



Technical Note

## Removal of Hydrogen Sulfide from Biogas Using a Bubbling Tank Fed with Aerated Wastewater

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### ABSTRACT

The work develops a simple bubbling tank scrubber that is fed with aerating wastewater for the removal of hydrogen sulfide (H<sub>2</sub>S) in biogas. A 2,000 L plastic tank, in which fixed liquid levels 0.80 and 1.0 m and volumes of 1.1 and 1.4 m<sup>3</sup> was kept, was used for the scrubbing tests. A polyvinyl chloride (PVC) pipe with holes of 1 mm diameter was used to sparge the biogas into the tank liquid. Results indicate that with an influent liquid of pH 7.5–7.7, a flow rate of 23–25 L min<sup>-1</sup>, influent biogas flow rates of 0.050–0.200 m<sup>3</sup> min<sup>-1</sup>, and a H<sub>2</sub>S concentration of 907 ± 212 ppm, the pH of the effluent liquid stabilized at 6.6–6.9. With gas/liquid rate ratio of 2–8 m<sup>3</sup> m<sup>-3</sup> liquid and volumetric gassing intensities of 0.04–0.20 m<sup>3</sup> m<sup>-3</sup> liquid min<sup>-1</sup>, average H<sub>2</sub>S removals of 86–71% were obtained. Absorption of CO<sub>2</sub> in the tested digester gas into the scrubbing liquid caused a decrease in the pH, thus decreasing the H<sub>2</sub>S removal efficiency. Increasing pH of the scrubbing liquid to 8.0 improved the H<sub>2</sub>S removal efficiency to as high as 99%.

**Keywords:** Hydrogen sulfide; Bubbling scrubbing; Digester gas; Air pollution control.

### INTRODUCTION

Biogas contains H<sub>2</sub>S which is corrosive to power generators and other metal components. The presence of H<sub>2</sub>S is a concern to not only owners of anaerobic digesters but also workers in biogas plants. H<sub>2</sub>S reacts with oxygen in air to form H<sub>2</sub>SO<sub>4</sub>, which is corrosive to most metals in the presence of water. Sulfate in air is also a main component of secondary inorganic aerosols in the atmosphere (Jiang *et al.*, 2018; Li *et al.*, 2018a; Li *et al.*, 2018b; Tseng *et al.*, 2019)

Another concern is the conversion of H<sub>2</sub>S to sulfur dioxide (SO<sub>2</sub>) during the combustion of biogas in power generator (Potivichayanon *et al.*, 2006; Beristain-Cardoso *et al.*, 2008; Krischan *et al.*, 2012; Smith and Ndegwa, 2012; Solcia *et al.*, 2014). Thus, the presence of H<sub>2</sub>S has been identified as a technological barrier to the production and utilization of biogas.

Techniques for removing H<sub>2</sub>S from biogas or industrial waste gases comprise physical, chemical, and biological methods. Chemical methods, such as the oxidative absorption of H<sub>2</sub>S into an aqueous solution of ferric sulfate, involve expensive chemicals or require the management of the sulfur slurry that is formed from H<sub>2</sub>S (Krischan *et al.*, 2010;

Liu and Wang, 2017, 2019; Pei and Wang, 2019). Physical methods, such as water scrubbing or adsorption, require the replacement of saturated scrubbing water or activated carbon (Pipatmanomai *et al.*, 2009; Lien *et al.*, 2014; Huang *et al.*, 2019; Mao *et al.*, 2020). In terms of microbiological methods, the removal of H<sub>2</sub>S has been intensively studied. Most studies have focused on fixed-film processes such as the use of biofilters (BFs), or biotrickling filters (BTFs), and bioscrubbing towers (BSTs) (Gadre, 1989; Nitta and Hirura, 1993; Yang and Allen, 1994; Jensen and Webb, 1995; Nishimura and Motoyuki, 1997; Potivichayanon *et al.*, 2006; Liang and Liang, 2013; Lin *et al.*, 2013; Su *et al.*, 2013; Solcia *et al.*, 2014; Su *et al.*, 2014).

H<sub>2</sub>S in a gas stream can also be removed by bubbling the stream through gas spargers into an activated sludge tank. Water-soluble H<sub>2</sub>S is absorbed into the mixed liquor and subsequently degraded by the microorganisms in the liquor (Sublette *et al.*, 1994; Chou *et al.*, 2010). The bubbling method can be easily applied when the activated sludge system is located near the waste gas stream(s). The process can be used to remove H<sub>2</sub>S in gases that are emitted from anaerobic digesters, landfill fields, lift wells for sewage treatment, and paper and pulp plants (Syed *et al.*, 2006; Zhang *et al.*, 2018). Sublette *et al.* (1994) developed a process that uses flocculated *Thiobacillus denitrificans* to remove up to 1,500 ppm of H<sub>2</sub>S from sour gas. Using a 0.5-m<sup>3</sup> pilot-scale bubble column, up to 97% of H<sub>2</sub>S was removed by complete oxidation to sulfate, which accumulated in the reactor medium. H<sub>2</sub>S removal was

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limited by mass transfer rather than the biodegradation rate of the system. Amano *et al.* (1999) used a suspension of *T. thiooxidans* with sodium citrate as a buffering agent to remove  $\text{H}_2\text{S}$  from a gas stream. They obtained a removal rate of  $0.96 \text{ g H}_2\text{S m}^{-3} \text{ d}^{-1}$ . Shimko *et al.* (1987) also proposed a patented process that involves bubbling a gas stream with  $1,700\text{--}5,400 \text{ mg H}_2\text{S m}^{-3}$  and  $1,800\text{--}5,100 \text{ mg CS}_2 \text{ m}^{-3}$  into an activated sludge tank with a liquor depth of 3–4 m. Chou *et al.* (2010) used an activated sludge aeration tank (width  $\times$  length  $\times$  height =  $0.4 \text{ m} \times 0.4 \text{ m} \times 3 \text{ m}$ ) with a 2 mm-orifice air sparger to treat gaseous  $\text{H}_2\text{S}$ . They tested the operational stability and the relationships between the removal of  $\text{H}_2\text{S}$  and the influent  $\text{H}_2\text{S}$  concentration (50–900 ppm), aeration intensity ( $0.083\text{--}0.50 \text{ m}^3 \text{ m}^{-3} \text{ min}^{-1}$ ), liquid depth (0.5–3 m), and concentration of mixed-liquor-suspended solids (MLSS =  $970\text{--}2,800 \text{ mg L}^{-1}$ ). They experimentally obtained  $\text{H}_2\text{S}$  removal efficiencies of 96% and  $< 98\%$  at liquid depth values of 0.5 m and  $< 1 \text{ m}$ , respectively, under their specified operational conditions. Their experimental results also revealed that no sludge bulking problem occurred at total sulfide loadings of  $47\text{--}148 \text{ g S kg}^{-1} \text{ MLSS d}^{-1}$ .

The bubbling approach requires a column or tank fed with a stream of activated sludge liquor that may be supplied from an existing aerating pond or fed with supplemental nutrients (such as carbon, nitrogen, and phosphorus) to sustain the microorganisms that oxidize the absorbed sulfide. This requirement limits the practical application of the approach because considerable attention must be paid to maintaining

the health of the microorganisms.

This study developed a simple bubbling tank scrubber that is fed with aerated wastewater for the removal of  $\text{H}_2\text{S}$  from biogas that is vented from anaerobic digesters used to treat wastewater from dairy farms. The effects of the bubbling rate, liquid depth, and the pH of the scrubbing liquid on the degree and rate of  $\text{H}_2\text{S}$  removal were investigated.

## METHODS

The experimental setup comprised a full-scale bubbling tank and an influent gas supply system (Figs. 1 and 2). A 2,000-L plastic tank with an inner diameter of 1.33 m; fixed water levels of 0.80–1.0 m; and 1,100–1,400 L of scrubbing liquid was used for the scrubbing tests. A 2-inch polyvinyl chloride (PVC) perforated pipe was formed into a rectangle and used to sparge the biogas into the tank liquid. A total of 536 holes with a diameter of 1 mm and a constant pitch of 10 mm were present along the pipe, and four holes were present  $90^\circ$  apart along the perimeter of the pipe. Biogas from the digesters of a dairy wastewater plant was collected in a full-scale plastic bag. The biogas was filtered and then passed through a ring-type blower and sparged into the tank liquid. Aerating wastewater for the aerobic treatment of the effluent from anaerobic digesters was fed into the tank as a scrubbing liquid and flowed over the tank into the aerobic pond under the influence of gravity. Flow rates of both the gas and scrubbing liquid were regulated using rotameters.

