

Effect of pH on the performance of an acidic biotrickling filter for simultaneous removal of H₂S and siloxane from biogas

Yuyao Zhang, Kazuyuki Oshita , Masaki Takaoka , Yu Kawasaki, Daisuke Minami, Go Inoue and Toshihiro Tanaka

ABSTRACT

Acidic biotrickling filters (BTF) can be used for simultaneous removal of hydrogen sulfide (H₂S) and siloxane from biogas. In this study, the performance of a BTF under different acidic pH conditions was investigated. The removal profile of H₂S showed that 90% of H₂S removal was achieved during the first 0.4 m of BTF height with down-flow biogas. Decamethylcyclopentasiloxane (D5) removal decreased from 34.5% to 15.6% when the pH increased from 0.88 to 3.98. Furthermore, the high partition coefficient of D5 obtained in under higher pH condition was attributed to the higher total ionic strength resulting from the addition of sodium hydroxide solution and mineral medium. The linear increase in D5 removal with the mass transfer coefficient (k_L) indicated that the acidic recycling liquid accelerated the mass transfer of D5 in the BTF. Therefore, the lower partition coefficient and higher k_L under acidic pH conditions lead to the efficient removal of D5. However, the highly acidic pH 0.9 blocked mass transfer of H₂S and O₂ gases to the recycling liquid. Low sulfur oxidation activity and low *Acidithiobacillus* sp. content also deteriorated the biodegradation of H₂S. Operating the BTF at pH 1.2 was optimal for simultaneously removing H₂S and siloxane.

Key words | biogas, biotrickling filter, hydrogen sulfide, pH, siloxane

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HIGHLIGHTS

- Effect of pH on the performance of acidic BTF for simultaneous removal of H₂S and siloxane was investigated.
- A linear positive correlation was observed between the mass transfer coefficient and the removal efficiency of D5.
- Evolution in microbial community under various acidic pH conditions was investigated.
- Operating the BTF at pH 1.2 was optimal for simultaneous efficient removal of H₂S and siloxane from biogas.

INTRODUCTION

Biogas from anaerobic digestion of organic compounds is a promising renewable biofuel that can be used to produce heat, steam, electricity, fuel, or for gas-grid injection (Chen

et al. 2015). Apart from methane (CH₄) and carbon dioxide (CO₂), biogas contains trace impurities, such as hydrogen sulfide (H₂S) (50–10,000 ppm_v) (Pipatmanomai *et al.* 2009) and siloxanes (10–400 mg/m³) (Dewil *et al.* 2006; Oshita *et al.* 2010; Raich-Montiu *et al.* 2014; Zhang *et al.* 2020). During biogas combustion, H₂S can corrode engines and metal piping and emit sulfur dioxide (SO₂) (Pipatmanomai

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et al. 2009), while silicon dioxide (SiO₂) crystals formed from trace siloxanes lead to abrasion of turbines or to layers deposition, inhibiting essential heat conduction (Dewil *et al.* 2006). Therefore, strict H₂S and siloxane limits are required for different biogas applications. For example, H₂S is limited to 1–250 ppm_v (Sun *et al.* 2015; Khan *et al.* 2017) and siloxanes to 0.1–30 mg/m³ (Dewil *et al.* 2006; Ryckebosch *et al.* 2011; Arespacochaga *et al.* 2014b; Hepburn *et al.* 2015; Tansel & Surita 2016).

Currently, commercially available methods for the removal of H₂S and siloxanes are applied separately (Appels *et al.* 2008; Calbry-Muzyka *et al.* 2019). These methods include iron-oxide-based materials (Cherosky & Li 2013; Arespacochaga *et al.* 2014b; Cristiano *et al.* 2020) or biological degradation (Arespacochaga *et al.* 2014a; Tu *et al.* 2016) for H₂S abatement, and activated carbon (AC) adsorption (Cabrera-Codony *et al.* 2014, 2018) or biological degradation (Popat & Deshusses 2008; Li *et al.* 2014) for siloxanes. These separate disposal technologies complicate biogas purification and increase installation costs. Hence, developing an integrated biogas purification technology is crucial for increasing the benefits available by combining H₂S and siloxanes abatement technologies. In our previous study, the feasibility of simultaneous removal of H₂S and siloxanes directly from biogas was demonstrated using an acidic biotrickling filter (BTF) (Zhang *et al.* 2020). Unlike pH-neutral BTFs inoculated with *Phyllobacterium myrsinacearum* (Wang *et al.* 2014), *Pseudomonas* sp. (Li *et al.* 2014; Santos-Clotas *et al.* 2019), and *Methylobium* sp. (Boada *et al.* 2020) for biodegrading siloxanes, the degradation of decamethylcyclopentasiloxane (D5) is attributed to hydrolysis promoted by the acidic recycling liquid that results from the biodegradation of H₂S by *Acidithiobacillus* sp. in the acidic BTF (Zhang *et al.* 2020). Cyclic D5 undergoes ring-opening hydrolysis to form linear oligomeric hexamethyltrisiloxane-1,5-diol and tetramethyldisiloxane-1,3-diol and is finally hydrolyzed to dimethylsilanediol. This is a similar degradation pathway to that of octamethylcyclotetrasiloxane (D4) in soil (Xu 1999). Therefore, in aquatic environments and especially under extremely acidic conditions, hydrolysis is considered one of the major degradation pathways of siloxanes.

