different gases involved were determined (CH_4, CO_2, H_2S, O_2, N_2). The formation of a biofilm over the membrane surface was observed on the biogas side, similar to that formed on the surfaces of the headspace of anaerobic reactors subjected to microaeration. On the other hand, Camiloti et al. (2013, 2014) reported the application of silicone tubes for the microaeration of the liquid phase of anaerobic reactors for wastewater treatment. In this case, a biofilm containing SOB was also formed, which was identified as responsible for a large part of the sulfur oxidation. The application of membranes with selective permeability for oxygen represents a great opportunity, since they may partially reduce the dilution of the biogas with nitrogen, when air is used as oxygen source. Moreover, membranes preventing methane permeation would be required to avoid emissions of this gas to the atmosphere.

5.5.2 Microaeration in separate compartments

In the second category, a microaerobic unit (or compartment) is added to the process, thus maintaining the core anaerobic digestion unaerated. This allows the utilization of higher O_2 rates and avoids the accumulation of elemental sulfur in the headspace of the anaerobic digester. Hence, anaerobic baffled reactors (ABR) can be designed with a final compartment where microaeration is performed to remove the H_2S produced in the initial chambers under anaerobic conditions (Bekmezci et al. 2011; Fox and Venkatasubbiah 1996). In a similar way, the sulfide-rich liquor and biogas, or the biogas alone, produced during anaerobic digestion can be treated in a sulfide oxidation unit (SOU) where microaeration is performed. When liquid and biogas were introduced into the SOU, increasing the ORP to around −265 from the natural anaerobic level of −290, H_2S was removed with efficiency higher than 99 % (Khanal and Huang 2006). Alternatively, the raw biogas produced in the digester can be treated in a SOU, inoculated with anaerobic sludge, which simulates the microaerobic conditions within the headspace of digesters. In this way S^0 can be easily removed without affecting the digester (Ramos et al. 2013).

5.6 Microaeration process control

A variable oxygen rate is necessary in most reactors, as the consequence of feed composition/rate variations

resulting in the varying production of sulfide. Besides, residual oxygen in the biogas must meet the requirements of the biogas utilization technology that will be employed afterwards. Oxygen content below 1 % is required for fuel cells and below 3–0.5 % (after carbon dioxide removal) for vehicle fuels or injection of upgraded biogas into the natural gas grid (Petersson and Wellinger 2009). Optimal process control is the key to the successful microaeration in such cases. Oxygen supply can be controlled to cope with the changes of H_2S concentration and biogas flow (Ramos and Fdz-Polanco 2014). Proportional-integral-derivative (PID) controller was used to control the oxygen flow rate according to the H_2S concentration in biogas (Ramos and Fdz-Polanco 2014). Oxygen flow rate was set according to the difference (e) between the measurement and target H_2S concentration. H_2S concentration in biogas dropped below the set-point (0.01 %) in a time range from 4.0 to 5.5 h, subsequently stabilizing at zero, while oxygen content remained around 0.05 %. The microoxygenation level was optimal since it kept the removal efficiency above 99 % with a minimum oxygen concentration in biogas. The flow of biogas was another parameter used for the control of H_2S concentration in biogas and for the control of oxygen supply in this paper. Approximately 3.5 and 5.0 L of O_2 per 1 m^3 of biogas was needed to successfully remove 0.33 and 0.5 % of H_2S from biogas, respectively. The average H_2S removal efficiency was 99 % with 0.08 % of oxygen in biogas. Ramos and Fdz-Polanco (2014) suggested that biogas production could be an efficient regulating parameter under variable organic loading rate and steady sulfur load, while under non-steady sulfur load, H_2S concentration should be used as a regulating parameter instead.

When using biogas production as a control parameter, there is a danger that overdosing by air would increase apparent biogas production which would induce the increase of air dosage. Therefore this strategy would only work in the case when the changes in biogas flow are considerably greater than the potential overdose by air. This was the case of the study by Ramos and Fdz-Polanco (2014).

ORP has also been used for the control of oxygen dosing, in a chemostat (Khanal and Huang 2003a) and a UAF system (Khanal and Huang 2003b, 2006; Khanal et al. 2003). In general, oxygen injection was automatically turned on whenever the reactor ORP was 10 mV below the target value. Pure oxygen was injected to the reactor until ORP was raised to 10 mV above the target level. During the operation of the chemostat, a target ORP value of −230 mV (50 mV above the anaerobic ORP level of −280 mV) almost completely removed the dissolved and gaseous sulfide (Khanal and Huang 2003a). In the UAF, the target ORP value of −265 mV (25 mV above the ORP level of −290 mV) was set, which provided a dissolved sulfide removal over 98.5 %,by converting it mainly to elemental sulfur with a production of small amount of thiosulfate (Khanal and Huang 2003b, 2006; Khanal et al. 2003). ORP as a tool for controlling microoxygenation was also used by Nghiem et al. (2014). In their case, an ORP probe was connected to a supervisory control and data acquisition (SCADA) system to control the digester. SCADA system was set to control valve dosing oxygen to maintain ORP level between −310 and −290 mV (the natural ORP level was −485 mV). Under such conditions, H_2S concentration decreased from over 6000 mg L^{-1} to just 30 mg L^{-1}.

No study was published that would use sulfide concentration in the liquid phase as the control parameter for the dose of air into the microaerobic reactor. This is most probably because the relation between H_2S concentration in biogas and in the liquid phase is not straightforward and large variations in H_2S concentrations in biogas often correspond to small or negligible variations in the liquid phase. This would largely depend on the oxygen dosing point (see chapter 5.1). However, even if air is dosed directly into the liquid phase, the changes in H_2S concentrations in liquid phase are relatively small compare to the changes in H_2S concentrations in biogas.

6 Mathematical modelling of sulfide oxidation

Mathematical modelling is an important tool which can provide valuable information that can help to understand the behavior of complex systems. There are many papers describing the kinetics of chemical oxidation of sulfide. The basic relation for the kinetic model can be expressed as follows (O'Brien and Birkner 1977):

$$R_{chem.ox.} = k_m \cdot (S_{H_2S})^{\alpha} \cdot (S_{O_2})^{\beta} \quad (4)$$

Table 4 The kinetic parameters of chemical oxidation of sulfide described by the Eq. 4

k (min^{-1})	α	β	c (S^{2-}) (mmoL L^{-1})	c (O_2) (mmoL L^{-1})	References
17.46	1.02	0.80	0–5.00	0.15	Klok et al. (2013)[a]
0.1165	1.00	1.00	0.04–0.10	Saturated (25 °C)	Luther et al. (2011)
0.57	0.41	0.39	0.16–9.38	0.003–0.266	Buisman et al. (1990a)
0.055	0.38	0.21	0.09–0.30	0.16–0.62	Wilmot et al. (1988)
67.6	1.15	0.69	0.05–0.20	0.60	Jolley and Forster (1985)
1.44	1.02	0.80	0.02–1.21	0.21–1.10	O'Brien and Birkner (1977)

[a] Measured in the gas phase

where $R_{chem.ox.}$ is the sulfide oxidation rate (mmoL L^{-1} min^{-1}), k_m is the rate constant (min^{-1}), S_{H_2S} is the H_2S concentration (mmoL L^{-1}), S_{O_2} is the O_2 concentration (mmoL L^{-1}), α is the reaction order with respect to the sulfide concentration (–), and β is the reaction order with respect to the oxygen concentration (–).

