Hydrogen sulfide removal from livestock biogas by a farm-scale bio-filter desulfurization system

J.-J. Su, Y.-C. Chang, Y.-J. Chen, K.-C. Chang and S.-Y. Lee

ABSTRACT

A farm-scale biogas desulfurization system was designed and tested for H₂S removal efficiency from livestock biogas. This work assesses the H₂S removal efficiency of a novel farm-scale biogas bio-desulfurization system (BBS) operated for 350 days on a 1,000-head pig farm. Experimental data demonstrated that suitable humidity and temperature can help sulfur-oxidizing bacteria to form active bio-films on the bio-carriers. The daily average removal rate increased to 879.16 from 337.75 g-H₂S/d with an average inlet H₂S concentration of 4,691 ± 1,532 mg/m³ in biogas. Thus, the overall (0–350 days) average H₂S removal efficiency exceeded 93%. The proposed BBS overcomes limitations of H₂S in biogas when utilizing pig farm biogas for power generation and other applications.

Key words | bio-desulfurization, biogas, hydrogen sulfide, piggery wastewater, sulfur oxidizers

INTRODUCTION

Anaerobic digestion of animal manure and other wastes produces H₂S in biogas of 2,800–8,400 mg/m³ (Syed et al. 2006). Biogas produced by anaerobic digestion of piggery wastewater mainly contains 60.06–76.95% CH₄ and 18.21–26.71% CO₂ (Su et al. 2005). Most industrial factories use a conventional water scrubber system to remove H₂S from biogas. A water scrubber system requires considerable amounts of water and electricity to dissolve H₂S in water, thereby increasing operating costs but making the reduction of H₂S in biogas feasible.

Certain photoautotrophic and chemotrophic bacteria immobilized in bioreactors remove H₂S from gas streams (H₂S → S⁰ → SO₄²⁻) (Kantachote et al. 2008). The five most effective microbiological devices developed to remove H₂S from gas streams are the gas-fed batch reactor, the continuous stir-tank reactor (CSTR), the bio-scrubber, the bio-filter, and the bio-trickling filter (Syed et al. 2006). Both the gas-fed batch reactor and the CSTR for H₂S removal require electricity consumption for oxygen supply, continuously stirred liquid, and lighting (Janssen et al. 1995; Basu et al. 1996; Kim et al. 1996).

Both the bio-scrubber system (fixed film) and the bio-trickling system for H₂S removal still require electricity consumption for recycling liquid and replacing fresh liquid (Moosavi et al. 2005; Potivichayanon et al. 2005). Hydrogen sulfide (20–6,500 mg/m³) removal efficiency is reported to achieve 85–99% using either a pilot- or bench-scale bio-trickling filter (Moosavi et al. 2005). Either pilot- or bench-scale bio-filters are used to treat H₂S (5.2–1,300 mg/m³) in biogas and achieve H₂S removal efficiency of 29.7–100% with various bio-carriers (Moosavi et al. 2005). Notably, no bio-filter in these studies was farm-scale.

A bio-filter is a three phase bioreactor (gas, liquid, and solid) with a filter bed that has a high porosity, buffer capacity, nutrient availability, and moisture retention capacity to ensure that the target bacteria can grow on it. The novelty of this work is to develop a high efficiency and cost-effective farm-scale biogas bio-desulfurization system (BBS) without recirculating and aerating flushing liquid. This work evaluates the H₂S removal efficiency of the BBS operated on a 1,000-head pig farm for 350 days. The optimal operating parameters for efficient H₂S removal from biogas are identified.

MATERIALS AND METHODS

Novel bio-carriers for the proposed BBS

All microorganisms for this work were isolated from a pre-pilot-scale bio-filter reactor (Su et al. 2008). The main bio-carriers were light-expanded clay aggregates (LECAs) and small Rasching rings (i.e. hollow spherical polypropylene balls) (Sheng-Fa Plastics, Inc., Taiwan). The LECA has a porous
matrix that can immobilize bacteria on the surface and inside the matrix. Notably, the LECA is resistant to low pH.