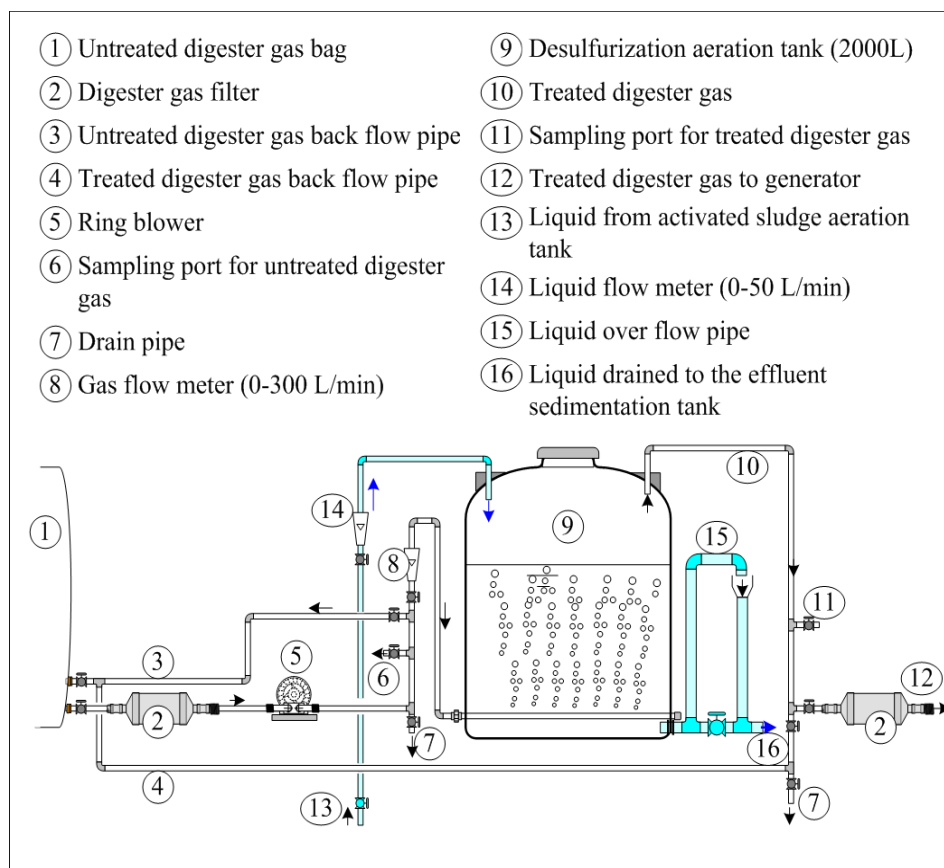


Fig. 1. Schematics of the experimental system.

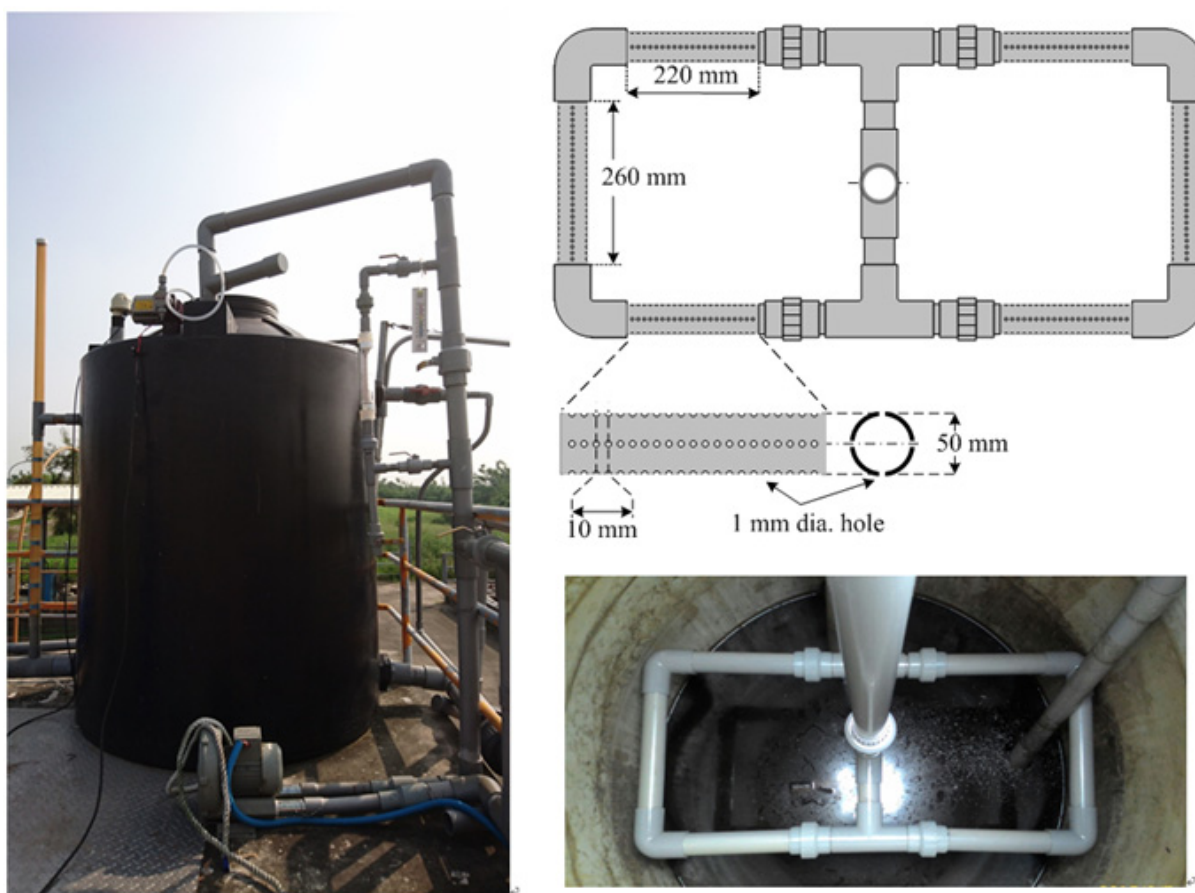


Fig. 2. The experimental bubbling tank and the gas sparger.

Initially, the tank was filled to a certain depth with the scrubbing liquid that was drawn from one of the aeration tanks; subsequently, the scrubbing liquid flow rate was adjusted to a preset value. A stream of biogas was then introduced into the tank and the flow rate was adjusted to a present value.  $\text{H}_2\text{S}$  concentrations in the influent and effluent biogas and the pH of the effluent scrubbing liquid were measured at the end of 10-min fixed intervals until both the  $\text{H}_2\text{S}$  concentration of the effluent biogas and the pH of the effluent scrubbing liquid reached quasi-steady values. Temperatures of the scrubbing liquid and gas were also measured during the operation. Concentrations of chemical oxygen demand (COD), suspended solids (SS), total solids (TS), dissolved oxygen (DO), and the basicity of the influent scrubbing liquid were measured during several runs.

Aqueous hydrogen sulfide has a  $\text{p}K_a$  of 7.1 at  $25^\circ\text{C}$  in the following ionization reaction:  $\text{H}_2\text{S}_{(\text{aq})} \rightleftharpoons \text{HS}^- + \text{H}^+$ . Consistent with this  $\text{p}K_a$  value, at pH 7, 55.7% of the total aqueous hydrogen sulfide ( $[\text{H}_2\text{S}_{(\text{aq})}] + [\text{HS}^-]$ ) is in an un-ionized state:  $\alpha = [\text{H}_2\text{S}_{(\text{aq})}] / ([\text{H}_2\text{S}_{(\text{aq})}] + [\text{HS}^-]) = 1 / (1 + 10^{7-7.1}) = 0.557$ . At a higher pH, such as 8,  $\alpha = 1 / (1 + 10^{8-7.1}) = 0.112$ . Thus, a scrubbing liquid with a higher pH and acidic buffering capacity favors the chemical absorption of  $\text{H}_2\text{S}$ . In the present study, for some cases, the scrubbing liquid was supplemented with sodium hydroxide solution (45%) by a dosing pump that was actuated by a pH controller to a preset pH range to test the effect of pH on  $\text{H}_2\text{S}$  removal efficiency. Either calcium or

magnesium hydroxide can also be used for pH control. However,  $\text{CaCO}_3$  or  $\text{MgCO}_3$  solids may form and precipitate in the scrubbing liquid and interfere with the operation. Sodium bicarbonate and carbonate are more expensive than sodium hydroxide.

