Removal of Hydrogen Sulfide in Biogas From Wastewater Treatment Sludge by Real Scale Biotrickling Filtration Desulfurization Process

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Abstract

High sulfur content in excess sludge impacts the production of biomethane during anaerobic digestion, meanwhile leads to hydrogen sulfide (H$_2$S) formation in biogas. This study aims to reveal the efficiency of the real-scale Biotrickling Filtration Process (BTF) in the removal of H$_2$S in the biogas formed in the anaerobic digester. The biogas was produced by stabilization of the treatment sludges formed in the processes of Urban Wastewater Treatment Plant with mesophilic anaerobic sludge digesters. It was determined that the anaerobic stabilization unit of the treatment plant was operated efficiently and the biogas with a high flow (18,123-21,383 m$^3$/day) was formed during the operation of the plant. The H$_2$S concentration in the biogas at the inlet of the BTF was 3,632 ppmv on average (2,900-4,400 ppmv) and 16 ppmv at the outlet. The elimination capacity of the system reached a maximum of 52.71 gH$_2$S m$^{-3}$h$^{-1}$. As a result, a real scale BTF unit was found to provide a sufficient removal efficiency (97.84-99.90%) for H$_2$S in the biogas.

1. Introduction

Anaerobic digestion (AD) is commonly used in the treatment of organic waste, such as agricultural waste, sewage sludge and organic form of municipal solid waste. During this process, approximately 95% of the organic matter and 95% of the energy present in the substrate are restrained in the biogas. (Guerrero et al. 2015). The biogas produced through anaerobic digestion is an environment friendly and important renewable energy resource (Oztürk 2007; Khoshnevisan et al. 2018). The produced biogas can be burned directly in combined heat and energy conversion plants and can be used as transportation fuel. Biogas is produced through anaerobic digestion of the treatment sludge originating from the wastewater treatment plants. The most important ingredients in the biogas produced by the digestion of the treatment sludges through anaerobic processes are: 60-70% methane (CH$_4$), 30-35% carbone dioxide (CO$_2$), 1-2% hydrogen sulphide (H$_2$S) and 0.3-3% other gases (Al Mamun and Shuichi Torii 2015; Rulkens 2008). The components of the biogas can vary depending on the used substrate for the production (Rasi et al. 2007). If the substrate used for biogas production contains sulphur, the formation of hydrogen sulphide (H$_2$S) is inevitable. (Chaiprapat et al. 2015, Dumont 2015).

The concentration of H$_2$S in biogas varies from a few hundred to ten thousand ppm depending on the amount of bioavailable sulfur compounds in the feedstock and the outcome of the competition among sulfate-reducing bacteria, acetogens and methanogens for the organic substrates (Stams et al. 2005). The presence of high concentration of H$_2$S causes corrosion on the equipment and increases the maintenance costs. Especially, due to the corrosive effect on the gas engines, engine life is shortened, the service/maintenance costs increase, and the conversion of biogas to electricity decreases. (Rasi et al. 2011). For this reason, H$_2$S must be removed from the produced biogas. By the removal of the H$_2$S, higher quality biogas is produced increasing electricity production and extending the life of equipment used. In addition, H$_2$S should be removed in terms of health and security (Deublein and Steinhauser 2008).

Actually, H$_2$S is produced under anaerobic conditions because sulphate (SO$_2^{4-}$) acts as an electron acceptor while organic compounds are decomposed biologically. H$_2$S is produced by anaerobic degradation of sulfur-containing compounds (mainly proteins) and reduction of anionic species (especially SO$_4^{2-}$) in the
feedstock of the digester (Ramos et al. 2013). Kuenen (1975) proposed the mechanism of HS removal that occurs through a series of physico-chemical processes and biological reactions, summarized by Equation (1)-(4) below.