The summary of available kinetic parameters and the tested range of sulfide and oxygen concentrations are shown in Table 4. The parameters vary significantly across the literature. Different researchers used different analytical methods to determine sulfide and sulfide oxidation rate, and used different buffer solutions. Reported experiments were also conducted at different sulfide and oxygen concentrations ranging from 0 to 9.38 and 0 to 1.10 mmoL L^{-1}, respectively. The reaction order of oxygen very likely depends on sulfide concentration (Buisman et al. 1990a). Due to the uniqueness of each system, it is very hard to summarize the results and to make a unified conclusion.

Sharma et al. (2014) proposed the following kinetic expression for chemical oxidation of sulfide:

$$R_{chem.ox.} = k_m \cdot (S_{H_2S})^{\alpha} \cdot \frac{S_{O_2}}{K_{O_2} + S_{O_2}} \quad (5)$$

with k_m being 4.46 h^{-1}, α 0.56, and K_{O_2} 1.30 mg L^{-1}. H_2S oxidation rate was independent of the O_2 concentration at the O_2 concentration above 5 mg L^{-1}, which they explained by Monod type equation.

Nielsen et al. (2004) included the effect of pH and temperature in their model of chemical oxidation of sulfide:

$$R_{chem.ox.} = \frac{k_0 + k_1 \cdot K_1/S_{H^+}}{1 + K_1/S_{H^+}} \cdot (S_{S^{2-}})^{\alpha} \cdot (S_{O_2})^{\beta} \cdot \theta^{T-20} \quad (6)$$

where $S_{S^{2-}}$ is the concentration of total sulfide (g m^{-3}), k_0 and k_1 are the rate constants for the

Table 5 The kinetic parameters of biological oxidation of sulfide to elemental sulfur

b_{SOB} (day^{-1})	μ_{SOB} (day^{-1})	$K_{s,S^{2-}}$ (mg S^{2-} L^{-1})	K_{s,O_2} (mg O_2 L^{-1})	Y_{SOB} (mg × mg^{-1} S^{2-})	Dominant microorganisms	References
n.a.	0.67	11.00	0.0002	0.0900 (x = VSS)	SOB from activated sludge	Xu et al. (2013)
0.130	n.a.	n.a.	n.a.	0.0380 (x = COD)	SOB of *γ-Proteobacteria* and *Halothiobacillaceae* class	Munz et al. (2009)
0.034	8.64	63.68	n.a.	0.0006 (x = ATP)	*Thiomicrospira* sp.	Gadekar et al. (2006)
n.a.	n.a.	8.96	n.a.	0.0891 (x = protein)	*Thiobacilli* sp.	Alcántara et al. (2004)
n.a.	7.20	0.32	n.a.	0.0969 (x = protein)	Pure culture of *Thiobacillus thioparus*	De Zwart et al. (1997)

n.a. not available

oxidation of H_2S and HS^-, respectively [(g S m^{-3})$^{1-\alpha}$ (g O_2 m^{-3})$^{-\beta}$ h^{-1}], θ is the Arrhenius constant, T is the temperature (°C), and K_1 is the first dissociation constant for H_2S ($\approx 1.0 \times 10^{-7}$). The reaction order α and β were 0.9 and 0.2 respectively, θ was 1.06, and k_0 and k_1 fluctuated from 0.02 to 0.08 and from 0.25 to 1.00, respectively. The rate constants varied significantly and should be employed with caution. Moreover, the rate equation is valid within the pH and temperature intervals of 6–9 and 5–25 °C, respectively (Nielsen et al. 2004).

For biochemical oxidation of sulfide, Monod-type equation for substrate utilization should be used as follows (Xu et al. 2013):

$$\frac{dS_{S^{2-}}}{dt} = -\frac{\mu_{SOB}}{Y_{SOB}} \cdot \frac{S_{S^{2-}}}{K_{s,S^{2-}} + S_{S^{2-}}} \cdot \frac{S_{O_2}}{K_{s,O_2} + S_{O_2}} \cdot X_{SOB} \quad (7)$$

where μ_{SOB} is the maximum specific growth rate (h^{-1}), Y_{SOB} is the yield coefficient for SOB (g VSS g^{-1} S^{2-}), $K_{s,S^{2-}}$ and K_{s,O_2} are sulfide and oxygen affinity constants (kg m^{-3}), $S_{S^{2-}}$ and S_{O_2} are sulfide and oxygen concentrations (kg m^{-3}), and X_{SOB} is the concentration of SOB (kg m^{-3}).

Xu et al. (2013) presented an integrated model describing sulfur cycle processes of sulfate reduction, sulfide oxidation and sulfur bioreduction. They found out that the ratio of oxygen to sulfide is a key factor for controlling elemental sulfur formation.

Kinetic data for biological oxidation of sulfide found in the literature are summarized in Table 5. However, these kinetic studies were made in aerobic environments. It has been reported that the maximum specific activity for sulfide oxidation by SOB is different under aerobic and anaerobic conditions (McComas et al. 2001), i.e. 23.7 and 8.6 mg HS^- $g_{protein}^{-1}$ min^{-1}, respectively. Yu et al. (2014) studied the microbial community structures in a biological desulfurization reactor under microaerobic conditions (0.02–0.33 mg L^{-1}). The results indicated that the microbial community functional compositions and structures were dramatically altered with elevated dissolved oxygen levels. Genes involved in sulfate reduction processes significantly decreased at relatively high dissolved oxygen concentration (0.33 mg L^{-1}), while genes involved in sulfur/sulfide oxidation processes significantly increased in low dissolved oxygen concentration conditions (0.09 mg L^{-1}) and then gradually decreased with continuously elevated DO levels. Therefore, the oxidation of sulfide under microaerobic (oxygen limited) conditions must be further studied.

Botheju et al. (2009) developed a model of oxygen effect in anaerobic digestion, however, the model focused on aerobic oxidation of soluble carbon and inhibition of strict anaerobic organisms, not on sulfide oxidation. Biomass dependent first order hydrolysis kinetics was used to relate increased hydrolysis rate to oxygen induced increase in biomass growth rate (Botheju et al. 2009, 2010). An integrated model describing the effects of microaeration on biological and chemical oxidation of sulfide in anaerobic digestion has not been addressed yet. Therefore, mathematical modelling remains a research gap in microaeration.