$\text{H}_2\text{S}$  concentrations in the gas samples were measured using detection tubes ( $\text{H}_2\text{S}$  detector tubes, Gastec Corporation, Japan) and a portable multiple gas analyzer (Dräger X-am 7000, Dräger Safety AG & Co. KGaA, Germany). The gas analyzer could also provide data on gaseous  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{O}_2$ . Data from 25 samples of the influent digester gas to the tank indicated  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{O}_2$  contents of  $64.5 \pm 2.7\%$ ,  $28.2 \pm 1.5\%$ , and  $0.53 \pm 0.22\%$ , respectively, and  $\text{H}_2\text{S}$  content was  $1090 \pm 300$  ppm. The detected gases accounted for > 93% of all the components, with the remaining gases likely to be  $\text{N}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{H}_2$  (Seadi *et al.*, 2008). Both detection tubes and the analyzer were calibrated using standard  $\text{H}_2\text{S}$  gas at concentrations of 5, 10, 20, and 50 ppm. Liquid pH was detected using a pH meter (pH/mV Pocker Meter pH 330i, WTW, Germany), and COD, SS, TSS, DO, and basicity were measured according to the APHA (1989).

## RESULTS AND DISCUSSION

Table 1 details the scrubbing liquid qualities and Table 2 details the properties of the raw and scrubbed biogases of the present study.

**Table 1.** Scrubbing liquid qualities.

	Influent	Effluent
Chemical oxygen demand, COD (mg L <sup>-1</sup> )	817 ± 67	797 ± 80
Suspended solids, SS (mg L <sup>-1</sup> )	262 ± 35	225 ± 28
Total solids, TS (mg L <sup>-1</sup> )	2160 ± 181	2160 ± 154
Dissolved oxygen, DO (mg L <sup>-1</sup> )	0.10 ± 0.02	-
Basicity (titration to pH 7.00) (meq L <sup>-1</sup> )	6.13 ± 0.33	-

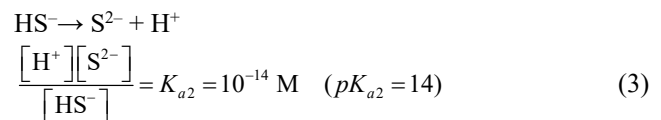
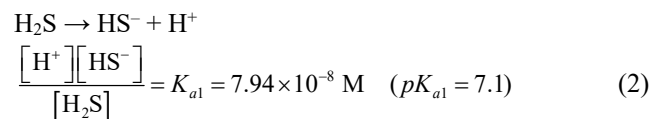
**Table 2.** Some operation data.

flowrate (L min <sup>-1</sup> )	Influent biogas to the tank				Effluent biogas @ quasi-steady state					Influent scrubbing liquid	Effluent scrubbing liquid	
	CH <sub>4</sub> (%)	CO <sub>2</sub> (%)	O <sub>2</sub> (%)	H <sub>2</sub> S (ppm)	T (°C)	CH <sub>4</sub> (%)	CO <sub>2</sub> (%)	O <sub>2</sub> (%)	H <sub>2</sub> S (ppm)	pH	pH	T (°C)
50	68	27	0.7	570	34.0	66	21	0.8	21	7.78	7.04	24.6
	63	29	0.8	1,410	34.0	65	26	0.6	68	7.73	7.19	31.4
	68	29	0.6	1,480	34.0	63	25	0.8	206	7.99	7.14	31.2
60	60	29	0.8	1,150	40.2	63	28	0.4	182	7.89	7.07	33.1
	62	30	0.5	1,055	40.5	64	29	0.4	177	7.92	6.98	33.9
100	65	25	0.4	1,020	30.0	70	23	0.4	156	7.78	6.93	23.8
	70	26	0.6	870	33.8	68	23	0.7	151	7.63	6.95	24.0
	66	26	0.8	570	31.0	65	24	1.1	62	7.67	6.95	24.8
	63	30	0.4	890	42.5	64	27	0.4	164	7.85	6.94	32.2
	63	29	0.6	1,510	39.0	64	27	0.3	236	7.95	7.04	31.8
	63	27	0.8	1,395	35.6	60	26	0.5	195	7.93	7.04	31.4
	62	28	0.5	1,190	37.0	64	26	0.4	170	7.92	7.11	32.0
150	62	29	0.5	1,290	36.0	63	29	0.4	230	7.96	7.02	33.1
	66	29	0.4	890	29.0	68	26	0.4	189	7.60	6.68	24.0
	70	26	0.6	1,320	30.5	70	25	0.3	464	7.75	6.84	24.8
	63	29	0.4	800	39.4	62	25	0.6	164	7.93	7.11	32.2
	61	29	1	1,245	40.2	64	29	0.3	244	8.06	7.12	33.3
	68	26	0.6	1,310	26.0	66	25	0.4	360	7.31	6.60	25.0
	66	29	0	620	25.5	68	29	0.4	166	7.58	6.70	24.5
200	68	29	0.2	1,410	39.0	66	27	0	414	7.68	6.68	25.8
	64	27	0.5	1,390	43.6	64	27	0.5	228	8.02	7.07	32
	63	30	0.4	915	42.4	66	27	0.3	195	7.97	7.07	32.1
	61	29	0.3	1,330	36.2	60	29	0.7	278	7.94	6.98	32.8

In general, the mechanistic model developed by Bielefeldt and Stensel (1999) describes the removal of VOCs from a contaminated gas stream sparged into a completely mixed activated sludge reactor as a function of the gas-liquid mass transfer and liquid VOC concentrations. The model can be modified and applied to the present system as follows:

$$C-mx = (C_0-mx) \exp [-K_{GA}Z/(G/A)] \quad (1)$$

where  $C$  and  $C_0$  represent H<sub>2</sub>S concentrations in the exit and the influent biogas streams (mg m<sup>-3</sup>), respectively;  $m$  is the dimensionless Henry's law coefficient;  $x$  is the molecular H<sub>2</sub>S concentration in the liquid phase (mg m<sup>-3</sup>);  $K_{GA}$  is the overall volumetric mass transfer coefficient of H<sub>2</sub>S in biogas (min<sup>-1</sup>);  $Z$  is the depth of the liquid over the sparger (m);  $G$  is the influent gas flow rate (m<sup>3</sup> min<sup>-1</sup>), and  $A$  is the cross-sectional area of the sparging tank (m<sup>2</sup>). In liquid phase, molecular hydrogen sulfide ionizes according to the following equations:



Un-dissociated or molecular H<sub>2</sub>S in water ( $x$  or [H<sub>2</sub>S]) can then be related to the total sulfide ([H<sub>2</sub>S] + [HS<sup>-</sup>] + [S<sup>2-</sup>]) in water by the following equation:

$$f = \frac{[\text{H}_2\text{S}]}{[\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}]} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}} \quad (4)$$

Table 3 shows dependence of  $f$  on water pH. Water with a higher pH gives a lower  $x$  or  $[H_2S]$  value which favors the absorption of gaseous  $H_2S$ , according to Eq. (1). In addition, molecular or ionized  $H_2S$  in the liquid may be chemically or biologically oxidized to elementary sulfur, sulfite, or sulfate by utilizing molecular oxygen in the liquid. The reactions help to gaseous  $H_2S$  removal by enhancing its transfer to the liquid.

According to Eq. (1), bubbling gas flow rate ( $G$ ), influent gas  $H_2S$  concentration ( $C_o$ ), liquid depth ( $Z$ ), mass-transfer coefficient ( $K_G a$ ), molecular  $H_2S$  concentration in the liquid phase ( $x$ , depends on pH), and  $m$  (depends mainly on liquid temperature) are among the affecting factors to the  $H_2S$  removal. In the present study, effects of  $G$ , liquid pH, and  $Z$  on the  $H_2S$  removal were tested and results discussed. Effect of  $C_o$  on the removal was also discussed.

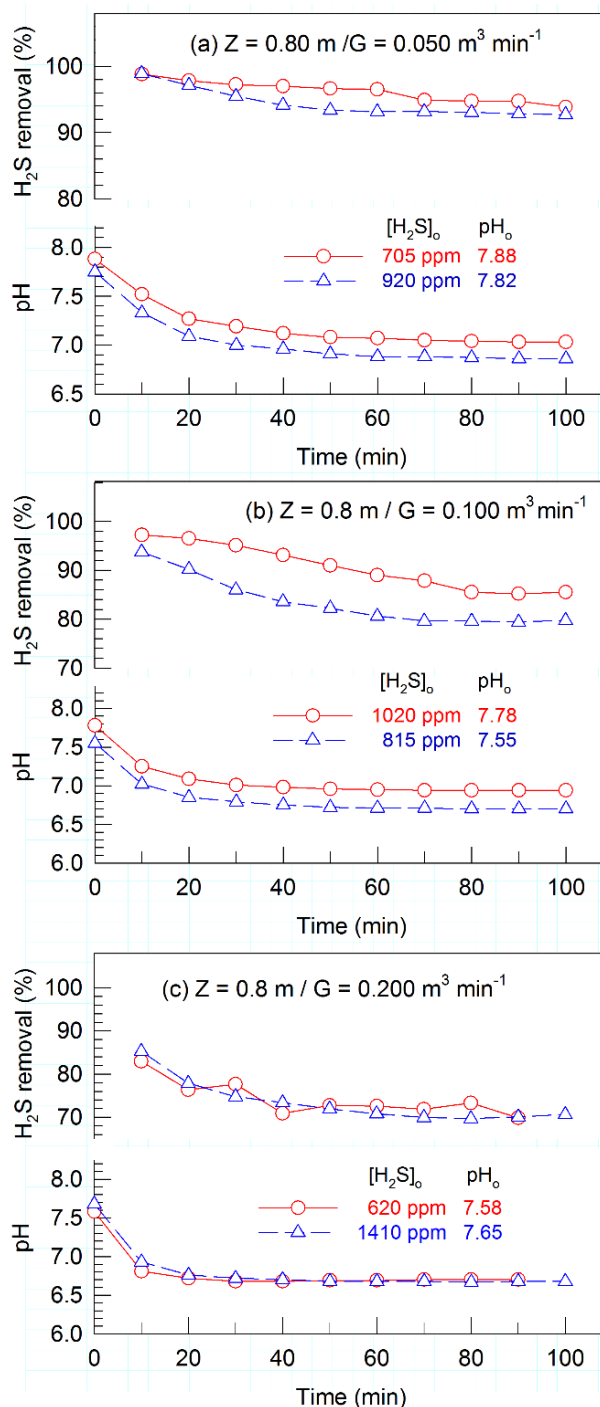
**Effects of Bubbling Rate, Scrubbing Liquid pH, and Depth on  $H_2S$  Removal**