(a) H$_2$S$_{(g)}$ dissolution in water

$$H_2S_{(g)} \rightarrow H_2S_{aq} \quad (1)$$

(b) H$_2$S biological oxidation to SO$_4^{2-}$

$$H_2S_{(aq)} + 2O_{2(g)} \rightarrow 2H^+ + SO_4^{2-} \quad (2)$$

(c) H$_2$S biological oxidation to S$_{(s)}$

$$2H_2S_{(aq)} + O_{2(g)} \rightarrow 2S_{(s)}^{0} + 2H_2O \quad (3)$$

(d) S$_{(s)}$ biological oxidation to SO$_4^{2-}$

$$2S_{(s)}^{0} + 3O_{2(g)} + 2H_2O \rightarrow 2H^+ + SO_4^{2-} \quad (4)$$

All of the processes lead to changes in terms of pH, dissolved oxygen and oxidation-reduction potential (ORP), which can be used to follow and control process performance (Janssen et al. 1998). There are also other reactions that have been reported, including non-biological oxidation of H$_2$S to thio-sulphate and the further biological oxidation of thio-sulphate to sulphuric acid (Fortuny et al. 2011).

For the removal of H$_2$S in biogas; solid phase adsorption, liquid phase absorption, membrane separation, chemical, biological, and thermal methods are used (Abatzoglou and Boivin 2009; Wellinger and Linberg 2000; Rasi et al. 2011; Lin 2013; Angelidaki et al. 2018; Diaz et al. 2011; Peluso et al. 2019). The biological desulphurisation of biogas can be performed in additional units mainly using bio-filters and bio-trickling filters during digestion process and by applying microaerobic conditions directly in anaerobic digestors (Ramos et al. 2013). This biological desulphurisation treatment method for the cleaning the contaminated biogas is a relatively new trend and is of great interest. On the other hand other gas desulphurisation methods have high operation costs and produce wastes that must be disposed. Biological desulphurisation method is economically more advantageous and more environment friendly than the other methods. Biological desulphurisation of biogas takes place under low temperature and pressure and can proceed with limited reactive consumption or no reactive consumption (Alverez 2003; Syed et al. 2006). This treatment method is also more useful because the gas stream contains biodegradable or biconvertable compounds (Gabriel and Deshusses 2003; Tomas et al. 2009).

In bioreactor systems, first hydrogen sulfide in the gas phase is dissolved into sulfur oxidizing bacteria (SOB) containing microbial media, followed by the oxidization of hydrogen sulfide by bacteria with oxygen in the liquid phase (Duan et al. 2006; Park et al. 1999). High elimination capacity and stability in the presence of severe operating conditions are required for bioreactor systems to be able to apply biological methods for the removal of high-strength hydrogen sulfide in a biogas stream. A large number of biodesulfurization processes are present, such as the biofilter processes (Rodriguez et al. 2014; Montebello et al. 2014; Ramos and Fdz-Polanco 2014), the bioscrubber processes (Hansen and Rindel 2000; Valero et al. 2019), and the process using
headspace of the digesters (headspace process) (Ramos and Fdz-Polanco 2012). The differences between these systems are the phase of the biomass (suspended or fixed), the state of the liquid phase (flowing or stationary) and the state of having or not having a carrier material (Ramirez et al. 2009). BTF, the waste air stream passes through a bed which is packed and which has pollutant-degrading organisms immobilized in the form of biofilms. The contaminant either passes from gas phase to liquid phase and later to the biofilm, or directly from gas phase to the biofilm, where it is eventually degraded biologically to harmless compounds (Gabriel and Deshusses 2003). The usage areas of BTF are large-scale gas applications to control and other odorous emissions from WWTPs and other industries (Khanongnuch et al. 2019). Its major advantages are having low operation cost, requiring low-energy and chemicals and having high removal efficiencies (REs), mostly above 99% (Aita et al. 2016). Thus, the aim of the present study is to eliminate H$_2$S from biogas generated in Konya advanced biological urban wastewater treatment plant sludge through anaerobic processes with the use of real scale biotrickling filtration desulphurisation method.