The farm-scale BBS

Structure and operation of the BBS

The farm-scale BBS was installed and operated on a 1,000-head pig farm, the Yuo-Shun Pig Farm, Taiwan. The BBS comprised: (1) a bio-filter (50.8 cm i.d. × 360 cm H), (2) humidifier (30.48 cm i.d. × 70 cm H), (3) absorption cylinder (40.6 cm i.d. × 100 cm H), and (4) sulfur settlement basin (100 cm × 40 cm × 60 cm) (L × W × H) (Figure 1). The bio-filter unit was assembled using three identical polypropylene columns (50.8 cm i.d. × 100 cm H each) (total working volume = 730 L) packed with bio-carriers (608 L); initial biogas flow rate was 50 L/min. Moreover, a 51-L humidifier containing 23 L clean tap water was installed, followed by the BBS to ensure that the humidity of biogas entering the BBS was ≥85%.

The inocula liquid (360 L) contained sludge (282 L), pond water (72 L), mud (100 g), and a sulfur-oxidizing bacterial suspension (6 L) as inocula for the bio-filter. The inocula liquid was re-circulated throughout the packed bio-filter by pumping the suspension via a 1/4 hp pump (TECO Co., Taiwan) from settlement basins for inoculation and then back to the settlement basins; this cycle was repeated for 24 h. The average temperature inside the bio-filter was maintained at 25–30°C. The biogas, after biosulfurization, was stored in bags for subsequent use. Activated sludge was added monthly (480 L/month) to the bio-filter. Piggery effluent from a piggery wastewater treatment facility was utilized to flush the bio-carriers three times a week (480 L/time) for providing nutrients to microbes on bio-carrier surfaces.

Inlet and outlet H$_2$S were determined using H$_2$S detector tubes; H$_2$S removal efficiency was then calculated. Inlet temperature, outlet temperature, and relative humidity were recorded simultaneously. However, outlet biogas temperature was determined after the air pump resulting in higher biogas temperature than that of ambient atmosphere. Three liquid samples from the bio-filter were subjected to ion chromatography (IC) analysis. The liquid samples were (1) effluent (treated wastewater discharged from a wastewater treatment system), (2) flushing water (effluent containing sulfur and other residues flushed out of the bio-filter), and (3) dropping water (condensed water dropping from bio-carriers with bio-films attached inside the bio-filter).

Novel operation mode by introducing adequate amount of oxygen to the BBS

A 1/2 hp air pump (TECO Co., Taiwan) was installed at the bio-filter outlet to withdraw biogas from biogas storage bags.
(83.4 m³), and introduce the biogas into the bio-filter through a flow meter (Tohama 10B; Yeong Shin Co. Ltd, Taiwan), humidifier, and bio-filter before withdrawing the biogas using an air pump. Oxygen was essential for growing sulfur-oxidizing bacteria in the BBS through an annulus gap in the connector of a biogas inlet pipeline by removing just an O-ring from the connector. The oxygen concentration was measured from the outlet biogas flow by a portable multi-gas leak detector (Resolution = 0.1%) (MX6 iBRID, Industrial Scientific Co., USA). The BBS operation was automatically controlled by a programmable logic controller (PLC) module.

Analysis

Analysis of CH₄, CO₂, and N₂ in biogas

Gas samples were analyzed for CH₄, CO₂, and N₂ by gas chromatography with a thermal conductivity detector (GC/TCD) (Perkin-Elmer, USA) (Su et al. 2005, 2008).

Analysis of liquid samples

Liquid samples were filtered and the filtrates were analyzed by IC (Metrohm ion analysis; Metrohm Ltd., Switzerland) (Su et al. 2008). Liquid samples were analyzed for chemical oxygen demand (COD), biochemical oxygen demand (BOD), and suspended solids (SS) concentrations using Standard Methods (APHA 1998).

Determining H₂S, temperature, and relative humidity of biogas

Inlet and outlet H₂S were determined using detector tubes (Gastec Co., Japan) and a gas sampling pump (GV-100C; Gastec Co., Japan) (detection range of 0–61,560 mg/m³). A portable electronic H₂S detector was used to complement H₂S measurements for outlet biogas (PortaSens II, Analytical Technology, Inc., USA) (accuracy, ±5%; sensitivity, 1% of sensor module range). Inlet and outlet temperatures and relative humidity were determined simultaneously by thermal/humidity meters (TES-1364; TES Electrical Co., Taiwan).