7 Adverse effects of oxygen in anaerobic treatment

7.1 Oxygen toxicity to methanogens

Strict absence of oxygen has previously been considered as vital for anaerobic digestion, because of the toxicity of oxygen to methanogens (Zehnder 1988). Later, methanogens were shown to be tolerant to certain oxygen concentrations or protected by facultative anaerobic bacteria in both granular (Guiot et al. 1992; Kato et al. 1993a, b; Shen and Guiot 1996) and suspended sludge (Estrada-Vazquez et al. 2003). Methanogens in granular sludge appear to be more tolerant to the presence of oxygen than methanogens in flocculent sludge. Based on the multilayer structure of anaerobic granular sludge, facultative anaerobes are predominant in the periphery of the granules, while oxygen-sensitive methanogens are located in the deeper layers, protected from the exposure to air (Guiot et al. 1992; Shen and Guiot 1996). In most studies, no significant oxygen inhibition (Díaz et al. 2010, 2011b; Fdz-Polanco et al. 2009; Jenicek et al. 2011a, 2014; Krayzelova et al. 2014a; Nghiem et al. 2014; Ramos and Fdz-Polanco 2014; Tang et al. 2004; Zhou et al. 2007) of methanogens was observed during microaeration. Only two studies (Jenicek et al. 2010; Zitomer and Shrout 2000) reported slightly lower specific methanogenic activity in microaerobic reactor compared to anaerobic reactor.

7.2 Explosion risks of methane/oxygen mixtures

In general, mixing oxygen or air with biogas is undesirable because of the increased explosion risks of methane/oxygen mixture. However, the amount of oxygen dosed in microaerobic digestion is very small and it is quickly consumed. Therefore, it is far from the flammable range, which is typically 85–95 % of air and 5–15 % of methane by volume (Appels et al. 2008; Wase and Forster 1984). The leakage of biogas in air should be considered as the higher threat compare to the mixing of a small amount of air/oxygen with biogas. During microaeration, the amount of oxygen or air in biogas should never reach these values. Most authors mentioned almost no or very limited amount of oxygen detected in biogas during microaeration (Krayzelova et al. 2014a; Ramos and Fdz-Polanco 2013, 2014). Nonetheless, the explosion risk is always present when working with biogas and should not be underestimated.

7.3 Partial oxidation of organic substrate

When oxygen is present in anaerobic treatment methanogenic substrates or methane can be partially oxidized. However, the oxygen dosing rate typically applied during microaerobic removal of sulfide (0.001–0.01 kg m^{-3} day^{-1}) and organic loading rate (ORL) of digesters expressed in COD in the same oxygen units (1–10 kg m^{-3} day^{-1}) are three orders of magnitude different. Therefore, the amount of oxidized substrate cannot be significant. Some authors observed lower methane production in microaerobic reactors compare to anaerobic reactors caused probably by an aerobic degradation of organic matter (Khanal and Huang 2003a; Kobayashi et al. 2012; Ramos and Fdz-Polanco 2013; Rodriguez et al. 2012). However, most authors report no or negligible decrease of methane production due to microaeration (Díaz et al. 2010, 2011a, b; Fdz-Polanco et al. 2009; Jenicek et al. 2010; Krayzelova et al. 2014a; Nghiem et al. 2014). In these cases the dose of oxygen was not controlled according to the sulfide content (or it was controlled very roughly by ORP). Therefore, oxygen was apparently overdosed or digesters were in unbalanced conditions which contributed to the decrease of methane production.

The partial oxidation of organic compounds in anaerobic digester can improve the efficiency of volatile suspended solids removal (VSS). The evaluation of side-effects of microaerobic sulfide removal during anaerobic digestion showed the decrease in VSS/TSS ratio of the digested sludge in all experiments with microaerobic conditions, due to its better VSS degradation (Jenicek et al. 2008).

7.4 Clogging the walls and pipes of microaerobic reactor with elemental sulfur

According to some authors, microaeration takes place solely or almost solely in reactor headspace (Díaz et al. 2011b; Kobayashi et al. 2012; Ramos et al. 2014b; Rodriguez et al. 2012). The whitish deposition of elemental sulfur on the walls and pipes can clog the system resulting in headspace overpressure and biogas leakage. de Arespacochaga et al. (2014) operated a biotrickling filter with a solid oxide fuel cell for on-site electricity and thermal energy production. Around 70 % of H_2S removal was done by partial oxidation to elemental sulfur which increased the pressure drop over the column, reduced the availability of the treatment line, and eventually led to a fuel cell shutdown. A cleaning interval of less than 14 months is necessary to minimize microaeration costs (Ramos et al. 2014b). Ramos et al. (2014b) opened their microaerobic reactors, cleaned the surface of its headspace, removed the liquid interface, and restarted microaeration. Hydrogen sulfide removal was not affected, however, it was not clear which mechanism (biological or chemical oxidation) played the main role in this set-up. The collection of elemental sulfur is a remaining challenge in microaeration technology and requires further research, especially in full-scale applications.

7.5 Dilution of biogas by nitrogen from air

By using air for microaeration, nitrogen will remain and dilute biogas. This is especially challenging when biogas with low amount of methane (around 50 %) is produced, e.g. from lignocellulose (Chandraa et al. 2012), because then, even small dilution of biogas may complicate its further use in cogeneration unit. Celis (2012) reported that when extremely high H_2S concentrations (around 12,000 ppm) must be removed, the concentration of N_2 to increased up to 20 % in biogas. It caused a decrease of methane concentration below 50 % and such concentration is

too low for most cogeneration units. However, the replacement of air by oxygen solved the nitrogen dilution of biogas without affecting digestion and desulfurization efficiency.

8 Additional advantages of microaeration

8.1 Enhancement of hydrolysis

Since hydrolysis is often considered as the bottleneck of the anaerobic digestion of solid materials (Myint et al. 2007), improving this limiting step can improve the whole process (Botheju and Bakke 2011). An adequate microaeration intensity can significantly enhance the hydrolysis of carbohydrate and protein in food waste by 21–27 and 38–64 %, respectively (Xu et al. 2014). A sufficient microaeration strategy should be employed during the early period of digestion to enhance the hydrolysis of easily biodegradable organics, promote acidogenesis, and avoid the accumulation of lactic acid (Zhu et al. 2009). Johansen and Bakke (2006) studied the effects of microaeration on hydrolysis of primary sludge and observed 50–60 % increase in the rate of the hydrolysis of carbohydrates and proteins. The extra hydrolyzed products were oxidized to carbon dioxide or incorporated into new biomass. The increase of soluble proteins due to microaeration was also observed by Diak et al. (2013) together with the increase of ammonia. Microaeration effectively solubilized COD, and improved the subsequent degradation of COD. However, the increase of carbohydrates was not observed. On the other hand, Nguyen et al. (2007) reported no enhancement of hydrolysis by microaeration, but the applied amount of air per kilogram of total solids per day was 10× lower than in the study of Johansen and Bakke (2006).

Moreover, microaerobic assays presented shorter lag-phase than the anaerobic assays in the study conducted by Díaz et al. (2011c). This resulted in faster production of methane during the first steps of the cellulose degradation. The maximum methane production in the anaerobic assay was observed on day 19 while in the microaerobic assay it was observed before day 15.