Furthermore, hydrolysis of polydimethylsiloxane fluids is much faster at pH 2–4 than at pH 6 (Ducom *et al.* 2013). Siloxanes hydrolysis further promotes their mass transfer from biogas to the BTF recycling liquid, implying that operating BTFs at lower pH values should improve siloxanes abatement. Moreover, acidic BTFs were found to lead to specialization of the bacterial community and the

prevalence of *Acidithiobacillus* sp. (Montebello *et al.* 2013; Arespacochaga *et al.* 2014a; Tu *et al.* 2016). However, an extremely acidic pH would deteriorate H₂S biodegradation because high SO₄²⁻ concentrations at low pH are toxic to microorganisms (Jin *et al.* 2005). Furthermore, faster growing *Ferroplasma acidiphilum* displaces *Acidithiobacillus* sp. in highly acidic environments (Zhang *et al.* 2020). In this case, the H₂S is degraded to sulfur, which clogs the packing layer of the BTF. Correspondingly, the gas–liquid mass transfer of siloxanes is blocked, leading to deterioration of their abatement. Therefore, pH is a key parameter that directly effects the operational performance of a BTF, especially for achieving effective removal of H₂S and siloxane simultaneously.

In this study, biogas from anaerobic digestion of sewage sludge was used as the gas feedstock of an acidic BTF to investigate the performance of BTF under five acidic pH conditions. A gas–liquid partition test was also carried out to evaluate the mass transfer coefficients of D5. Furthermore, the microbial community in the BTF under various acidic pH conditions was analyzed and compared to explain the changing performances of the BTF.

MATERIALS AND METHODS

BTF setup and operating conditions

The study was carried out on-site using an experimental BTF that was installed at a wastewater treatment plant with a sewage-treatment capacity of 847,000 m³/day, located in Kyoto, Japan. Biogas from a thermophilic anaerobic digestion tank of thickened primary sludge (maintained at 55°C for 10 days) was fed to the BTF. The biogas production reached 1,200 Nm³/h, and contained H₂S (600–1,100 ppm_v), D5 (15.5–52.8 mg/m³), and D4 (2.3–12.3 mg/m³). The experimental apparatus (Zhang *et al.* 2020) was a polyvinyl chloride column with a 15 cm inner diameter was filled with commercial polypropylene carrier (KG-088-O15; KansaiKako Co., Osaka, Japan) and packed to a height of 1.0 m. The length, particle diameter, and specific surface area of polypropylene carrier were 15 mm, 15 mm, and 960 m²/m³, respectively. The inner temperature of the column was maintained at 30°C using a water heating system.

According to Tu *et al.* (2016), inoculation with *Acidithiobacillus* sp. is an ideal way to reduce the acclimation times of a BTF with a high H₂S-degrading capability. Therefore, start-up of the acidic BTF used 40 L of recycling liquid at pH 1.5 from the nutrient solution tank because it contains

Acidithiobacillus sp. (Zhang *et al.* 2020). The BTF was operated in the down-flow condition. Initially, 40 L of recycling liquid was recirculated at 0.9 L/min along the packing material for 4 h without gas feeding, after which the flow rates of inlet gas was set to 18 L/min. After 2 weeks' acclimation, the recycling liquid had stabilized at pH 0.9 and the variations in the inlet and outlet concentrations of H₂S, D5, and D4 (C_{in,H_2S} ; $in,D5$; $in,D4$ and C_{out,H_2S} ; $out,D5$; $out,D4$) were measured. The corresponding loading rates (LRs), removal efficiency (REs) and elimination capacity (ECs) of H₂S, D5, and D4 ($LR_{H_2S,D5,D4}$, $RE_{H_2S,D5,D4}$ and $EC_{H_2S,D5,D4}$) were calculated based on these measurements and the detailed equations were described in our previous report (Zhang *et al.* 2020). The pH of the recycling liquid was adjusted daily to the set value (Table 1) using sodium hydroxide (NaOH) (Nacalai Tesque Inc., Kyoto, Japan). In addition to the irregular supply of water to the recycling liquid, 20 mL of mineral medium (elemental analysis: N, 6,618; P, 1,032; K, 1,120; Fe, 11.8; Mn, 0.4; Al, 1.0; Na, 25.4; Ca, 6.0; Mg, 9.8; S, 17.8; and B, 0.4 mg/L) was added daily into the nutrient solution tank.

The empty bed residence time (EBRT) is the length of time that gas spends in contact with the inside chamber of the BTF. As shown in Table 1, the EBRT was stable at 60 s through all operational stages in this study. Moreover,

during day 110–111 in stage 4, the acidic BTF was operated under different EBRTs (18–106 s) to investigate the effect of EBRT on the RE_{D5} . On the 110th day, the EBRT was suddenly changed to 106 s from 60 s, and after the stable operation of the BTF for 1 h, the inlet and outlet gas were then sampled for measuring the $C_{in,D5}$ and $C_{out,D5}$. When the EBRT was changed in sequence from 106 s to 66 s, 53 s, 35 s, 27 s, 21 s, and 18 s, the same procedure was performed, i.e. gas sampling after 1 h of stable operation of the BTF. The same changes of EBRT were repeated on the 111th day. NaOH solution was added every hour to maintain the pH of the recycling liquid at 2.73.