Determining sulfur in flushing water samples

Sulfur in samples was extracted by the methods of Hurse & Abeydeera (2002) and analyzed by high-performance liquid chromatography (HPLC) (Hitachi, Japan) (Rethmeier et al. 1997; McGuire & Hamers 2000).

Statistical analysis

Experimental data for different samples were analyzed using the analysis of variance (ANOVA) procedure in SAS (SAS 1992). When ANOVA identified a significant effect, differences among experimental data groups were tested using Duncan’s new multiple range test (Snedecor & Cochran 1980).

RESULTS AND DISCUSSION

Hydrogen sulfide removal by the BBS

Overall (0–350 days) average H₂S, in the inlet and outlet biogas streams, was 4,691 ± 1,532 mg/m³ (1,231–8,465 mg/m³) and 320 ± 750 mg/m³ (0–4,001 mg/m³), respectively (Figure 2). Pig farmers normally add methionine and cystine to feed, which may explain high H₂S in the biogas. Variations in inlet and outlet H₂S concentrations were due to anaerobic digestion of sulfur-containing amino acids and unstable bio-desulfurization of biogas by the biofilm in the start period.

The start period of the BBS was at least 30 days under humidity ≥90% and mesophilic conditions for enrichment of biofilm. Elemental sulfur and sulfate were formed by microbial sulfide oxidation when bio-film was proliferated on the bio-carriers. The start period (the first 21–30 days) comprised the enrichment of sulfur-oxidizing bacteria on the bio-carriers. Operating results indicate that average

![Figure 2](https://iwaponline.com/wst/article-pdf/67/6/1288/440750/1288.pdf)
H₂S in inlet and outlet biogas was 4,312.00 ± 725.37 mg/m³ (3,560–5,600 mg/m³) and 758.80 ± 870.90 mg/m³ (0–2,520 mg/m³), respectively; the H₂S removal efficiency was 83.35 ± 18.61% (50–100%).

In the pre-mature period (days 35–46), average H₂S in the inlet and outlet biogas was 3,795.55 ± 1,015.76 mg/m³ (1,680–5,600 mg/m³) and 134.30 ± 220.35 mg/m³ (0–700 mg/m³), respectively; the H₂S removal efficiency was 96.30 ± 6.64% (75–100%). During the stable operation period (days 47–350), H₂S removal ranged from 96.71 ± 18.61% to 98.48 ± 3.32 under mesophilic conditions (20–37°C). Daily maximum biogas treatment volume increased to 187.2 from 72 m³ when the biogas flow rate was increased to 150 from 50 L/min after 280 days; average H₂S removal efficiency still exceeded 95%. The overall average H₂S removal from biogas was 93.16 ± 15.61% (7.7–100%).

**Bio-film formation and humidity build-up**

Piggery effluent was pumped into the packed bio-filter with dried bio-carriers and re-circulated for 24 h to increase bio-carrier humidity prior to inoculation. Dried LECA beads absorb large amounts of effluent inside the BBS and then highly water content LECA beads can facilitate bio-film formation. The bio-film formation period was at least 35 days under adequate humidity and mesophilic conditions. Mature bio-film formation was achieved when low pH of dropping water samples was detected. Overall (0–350 days) average humidity of inlet and outlet biogas and that of the ambient atmosphere was 92.89 ± 8.85% (66.5–99.9%), 96.27 ± 6.55% (61.6–99.9%), and 76.05 ± 14.43% (41.4–99.9%), respectively. Average humidity of inlet and outlet biogas and that of the ambient atmosphere was 84.74 ± 6.27% (74.4–94.5%), 89.64 ± 10.87% (69.5–99.9%), and 70.71 ± 15.12% (44.5–96.9%) during days 21–34, respectively (Table 1).