Fig. 3 details the variations in  $H_2S$  removal and liquid pH over time during operation at a liquid depth ( $Z$ ) of 0.8 m and gas injection rates ( $G$ ) of 0.050, 0.100, and 0.200  $m^3 \text{ min}^{-1}$ . When  $G$  was 0.050  $m^3 \text{ min}^{-1}$  at 30–32°C or when the volumetric gasing intensity ( $G/V$ ) (gas injection rate per unit liquid volume) was 0.0455  $m^3 \text{ m}^{-3} \text{ min}^{-1}$ ,  $H_2S$  removal was 86.4% ± 8.9% at pH 6.92 ± 0.12 for an influent  $H_2S$  concentration of 918 ± 18 ppm and a scrubbing liquid influent flow rate of 25 ± 1  $L \text{ min}^{-1}$  in the quasi-steady state. As the gas injection rate increased from 0.050 to 0.200  $m^3 \text{ min}^{-1}$ , the proportion of  $H_2S$  removed was reduced from 86.4% ± 8.9% to 70.6% ± 1.1%, and the pH of the scrubbing liquid decreased from 6.92 ± 0.12 to 6.75 ± 0.11. The influent  $H_2S$  concentration did not affect its removal efficiency (Fig. 3). At the influent  $H_2S$  concentrations of 620 and 1,410 ppm, the removal efficiency was approximately 70%, and the pH was 6.75 at the end of each operation (Fig. 3(c)). This could be because the efficiency was mass-transfer-controlled when the influent  $H_2S$  concentration increased from 620 to 1410 ppm and the removal efficiency remained constant (at around 70%) (Chou *et al.*, 2010). Increase in the biogas injection flow rate, which reduced the pH of the scrubbing liquid, affected the removal efficiency of  $H_2S$ .

Fig. 4 details the time variations in the mean proportions of  $H_2S$  removed and the liquid pH in the operations where  $G = 0.150 \text{ m}^3 \text{ min}^{-1}$  and  $Z$  was 0.8, 0.9, and 1 m. Higher pH values of the influent and effluent liquid were associated with the removal of a higher amount of  $H_2S$ .

**Table 3.** Dependence of  $f$  on water pH.

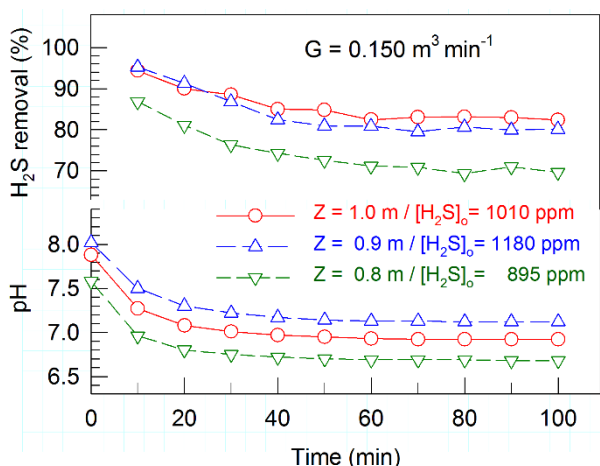
pH	$f = \frac{[H_2S]}{[H_2S] + [HS^-] + [S^{2-}]}$
6.50	0.799
7.00	0.557
7.50	0.285
8.00	0.112
8.50	0.0383
9.00	0.0124



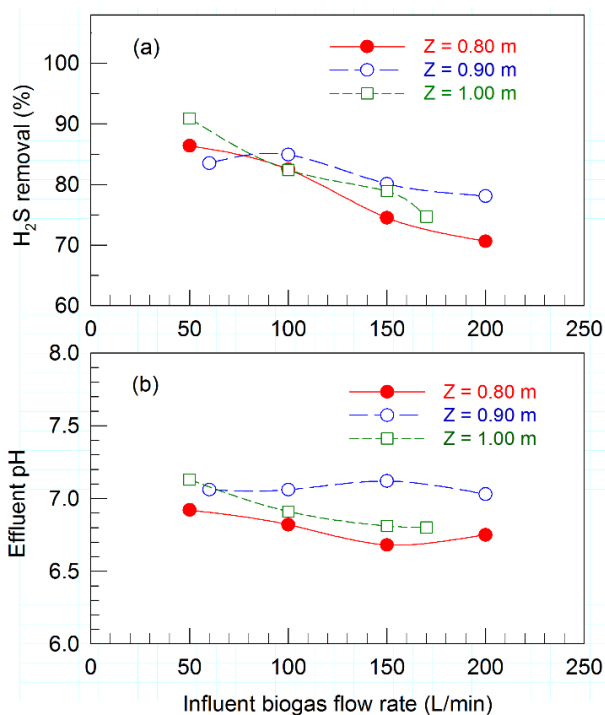
**Fig. 3.** Time variations of  $H_2S$  removal and liquid pH with operations of liquid depth  $Z = 0.8 \text{ m}$  and gas injection rate  $G$  of (a) 0.050, (b) 0.100, and (c) 0.200  $m^3 \text{ min}^{-1}$ .

Fig. 5 presents the effects of the influent biogas flow rate on the removal efficiency of  $H_2S$  and the pH of the effluent liquid. When  $Z$  was 0.80 m, because the pH of the liquid decreased, the removal efficiency drastically decreased as the gas flow rate increased. When  $Z$  was 0.90 and 1.0 m, higher liquid pH values at all gas flow rates caused variations in efficiency; the gas flow rate and liquid level were lower than those when  $Z$  was .8 m.





**Fig. 4.** Time variations of average values of H<sub>2</sub>S removal and liquid pH with operations of gas injection rate  $G = 0.150 \text{ m}^3 \text{ min}^{-1}$  and liquid depths  $Z =$  of 0.8, 0.9, and 1.0 m.



**Fig. 5.** Influences of influent biogas flow rate on the H<sub>2</sub>S removal and effluent liquid pH at quasi-steady states.

#### Mechanisms of H<sub>2</sub>S Removal Other than Water Absorption

As detailed in Table 2, the oxygen concentrations in the influent biogas added to and the effluent biogas derived from the absorbing liquid were  $0.53\% \pm 0.22\%$  and  $0.50\% \pm 0.22\%$ , respectively. On average, only 0.03%, or 300 ppm, of O<sub>2</sub> in the biogas was absorbed by the absorbing liquid, and the oxygen could be used to oxidize either 150 ppm of H<sub>2</sub>S that was transferred from the biogas (according to  $\text{HS}^- + 2\text{O}_2 \rightarrow \text{HSO}_4^-$ ) or 600 ppm of H<sub>2</sub>S (according to  $2\text{HS}^- + \text{O}_2 \rightarrow 2\text{S}^0 + 2\text{OH}^-$ ) (González-Sánchez and Revah, 2007). This amount of H<sub>2</sub>S (150–600 ppm) was approximately 14%–55% of

$1,090 \pm 300$  ppm of H<sub>2</sub>S in the influent biogas. DO in the influent absorbing liquid at an average flow rate of  $25 \text{ L min}^{-1}$  was approximately  $1 \text{ mg L}^{-1}$ , and the total DO input to the absorbing tank was  $25 \text{ mg min}^{-1}$ . This amount of oxygen could oxidize 13 and  $53 \text{ mg H}_2\text{S min}^{-1}$  (according to the two aforementioned equations), respectively. The DO could oxidize 95–380 ppm of H<sub>2</sub>S that was absorbed from the biogas at an influent flow rate of  $100 \text{ L min}^{-1}$ , at, for example, approximately 30°C. Therefore, at most 245–980 ppm of H<sub>2</sub>S that was absorbed from the biogas with 1,090 ppm H<sub>2</sub>S could possibly be oxidized to elementary sulfur or various oxidation compounds of sulfur (such as  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_3^{2-}$ , and  $\text{SO}_4^{2-}$ ) (Cline and Richards, 1969; Jorgensen, 1990; Zhang et al., 2008). Therefore, the H<sub>2</sub>S removal mechanisms in this process might include liquid absorption and chemical or biological oxidation.