2. Material And Methods

2.1. Real-Scale Biotrickling Filtration (BTF) Process

This study performed at Konya advanced biological urban wastewater treatment plant with an equivalent population of 1,000,000 and a flow rate of 200 00 m$^3$/day. BTF was used for the purification of H$_2$S in the biogas collected at the anaerobic digester output used for sludge stabilization. In this process, the H$_2$S is removed from biogas and biogas is cooled to condense the moisture in it and the condensate is disposed. Biogas collected from anaerobic sludge digesters is transferred to the feeding chamber at the bottom of the closed tower where the BTF unit is located. The biogas moves from bottom to the top and in the tower that contains layers of polypropylene media filling circles (Table 1) where desulphurisation occurs. A complexed culture of sulfur oxidizing bacteria (SOB) dominated by Acidithiobacillus thiooxidans acclimated from activated sludge was used as the bacterial strain and a biofilm was formed. In order to supply the substrate for the SOB, treated wastewater was fed into the feeding chamber at the bottom of the tower. The feeding water was passed through heat exchangers to adjust the temperature to 35-36 °C and it was sprayed to the media material from the top of the tower. Some authors reported for similar sulfide-oxidizing microorganisms, an optimum growth temperature at around 30 °C (Ravichandra et al. 2006; Sanchez et al. 2014). Operation of H$_2$S biofiltration reactors report 100% removal efficiency at 30-50 °C, but only 20% at temperatures below 10 °C (Yang and Allen 1994). At the entrance point of the desulphurisation unit 1.5-3.5% air was added to the biogas. In this process, O$_2$/H$_2$S ratio was 2/1. The end product of oxidation, sulfate (high O$_2$/H$_2$S ratio in biofilm) or elemental sulfur (low O$_2$/H$_2$S ratio), should vary depending on the availability of oxygen for microorganisms in the bioreactor. If the oxygen is more than the stoichiometric requirement, the formation of elemental sulfur decreases (Buisman et al. 1991). The treated biogas was passed through cooling units to decrease the temperature and moisture before it was fed into the gas conversion engines. The filtrate collected at the bottom of the unit was discharged into the sulphur fertiliser tank. The sludge layer accumulated on the polypropylene material was disposed from the system by back-washing. The flow diagram of Biotrickling Filtration process is given in Figure 1.

Table 1. BTP media material characteristics
Material | Polypropylene (PP)
Shape | Perforated rings
Size (D1-D2/L) (mm) | 100-90/50-35
Colour | Black
Porosity | 92%
Specific surface area (m²/m³) | 140
Weight (gr/adet) | 39
Pieces per unit volume (pieces/m³) | 2080
Density (kg/m³) | 80

2.2. BTF Operational Conditions

Real scale BDP design criteria are given in Table 2. The produced biogas consists of 65% methane (CH₄), 34% carbon dioxide (CO₂), and 1% H₂S and other gases. The process was designed for biogas average temperature to be 30 °C and the dilution water average temperature to be 15 °C.

Table 2. Biological desulphurisation process design criteria

| Parameter                     | Unit   | Value |
|-------------------------------|--------|-------|
| Flow rate                     | Nm³/hour | 1,500 |
| Inlet H₂S concentration       | ppm    | 5,000 |
| Outlet H₂S concentration      | ppm    | 200   |
| Inlet biogas temperature      | °C     | 30    |
| Inlet biogas temperature      | °C     | 5     |
| Biogas pressure               | mbar   | 15    |
| Methane (CH₄)                 | %      | 65    |
| Carbon dioxide (CO₂)          | %      | 34    |
| Nitrogen (N₂)                 | %      | 7     |
| Oxygen (O₂)                   | %      | 2     |