Partition tests

Mass transfer limitations are the main challenge to the efficient removal of siloxanes by BTFs (Popat & Deshusses 2008; Li *et al.* 2014; Santos-Clotas *et al.* 2019). A second phase can be used to improve the performance of a BTF for siloxanes abatement, e.g. oleyl alcohol (Popat & Deshusses 2008), biosurfactants (Li *et al.* 2014), and AC (Santos-Clotas *et al.* 2019). Furthermore, the time-dependent dimensionless partition coefficient and mass transfer coefficients (k_L) are two important factors that govern the mass transfer process of siloxanes from biogas to the acidic BTF

Table 1 | Performance data of the BTF as a function of pH

Parameters	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
Period (d)	0–38	39–78	79–104	105–124	125–149
pH (–)	0.9 ± 0.05	1.2 ± 0.1	2.0 ± 0.3	3.0 ± 0.4	4.0 ± 0.2
EBRT (s)	60	60	60	60	60
C_{in,H_2S} (ppm _v)	425 ± 98	400 ± 87	429 ± 86	570 ± 27	436 ± 36
C_{out,H_2S} (ppm _v)	0	0	0	0	0
LR_{H_2S} (g/(m ³ ·h))	18 ± 4	17 ± 4	18 ± 4	24 ± 1	18 ± 2
RE_{H_2S} (%)	100	100	100	100	100
EC_{H_2S} (g/(m ³ ·h))	18 ± 4	17 ± 4	18 ± 4	24 ± 1	18 ± 2
$C_{in,D4}$ (mg/m ³)	3 ± 1	4 ± 2	6 ± 3	3 ± 2	6 ± 2
$C_{out,D4}$ (mg/m ³)	2 ± 0	3 ± 1	5 ± 2	3 ± 0	5 ± 2
EC_{D4} (mg/(m ³ ·h))	47 ± 7	36 ± 9	30 ± 7	17 ± 7	30 ± 12
RE_{D4} (%)	20 ± 13	17 ± 9	11 ± 9	8 ± 4	11 ± 2
$C_{in,D5}$ (mg/m ³)	19 ± 6	20 ± 8	28 ± 8	27 ± 6	27 ± 7
$C_{out,D5}$ (mg/m ³)	14 ± 4	16 ± 6	22 ± 9	23 ± 5	23 ± 8
LR_{D5} (mg/(m ³ ·h))	1,182 ± 367	1,249 ± 512	1,691 ± 514	1,674 ± 396	1,626 ± 430
RE_{D5} (%)	26 ± 19	21 ± 13	18 ± 9	17 ± 3	12 ± 9
EC_{D5} (mg/(m ³ ·h))	316 ± 45	246 ± 20	324 ± 33	289 ± 29	222 ± 41

Note: Values are quoted as means ± standard deviation.

recycling liquid. Hence, partition tests for D5 between the gas and the recycling liquid of the BTF were conducted under different pH conditions according to the protocol reported in our previous study (Zhang *et al.* 2020). Samples of recycling liquids taken from the nutrient solution tank of BTF were directly used as the test liquids in partition tests; the pH of these samples ranged from 0.88 to 3.98 (Table 2). However, the liquid with pH 5.64 was obtained by diluting the recycling liquid with a pH 3.98 with deionized water rather than adding NaOH solution.

The initial D5 concentration in the headspace of 250 mL flasks containing 100 mL of the tested liquid was about 1,000 mg/m³. Several flasks were placed in a water-bath shaker at 30 °C and agitated at 150 times/min. At selected time intervals, the D5 concentrations in the headspace (C_G^*) and the liquid phase (C_L^*) of the flasks were measured and the corresponding gas–liquid partition coefficient of D5 were calculated according to Equation (1). According to the mass transfer model (Popat & Deshusses 2008), the mass transfer rate of D5 across a gas–liquid interface is expressed by Equation (2), which integrates to form Equation (3) as follows:

$$P = \frac{C_G^*}{C_L^*} \quad (1)$$

$$V_G \frac{dC_G}{dt} = -k_L A \left(\frac{C_G}{P} - C_L \right) \quad (2)$$

$$C_G = c \cdot \exp\left(-\frac{k_L A}{V_G P} \cdot t\right) + C_L P \quad (3)$$

where P is the partition coefficient, k_L is the mass transfer coefficient of D5 (m/h), V_G is the volume of the headspace of the flask (150 mL), C_G is the concentration (mg/m³) of D5 in the headspace, C_L is the equilibrium concentration

(mg/m³) of D5 in the liquid phase, c is a constant, and A is the interfacial area for mass transfer in the flasks, which was estimated at 0.005 m².

Extraction and analysis of siloxanes from liquid and gas samples

Siloxanes were extracted from the liquid before gas chromatography-mass spectrometry (GC-MS) analysis to determine their concentrations. First, 100 mL of recycling liquid sample and 50 mL of n-hexane (minimum purity 96%; Kanto Chemical Co. Inc., Tokyo, Japan) were added to a separating funnel, which was then shaken for 5 min. The mixture was treated with 8 g of anhydrous Na₂SO₄ to remove water, and the liquid was transferred to a conical flask and magnetically stirred at 1,000 rpm for 20 min (SR100; Toyo Roshi Kaisha, Ltd, Tokyo, Japan). After the mixture had been centrifuged (3,000 rpm, 3 min), the hexane layer was separated using a disposable pipette. In the case of gas samples, the siloxanes in adsorbents were Soxhlet-extracted with n-hexane for 10 h at 65 °C and then analyzed by GC-MS under the analytical conditions reported by Zhang *et al.* (2020).