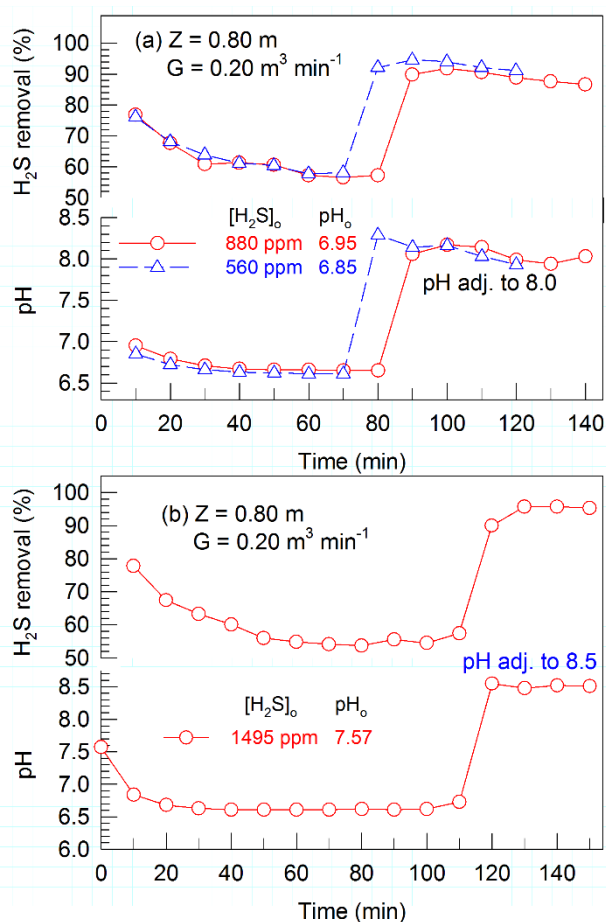
There existed biological activity in the influent scrubbing liquid drawn from one of the aeration ponds for treating the dairy wastewater, and the activities responded for the microbial oxidation of the absorbed H<sub>2</sub>S. The aeration ponds were operated 24 hours a day and biological activity was kept at a quasi-steady state. The biological activity in the scrubbing liquid were assumed to be constant throughout the 100-minute operation time.

#### Adjustment of Liquid pH to Improve H<sub>2</sub>S Removal Efficiency

Fig. 6 details the effect of liquid pH on the removal efficiency of H<sub>2</sub>S when  $Z$  is 0.8 m. The pH was adjusted when the system reached a quasi-steady state. Data in Fig. 6 indicate that the condition where  $G$  is  $0.100 \text{ m}^3 \text{ min}^{-1}$  and the effluent or absorbing liquid was of pH 8 resulted in 99% removal of 760 ppm H<sub>2</sub>S in the influent gas. At pH 8, the H<sub>2</sub>S removal efficiency decreased as the gas injection rate increased, possibly because of a decrease in the mass transfer rate of the gaseous H<sub>2</sub>S to the scrubbing liquid at the higher gas injection rate, as Eq. (1) shows. The additional increase in the H<sub>2</sub>S removal rate when the liquid pH was adjusted to 8.5 was less than that when the liquid pH was adjusted to 8. Supplementation with an additional caustic solution to increase the pH to 8.5 was unnecessary.

#### Limitation of H<sub>2</sub>S Transfer Rate

According to data in Fig. 6, the H<sub>2</sub>S removal rates were  $> 94\%$  when  $G$  was  $\leq 0.150 \text{ m}^3 \text{ min}^{-1}$  and the pH of the absorbing water was adjusted to 8.0 or 8.5. The mass transfer rate,  $R$ , of gaseous H<sub>2</sub>S to the scrubbing liquid can be described as  $R = K_{\text{Ga}}(C - mx)$  as shown in Eq. (1). Table 3 shows dependence of  $f$  on water pH. Water with a higher pH gives a lower [H<sub>2</sub>S] or  $x$  value which favors the absorption of gaseous H<sub>2</sub>S. When the scrubbing liquid pH is  $> 8.0$ ,  $mx \ll C$ , and  $R$  equals approximately  $K_{\text{Ga}} C$ . This explains why when pH is  $> 8$ , the H<sub>2</sub>S removal efficiency could reach a high value at the fixed operating conditions of liquid depth, liquid temperature, liquid flow rate, and biogas flow rate. In addition, sparging holes with 2.0 mm (rather than 1.0 mm in the present study) in diameter had been used by authors and much lower H<sub>2</sub>S removal efficiencies got due to their lower gas-liquid interfacial area (a) available for the transfer.



**Fig. 6.** Time variations of H<sub>2</sub>S removal and liquid pH with operations of liquid depth Z = 0.8 m and gas injection rate G = 0.20 m<sup>3</sup> min<sup>-1</sup> and liquid pH adjusted to (a) 8.0 after time of 70–80 minutes and (b) 8.5 after time of 110 minutes.

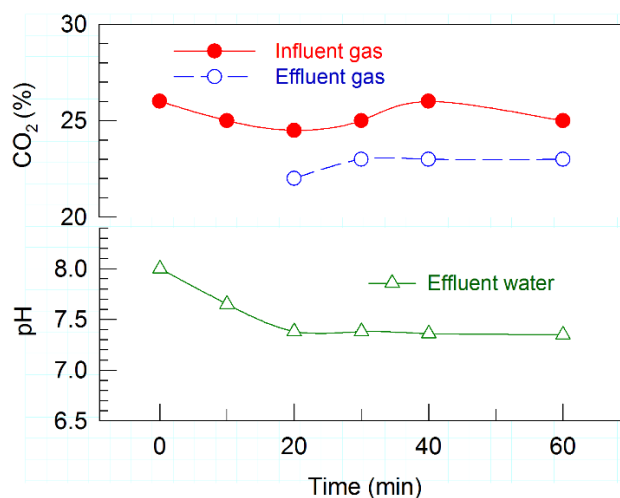
### Effects of Biogas Absorption on the Basicity of the Scrubbing Liquid

Table 1 reveals that COD, SS, and TS did not differ significantly between the influent and effluent scrubbing liquids for H<sub>2</sub>S absorption. The decrease in the pH of the effluent liquid that was caused by the absorption of H<sub>2</sub>S and CO<sub>2</sub> from the injected biogas reduced the H<sub>2</sub>S removal efficiency. Temperature may affect the H<sub>2</sub>S removal rate. The influent gas temperatures were between 33–47°C from April to September and 20–35°C from October to March. The effluent gas temperatures were 2–5°C lower than the influent ones due to a chilling effect from the gas bubbling through the scrubbing liquid. The scrubbing liquid temperatures were 30–34°C from April to September and 24–30°C from October to March. No temperature control for both the biogas and scrubbing liquid was conducted during the tests. Similar studies have not considered biogas and scrubbing water temperatures (Hagen *et al.*, 2001; Lien *et al.*, 2014). Tilahun *et al.* (2017, 2018) used membrane contactors to separate H<sub>2</sub>S from biogas; however, the mechanism of H<sub>2</sub>S removal is its diffusion through a porous membrane rather than a gas film (as in this study). The effects of biogas and scrubbing liquid temperatures on H<sub>2</sub>S removal will be

investigated in a further study.

According to Fig. 3(c), when G was 0.200 m<sup>3</sup>·min<sup>-1</sup>, the mean effluent gas temperature was 38°C, the average influent H<sub>2</sub>S concentration was 1,410 ppm, and the influent H<sub>2</sub>S mass flow rate was 11.1 mmol min<sup>-1</sup> (1,410 ppm × 0.200 Am<sup>3</sup> min<sup>-1</sup> × 10<sup>-6</sup> ppm<sup>-1</sup> × 273 Nm<sup>3</sup>/[38 + 273] Am<sup>3</sup>/22.4 Nm<sup>3</sup> kmol<sup>-1</sup> = 11.1 mmol min<sup>-1</sup>). Total absorption of the injected H<sub>2</sub>S into the influent liquid at a flow rate of 25 L min<sup>-1</sup> may have reduced the water basicity by 0.336 meq L<sup>-1</sup> from that of the influent water (11.1 mmol min<sup>-1</sup>/(25 L min<sup>-1</sup>) = 0.444 meq L<sup>-1</sup> according to H<sub>2</sub>S<sub>(aq)</sub> → HS<sup>-</sup> + H<sup>+</sup>). The decrease in basicity was only 7.25% of that of 6.13 ± 0.3 meq L<sup>-1</sup> in the influent liquid when titrated to pH 7 (Table 1).