8.2 Better recovery from shock loading or serious decrease of pH

Wang et al. (2014) described that microaeration was a promising strategy to handle shock loading in anaerobic treatment of coal gasification wastewater. The recovery time was shortened from 23 to 11 days under natural condition. Ramos and Fdz-Polanco (2013) subjected microaerobic digester to a hydraulic overload. Microaeration improved the biogas quality and oxygen seemed to contribute to a stable digestion system, which increased the ability to deal with overloads. Also Jenicek et al. (2010) observed faster methanogenic bacteria recovery after the inhibition caused by overloading. Aero-tolerant methanogenic culture was added to anaerobic digester to improve the recovery time after organic overload or toxicity upset (Tale et al. 2015). In contrast to the anaerobic enrichment, the aerated enrichments were more effective, resulting in faster recovery of methane and COD removal rates.

After a shock-load of sucrose, the pH in the complete-mix methanogenic reactors recovered more quickly under microaeration conditions (Zitomer and Shrout 1998). Aeration may prevent pH decreases in other highly loaded systems since volatile acids were potentially oxidized and carbon dioxide and hydrogen were stripped out. O'Keefe et al. (2000) observed no adverse effect of aeration on the microbial activities in anaerobic digester.

8.3 Better sludge quality

Microaeration also appeared to improve the quality of the digested sludge in the way of lower foaming potential and better dewaterability (Jenicek et al. 2011a, b, 2014). The extent of foaming problems was lower in microaerobic digester compare to anaerobic digester.

8.4 Production of elemental sulfur

As mentioned previously, there is a lack of technology available to recover elemental sulfur from bioreactors where microaeration is applied. However, if this technology were to be developed, the elemental sulfur could be used in bioleaching processes (Tichý et al.

1994) or for the autotrophic sulfur-oxidizing denitrification (Krayzelova et al. 2014b; Zhou et al. 2011). The biologically produced elemental sulfur has some distinctly different properties as compared to "normal" inorganic (orthorhombic) sulfur (Kleinjan et al. 2003). The density of biologically produced sulfur is lower and the particles have hydrophilic properties whereas orthorhombic sulfur is known to be hydrophobic with higher density. Due to this, the biologically produced sulfur could be more available and suitable for microorganisms compared to the chemically produced one. More information about biologically produced elemental sulfur can be found in the papers by Janssen et al. (2009) and Kleinjan et al. (2003).

9 Economic considerations

When considering microaeration to remove sulfide, air is, at least initially, the most economical alternative; however, biogas dilution with nitrogen (1–8 %) when air is employed may result in a lower performance of biogas combustion or higher costs during biogas upgrading to remove nitrogen. In fact, a recent economic evaluation revealed that the utilization of concentrated oxygen (92–98 %) presented higher net present value (NPV5 and NPV20) than the utilization of pure oxygen or air to substitute the current addition of $FeCl_3$ to the anaerobic digesters of a full-scale WWTP producing 550 m^3 h^{-1} of biogas. This alternative presented the lowest operational costs per cubic meter of biogas treated (0.0019 EUR) compared to air, pure oxygen supply and the addition of $FeCl_3$ (0.0027 EUR, 0.0039 EUR and 0.0100 EUR, respectively) (Díaz et al. 2015).

10 Needs for further research

Microaeration as a method for biogas desulfurization has been gaining attention over the past years and it has been often used in full-scale digesters in agricultural applications [personal communications with plant operators and Schneider et al. (2002)]. However, some theoretical and practical aspects of microaeration still remain unclear and need further research. This is important both for introduction of microaeration into new fields (high rate digesters for wastewater treatment) and for optimization of microaeration in current application (agricultural digesters).

10.1 Mechanism of sulfide oxidation

There is still discussion to what extend bacteria are responsible for the oxidation of sulfide under microaerobic condition. It is clear that both biotic and abiotic processes run in parallel (Buisman et al. 1990a), but the rates of these processes in microaerobic digesters are not well quantified yet.

Moreover, the exact metabolic pathway of sulfide oxidation under microaerobic condition is not well defined. It is not clear yet, what is the role of intermediate sulfur species such as sulfite, thiosulfate, polysulfide, and polythionates. It is also not clear, to what extend can be elemental sulfur repeatedly reduced to sulfide and how this process contributes to the overall oxygen consumption and reduction of methane yield.

10.2 Control of microaeration

To maximize the efficiency of microaeration, precise control of air dosing is needed. In the current applications, microaeration often cannot cope with sudden changes of sulfide concentration in biogas induced e.g. by the start of intermittent mixing (personal communication with plant operators). It can be expected that similar problems will take place in high-rate digesters should microaeration be introduced for them too.

The spatial control of microaeration, i.e. the spatial distribution of the formation of elemental sulfur is even more pressing problem. In current applications, most of sulfur forms on the walls of reactor's headspace (Kobayashi et al. 2012; Ramos et al. 2012, 2014b; Rodriguez et al. 2012) and is expected to continually fall of into the liquid effluent (Ramos et al. 2014c). However, partial or complete clogging of biogas piping has also been reported (de Arespacochaga et al. 2014). When introduced into high-rate digesters such as UASB, IC or EGSB, formation of sulfur will partially take place in the three-phase separators of these reactors (Krayzelova et al. 2014a) which may seriously impair the function of the digester. Therefore, new methods for controlled safe sulfur formation in dedicated compartments of the

digesters should be developed. The application of biomembranes (biofilm grown on the surface of membrane modules) for air delivery is one of the promising options (Alvarez 2014). This technique would facilitate sulfur formation directly on the surface of these membranes and thus preventing the clogging of three-phase separators.

10.3 Microbiology

There are several reports describing the microbiological composition of microaerobic biofilms, but there has been very little systematic work on this topic. Most of the knowledge on SOB microbiology is derived from studies with pure SOB cultures (De Zwart et al. 1997) or environments different from microaerobic digesters such as activated sludge biotrickling filters etc. (Alcántara et al. 2004; Munz et al. 2009; Xu et al. 2013).

10.4 Mathematical modelling

Microaeration as a method for biogas desulfurization in anaerobic digestion has not been modelled yet and remains an important research gap. Although, there are a few papers describing sulfate reduction and sulfide oxidation (Xu et al. 2013), the conditions of limited amount of oxygen are specific and require its own modelling approach.

11 Conclusions

Although the interest in microaeration for hydrogen sulfide removal from biogas in full-scale has been steadily growing, only over 40 papers on this topic have been published during the last decade. Interestingly, while microaeration has been widely applied in full-scale anaerobic digesters for solid substrates (biogas plants), microaeration in anaerobic reactors for wastewater treatment such as UASB reactor has been rarely studied or applied.