High-throughput sequence analysis of the microbial community

The microorganism community in the BTF at pH 1.5 was reported previously (Zhang *et al.* 2020). To better understand the evolution of the microbial community with increasing pH, the recycling liquid with pH 4.0 on day 150 was collected for 16S rRNA gene analysis. The DNA was extracted and purified using an Extrap Soil DNA Kit Plus v. 2 (Nippon Steel, Japan). The V4–V5 hypervariable regions of the 16S rRNA genes were polymerase chain reaction (PCR)-amplified using the universal primers U515F (5'-GTGYCAGCMGCCGCGGTA-3')

Table 2 | Partition coefficient of D5 between gas and liquid phases as a function of pH

Equilibration time (h)	Air-recycling liquid as function of pH							
	0.88	0.94	1.15	1.66	2.51	2.90	3.98	5.64
0.25	2.3 ± 0.1	7.3 ± 2.0	18.4 ± 2.4	29.3 ± 3.7	23.5 ± 7.0	24.8 ± 2.9	6.3 ± 0.3	5.7 ± 0.8
0.5	0.7 ± 0	4.9 ± 0.7	10.4 ± 2.0	22.7 ± 1.5	22.6 ± 7.0	19.8 ± 1.9	5.8 ± 0.3	3.8 ± 1.3
1.0	0.4 ± 0.1	2.9 ± 0.8	5.6 ± 1.0	15.5 ± 2.0	15.7 ± 3.6	14.1 ± 1.1	4.9 ± 0.2	2.9 ± 1.0
2.0	0.2 ± 0.1	2.4 ± 0.6	4.3 ± 0.1	10.6 ± 1.7	7.3 ± 0.8	8.3 ± 0.4	4.4 ± 0.2	2.2 ± 0.7
4.0	0.2 ± 0	1.2 ± 0	2.0 ± 1.2	4.8 ± 0.3	4.6 ± 0.4	6.2 ± 0.3	4.3 ± 0.2	1.9 ± 0.6
16.0	–	0.9 ± 0.1	1.0 ± 0.5	–	–	–	–	–
19.0	–	–	–	4.0 ± 0.2	3.5 ± 0.3	2.8 ± 0.1	3.1 ± 0.1	1.4 ± 0.4

and 926R (5'-CCGYCAATTCMTTTRAGTT-3'). The purified PCR amplicon was quantified using a PicoGreen dsDNA Assay Kit (Invitrogen, USA) and then pair-end sequenced by MiSeq (Illumina, USA).

The sequence data were processed using Quantitative Insights Into Microbial Ecology (QIIME) Pipeline (Caporaso *et al.* 2010). The sample was rarefied to exhibit the lowest number of reads (10,000 sequences) for alpha-diversity analyses, for which the rarefaction curves were generated from the observed species. Sequences were then phylogenetically assigned using the Greengene and Silva's Living Tree Database Project classifiers and allocated to phylum, class, family, and species levels (Zhang *et al.* 2020). Sequences were clustered into operational taxonomic units (OTUs) using a 97% identity threshold. Those OTUs with abundances exceeding 0.1% were selected to compare the microbial communities of the BTFs.

RESULTS AND DISCUSSION

BTF performance as a function of pH

After starting-up successfully at pH 0.9, the BTF was operated continuously under five different acidic conditions (pH 0.9, 1.2, 2.0, 3.0, and 4.0) for 150 days (Figure 1). The mean values of the corresponding parameters are shown in Table 1. The RE_{H₂S} was stable at 100% and the EC_{H₂S} was in the range of 17–24 g/(m³·h) during operating stages 1–5, although C_{in,H₂S} fluctuated within the range of 400–600 ppm_v. Meanwhile, C_{in,D5} and C_{in,D4} maintained levels of 19–28 mg/m³ and 3–6 mg/m³, respectively. The RE_{D5} and EC_{D5} of the BTF at the same LR_{D5} of 1,200 mg/(m³·h) or 1,700 mg/(m³·h) were compared; both showed decreasing trends with increasing pH. Table 1 shows that the RE_{D5} decreased from 26% to 12% as the pH increased from 0.9 to 4.0. Meanwhile, the EC_{D5} decreased from 316 mg/(m³·h) to 246 mg/(m³·h) as the pH increased from 0.9 to 1.2 at the LR_{D5} of 1,200 mg/(m³·h) and decreased from 324 mg/(m³·h) to 222 mg/(m³·h) as the pH increased from 2.0 to 4.0 at the LR_{D5} of 1,700 mg/(m³·h).

Furthermore, the fluctuations in RE_{D5} and EC_{D5} were attributed to changes in LR_{D5} and pH and also to the variation in C_{in,H₂S}. For example, lower C_{in,H₂S} resulted in higher RE_{D5} in the pH 0.9 case (2–14 day) and 1.2 case (39–57 day) (Figure 1). At extremely acidic pH values such as 0.9 and 1.2, the H₂S was mainly biodegraded to S⁰ rather than to SO₄²⁻ due to the prevalence of *F. acidiphilum* (Zhang *et al.* 2020), i.e. deteriorated biodegradation of H₂S