The major drop in the basicity of the scrubbing liquid is caused by the absorption of CO<sub>2</sub> from the biogas. Fig. 7 presents the time variations in the concentrations of CO<sub>2</sub> in the influent and effluent gases and the pH of the effluent liquid when Z, G, and L were 0.8 m, 0.16 m<sup>3</sup> min<sup>-1</sup>, and 25 L min<sup>-1</sup>, respectively. In the quasi-steady state, an average of approximately 2.33% of the CO<sub>2</sub> in the influent biogas was absorbed into the liquid. The absorbed CO<sub>2</sub> mass flow rate was 146 mmol min<sup>-1</sup> (2.33% × 0.160 Am<sup>3</sup> min<sup>-1</sup> × 10<sup>-2</sup> %<sup>-1</sup> × 273 Nm<sup>3</sup>/[(38 + 273)Am<sup>3</sup>/(22.4 Nm<sup>3</sup> kmol<sup>-1</sup>)] = 146 mmol min<sup>-1</sup>). The absorption of the CO<sub>2</sub> into the influent liquid at a flow rate of 25 L min<sup>-1</sup> reduced the basicity by 5.84 meq L<sup>-1</sup> from that of the influent liquid (146 mmol min<sup>-1</sup>/(25 L min<sup>-1</sup>) = 5.84 mmol L<sup>-1</sup> = 5.84 meq L<sup>-1</sup>, according to CO<sub>2(aq)</sub> + H<sub>2</sub>O → HCO<sub>3</sub><sup>-</sup> + H<sup>+</sup>). This basicity of 5.84 meq L<sup>-1</sup> was approximately 95% of 6.13 ± 0.33 meq L<sup>-1</sup> in the influent liquid (Table 1). The decrease in pH is attributable to CO<sub>2</sub> absorption into the scrubbing liquid, which reduced the H<sub>2</sub>S removal efficiency. Therefore, with an increase in G/L (gas/liquid rate ratio), the scrubbing liquid absorbs a much more CO<sub>2</sub> from the biogas and this results in the decrease in liquid pH and H<sub>2</sub>S removal efficiency. Fig. 5 displays that at a constant L of 25 L min<sup>-1</sup>, H<sub>2</sub>S removal efficiencies decreased with increasing gas flow rate (G) or G/L, and decreasing pH. With G extra plotting to



**Fig. 7.** Time variations of CO<sub>2</sub> concentrations in the influent and effluent gases and effluent liquid pH (Liquid depth Z = 0.8 m, gas injection rate G = 0.16 m<sup>3</sup> min<sup>-1</sup>, and water flow rate L = 25 L min<sup>-1</sup>).

0 at  $Z = 1.00$  m,  $H_2S$  might approach to 100% as shown in Fig. 3(a). The attribution of  $CO_2$  in the biogas to the lowering liquid pH also supports the results that the  $H_2S$  removal efficiencies were nearly independent with the influent  $H_2S$  concentrations of  $< 1,500$  ppm.

#### Comparisons of Biogas Desulfurization Methods

Table 4 compares biogas desulfurization methods. Tilahun *et al.* (2018) used a polydimethylsiloxane membrane contactor for selective  $H_2S$  removal from the biogas. The  $H_2S$  and  $CH_4$  in the biogas diffused through the membrane to an absorbing liquid. The results revealed that at the lowest loading rate ( $91 \text{ mg } H_2S \text{ m}^{-2} \text{ h}^{-1}$ ), absorption efficiencies of more than 98% for  $H_2S$  and 59% for  $CO_2$  were achieved. Increasing the absorbing liquid pH (from 7 to 10) and the loading rate (from 91 to  $355 \text{ mg } H_2S \text{ m}^{-2} \text{ h}^{-1}$ ) increased the  $H_2S$  absorption capacity. Tilahun *et al.* (2017) also used a

hybrid membrane gas absorption and bio-oxidation process for the removal of hydrogen sulfide from biogas. Membrane processes have promising real scale applications if they are cost-effective.

Unlike the water scrubbing method in which the saturated scrubbing water must be replaced (Lien *et al.*, 2014), an activated sludge mixed liquor for polishing the effluent wastewater from the anaerobic digester(s) was used in the current approach. No additional fresh water is required for this proposed process. The effluent liquid from the simple absorption tank can be further treated to oxidize the absorbed  $H_2S$  to sulfate, which is considerably less harmful to aqueous environments than sulfide ions.

Compared with biological approaches such as those involving BFs or BTFs, which require organic or inert packing materials, the proposed method neither requires these materials nor the need to control the microbial activities

**Table 4.** Comparisons of biogas desulfurization methods.

Method	Characteristics	Advantages	Limitations	Literature
Addition of $Fe^{2+}$ to anaerobic digester	$Fe^{2+}$ reacts with sulfide ions to form $FeS$	$H_2S$ levels of 100 to 150 ppm in the biogas can be reached	When using raw materials that are rich in sulfur containing molecules, this method is rather expensive	Hagen <i>et al.</i> , 2001
Chemical adsorption of $H_2S$ by $Fe_2O_3$	Oxidation of $H_2S$ to S by $Fe^{3+}$	High $H_2S$ removal can be reached	Needs expensive chemicals and require that the sulfur slurry that is formed from hydrogen sulfide to be handled	Hagen <i>et al.</i> , 2001
Chemical absorption of $H_2S$ by ferric sulfate	Ibid.	Ibid.	Ibid.	Krischan <i>et al.</i> , 2010
Biological oxidation of $H_2S$	Addition of 5–10% air to the biogas in a bioreactor to convert $H_2S$ to sulfur	Ibid.	Ibid.	Gadre, 1989; Nitta and Hirura, 1993; Yang and Allen, 1994; Jensen and Webb, 1995; Nishimura and Motoyuki, 1997; Potivichayanon <i>et al.</i> , 2006; Liang and Liang, 2013; Lin <i>et al.</i> , 2013; Su <i>et al.</i> , 2013; Solcia <i>et al.</i> , 2014; Su <i>et al.</i> , 2014
Adsorbed on activated carbon	Addition of air to the biogas to catalytically oxidize $H_2S$ to sulfur	Ibid.	Saturated carbon is usually spent without regeneration.	Hagen <i>et al.</i> , 2001; Pipatmanomai <i>et al.</i> , 2009
Membrane filtration	Selective membrane filtration of $H_2S$ and $CO_2$ from biogas	High $H_2S$ removal and moderate $CO_2$ removal can be reached	Cost of	Tilahun <i>et al.</i> , 2017, 2018
Water scrubbing	Use water to scrub $H_2S$ from biogas	Equipment is simple	Needs replacement and treatment of saturated scrubbing water	Lien <i>et al.</i> , 2014
Wastewater scrubbing	Use wastewater in aeration to scrub $H_2S$ from biogas	Equipment is simple	Needs enough wastewater to reach a high $H_2S$ removal	Present study



of the biofilms that are either inside or attached to the packing materials. In addition, the H<sub>2</sub>S removal efficiency from BFs may be unstable because of fluctuations in biological activity. The H<sub>2</sub>S removal efficiency of the proposed method can be stabilized by maintaining the scrubbing liquid depth, liquid pH, and the ratio of gas flow rates to liquid flow rates. However, the proposed method requires at least one activated aeration tank, a low-head liquid pump to deliver the scrubbing liquid, and a medium-pressure (approximately 0.1 bar) or a 1,000 mm water head blower to sparge the digester gas into the scrubbing liquid. The operating electrical energy cost of the proposed method is also higher than that of the method that uses biofilters.

Compared with the activated sludge tank bubbling processes (Shimko *et al.*, 1987; Sublette *et al.*, 1994; Amano *et al.*, 1999; Chou *et al.*, 2010), the proposed method requires no nutrients to sustain microbial growth and activity. In the proposed method, no attention is required to be paid to the health of the microorganisms to maintain H<sub>2</sub>S removal efficiency.

Biological processes such as those cited in Muñoz *et al.* (2015) may have H<sub>2</sub>S removal efficiencies higher than 90%. Compared with biological methods, the main limitation of the proposed process is its increased cost from additional chemicals (caustic soda) that are usually required to adjust the absorbing liquid to a pH of > 8 to obtain a H<sub>2</sub>S removal efficiency of more than 90%. However, this cost can be reduced to as low as zero by increasing the ratio of scrubbing liquid flow rate to gas flow rate, allowing the removal of over 90% of H<sub>2</sub>S in the influent biogas. The scrubbing liquid can be drawn from existing biological aeration tank(s) and drained back to the tank(s) to biologically oxidize the absorbed H<sub>2</sub>S to sulfate ions. The pumping cost should be taken into account.