2.3 Monitoring and Analytical Methods

The pH is an important parameter affecting the process efficiency and the system was operated in the pH range of 1.5-3.5. The optimum pH should be in the range of 2-3.5 for activities of sulphate oxidising *Acidithiobacillus thiooxidans* bacteria (Syed et al. 2004; Montebello 2013; Rodriguez et al. 2014). Kim and Deshusses (2005) reported that the biological activity of microorganisms was inhibited due to the low pH and high sulfate content.
(at pH 2 the sulfate content in the water was 1,900 ppm). In order to monitor and control of the environment conditions of sulphur bacteria taking active role in the system, full otomation (SCADA) system was used. In this biological desulphurisation process; biogas flow meter, air flow meter, circulation liquid flow meter, pH and temperature measurement devices, dilution (addition) liquid indicators, biogas oxygen analysis system, sulphur removal tower, tank level indicator, gas detector, pressure indicator, and other instruments were used. In order to compare the ability of biofilters on the same basis, the elimination capacity (EC) was used. It represents the ability in removing pollutants in gaseous form compared to the incoming pollutant mass, expressed as the mass of pollutant removed per unit time per bed volume. The parameters used in this study to describe the operating conditions and for the determination of the removal performances are given in Table 3.

Table 3. Process control parameters used in this study

| Parameter                                | Formula                                      | Nomenclature                                                                 |
|------------------------------------------|----------------------------------------------|------------------------------------------------------------------------------|
| Loading rate (gH₂S m⁻³h⁻¹)               | \( LR = \frac{Q}{V}C_m \)                   | \( C_m \): concentration of H₂S in gas entering biofilter (ppm₀)             |
| Elimination capacity (gH₂S m⁻³h⁻¹)       | \( EC = \frac{Q}{V}(C_{in} - C_{out}) \)   | \( C_{out} \): concentration of H₂S in gas exiting biofilter (ppm₀)         |
| Removal efficiency (%)                   | \( RE(\%) = \frac{(C_m - C_{out})}{C_m} \times 100 \) | Q: Flow rate of mixed gas entering biofilter (m³/h)                           |
| Empty Bed Residence Time (min)           | \( EBRT = \frac{V}{Q} \)                    | V: Empty packed bed volume (m³)                                              |

H₂S removal efficiency of real scale BTF system was monitored for twelve months between January 2017 and December 2017 and the performance of the process was evaluated. During this period, the flow rate of biogas produced in the anaerobic sludge digesters, minimum, maximum, and average values of H₂S level in the biogas and at the process outlet were monitored on a monthly basis to determine the H₂S removal efficiency of the process. During this study, biogas flow was measured by flow meter (Drager) and H₂S concentration was measured by H₂S measurement tubes (Rea) and analyzed by colourmatic method (TS EN 1231: 2000).

3. Results And Discussion

3.1 Anaerobic Digester and Biogas Production

The flow rate of biogas and the H₂S concentration in the biogas were measured for the efficient process operation. The operational parameters of the mesophilic anaerobic sludge digester (pH, organic loading rate, sludge feeding rate, ambient temperature, volatile organic acid concentration, sludge retention time) during the operation of the biological desulphurisation process, were given in Table 4. The characteristics of sludge at the inlet and outlet of sludge digester (total solid material, chemical oxygen demand, protein, alcalinity) were given in Table 5. The most important indicator showing the efficient operation of the anaerobic sludge digesters is the biogas production. During the working period, the flow rate of biogas produced in anaerobic sludge digesters varied between 18,123-21,383 m³/day and an average of 19,519 m³/day (Table 6) (Figure 2). However, the
range of percentage composition of the biogas produced from AD processes is dependent upon several factors including the digestibility of organic matter, digestion kinetics, digester retention time, and the digestion temperature (Dobre et al. 2014).