The following highlights were extracted from recent literature:

- The accumulation of elemental sulfur and the growth of SOB biofilm have been most often observed in the headspace (or on the gas–liquid interphase) of anaerobic bioreactors, as the result of microaeration taking place in the gas phase. However, there are reports showing that microaeration can take place also in the liquid phase.
- The residence time of biogas in the headspace and available surface area are the key factors affecting the efficiency of hydrogen sulfide removal through sulfur oxidation in the headspace.
- Intensified contact between oxygen and anaerobic biomass may improve the removal of dissolved sulfide, decrease the amount of oxygen in biogas and increase the rate of hydrolysis. This effect can be facilitated when the reactor is mixed by biogas or when air/oxygen is dosed into the liquid phase.
- An integrated mathematical model describing microaeration has not been developed so far. Such model would greatly improve the understanding of the process and research on this topic is of high priority.

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References

Alcántara S, Velasco A, Muñoz A, Cid J, Revah S, Razo-Flores E (2004) Hydrogen sulfide oxidation by a microbial consortium in a recirculation reactor system: sulfur formation under oxygen limitation and removal of phenols. Environ Sci Technol 38(3):918–923

Alvarez A (2014) Use of a silicone bio-membrane for H_2S removal from biogas. In: Department of Water Technology and Environmental Engineering, M.Sc., University of Chemistry and Technology Prague, pp 87

Annachhatre AP, Suktrakoolvait S (2001) Biological sulfide oxidation in a fluidized bed reactor. Environ Technol 22(6):661–672

Appels L, Baeyens J, Degrève J, Dewil R (2008) Principles and potential of the anaerobic digestion of waste-activated sludge. Prog Energy Combust Sci 34(6):755–781

Bandosz TJ (2002) On the adsorption/oxidation of hydrogen sulfide on activated carbons at ambient temperatures. J Colloid Interface Sci 246(1):1–20

Bekmezci OK, Ucar D, Kaksonen AH, Sahinkaya E (2011) Sulfidogenic biotreatment of synthetic acid mine drainage and sulfide oxidation in anaerobic baffled reactor. J Hazard Mater 189(3):670–676

Botheju D, Bakke R (2011) Oxygen effects in anaerobic digestion—a review. Open Waste Manag J 4:1–19

Botheju D, Lie B, Bakke R (2009) Oxygen effects in anaerobic digestion. Model Identif Control 30(4):191–201

Botheju D, Lie B, Bakke R (2010) Oxygen effects in anaerobic digestion—II. Model Identif Control 31(2):55–65

Buisman C, Post R, Ijspeert P, Geraats G, Lettinga G (1989) Biotechnological process for sulphide removal with sulphur reclamation. Acta Biotechnol 9(3):255–267

Buisman CJN, Geraats BG, Ijspeert P, Lettinga G (1990a) Optimization of sulphur production in a biotechnological sulphide-removing reactor. Biotechnol Bioeng 35(1):50–56

Buisman C, Uspeert P, Janssen A, Lettinga G (1990b) Kinetics of chemical and biological sulphide oxidation in aqueous solutions. Water Res 24(5):667–671

Camiloti PR, Rodriguez RP, Zaiat M (2013) Silicon membrane for micro-aeration and sulfide oxidation control. In: 13th world congress on anaerobic digestion. Santiago de Compostela, Spain

Camiloti PR, Valdés F, Bartacek J, Nuñes DJ, Zaiat M (2014) Sulfate reduction and sulfide oxidation in an UASB reactor combined to a membrane aerated biofilm reactor (MABR). In: 11th Latin-American symposium of anaerobic digestion. La Habana, Cuba

Cardoso RB, Sierra-Alvarez R, Rowlette P, Flores ER, Gomez J, Field JA (2006) Sulfide oxidation under chemolithoautotrophic denitrifying conditions. Biotechnol Bioeng 95(6):1148–1157

Celis CA (2012) Improvement of anaerobic digestion by using of microaerobic conditions. In: Department of Water Technology and Environmental Engineering, Ph.D., Institute of Chemical Technology in Prague. Prague, pp 181

Chandraa R, Takeuchi H, Hasegawa T (2012) Methane production from lignocellulosic agricultural crop wastes: a review in context to second generation of biofuel production. Renew Sustain Energy Rev 16(3):1462–1476

Chen KY, Morris JC (1972) Kinetics of oxidation of aqueous sulfide by oxygen. Environ Sci Technol 6(6):529–537

Chu L-B, Zhang X-W, Li X, Yang F-L (2005) Simultaneous removal of organic substances and nitrogen using a membrane bioreactor seeded with anaerobic granular sludge under oxygen-limited conditions. Desalination 172(3):271–280

Cote P, Bersillon JL, Huyard A, Faup G (1988) Bubble-free aeration using membranes: process analysis. J Water Pollut Control Fed 60(11):1986–1992

Couvert A, Sanchez C, Laplanche A, Renner C (2008) Scrubbing intensification for sulphur and ammonia compounds removal. Chemosphere 70(8):1510–1517

Cytryn E, Minz D, Gelfand I, Neori A, Gieseke A, De Beer D, Van Rijn J (2005) Sulfide-oxidizing activity and bacterial community structure in a fluidized bed reactor from a zero-discharge mariculture system. Environ Sci Technol 39(6):1802–1810

de Arespacochaga N, Valderrama C, Mesa C, Bouchy L, Cortina JL (2014) Biogas biological desulphurisation under extremely acidic conditions for energetic valorisation in solid oxide fuel cells. Chem Eng J 255:677–685

De Zwart J, Sluis J, Kuenen JG (1997) Competition for dimethyl sulfide and hydrogen sulfide by *Methylophaga sulfidovorans* and *Thiobacillus thioparus* T5 in continuous cultures. Appl Environ Microbiol 63(8):3318–3322

Diak J, Ormeci B, Kennedy KJ (2013) Effect of micro-aeration on anaerobic digestion of primary sludge under septic tank conditions. Bioprocess Biosyst Eng 36(4):417–424

Díaz I, Donoso-Bravo A, Fdz-Polanco M (2011a) Effect of microaerobic conditions on the degradation kinetics of cellulose. Bioresour Technol 102(21):10139–10142

Díaz I, Fdz-Polanco M (2012) Robustness of the microaerobic removal of hydrogen sulfide from biogas. Water Sci Technol 65(8):1368–1374

Díaz I, Lopes AC, Perez SI, Fdz-Polanco M (2011b) Determination of the optimal rate for the microaerobic treatment of several H_2S concentrations in biogas from sludge digesters. Water Sci Technol 64(1):233–238

Díaz I, Lopes AC, Pérez SI, Fdz-Polanco M (2010) Performance evaluation of oxygen, air and nitrate for the microaerobic removal of hydrogen sulphide in biogas from sludge digestion. Bioresour Technol 101(20):7724–7730

Díaz I, Pérez SI, Ferrero EM, Fdz-Polanco M (2011c) Effect of oxygen dosing point and mixing on the microaerobic removal of hydrogen sulphide in sludge digesters. Bioresour Technol 102(4):3768–3775

Díaz I, Ramos I, Fdz-Polanco M (2015) Economic analysis of microaerobic removal of H_2S from biogas in full-scale sludge digesters. Bioresour Technol 192:280–286

Duangmanee T, Kumar S, Sung S (2007) Micro-aeration for sulfide removal in anaerobic treatment of high-solid wastewater: a pilot-scale study. Proc Water Environ Fed 2007(16):2748–2760