Khoshnevisan *et al.* (2017) demonstrated that the sufficient residence time (RT) for biogas in biotrickling filters is a key factor for successful microaerobic desulfurization. A RT of greater than 5 h yields removal efficiencies (REs) of up to 90%. REs of 88% and 72% were obtained when an RT of approximately 2.5 h was tested. A study demonstrated a successful RE of 96% under variable RTs (from 59 to 97 min). However, a long RT, for example, of 1 h, implies that a big reactor is required to treat a sufficiently large flow of biogas. In the present study, a biogas rate of 200 L min<sup>-1</sup> requires an absorbing water volume of only 1,100 L to attain an RE of more than 80%. Data are equivalent to an RT of approximately 5 min.

Another disadvantage of BTFs is the formation of elemental sulfur in the reactors. The sulfur gradually increases the pressure required for driving the gas through the filters and eventually clogs the filters. One approach to solving the clogging problem is to withdraw the accumulated solids from the packing materials after shutting down the filtration systems. The present system has no problems with clogging because most of the absorbed H<sub>2</sub>S is in H<sub>2</sub>S and HS<sup>-</sup> aqueous states. Moreover, the suspended elemental sulfur, if any, flows out with the effluent absorbing liquid.

Pokorná *et al.* (2015) described microaeration as a straightforward, highly efficient, and economically viable

technique for H<sub>2</sub>S removal from biogas. In the method, sulfide is oxidized to elemental sulfur by the action of sulfide oxidizing bacteria. However, the limitations of microaeration, such as partial oxidation of the soluble substrate, clogging in the walls and pipes by elemental sulfur, and toxicity to methanogens, were noted. The proposed method has no such problems.

### **Feasibility of the Process and Further Studies**

A tank with a reasonable size and liquid depth is required for the practical application of the proposed method. Recebli *et al.* (2015) discovered that an average of 25 kg of manure per day (8.44% dry solids) produced from one bovine animal can generate 0.90 m<sup>3</sup> of digester gas per day with 62% of CH<sub>4</sub> at 25–40°C. Thus, a ranch that has 200 bovine animals can produce 180 m<sup>3</sup> of digester gas per day (average: 0.125 m<sup>3</sup> min<sup>-1</sup>) if all the manure is anaerobically fermented. A system size similar to the one tested in the present study can be used to remove 80% of H<sub>2</sub>S from the biogas when the scrubbing liquid flow is 25 L min<sup>-1</sup>. The liquid can be introduced from either an aerobic pond or the effluent pond of the wastewater treatment plant for the ranch and discharged back to the aerobic pond to oxidize the absorbed sulfides. The installation cost for the system is around 3,000 USD. The operation consumes electricity for the 1 HP ring blower and 1 HP water pump, both operated at around 50% capacity. Daily electricity cost is estimated to be around 1.8 USD for 18 kWh electricity. The cost is equivalent to USD 10 for 1,000 m<sup>3</sup> of the biogas. The cost is around 3.3% of USD 300 for 1,000 m<sup>3</sup> biogas cost.

This study presents only experimental data and discusses some influencing factors on the H<sub>2</sub>S removal from the biogas. Based on the data, theoretical analyses should be done in further studies to show quantitatively the influence of the key affecting factors on the H<sub>2</sub>S removal. In addition, H<sub>2</sub>S in the biogas from digesters for swine wastes were reported to be as high as 5,000 ppm (Su *et al.*, 2014). Further studies should account for the high H<sub>2</sub>S concentrations in some biogases.

### **CONCLUSIONS**

The results revealed that H<sub>2</sub>S in an anaerobic digester gas can be effectively removed by directly sparging it into a tank that is filled with liquid to a depth of 0.8–1 m. The liquid was obtained from an aerobic pond to treat the effluent from the digester of a dairy wastewater treatment plant. With an influent liquid of pH 7.5–7.7, a flow rate of 23–25 L min<sup>-1</sup>, influent biogas flow rates of 0.050–0.200 m<sup>3</sup> min<sup>-1</sup>, and a H<sub>2</sub>S concentration of 907 ± 212 ppm, the pH of the effluent liquid stabilized at 6.6–6.9. The operation conditions were as follows: gas/liquid ratio of 2–8 m<sup>3</sup> m<sup>-3</sup> liquid), volumetric gassing intensities of 0.04–0.20 m<sup>3</sup> m<sup>-3</sup> liquid min<sup>-1</sup>), and an average tank liquid volume of 1.25 m<sup>3</sup>. Average H<sub>2</sub>S REs of 86.4%, 82.5%, 74.4%, and 70.6% were obtained at influent biogas rates of 0.050, 0.100, 0.150, and 0.200 m<sup>3</sup> min<sup>-1</sup>, respectively. Data indicate that increasing the pH of the scrubbing liquid improved the H<sub>2</sub>S removal efficiency from biogas. CO<sub>2</sub> absorption into the scrubbing liquid caused a decrease in the pH, thus decreasing the H<sub>2</sub>S removal efficiency.

## ACKNOWLEDGMENTS

The authors would like to thank the Livestock Research Institute, Council of Agriculture, Executive Yuan of Taiwan, R.O.C. for financially supporting this research under Contract No 107AS-2.4.1-LI-L2.

## REFERENCES

- Amano, Y., Hirano, T., Kurosawa, H. and Nakamura, K. (1999). Simultaneous removal of hydrogen sulfide and triethylamine by a bacterial deodorant. *J. Ferment. Bioeng.* 81: 337–342.
- American Public Health Association (APHA) (1989). *Standard Methods for Examination of Water and Wastewater*. 17<sup>th</sup> Edition, American Public Health Association, Washington DC.
- Bellová, R., Melicherčíková D. and Tomčík P. (2016). Calculation of conditional equilibrium in serial multiple precipitation of metal sulfides with hydrogen sulfide stream generated from sodium sulfide: A didactic tool for chemistry teaching. *Quim. Nova* 39: 765–769.
- Beristain-Cardoso, R., Texier, A.C., Sierra, S.Á., Field, J. A., Elías RF. and Gómez, J. (2008). Simultaneous sulfide and acetate oxidation under denitrifying conditions using an inverse fluidized bed reactor. *J. Chem. Technol. Biotechnol.* 83: 1197–1203.
- Bielefeldt, A.R. and Stensel, H.D. (1999). Treating VOC-contaminated gases in activated sludge: Mechanistic model to evaluate design and performance. *Environ. Sci. Technol.* 33: 3234–3240.
- Chou, M.S., Perng, C.H., Li, T.H. and Chen, J.Y. (2010). Biooxidation of gaseous hydrogen sulfide in an activated sludge aeration tank. *J. Environ. Eng. Manage.* 20: 57–62.
- Cline J.D. and Richards F.A. (1969). Oxygenation of hydrogen sulfide in seawater at constant salinity, temperature and pH. *Environ. Sci. Technol.* 3: 838–843.
- Gadre, R.V. (1989). Removal of hydrogen sulfide from biogas by chemoautotrophic fixed-film bioreactor. *Biotechnol. Bioeng.* 34: 410–414.
- González-Sánchez, A. and Revah, S. (2007). The effect of chemical oxidation on the biological sulfide oxidation by an alkaliphilic sulfoxidizing bacterial consortium. *Enzyme Microb. Technol.* 40: 292–298.
- Hagen, M., Polman, E., Myken, A., Jensen, J., Jönsson, O. and Dahl, A. (2001). Adding gas from biomass to the gas grid. Final Report Contract ENS-51161/99-0034; ALTENER-XVII/4.1030/Z/99-412, Denmark.
- Huang, Y., Su, W., Wang, R. and Zhao, T. (2019). Removal of typical industrial gaseous pollutants: from carbon, zeolite, and metal-organic frameworks to molecularly imprinted adsorbents. *Aerosol Air Qual. Res.* 19: 2130–2150.
- Jensen, A.B. and Webb, C. (1995). Treatment of H<sub>2</sub>S containing gases: A review of microbiological alternatives. *Enzyme Micro. Technol.* 1: 2–10.
- Jiang, N., Dong, Z., Xu, Y., Yu, F., Yin, S., Zhang, R. and Tang, X. (2018). Characterization of PM<sub>10</sub> and PM<sub>2.5</sub> source profiles of fugitive dust in Zhengzhou, China. *Aerosol Air Qual. Res.* 18: 314–329.
- Jiang, X., Yan, R. and Tay, J.H. (2009). Simultaneous autotrophic biodegradation of H<sub>2</sub>S and NH<sub>3</sub> in a biotrickling filter. *Chemosphere* 75: 1350–1355.
- Jorgensen, B.A. (1990). Thiosulfate shunt in the sulfur cycle of marine sediments. *Science* 249: 152–154.
- Khoshnevisan, B., Tsapekos, P., Alfaro, N., Díaz, I., Fdz-Polanco, M., Rafiee, S. and Angelidaki, I. (2017). A review on prospects and challenges of biological H<sub>2</sub>S removal from biogas with focus on biotrickling filtration and microaerobic desulfurization. *Biofuel Res. J.* 16: 741–750.
- Krischan, J., Makaruk, A. and Harasek, M. (2010). Design and scale-up of an oxidative scrubbing process for selective removal of hydrogen sulfide from biogas. *J. Hazard. Mater.* 49: 215–216.
- Li, P., Sato, K., Hasegawa, H., Huo, M., Minoura, H., Inomata, Y., Take, N., Yuba, A., Futami, M., Takahashi, T. and Kotake, Y. (2018a). Chemical characteristics and source apportionment of PM<sub>2.5</sub> and long-range transport from Northeast Asia Continent to Niigata in Eastern Japan. *Aerosol Air Qual. Res.* 18: 938–956.
- Li, Y.C., Shu, M., Ho, S.S.H., Yu, J.Z., Yuan, Z.B., Liu, Z.F., Wang, X.X. and Zhao, X.Q. (2018b). Effects of chemical composition of PM<sub>2.5</sub> on visibility in a Semi-Rural City of Sichuan Basin. *Aerosol Air Qual. Res.* 18: 957–968.
- Liang, M.S. and Liang, Y. (2013). Biological removal of H<sub>2</sub>S from the livestock manure using a biofilter. *Biotechnol. Bioprocess Eng.* 18: 1008–1015.
- Lien, C.C., Lin, J.L. and Tin, C.H. (2014). Water scrubbing for removal of hydrogen sulfide [H<sub>2</sub>S] in biogas from hog farms. *J. Agri. Chem. Environ.* 3: 1–6.
- Lin, W.C., Chen, Y.P. and Tseng C.P. (2013). Pilot-scale chemical-biological system for efficient H<sub>2</sub>S removal from biogas. *Bioresour. Technol.* 135: 283–291.
- Liu, X. and Wang, R. (2017). An innovative approach to oxidative removal of hydrogen sulfide using the solution of peroxy heteropolyacid. *Aerosol Air Qual. Res.* 17: 1341–1346.
- Liu, X. and Wang, R. (2019). Study on macro kinetics of the desulfurization processes of heteropoly compounds in ionic liquids and aqueous solutions. *Aerosol Air Qual. Res.* 19: 2899–2907.
- Mao, J., Ma, Y., Zang, L., Xue, R., Cong Xiao, C. and Ji, D. (2020). Efficient adsorption of hydrogen sulfide at room temperature using fumed silica-supported deep eutectic solvents. *Aerosol Air Qual. Res.* 20: 203–215.
- Muñoz, R., Meier, L., Diaz, I. and Jeison, D. (2015). A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading. *Rev. Environ. Sci. Biotechnol.* 14: 727–759.
- Nishimura, S. and Motoyuki, Y. (1997). Removal of hydrogen sulfide from an anaerobic biogas using a bio-scrubber. *Water Sci. Technol.* 36: 349–356.
- Nitta, M. and Hirura, H. (1993). Biofiltration system for gas-deodorizing. *J. Bioeng.* 3: 29–33.
- Pei, X. and Wang, R. (2019). Desulfurization performance