Table 4. Anaerobic sludge digester operation parameters

| Parameters                                | Value         |
|-------------------------------------------|---------------|
| pH                                        | 7.3-8.1       |
| Organic loading ratio (OLR) (kg/ gün/ m³) | 1.2–1.5       |
| Sludge feed flow (m³/h)                   | 16–17         |
| Temperature (°C)                          | 36-41         |
| Volatile fatty acid (VFA)/Alkalinity      | 0.02-0.08     |
| Sludge Retention Time (SRT) (day)         | 17            |

Table 5. Sludge characteristics in anaerobic sludge digester

| Parameters                | Feed Sludge      | Anaerobic sludge digester outlet |
|---------------------------|-------------------|----------------------------------|
| TS (mg/L)                 | 25,100-37,500     | 21,000–30,100                    |
| COD (mg/L)                | 19,100–32,000     | 9,400–19,000                     |
| TKN (mg/L)                | 1,500–4,150       | 1,300–4,700                      |
| Protein (mg/L)            | 11,000–23,100     | 7,400–22,000                     |
| Alkalinity (mg/L)         | 720-1300          | 2,450–3,900                      |
| VFA (mg/L)                | 450-1450          | 60–230                           |

3.1. Hydrogen Sulfide Removal from Biogas

The inlet H₂S concentration was routinely measured per day to assess the variation of the inlet H₂S load. H₂S concentration of biogas at the inlet of the BTF unit varied between 2,900–4,400 ppm and an average of 3,632 ppm (Table 6). The H₂S concentration in biogas is consistent with the literature (Jenicek et al. 2008; Charnnok et al. 2013; Reddy et al. 2019). The biogas generated in anaerobic digestion facilities in WWTPs contains average concentrations of H₂S in the range from 0.1 to 0.5 vol. % (1000-5000 ppmv) (Walsh et al. 1998). At the outlet of the BTF process, H₂S concentration varied between 4-63 ppm and an average of 16 ppm (Figure 3). No relation was determined between the biogas flow rate produced in anaerobic sludge digester and the H₂S concentration in the biogas. It is thought that H₂S is produced depending on the other factors (protein and sulphate concentrations in wastewater, etc.) completely independent from the produced biogas quantity.
| Time       | Biogas (m³/d) | Inlet [H₂S] biogas (ppmᵥ) | Outlet [H₂S] biogas (ppmᵥ) | H₂S LR (gH₂S m⁻³h⁻¹) | EBRT (min) | EC (gH₂S m⁻³h⁻¹) | H₂S removal efficiency (%) |
|------------|---------------|-----------------------------|----------------------------|------------------------|------------|-------------------|-----------------------------|
| January    | 19,627        | 2,923                       | 63                         | 33.47                  | 7.34       | 32.74             | 97.84                       |
| February   | 19,581        | 3,233                       | 14                         | 36.93                  | 7.35       | 36.77             | 99.57                       |
| March      | 19,673        | 3,200                       | 23                         | 36.72                  | 7.32       | 36.46             | 99.28                       |
| April      | 19,714        | 2,900                       | 12                         | 33.35                  | 7.30       | 33.21             | 99.59                       |
| May        | 19,526        | 3,253                       | 17                         | 37.05                  | 7.37       | 36.86             | 99.48                       |
| June       | 18,233        | 4,103                       | 6                          | 43.64                  | 7.90       | 43.58             | 99.85                       |
| July       | 18,123        | 4,000                       | 20                         | 42.29                  | 7.95       | 42.08             | 99.50                       |
| August     | 18,683        | 3,900                       | 4                          | 42.50                  | 7.71       | 42.46             | 99.90                       |
| September  | 20,583        | 4,400                       | 10                         | 52.83                  | 7.00       | 52.71             | 99.77                       |
| October    | 21,383        | 4,133                       | 4                          | 51.55                  | 6.73       | 51.50             | 99.90                       |
| November   | 18,617        | 3,433                       | 11                         | 37.28                  | 7.73       | 37.16             | 99.68                       |
| December   | 20,483        | 4,100                       | 12                         | 48.99                  | 7.03       | 48.85             | 99.71                       |
| **Average**| **19,519**    | **3,632**                   | **16**                     | **41.38**              | **7.39**   | **41.20**         | **99.55**                   |