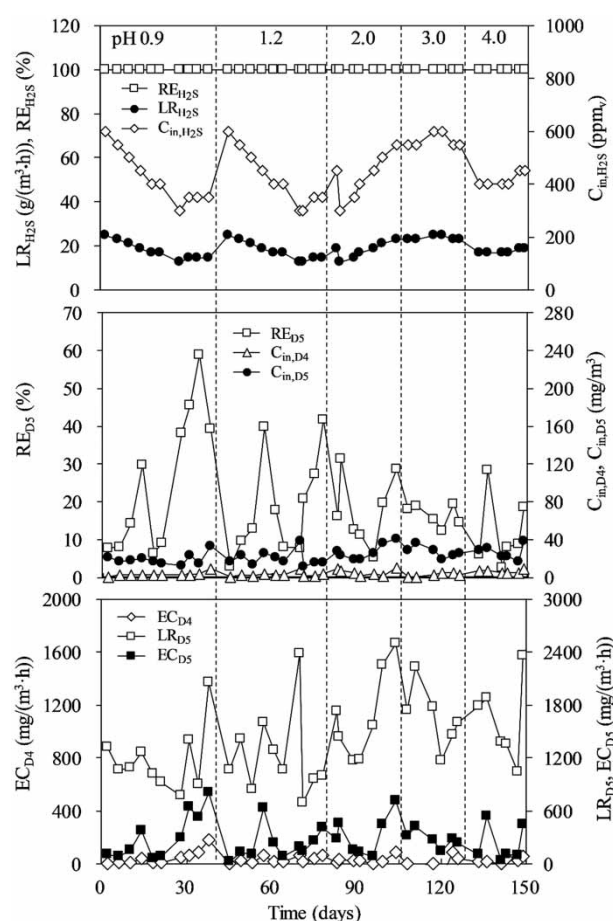


Figure 1 | Performance data of the BTF.

led to sulfur deposition once the H₂S concentration was too high. Sulfur deposition on the packing layer of the BTF blocked the mass transfer of siloxane from the gas to the recycling liquid. Therefore, lower C_{in,H₂S} was beneficial for both H₂S and siloxane abatement using the BTF under extremely acidic pH.

Removal profiles of H₂S

Figure 2 shows the removal profiles of H₂S and the LR_{H₂S} for the BTFs under five acidic pH conditions. The experimental points were the C_{out,H₂S} at different BTF heights and the corresponding RE_{H₂S}. The lines in Figure 2 facilitate interpretation of the data. The C_{out,H₂S} increased and the RE_{H₂S} decreased with increasing LR_{H₂S} for all tested pH conditions. Notably, 90% of the H₂S removal was achieved during the first 0.4 m of the BTF. This observation is consistent with that of Tu *et al.* (2016), who found that H₂S elimination occurred near the gas inlet section of the filter bed.

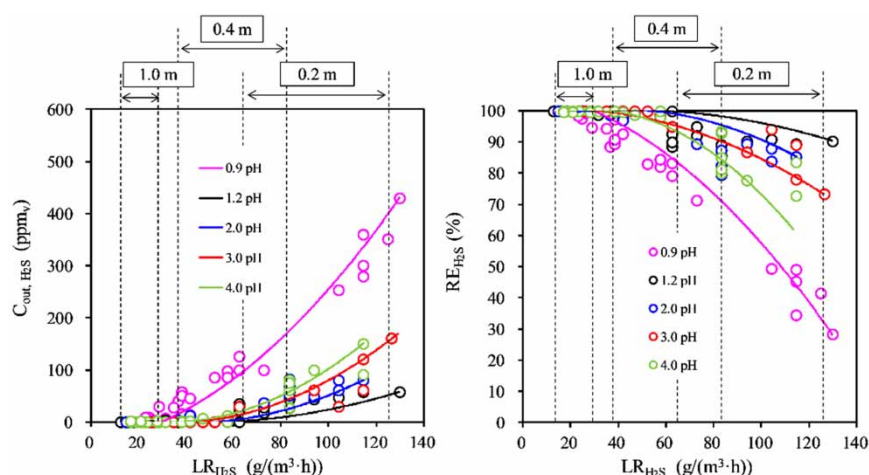


Figure 2 | Relationship between H₂S concentration from different parts of the BTF and H₂S loading.

However, when the pH decreased from 4.0 to 1.2 and then to 0.9, the maximum $C_{\text{out,H}_2\text{S}}$ at 0.2 m of BTF decreased correspondingly from 150 ppm_v to 60 ppm_v, and then increased to 420 ppm_v. Decreasing the pH to very low levels reduces H₂S and O₂ solubility (Chaiprapat et al. 2011; Jaber et al. 2016). Similar variation was also observed in the $RE_{\text{H}_2\text{S}}$ because H₂S removal is limited by the mass transfer of both H₂S and O₂ under acidic conditions (Tu et al. 2016). Additionally, Figure 3 shows that 91.9% of the sequence reads in the pH 4.0 recycling liquid were associated with *Acidithiobacillus* sp., among which the relative abundances of *A. caldus* and *A. thiooxidans* were 83.6% and 8.3% respectively, while 85.5% of the sequence reads in the pH 1.5 recycling liquid belonged to *F. acidiphilum* (Zhang et al. 2020). Compared with the pH-neutral BTF (Montebello et al. 2013; Tu et al. 2016), our results indicate that an acidic BTF led to specialization of the bacterial community and the prevalence of *Acidithiobacillus* sp.

However, excessively acidic pH led to the replacement of *Acidithiobacillus* sp. by *F. acidiphilum*, which is a major ferrous-iron oxidizing microbe (Zhang et al. 2020).