Estrada-Vazquez C, Macarie H, Kato MT, Rodriguez-Vazquez R, Esparza-Garcia F, Poggi-Varaldo HM (2003) The effect of the supplementation with a primary carbon source on the resistance to oxygen exposure of methanogenic sludge. Water Sci Technol 48(6):119–124

Fdz-Polanco M, Diaz I, Perez SI, Lopes AC, Fdz-Polanco F (2009) Hydrogen sulphide removal in the anaerobic digestion of sludge by micro-aerobic processes: pilot plant experience. Water Sci Technol 60(12):3045–3050

Fox P, Venkatasubbiah V (1996) Coupled anaerobic/aerobic treatment of high-sulfate wastewater with sulfate reduction and biological sulfide oxidation. Water Sci Technol 34(5–6):359–366

Friedrich CG, Mitrenga G (1981) Oxidation of thiosulfate by *Paracoccus denitrificans* and other hydrogen bacteria. FEMS Microbiol Lett 10(2):209–212

Gadekar S, Nemati M, Hill GA (2006) Batch and continuous biooxidation of sulphide by *Thiomicrospira* sp. CVO: reaction kinetics and stoichiometry. Water Res 40(12):2436–2446

Gadre RV (1989) Removal of hydrogen sulfide from biogas by chemoautotrophic fixed-film bioreactor. Biotechnol Bioeng 34(3):410–414

Guiot SR, Pauss A, Costerton JW (1992) A structured model of the anaerobic granule consortium. Water Sci Technol 25(7):1–10

Hao OJ, Chen JM, Huang L, Buglass RL (1996) Sulfate-reducing bacteria. Crit Rev Environ Sci Technol 26(2):155–187

Horikawa MS, Rossi F, Gimenes ML, Costa CMM, Silva MGCD (2004) Chemical absorption of H_2S for biogas purification. Braz J Chem Eng 21:415–422

Hulshoff Pol LW, Lens PNL, Stams AJM, Lettinga G (1998) Anaerobic treatment of sulphate-rich wastewaters. Biodegradation 9(3):213–224

Ikbal, Tang Y, Shigematsu T, Morimura S, Kida K (2003) Methanogenic activity and repression of hydrogen sulfide evolved during high rate thermophilic methane fermentation of municipal solid waste. Jpn J Water Treat Biol 39(1):17–24

Janssen AJ, Lens PN, Stams AJ, Plugge CM, Sorokin DY, Muyzer G, Dijkman H, Van Zessen E, Luimes P, Buisman CJ (2009) Application of bacteria involved in the biological sulfur cycle for paper mill effluent purification. Sci Total Environ 407(4):1333–1343

Janssen AJH, Sleyster R, Van der Kaa C, Jochemsen A, Bontsema J, Lettinga G (1995) Biological sulphide oxidation in a fed-batch reactor. Biotechnol Bioeng 47(3):327–333

Jenicek P, Celis CA, Koubova J, Pokorna D (2011a) Comparison of microbial activity in anaerobic and microaerobic digesters. Water Sci Technol 63(10):2244–2249

Jenicek P, Celis CA, Koubova J, Ruzickova I (2011b) Change of the digested sludge quality at microaerobic digestion. J Residuals Sci Technol 8:39–44

Jenicek P, Celis CA, Krayzelova L, Anferova N, Pokorna D (2014) Improving products of anaerobic sludge digestion by microaeration. Water Sci Technol 69(4):803–809

Jenicek P, Celis C, Picha A, Pokorna D (2013) Influence of raw sludge quality on the efficiency of microaerobic sulfide removal during anaerobic digestion of sewage sludge. J Residuals Sci Technol 10(1):11–16

Jenicek P, Keclik F, Maca J, Bindzar J (2008) Use of microaerobic conditions for the improvement of anaerobic digestion of solid wastes. Water Sci Technol 58:1491–1496

Jenicek P, Koubova J, Bindzar J, Zabranska J (2010) Advantages of anaerobic digestion of sludge in microaerobic conditions. Water Sci Technol 62(2):427–434

Jensen AB, Webb C (1995) Treatment of H_2S-containing gases: a review of microbiological alternatives. Enzyme Microb Technol 17(1):2–10

Johansen JE, Bakke R (2006) Enhancing hydrolysis with microaeration. Water Sci Technol. 53:43–50

Jolley RA, Forster CF (1985) The kinetics of sulphide oxidation. Environ Technol Lett 6(1–11):1–10

Kapdi SS, Vijay VK, Rajesh SK, Prasad R (2005) Biogas scrubbing, compression and storage: perspective and prospectus in Indian context. Renew Energy 30(8):1195–1202

Kato MT, Field JA, Lettinga G (1993a) High tolerance of methanogens in granular sludge to oxygen. Biotechnol Bioeng 42(11):1360–1366

Kato MT, Field JA, Lettinga G (1993b) Methanogenesis in granular sludge exposed to oxygen. FEMS Microbiol Lett 114(3):317–323

Khanal SK, Huang J-C (2003a) ORP-based oxygenation for sulfide control in anaerobic treatment of high-sulfate wastewater. Water Res 37(9):2053–2062

Khanal SK, Huang JC (2003b) Anaerobic treatment of high sulfate wastewater with oxygenation to control sulfide toxicity. J Environ Eng 129(12):1104–1111

Khanal SK, Huang JC (2006) Online oxygen control for sulfide oxidation in anaerobic treatment of high-sulfate wastewater. Water Environ Res 78(4):397–408

Khanal SK, Shang C, Huang JC (2003) Use of ORP (oxidation-reduction potential) to control oxygen dosing for online sulfide oxidation in anaerobic treatment of high sulfate wastewater. Water Sci Technol 47(12):183–189

Kleinjan W, Keizer A, Janssen AH (2003) Biologically produced sulfur. In: Steudel R (ed) Elemental sulfur and sulfur-rich compounds I, vol 230. Springer, Berlin, pp 167–188

Klok JBM, de Graaff M, van den Bosch PLF, Boelee NC, Keesman KJ, Janssen AJH (2013) A physiologically based kinetic model for bacterial sulfide oxidation. Water Res 47(2):483–492

Kobayashi T, Li YY, Kubota K, Harada H, Maeda T, Yu HQ (2012) Characterization of sulfide-oxidizing microbial mats developed inside a full-scale anaerobic digester employing biological desulfurization. Appl Microbiol Biotechnol 93(2):847–857

Kohl AL, Nielsen R (1997) Gas purification. Elsevier, Amsterdam

Krayzelova L, Bartacek J, Kolesarova N, Jenicek P (2014a) Microaeration for hydrogen sulfide removal in UASB reactor. Bioresour Technol 172:297–302

Krayzelova L, Lynn TJ, Banihani Q, Bartacek J, Jenicek P, Ergas SJ (2014b) A tire-sulfur hybrid adsorption denitrification (T-SHAD) process for decentralized wastewater treatment. Water Res 61:191–199