Since the produced biogas is used in the production of electrical energy, H₂S needs to be removed due to the corrosive effect of H₂S on gas engines and other auxiliary equipment. For this reason, H₂S concentration should be reduced up to the limit value (≤ 260 ppm) determined for gas engines before biogas is given to gas engines. The recommended level of H₂S in the produced biogas is in the range of 0.02 to 0.05% (w/w) (200 to 500 ppm) while H₂S-free biogas is more desirable (Rodriguez al. 2014). During the working period, the H₂S removal efficiency ranged between 97.84-99.90% and an average of 99.55%. (Table 6). In January 2017, when the performance of the process started to be monitored, H₂S removal efficiency was observed to be 97.8% and increased during operation to 99% (Figure 4). It was determined that the H₂S concentration at the outlet of BTF process was well below the determined limit value.

The elimination capacity (EC) and RE as functions of the load supplied to the system were analyzed for BTF reactor. Figure 4 shows the removal efficiency and elimination capacity of H₂S monthly. EC changes as a function of EBRT and LR values. In BTF process, EBRT values were between 6.3-7.95 min, LR values were between 33.35-52.83 g H₂S m⁻³h⁻¹, EC values were between 33.21-51.71 g H₂S m⁻³h⁻¹ (Figure 4). The average H₂S removal was 99.9% at EBRT of 7.39 min (i.e., a LR of 41.38 g H₂S m⁻³h⁻¹). In addition, the elimination capacity and H₂S removal efficiency of this study BTF process performance well when compared to the previous studies (Table 7).
Tablo 7. Comparison of the performance of BTF reported in the literature on the treatment of biogas polluted by H₂S
| Scale          | Type bed                  | Packed Bed volume | Inlet $\text{[H}_2\text{S]}$ (ppmv) | Gas residence time (EBRT) | Elimination capacity (EC) $\text{g H}_2\text{S m}^{-3} \text{h}^{-1}$ | $\text{H}_2\text{S RE} \%$ | Reference                          |
|---------------|---------------------------|-------------------|-------------------------------------|--------------------------|-----------------------------------------------------------------|-----------------|-----------------------------------|
| Lab-scale     | Polypropylene pall rings  | 1L                | 170                                 | 36 s                     | 20                                                              | 100             | Cox and Deshusses 2001            |
| Lab-scale     | HD-QPAC                   | 2 L               | 2000                                | 3 min                    | 55                                                              | 99              | Maestre et al. 2010               |
| Lab-scale     | Polypropylene rings       | 1L                | 5415                                | 5.5 min                  | 89.4                                                           | 100             | Zhou et al. 2015                  |
| Lab-scale     | Calgon AP460              | 6.4 L             | 20-100                              | 4-16 min                 | 22.1                                                           | 90              | Duan et al. 2005                  |
| Lab-scale (bench) | Plastic pall rings      | 5.15 m$^3$       | 1954±454                            | 180 min                  | 50 ± 11                                                         | 94              | Rodriguez et al. 2014            |
| Lab-scale     | HD Q-PAC                  | 2.15 L            | 2000-8000                           | 180 s                    | 50                                                             | 100             | Montebello et al. 2010           |
| Lab-scale (pilot) | Metallic Pall rings (AISI 316) | 2 L          | 2000                                | 180 s                    | 100-140                                                        | 95-100          | Montebello et al. 2012           |
| Lab-scale     | Polypropylene Pall rings  | 2 L               | 2000                                | 131 s                    | 50-100                                                         | 35-100          | Montebello et al. 2013           |
| Lab-scale     | Metallic Pall rings       | 2.4 L             | 2000-10000                          | 130 min                  | 100-140                                                        | 70-80           | Montebello et al. 2014           |
| Lab-scale     | HS- Q-PAC                 | 2.15 L            | 900 - 10000                         | 180 s                    | 200                                                            | 84              | Fortuny et al. 2008              |
| Lab-scale     | HD-Q-PAC                  | 2 L               | 2000                                | 167-180                  | 84                                                             | 97 ±0.3         | Fortuny et al. 2011              |
| Lab-scale     | Polypropylene pall rings  | 2.4 L             | 850-8500                            | 2.4-3.5                  | 99.8–130                                                      | 99              | Fernandez et al. 2014            |
| Lab-scale (pilot) | Polyurethane foam        | 600 m$^2$ m$^{-3}$ surface area | 5-25                             | 15-40 s                   | 15-95                                                         | 99              | Gabriel and Deshusses 2003       |
| Scale       | Material                  | Volume/L | Mass/kg | Time/s | K/L   | Temperature/°C | Reference                     |
|-------------|---------------------------|----------|---------|--------|-------|----------------|-------------------------------|
| Lab-(pilot) | Ceramic granules          | 1177     | 2.84±1.76 | 5-20   | 2.82-2.85 | 60-100          | Li et al. 2012                |
|             | Volcanic rocks            |          |         |        |       |                |                               |
| Full-scale  | Polypropylene pall rings  | -        | 3000    | 180    | 170    | 90             | Tomas et al. 2009             |
| Lab-(pilot) | BioSulfidEx               | 2.21     | 500-600 | 84     | 32.3   | 98             | Naegele et al. 2013           |
|             | Polyethylene (HDPE)       | 1        | 0-2040  | 120    | 78.57  | 100            | Vikromvarasiri et al. 2017   |
|             | Commercial polyester fibers| 12       | 1000-4000 | 10.29-72 | 14.58  | 100            | Soreanu et al., 2008          |
|             | Schist                    | 7.85     | 1100    | 300    | 30.3   | 100            | Jabera et al. 2017            |
|             | 3D-printed honeycomb monolith | 0.2     | 2000    | 41     | 122    | 95             | Qiu et al. 2017               |
|             | K1 packing material       | 0.5      | 200     | 40-100 | -      | 92.27±10.30    | Zhuo et al. 2019              |
|             | HDPE Plastics             | 1        | 2000    | 120    | 82.98  | 99.5           | Juntranapaporn et al. 2019    |
|             | Polypropylene Pall rings  | 4000     | 2000    | 15     | 29.5   | 94.6-99.6      | Reddy et al. 2019             |
|             | Bamboo charcoal           | 643      | 5-20    | 10.9-28.9 | 6.58 | 99.8          | Chen et al. 2019              |
|             | Polyurethane foam         | 3        | 1246-305 | 1.6 min | 98    | 95-99          | Tayar et al. 2019             |
|             | Polypropylene pall rings  | 2.8      | 2000    | 118    | 120    | 100            | Lopez et al. 2019             |
| Pilot       | Polypropylene spheres     | 440      | 1.2     | 40     | 122    | 100            | Xia et al. 2019               |
| scale       | PUF cubes                 | 3        | 4000    | 3 min  | 113.5  | 97             | Watsuntorn et al. (in press)  |
3.3. Microbial community