Moreover, the specific sulfur oxidation rate of the *A. thiooxidans* AZ11 and TAS cultures showed a maximum value at pH 1.3–1.5 and then decreased sharply with decreasing pH (Lee et al. 2006). In this study, a similar effect of pH is proposed for the sulfur oxidizing activity of *A. caldus* because it has a similar metabolism and ecophysiology to that of *A. thiooxidans* (Valdés et al. 2008). For *Acidithiobacillus* sp., the oxidation rate increased as the pH decreased from 4.0 to 1.2, and it exhibited a peak value near 1.2, and then decreased sharply as pH decreased to 0.9. Therefore, the excessively acidic pH of 0.9 blocked the mass transfer of H₂S and O₂ from the gas to the recycling liquid. The low sulfur oxidation activity and low proportion of *Acidithiobacillus* sp. further aggravated the deterioration in biodegradation of S⁰ to SO₄²⁻.

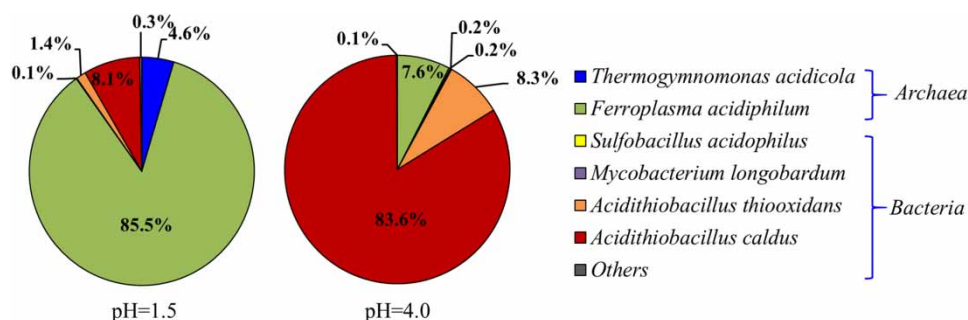


Figure 3 | Evolution of the microbial community in the BTF as a function of pH.

Removal profiles of D5

Prolonging the gas-liquid contact time improves the mass transfer of siloxanes. Hence, increasing the EBRT is widely used to increase the siloxane RE of BTFs (Popat & Deshusses 2008; Santos-Clotas *et al.* 2019; Zhang *et al.* 2020). The effect of EBRT on the RE_{D5} of the acidic BTF with pH 2.73 in stage 4 was investigated in this study (Figure 4). Similar to the result reported by Santos-Clotas *et al.* (2019), a positive correlation was observed between the D5 removal and EBRTs of 18–106 s, achieving the maximum D5 removal of 27.7% under the EBRT of 106 s. However, an EBRT of 10.1 min was required in a pH-neutral to achieve the same value of D5 removal (Santos-Clotas *et al.* 2019). This comparison indicates that acidic recycling liquid significantly improves gas-to-liquid mass transfer of D5.

Figure 5 presents the D5 removal profile of the BTF under different pH conditions. D5 removal decreased from 34.5% to 15.6% as the recycling liquid pH increased from 0.88 to 3.98. In our previous report, the removal of D5 in an acidic BTF was mainly attributed to absorption and further hydrolysis in the acidic recycling liquid (Zhang *et al.* 2020). Therefore, the variation in D5 RE under different pH conditions resulted from changes in the absorption rate of D5 from the biogas into the recycling liquid, because lower acidic pH significantly promoted hydrolysis of D5 to silanol.

Mass transfer coefficient of D5 from gas to recycling liquid under different pH conditions

The variation in the partition coefficient of D5 between the gas and recycling liquid under different pH conditions together with the equilibration time is presented in Table 2. The stable partition coefficient after partition equilibrium increased

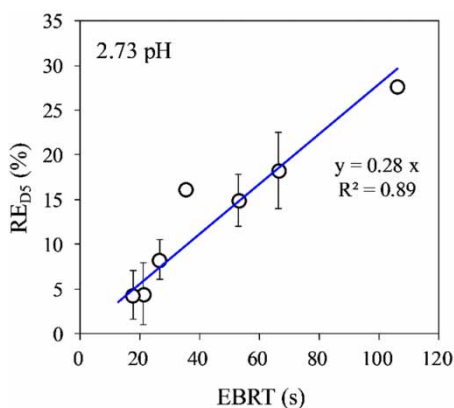


Figure 4 | Relationship between D5 RE and EBRT of biogas in the BTF.

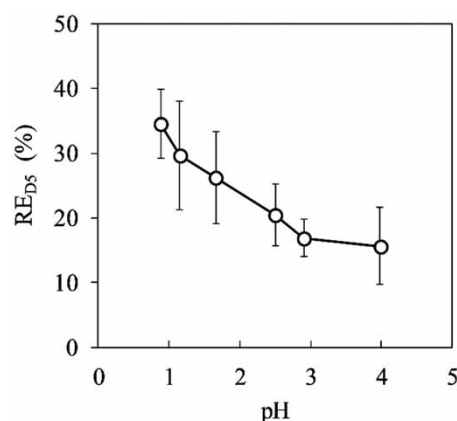


Figure 5 | D5 removal profile of the BTF as a function of pH.

from 0.2 to 3.1 as the pH increased from 0.88 to 3.98, and then decreased to 1.4 when the pH increased to 5.64. The variation in partition coefficient of D5 was related to the ionic strength of the recycling liquids, which changed with pH. During the daily operation of the BTF, some NaOH solution was added to the nutrient solution tank to adjust the recycling liquid pH to the set values (Table 1). Meanwhile, 20 mL of mineral medium was also added daily as a nutritional supplement for microbial growth. The addition of NaOH solution and mineral medium increases the total ionic strength of the recycling liquids. According to a previous report (Popat & Deshusses 2008), higher ionic strength mineral media increases the partition coefficient. Hence, a recycling liquid with higher pH had a higher partition coefficient: 0.2 for pH 0.88, 0.9–1.0 for pH 0.94–1.15, and 2.8–4.0 for pH 1.66–3.98. In the case of the pH 5.64, the addition of deionized water decreased the ionic strength of the recycling liquid, which led to a lower partition coefficient, 1.4.