Krishnakumar B, Majumdar S, Manilal VB, Haridas A (2005) Treatment of sulphide containing wastewater with sulphur recovery in a novel reverse fluidized loop reactor (RFLR). Water Res 39(4):639–647

Kuenen JG (1975) Colourless sulfur bacteria and their role in the sulfur cycle. Plant Soil 43(1–3):49–76

Kuenen JG, Veldkamp H (1973) Effects of organic compounds on growth of chemostat cultures of *Thiomicrospira pelophila*, *Thiobacillus thioparus* and *Thiobacillus neapolitanus*. Archiv für Mikrobiologie 94(2):173–190

Larkin JM, Strohl WR (1983) Beggiatoa, thiothrix, and thioploca. Annu Rev Microbiol 37(1):341–367

Lee EY, Lee NY, Cho K-S, Ryu HW (2006) Removal of hydrogen sulfide by sulfate-resistant *Acidithiobacillus thiooxidans* AZ11. J Biosci Bioeng 101(4):309–314

Lee C-M, Sublette KL (1993) Microbial treatment of sulfide-laden water. Water Res 27(5):839–846

Lohwacharin J, Annachhatre AP (2010) Biological sulfide oxidation in an airlift bioreactor. Bioresour Technol 101(7):2114–2120

Lopes AC (2010) Tratamiento anaerobio y microerobio de agua residual rica en sulfato (Anaerobic and microaerobic treatment of sulfate-rich wastewater), Ph.D. thesis, University of Valladolid (Spain)

Luo JF, Lin WT, Guo Y (2011) Functional genes based analysis of sulfur-oxidizing bacteria community in sulfide removing bioreactor. Appl Microbiol Biotechnol 90(2):769–778

Luther GW 3rd, Findlay AJ, Macdonald DJ, Owings SM, Hanson TE, Beinart RA, Girguis PR (2011) Thermodynamics and kinetics of sulfide oxidation by oxygen: a look at inorganically controlled reactions and biologically mediated processes in the environment. Front Microbiol 2:62

Ma Y, Zhao J, Yang B (2006) Removal of H_2S in waste gases by an activated carbon bioreactor. Int Biodeterior Biodegrad 57(2):93–98

Maestre JP, Rovira R, Alvarez-Hornos FJ, Fortuny M, Lafuente J, Gamisans X, Gabriel D (2010) Bacterial community analysis of a gas-phase biotrickling filter for biogas mimics desulfurization through the rRNA approach. Chemosphere 80(8):872–880

Mahmood Q, Zheng P, Cai J, Wu D, Hu B, Li J (2007) Anoxic sulfide biooxidation using nitrite as electron acceptor. J Hazard Mater 147(1–2):249–256

Matin A (1978) Organic nutrition of chemolithotrophic bacteria. Annu Rev Microbiol 32:433–468

McComas C, Sublette KL, Jenneman G, Bala G (2001) Characterization of a novel biocatalyst system for sulfide oxidation. Biotechnol Prog 17(3):439–446

McKinsey Zicari S (2003) Removal of hydrogen sulfide from biogas using cow-manure compost. In Faculty of the Graduate School, M.Sc., Cornell University

Migdisov AA, Williams-Jones AE, Lakshtanov LZ, Alekhin YV (2002) Estimates of the second dissociation constant of H_2S from the surface sulfidation of crystalline sulfur. Geochim Cosmochim Acta 66(10):1713–1725

Munz G, Gori R, Mori G, Lubello C (2009) Monitoring biological sulphide oxidation processes using combined respirometric and titrimetric techniques. Chemosphere 76(5):644–650

Myint M, Nirmalakhandan N, Speece RE (2007) Anaerobic fermentation of cattle manure: modeling of hydrolysis and acidogenesis. Water Res 41(2):323–332

Myung Cha J, Suk Cha W, Lee J-H (1999) Removal of organosulphur odour compounds by *Thiobacillus novellus* SRM, sulphur-oxidizing microorganisms. Process Biochem 34(6–7):659–665

Nelson D, Jannasch H (1983) Chemoautotrophic growth of a marine Beggiatoa in sulfide-gradient cultures. Arch Microbiol 136(4):262–269

Ng YL, Yan R, Chen XG, Geng AL, Gould WD, Liang DT, Koe LC (2004) Use of activated carbon as a support medium for H_2S biofiltration and effect of bacterial immobilization on available pore surface. Appl Microbiol Biotechnol 66(3): 259–265

Nghiem LD, Manassa P, Dawson M, Fitzgerald SK (2014) Oxidation reduction potential as a parameter to regulate micro-oxygen injection into anaerobic digester for reducing hydrogen sulphide concentration in biogas. Bioresour Technol 173:443–447

Nguyen PHL, Kuruparan P, Visvanathan C (2007) Anaerobic digestion of municipal solid waste as a treatment prior to landfill. Bioresour Technol 98:380–387

Nielsen AH, Vollertsen J, Hvitved-Jacobsen T (2004) Chemical sulfide oxidation of wastewater—effects of pH and temperature. Water Sci Technol 50(4):185–192

O'Brien DJ, Birkner FB (1977) Kinetics of oxygenation of reduced sulfur species in aqueous solution. Environ Sci Technol 11(12):1114–1120

O'Keefe DM, Brigmon RL, Chynoweth DP (2000) Influence of methane enrichment by aeration of recirculated supernatant on microbial activities during anaerobic digestion. Bioresour Technol 71(3):217–224

Ongcharit C, Shah YT, Sublette KL (1990) Novel immobilized cell reactor for microbial oxidation of H_2S. Chem Eng Sci 45(8):2383–2389

Petersson A, Wellinger A (2009) Biogas upgrading technologies—developments and innovations. http://typo3.dena.de/fileadmin/biogas/Downloads/Studien/IEA-BiogasUpgradingTechnologies2009.pdf. Accessed 9 Mar 2015

Prescott LM, Harley JP, Klein DA (2002) Microbiology. McGraw-Hill, New York

Ramos I, Diaz I, Fdz-Polanco M (2012) The role of the headspace in hydrogen sulfide removal during microaerobic digestion of sludge. Water Sci Technol 66(10):2258–2264

Ramos I, Fdz-Polanco M (2013) The potential of oxygen to improve the stability of anaerobic reactors during unbalanced conditions: results from a pilot-scale digester treating sewage sludge. Bioresour Technol 140:80–85

Ramos I, Fdz-Polanco M (2014) Microaerobic control of biogas sulphide content during sewage sludge digestion by using biogas production and hydrogen sulphide concentration. Chem Eng J 250:303–311

Ramos I, Peña M, Fdz-Polanco M (2014a) Where does the removal of H_2S from biogas occur in microaerobic reactors? Bioresour Technol 166:151–157

Ramos I, Pérez R, Fdz-Polanco M (2013) Microaerobic desulphurisation unit: a new biological system for the removal of H_2S from biogas. Bioresour Technol 142:633–640