In effective removal of H\textsubscript{2}S, microorganisms have important roles. Sulfide oxidizing bacteria (SOB) are gram negatives which can use sulfide and thiosulfate as an energy source. Due to their ability to tolerate a pH swing between 1.5 and 3.5, SOB *Acidithiobacillus thiooxidans* was found to be a major microorganism group in our biofilter in the present study. This bacterium is thought to be an ideal inoculum for the biofiltration of H\textsubscript{2}S in biogas and it is the most acidophilic SOB (Aita et al. 2016; Ramirez et al. 2016). It has a pH range between 0.5 and 5.5 and an optimum at pH 2-3 for growth (Wang et al. 2019). In this technology, the headspace of anaerobic digesters functions as a H\textsubscript{2}S abatement unit that causes the development of various microaerophilic SOBs such as *Acidithiobacillus sp.*, *Arcobacter sp.*, *Sulfuricuvum sp.*, *Sulfurimonas sp.*, *Thiobacillus sp.*, *Thiofaba sp.* and *Thiomonas sp.* in case of the development of limited amount of O\textsubscript{2} (Diaz et al. 2011; Kobayashi et al. 2012; Rodri Guez et al. 2012). This result is similar to the results of Lee et al. (2006) which showed that in degradation of H\textsubscript{2}S, *Thiobacillus thiooxidans* proliferating between pH 2 to 0.5 and *Acidithiobacillus thiooxidans*AZ11 could grow at pH as low as 0.2. It was reported that it was still possible to reach high removal efficiencies of 99.9%, 98.0%, and 94.0%, respectively. In acidic conditions, *Acidithiobacillus sp.* was reported to reach an H\textsubscript{2}S elimination capability (EC) of 113 (Aita et al. 2016), 150.3 (Charnnok et al. 2013) and 113.5 gH\textsubscript{2}S/m\textsuperscript{3}/h (Chaiprapat et al. 2011). Our EC 35 gH\textsubscript{2}S/m\textsuperscript{3}/h at the condition for H\textsubscript{2}S removal is similar to those reported in the aforementioned *Acidithiobacillus sp.* predominant experiments. pH of the recirculating fluid was found to decrease rapidly and vary between 1.5 and 3.5. It can be seen from the results that the SOB culture in the BTF reactor has already adapted to the condition of inlet H\textsubscript{2}S concentration and eliminated H\textsubscript{2}S in biogas.