The partition coefficient of D5 at the initial equilibration time of 0.25 h increased from 2.3 to 24.8 as the pH increased from 0.88 to 2.90, and then decreased to 6.3 at pH 3.98. The recycling liquid after long-term BTF operation contained some biomass flocs, which partly adsorbed D5. Generally, more biomass accumulated within the BTF operated under pH-neutral or lower acidic pH (Tu *et al.* 2017) because acidity inhibits the growth of many types of microorganisms (Tu *et al.* 2016). The total reads of microbial communities in the BTF recycling liquid at pH 1.5 and 3.98 were 31,800 and 47,267, respectively. The results indicate that more biomass accumulated in the BTF during operation at pH 3.98 than at pH 0.88–2.90. Therefore, the lower partition coefficient at pH values below 3.98 was attributed mainly to adsorption on the more numerous biomass flocs in the recycling liquid, although higher ionic strength also increased the partition coefficient.

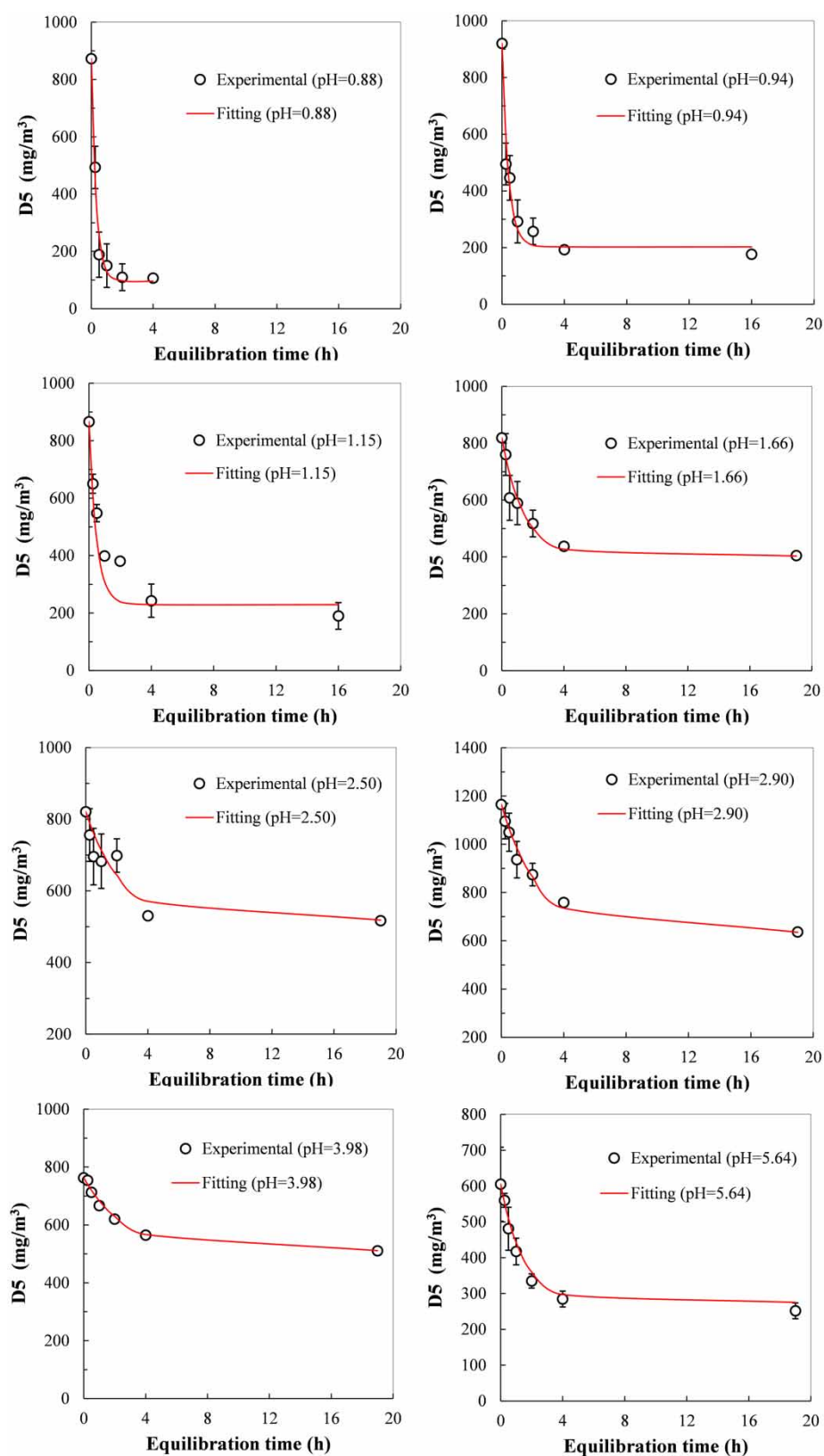


Figure 6 | D5 profile in the flask headspace during the partition test as a function of equilibration time and pH.