Ramos I, Pérez R, Fdz-Polanco M (2014b) The headspace of microaerobic reactors: sulphide-oxidising population and the impact of cleaning on the efficiency of biogas desulphurisation. Bioresour Technol 158:63–73

Ramos I, Pérez R, Reinoso M, Torio R, Fdz-Polanco M (2014c) Microaerobic digestion of sewage sludge on an industrial-pilot scale: the efficiency of biogas desulphurisation under different configurations and the impact of O_2 on the microbial communities. Bioresour Technol 164:338–346

Ravichandra P, Ramakrishna M, Gangagni RA, Annapurna J (2006) Sulfide oxidation in a batch fluidized bed bioreactor using immobilized cells of isolated *Thiobacillus* sp. (iict-sob-dairy-201) as biocatalyst. J Eng Sci Technol 1(1):21–30

Rodriguez E, Lopes A, Fdz-Polanco M, Stams AJ, Garcia-Encina PA (2012) Molecular analysis of the biomass of a fluidized bed reactor treating synthetic vinasse at anaerobic and micro-aerobic conditions. Appl Microbiol Biotechnol 93(5):2181–2191

Schneider RL, Quicker P, Anzer T, Prechtl S, Faulstich M (2002) Grundlegende Untersuchungen zur effektiven, kostengünstigen Entfernung von Schwefelwasserstoff aus Biogas. In: Biogasanlagen Anforderungen zur Luftreinhaltung. Ausburg

Sharma K, Derlon N, Hu S, Yuan Z (2014) Modeling the pH effect on sulfidogenesis in anaerobic sewer biofilm. Water Res 49:175–185

Shen CF, Guiot SR (1996) Long-term impact of dissolved O_2 on the activity of anaerobic granules. Biotechnol Bioeng 49(6):611–620

Stucki G, Hanselmann KW, Hurzeler RA (1993) Biological sulfuric acid transformation: reactor design and process optimization. Biotechnol Bioeng 41(3):303–315

Syed M, Soreanu G, Falletta P, Béland M (2006) Removal of hydrogen sulfide from gas streams using biological processes—a review. Can Biosyst Eng 48:2.1–2.14

Takano B, Koshida M, Fujiwara Y, Sugimori K, Takayanagi S (1997) Influence of sulfur-oxidizing bacteria on the budget

of sulfate in Yugama crater lake, Kusatsu-Shirane volcano, Japan. Biogeochemistry 38(3):227–253

Tale VP, Maki JS, Zitomer DH (2015) Bioaugmentation of overloaded anaerobic digesters restores function and archaeal community. Water Res 70:138–147

Tang K, Baskaran V, Nemati M (2009) Bacteria of the sulphur cycle: an overview of microbiology, biokinetics and their role in petroleum and mining industries. Biochem Eng J 44(1):73–94

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

Tartakovsky B, Mehta P, Bourque JS, Guiot SR (2011) Electrolysis-enhanced anaerobic digestion of wastewater. Bioresour Technol 102(10):5685–5691

Tichý R, Janssen A, Grotenhuis JTC, Lettinga G, Rulkens WH (1994) Possibilities for using biologically-produced sulphur for cultivation of Thiobacilli with respect to bioleaching processes. Bioresour Technol 48(3):221–227

van den Ende FP, van Gemerden H (1993) Sulfide oxidation under oxygen limitation by a *Thiobacillus thioparus* isolated from a marine microbial mat. FEMS Microbiol Ecol 13(1):69–77

van der Zee FP, Villaverde S, García PA, Fdz-Polanco F (2007) Sulfide removal by moderate oxygenation of anaerobic sludge environments. Bioresour Technol 98(3):518–524

Vannini C, Munz G, Mori G, Lubello C, Verni F, Petroni G (2008) Sulphide oxidation to elemental sulphur in a membrane bioreactor: performance and characterization of the selected microbial sulphur-oxidizing community. Syst Appl Microbiol 31(6–8):461–473

Vlasceanu L, Popa R, Kinkle BK (1997) Characterization of *Thiobacillus thioparus* LV43 and its distribution in a chemoautotrophically based groundwater ecosystem. Appl Environ Microbiol 63(8):3123–3127

Wang W, Zhang J, Wang S, Shen J, Pan S-L (2014) Oxygen-limited aeration for relieving the impact of phenolic compounds in anaerobic treatment of coal gasification wastewater. Int Biodeterior Biodegrad 95:110–116

Wase DAJ, Forster CF (1984) Biogas—fact or fantasy. Biomass 4(2):127–142

Wellinger A, Lindberg A (1999) Biogas upgrading and utilization, Task 24—energy from biological conversion of organic wastes. IEA Bioenergy, pp 1–20. http://www.seai.ie/Renewables/Bioenergy/Biogas_upgrading_and_utilisation_IEA_Bioenergy_Report.pdf

Wilmot PD, Cadee K, Katinic JJ, Kavanagh BV (1988) Kinetics of sulfide oxidation by dissolved oxygen. J Water Pollut Control Fed 60(7):1264–1270

Xu X, Chen C, Lee DJ, Wang A, Guo W, Zhou X, Guo H, Yuan Y, Ren N, Chang JS (2013) Sulfate-reduction, sulfide-oxidation and elemental sulfur bioreduction process: modeling and experimental validation. Bioresour Technol 147:202–211

Xu XJ, Chen C, Wang AJ, Fang N, Yuan Y, Ren NQ, Lee DJ (2012) Enhanced elementary sulfur recovery in integrated sulfate-reducing, sulfur-producing rector under micro-aerobic condition. Bioresour Technol 116:517–521

Xu S, Selvam A, Wong JWC (2014) Optimization of micro-aeration intensity in acidogenic reactor of a two-phase anaerobic digester treating food waste. Waste Manag 34(2):363–369

Yu H, Chen C, Ma J, Xu X, Fan R, Wang A (2014) Microbial community functional structure in response to micro-aerobic conditions in sulfate-reducing sulfur-producing bioreactor. J Environ Sci 26(5):1099–1107

Zehnder AJB (1988) Biology of anaerobic microorganisms. Wiley, Hoboken

Zhou W, Imai T, Ukita M, Li F, Yuasa A (2007) Effect of limited aeration on the anaerobic treatment of evaporator condensate from a sulfite pulp mill. Chemosphere 66(5):924–929

Zhou W, Sun Y, Wu B, Zhang Y, Huang M, Miyanaga T, Zhang Z (2011) Autotrophic denitrification for nitrate and nitrite removal using sulfur-limestone. J Environ Sci 23(11):1761–1769

Zhu M, Lü F, Hao L-P, He P-J, Shao L-M (2009) Regulating the hydrolysis of organic wastes by micro-aeration and effluent recirculation. Waste Manag 29(7):2042–2050

Zitomer DH, Shrout JD (1998) Feasibility and benefits of methanogenesis under oxygen-limited conditions. Waste Manag 18(2):107–116

Zitomer DH, Shrout JD (2000) High-sulfate, high chemical oxygen demand wastewater treatment using aerated methanogenic fluidized beds. Water Environ Res 72:90–97