- of rare earth mono-substituted heteropoly compounds. *Aerosol Air Qual. Res.* 19: 2888–2898.
- Pipatmanomai, S., Kaewluan, S. and Vitidsant, T. (2009). Economic assessment of biogas-to-electricity generation system with H<sub>2</sub>S removal by activated carbon in small pig farm. *Appl. Energy* 86: 669–674.
- Pokorná, L., Bartacek, J., Díaz, I., Jeison, D., Volcke., E. and Jenicek P. (2015). Microaeration for hydrogen sulfide removal during anaerobic treatment: A review. *Rev. Environ. Sci. Biotechnol.* 14: 703–725.
- Potivichayanon, S., Pokethitiyook, P. and Kruatrachue. M. (2006). Hydrogen sulfide removal by a novel fixed-film bioscrubber system. *Process Biochem.* 41: 708–715.
- Recebli, Z., Selimli, S., Ozkaymak, M. and Gonc, O. (2015). Biogas production from animal manure. *J. Energy Sci. Technol.* 10: 722–729.
- Seadi, T.A., Rutz, D., Prassl, H., Köttner, M., Finsterwalder, T., Volk, S. and Janssen, R. (2008). Biogas handbook, University of Southern Denmark Esbjerg, Niels Bohrs Vej 9-10, DK-6700 Esbjerg, Denmark 41.
- Shimko, I.G., Spasov, V.A., Chinennaya, S.K., Zakirova, R.I., Tananina, I.N., Perchugov, Y.G. and Pavlova, O.I. (1987). Biochemical methods of freeing gas-air mixtures from sulfur containing compounds, Translated from *Khimicheskie Volokna* 6: 7–10.
- Smith, S.A. and Ndegwa, P.M. (2012). Hydrogen sulfide concentrations in biogas from dairy manure digesters. In *Department of Ecology Report to the Legislature: Dairy Manure Anaerobic Digesters*, Newman, A. (Ed.), Air Quality Program Washington State Department of Ecology, Olympia, Washington, USA.
- Solcia, R.B., Ramíez, M., Fernández, M., Cantero, D. and Bevilaqua, D. (2014). Hydrogen sulphide removal from air by biotrickling filter using open-pore polyurethane foam as a carrier. *Biochem. Engrg. J.* 84: 1–8.
- Su, J.J., Chang, Y.C., Chen, Y.J., Chang, K.C. and Lee S.Y. (2013). Hydrogen sulfide removal from livestock biogas by a farm-scale bio-filter desulfurization system. *Water Sci. Technol.* 67: 1288–1293.
- Su, J.J., Chen, Y.J. and Chang, Y.C. (2014). A study of a pilot-scale biogas bio-filter system for utilization on pig farms. *J. Agri. Sci.* 152: 217–224.
- Sublette, K.L., Hesketh, R.P. and Hasan, S. (1994). Microbial oxidation of hydrogen sulfide in a pilot-scale bubble column. *Biotechnol. Progr.* 10: 611–614.
- Sun, J., Zhou, J., Shang, C. and Kikkert, G.A. (2014). Removal of aqueous hydrogen sulfide by granular ferric hydroxide-kinetics, capacity and reuse. *Chemosphere* 117: 324–329.
- Syed, M., Soreanu, G., Falletta, P. and Béland, M. (2006). Removal of hydrogen sulfide from gas streams using biological processes - A review. *Can. Biosyst. Eng.* 48: 2.1–2.14.
- Tilahun, E., Bayrakdar, A., Sahinkaya, E. and Çalli, B. (2017). Performance of polydimethylsiloxane membrane contactor process for selective hydrogen sulfide removal from biogas, *Waste Manage.* 61: 250–257.
- Tilahun, E., Sahinkaya, E. and Çalli, B. (2018). A hybrid membrane gas absorption and bio-oxidation process for the removal of hydrogen sulfide from biogas. *Int. Biodeterior. Biodegrad.* 127: 69–76.
- Truong, L.V.A. and Abatzoglou, N. (2005). A H<sub>2</sub>S reactive adsorption process for the purification of biogas prior to its use as a bioenergy vector. *Biomass Bioenergy* 29: 142–151.
- Tseng, Y.L., Yuan, C.S., Bagtasa, G., Chuang, H.L. and Li, T.C. (2019). Inter-correlation of chemical compositions, transport routes, and source apportionment results of atmospheric PM<sub>2.5</sub> in Southern Taiwan and the Northern Philippines. *Aerosol Air Qual. Res.* 19: 2645–2661.
- Widiana, D.R., Wang, Y.F., You, S.J., Yang, H.H., Wang, L.C., Tsai, J.H. and Chen, H.M. (2019). Air pollution profiles and health risk assessment of ambient volatile organic compounds above a municipal wastewater treatment plant, Taiwan. *Aerosol Air Qual. Res.* 19: 375–382.
- Yang, Y. and Allen, E.R. (1994). Biofiltering control of hydrogen sulfide 1. Design and operational parameters. *J. Air Waste Manage. Assoc.* 44: 863–868.
- Zhang, L., Schryver, P.D., Gussemme, B.D., Muynck, W.D., Boon, N. and Verstraete, W. (2008). Chemical and biological technologies for hydrogen sulfide emission control in sewer systems: A review. *Water Res.* 42: 1–12.
- Zhang, Y.B., Wang, Y.L., Li, W.H., Bao, L.N., Wang, L.H., Huang, X.H. and Huang, B. (2018). Biogas emission from an anaerobic reactor. *Aerosol Air Qual. Res.* 18: 1493–1502.

Received for review, December 27, 2019

Revised, February 17, 2020

Accepted, February 17, 2020