Furthermore, the D5 concentration in the flask headspace was simulated using Equation (3) to obtain the k_L of D5 in the BTF under different acidic pH conditions (Figure 6). Figure 7 and Table 3 show the various calculated k_L values. The k_L decreased rapidly from 0.075 m/h to 0.062 m/h when the pH increased from 0.88 to 1.15. In the pH range of 1.66–2.90, the k_L decreased slowly from 0.060 m/h to 0.035 m/h, and finally decreased to 0.029 m/h when at pH 5.64. These results indicate that the mass transfer of D5 from the headspace gas to the liquid at the bottom of the flask was accelerated by the acidic recycling liquids, especially under extremely acidic pH conditions.

According to the model reported by Ottengraf & Van den Oever (1983), pollutant conversion can be calculated from the gas-phase mass balance of the pollutant at the height (H) of the BTF (Equation (4)). Considering that the δ , C_{in} , A_{bio} , U , and H of BTF were constant in this study, the D5 removal follows Equation (5), which was simplified from Equation (4) as follows:

$$\frac{C_{in} - C_{out}}{C_{in}} = \frac{k\delta A_{bio} H}{C_{in} U} \quad (4)$$

$$RE = \alpha_1 k_L \quad (5)$$

where k is the kinetic coefficient ($\text{g}/(\text{m}^3_{\text{biofilm}} \cdot \text{h})$), δ is the biofilm thickness (m), C_{in} and C_{out} are the inlet and outlet

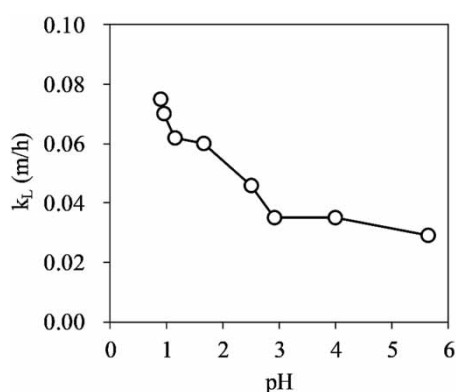


Figure 7 | Mass transfer coefficient of D5 from air to the recycling liquid as a function of pH.

Table 3 | Mass transfer coefficient of D5 between gas and liquid phases as a function of pH

Air-recycling liquid as a function of pH								
Scenario	0.88	0.94	1.15	1.66	2.51	2.90	3.98	5.64
k_L (m/h)	0.075	0.070	0.062	0.060	0.046	0.035	0.035	0.029
R^2	0.98	0.96	0.88	0.94	0.85	0.98	0.99	0.97

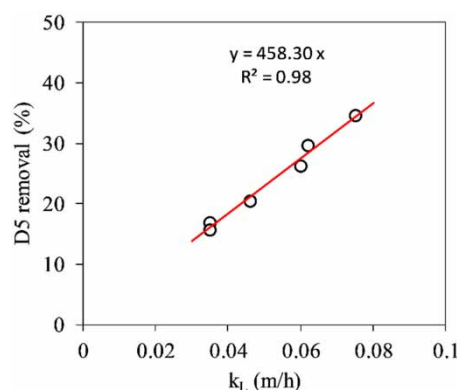


Figure 8 | Relationship between decamethylcyclotrisiloxane (D5) RE and mass transfer coefficient.

pollutant concentrations (mg/m^3), A_{bio} is the biofilm surface area per volume of packing material ($\text{m}^2_{\text{biofilm}}/\text{m}^3_{\text{packing material}}$), U is the gas velocity (m/s), and α_1 is a constant (h/m).

To quantify the contribution of k_L for D5 removal, the calculated k_L was correlated with the RE of D5 in the BTF under different pH conditions. Figure 8 shows that a positive linear relationship was obtained between the RE_{D5} and k_L . Actually, hydrolysis of D5 in the acidic recycling liquid is the major reaction for D5 abatement in an acidic BTF. Hydrolysis is commonly recognized as the rate-limiting step, and the removal of D5 in an acidic BTF follows zero-order kinetics with reaction limitation (Ottengraf & Van den Oever 1983; Dumont 2017). Furthermore, the high k_L values under extremely acidic pH conditions indicated a significant reduction in the resistance to gas-liquid mass transfer. Hence, it is feasible to decrease the pH of the recycling liquid for efficient D5 removal performance by an acidic BTF while simultaneously achieving high H₂S removal. Acid washing may be a promising alternative approach to remove siloxanes from biogas.

CONCLUSIONS

The performance of a BTF under different acidic pH conditions (0.9, 1.2, 2.0, 3.0, and 4.0) indicated that pH was a key parameter that directly affected operational

performance. The removal of D5 increased linearly with decreasing pH because the acidic recycling liquid accelerated the mass transfer of D5 in the BTF. However, the removal profile of H₂S and the variation in the microbial community within the BTF indicated that excessively acidic pH blocked the mass transfer of H₂S and O₂ from the gas to the recycling liquid. The low sulfur oxidation activity and low proportion of *Acidithiobacillus* sp. also led to S⁰ deposition. The optimal pH was about 1.2, and under this acidic condition the BTF simultaneously achieved effective removal of H₂S and D5 from biogas.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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