During the pre-mature period (days 35–46), average humidity of the ambient atmosphere was 68.17 ± 13.33% (43.7–96.3%), and average humidity of the inlet and outlet biogas was 86.04 ± 10.07% (66.5–99.9%) and 91.17 ± 9.31% (61.6–99.9%), respectively. During days 47–78, average humidity of the ambient atmosphere was 69.18 ± 14.30% (43.7–96.3%), and average humidity of inlet and outlet biogas was 84.57 ± 11.06% (66.5–99.9%) and 95.24 ± 7.18% (81.2–99.9%), respectively (Table 1). When biogas humidity exceeded 85%, bio-films were easily formed on the bio-carrier with higher bio-film activity. Thus, H₂S removal efficiency increased as bio-film activity increased. One of the biofilm scanning electron microscope (SEM) photos on the surface of LECA inside the bio-filter after 350 days is shown in Figure 3.

### Biogas temperature and H₂S removal efficiency

Overall (0–350 days) average temperature of inlet and outlet biogas was 29.46 ± 7.17°C (11.5–43.2°C) and 33.73 ± 8.27°C (14.6–48.2°C), respectively, and average ambient atmosphere temperature was 27.63 ± 6.24°C (12.7–41.9°C) (Table 1). During days 21–34, average temperature of inlet and outlet biogas and that of the ambient atmosphere was 31.51 ± 3.72°C (26.6–36.1°C), 39.31 ± 4.30°C (32.8–45.5°C) and 28.66 ± 2.12°C (25.2–31.1°C), respectively.

During days 35–46, average temperature of inlet and outlet biogas and that of the ambient atmosphere was 29.20 ± 5.16°C (19.2–34.3°C) and 33.56 ± 5.35°C (23.8–47.2°C) and 26.22 ± 2.85°C (19.2–33.2°C), respectively. During days 47–78, average temperature of inlet and outlet biogas and that of the ambient atmosphere was 29.80 ± 5.57°C (18.7–38.5°C), 35.56 ± 4.97°C (23.8–40.6°C) and 25.95 ± 3.25°C (19.2–33.2°C), respectively. Both adequate humidity and mesophilic conditions were also essential for maintaining activity of bio-film.

### Sulfur oxidation by the BBS

Analytical data demonstrate that average amounts of CH₄, CO₂, and N₂ in inlet biogas were 60.6 ± 1.6%, 35.0 ± 1.4%,

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Comparison of hydrogen sulfide removal efficiency at different outlet biogas temperatures and humidity percentages</th>
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</thead>
<tbody>
<tr>
<td>Operation (Days)</td>
<td>H₂S removal (%)</td>
</tr>
<tr>
<td>21–34</td>
<td>83.33 ± 18.61 (50–100)</td>
</tr>
<tr>
<td>35–46</td>
<td>96.30 ± 6.64 (75–100)</td>
</tr>
<tr>
<td>47–78</td>
<td>96.71 ± 6.89 (75–100)</td>
</tr>
<tr>
<td>78–204</td>
<td>98.48 ± 3.32 (84.6–100)</td>
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<tr>
<td>205–350</td>
<td>97.77 ± 5.53 (78.6–100)</td>
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*Data are mean ± SD.*
and 4.4 ± 1.5%, respectively; however, average amounts of CH₄, CO₂, and N₂ in outlet biogas were lower at 44.7 ± 4.8%, 27.0 ± 0.7%, and 28.3 ± 5.3%, respectively (Table 2). Roughly 5–10% air must be introduced into the bio-desulfurization unit for operation (Özmen & Aslanzadeh 2009). The oxygen (4–10%) was adequate for efficient H₂S removal in the stable operation period, with biogas flow rates of 50–130 L/min (winter through summer). Notably, all CH₄ in the inlet or outlet biogas exceeded 60% (Table 2).