4. Conclusion

In this study, the removal of H\textsubscript{2}S from the biogas that was produced at real scale anaerobic sludge digester by BTF process was investigated. Average biogas flow rate produced in mesophilic anaerobic sludge digesters varied between 18,123–21,383 m\textsuperscript{3}/day and H\textsubscript{2}S concentration varied between 2,923-4,400 ppm\textsubscript{v}. It was observed that the H\textsubscript{2}S concentration in the produced biogas is completely independent from the biogas flow rate. The removal of high concentrations of H\textsubscript{2}S in biogas was accomplished by real scale BTF process with SOB bacteria (*Acidithiobacillus Thiooxidans*) which active at acidic environment (pH 1.5–3.5.). BTF process was operated at; pH:1.5-3.5, O\textsubscript{2}/H\textsubscript{2}S:1/2, EBRT:6.3-7.95 minutes, LR:33.35-52.83 g H\textsubscript{2}S/ m\textsuperscript{3}h\textsuperscript{-1}. The H\textsubscript{2}S removal efficiency (RE) varied in the range of %97.84-99.90 and H\textsubscript{2}S elimination capacity (EC) varied in the range of 33.21-52.71 gH\textsubscript{2}S m\textsuperscript{3}h\textsuperscript{-1}. The process efficiency was found to be independent of inlet H\textsubscript{2}S concentration. The average H\textsubscript{2}S values in biogas desulphurized by BTF process ranged between 4-63 ppm. As a result, BTF process regardless of the biogas flow and inlet H\textsubscript{2}S concentration was found to be an effective and efficient process for the removal of H\textsubscript{2}S from biogas produced in the real scale anaerobic sludge digester.

Declarations
Ethics approval: Not applicable

Consent of Participate: Not applicable

Availability of data and materials: Not applicable

Competing interests: We declare that they have no conflict of interest.

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Code availability (software application or custom code): Not applicable

Consent for publication: Not applicable

Authors' contributions: All authors contributed to the study conception and design. Material preparation and data collection was done by SK. The study of analysis was performed by SA. The first draft of the manuscript was written by SA and SK commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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**Figures**

![Diagram of the biotrickling filtration process](image-url)

**Figure 1**

Real scale biotrickling filtration (BTF) process
Figure 2

Variation of biogas production
Figure 3

Variation of H2S concentration at BTF inlet and outlet
Figure 4

Variation of H2S removal efficiency and elimination capacity (EC).