To maintain stable operation activity of the BBS, piggery effluent was used to flush bio-carriers inside the bio-filter once a week. All dropping water (0.5–2.0 L/wk), flushing water, and effluent samples were collected from the BBS and analyzed by ion chromatography and pH meters periodically. Dropping water samples were obtained from the bottom of the bio-filter; dropping water formed by water vapor condensation inside the bio-filter. The pH value of dropping water, flushing water, and effluent was 1.54 ± 0.17, 2.25 ± 0.84, and 8.09 ± 0.18, respectively (p < 0.01). The average SO₄²⁻ in dropping water, flushing water, and effluent was 27,086 ± 3,956, 5,704 ± 2,701, and 67.03 ± 16.68 mg/L, respectively (p < 0.01). Further, average NH₄⁺ in dropping water, flushing water, and effluent was 1,412 ± 488.4, 693.4 ± 359.8, and 1,096.8 ± 86.3 mg/L, respectively (p < 0.05) by IC analysis. Average NO₃⁻ in dropping water, flushing water, and effluent differed significantly (p < 0.05).

The pH of dropping water, flushing water, and effluent was inversely proportional to average sulfate concentration. The high COD in dropping water samples resulted from high NO₃⁻ and SO₄²⁻ concentrations. Average SO₄²⁻ in dropping water samples (27,086 ± 3,956 mg/L) was roughly 4.7 times that in flushing water samples (5,704 ± 2,701 mg/L), likely resulting in COD in dropping water samples (1,456.00 ± 68.43 mg/L) roughly 4.5 times those in flushing water samples (322.01 ± 39.51 mg/L). Although large amounts of SS in flushing water samples were mostly from sulfur, the amount of sulfur did not increase the BOD in flushing water samples.

Average COD in dropping water, flushing water, and effluent was 1,456.00 ± 68.43, 322.01 ± 39.51, and 193.74 ± 57.30 mg/L, respectively (p < 0.01). Average BOD in dropping water, flushing water, and effluent was 102.17 ± 46.27, 139.14 ± 59.98, and 143.7 ± 42.24 mg/L, respectively (p < 0.05); additionally, average SS in dropping water, flushing water, and effluent was 90.07 ± 23.42, 1,279.33 ± 458.60, and 123.49 ± 72.27 mg/L, respectively (p < 0.01). Average sulfur in flushing water samples was 0.239 ± 0.008–0.357 ± 0.021 mol/L (recovery 78–85%) by HPLC. Large amounts of SS in flushing water samples was due to higher sulfur content in flushing water samples than the other samples.

A bio-scrubber composed of a gas/liquid contact tower and an aeration tank was used to remove 2,800 mg/m³ H₂S in the biogas from anaerobic digestion of potato processing wastewater (Nishimura & Yoda 1997). For full-scale operation, the H₂S removal efficiency in biogas (inlet H₂S = 7,000 mg/m³) exceeded 90% by the ‘BIO-Sulfex’ bio-filter (Schieder et al. 2005). The ‘BIO-Sulfex’ system requires extra electricity for recirculating and aerating flushing liquid to remove H₂S in the biogas. Notably, in this work, the average H₂S in the inlet biogas streams was 4,691 ± 1,532 mg/m³ (1,231–8,465 mg/m³) and H₂S removal efficiency was 95–100% by only one BBS module without recirculating and aerating flushing liquid.

In summary, the proposed BBS requires only a humidifier and bio-filter to remove H₂S from biogas, and sulfur can be recycled. Sulfur-oxidizing bacteria formed stable
bio-films on bio-carrier surfaces when dropping water samples had a pH < 2 (i.e. H\textsubscript{2}S $\rightarrow$ SO\textsubscript{4}\textsuperscript{2-}). Elemental sulfur formed in the BBS of this work was automatically flushed with piggy effluent periodically.

**CONCLUSIONS**

Farm test results demonstrate that the proposed BBS removes H\textsubscript{2}S from biogas efficiently without recirculating and aerating flushing liquid. Biogas flow rate increased to 130 from 50 L/min, i.e. biogas retention time decreased to 5.6 from 14.6 min during the 350-day test. Thus, daily average removal rate increased to 879.16 from 337.75 g with an average inlet H\textsubscript{2}S concentration in biogas of 4,691 $\pm$ 1,532 mg/m\textsuperscript{3} (1,231–8,465 mg/m\textsuperscript{3}). The overall average H\textsubscript{2}S removal efficiency exceeded 95%. The novelty of this work is to develop a simply operated and economical farm-scale BBS for promoting green livestock farming.

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