Sulfur Oxidizing Bacterial Biofilter for Removal of Hydrogen Sulfide (H_2S) from Biogas

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Abstract: Presence of hydrogen sulfide (H_2S) in biogas is a major problem for biogas utilization due to its corrosive property. H_2S contamination can be removed by chemical and physical methods but both of them have high capital costs and demand large energy inputs. The biological process e.g. Biofilter can change biogas into noncorrosive form. Pollutants (e.g. H_2S) are utilized by biofilm of microorganisms grown on packing material when contaminated gases stream pass through the filter bed. Many types of microorganisms, either autotrophic or heterotrophic, are capable of utilizing hydrogen sulfide for their growth. Sulfur oxidizing bacteria (SOB) convert hydrogen sulfide (H_2S) into elemental sulfur (S_0) by partial oxidation, or sulfate (SO_4^{2-}). Besides H_2S, other sulfur compounds like thiosulfate ($S_2O_3^{2-}$) and tetrathionate ($S_4O_6^{2-}$) can also be converted to sulfate. In this study, Sulfur oxidizing bacteria isolated from Fang hot-spring in Chaingmai province, from a bio-scrubber tank of cassava starch wastewater treatment plant at Saraburi province and mixed culture of bio-scrubber effluent and hot-spring bacterial biofilm were determined for their hydrogen sulfide removal efficiency in the biofilter (PVC pipe; diameter 0.2 m, height 1.5 m) packed with plastic bio-ball (6.29 m^2 surface area). Each biofilter was continuously fed with real biogas (H_2S concentration ~ 2,000-3,000 ppm) at the bottom with the flow rate of 0.6 m^3/h. Minerals medium was sprayed from a nozzle at the top of biofilter. Hydrogen sulfide concentration from biogas inlet and outlet was monitoring every 4 hours over 3 days and used to calculate the removal efficiency (%). The results showed that biofilter inoculated with hot-spring bacterial biofilm and bio-scrubber effluent biofilm had hydrogen sulfide removal efficiency of more than 75 and 80 %, respectively. A hydrogen sulfide removal efficiency of more than 85% was achieved when mixture of two bacterial sources were used.

Keywords: Bacterial biofilm; biofilter; hydrogen sulfide; sulfur oxidizing bacteria; sulfide removal efficiency.

1. Introduction

Biogas is a renewable and sustainable energy source which is produced by the anaerobic digestion of organic matter. The anaerobic fermentation of sulfur rich wastewater can produce hydrogen sulfide (H_2S) in biogas. Biogas from anaerobic processes at wastewater treatment plants can contain up to 2,000 ppm H_2S [1]. H_2S is a colorless, extremely toxic and flammable gas that has a characteristic odor of rotten eggs. It can cause injury to the central nervous system even at low dose, is toxic to microorganisms, and is corrosive to concrete and steel. Considerable amounts of hydrogen sulfide are emitted from industrial activities such as petroleum refining, pulp and paper manufacturing, wastewater treatment, food processing, livestock farming, and biogas processing. H_2S concentrations of 5-60 ppm were generally emitted from those processes [2-4].

Biogas is generally comprise of methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2) and sulfur containing molecules in which the most abundant sulfur containing molecules is hydrogen sulfide (H_2S). As the presence of H_2S in biogas causes the corrosion of engines and equipments, H_2S should be removed prior to use. H_2S gas may be treated by both chemical and physical methods but such methods have high capital costs, demand large energy inputs and result in the generation of secondary hazardous wastes. Biological methods e.g. Biofilter have advantages over physical and chemical methods since they are cost effective systems, have low maintenance, low toxic final disposal and high removal efficiency [5]. A biofilter system is a process by which contaminated gases passes through a biofilm with packing materials and pollutants are transported into the biofilm where they are utilized by microorganisms. The objective of this study was to develop a biofilter to treat a gaseous stream containing a high concentration of hydrogen sulfide (2,000-3,000 ppm). The efficiency of a biofilter system inoculated with selected sulfur-oxidizing bacteria for hydrogen sulfide removal was determined.

2. Materials and Methods

2.1 Inoculum seed and Cultivation

Microorganisms were collected from a bio-scrubber tank at cassava starch wastewater treatment plant at Saraburi province and a bacteria code F18 (isolated from Fang hot-spring in Chaingmai province) from our previous work were enriched by repeatedly transferring to fresh thiosulfate medium. In order to enrich microorganisms, 10 ml of microorganisms in thiosulfate medium flask were repeatedly transferred into 500 ml Erlenmeyer flask containing 250 ml of thiosulfate medium and incubated at 30°C, 180 rpm for 3 days. After that, the culture was transferred in to a 5L of thiosulfate medium in a 10L tank and was incubated at room temperature for 7 days under aerated conditions. The thiosulfate medium consisted of 2.0 g KNO_3, 1.0 g NH_4Cl, 2.0 g KH_2PO_4, 2.0 g $NaHCO_3$, 0.8 g $MgSO_4.7H_2O$, 5.0 g $Na_2S_2O_3.5H_2O$ and 1.0 ml trace element in 1,000 ml distilled water and the pH was adjusted to 6 with 1N KOH. The composition of trace element was as follows: 50.0 g Na_2-EDTA, 7.34 g $CaCl_2.2H_2O$, 5.0 g $FeSO_4.7H_2O$, 2.5 g $MnCl_2.4H_2O$, 2.2 g $ZnSO_4.7H_2O$, 0.5 g $(NH_4)_6Mo_7O_{24}.4H_2O$, 0.2 g $CaSO_4.5H_2O$ and 11.0 g NaOH dissolved in 1,000 ml of distilled water [6].

2.2 Experimental Setup

In this study, pilot biofilter consisted of two components. The first component, biofilter column (packed column), which was packed with plastic bio-ball using as supporting materials for microorganism attachment. The diameter and surface loading rate of the packing materials were 3.75 cm and 140 m^2/m^3, respectively; (2) the recirculation tank that serve as a liquid sump for supplying nutrients to microorganisms.

The schematic diagram of the pilot biofilter system is shown in Figure 1. The biofilter was made of polyvinyl chloride (PVC 8") pipe 0.2 m in diameter and 1.5 m in height and had a working volume of 0.047 m^3. The active height of the packing materials is 1.0 m with a working volume 0.031 m^3. The pilot biofilter was continuously fed with real biogas from TBEC Chao Khun Agro (CKA) Biogas Project (H_2S concentration varies about 2,000 - 3,000 mg/l) at the bottom and the treated biogas exhausted from the top.

Table 1. Operating parameters of the pilot biofilter.

Biogas flow rate	0.60	m^3/hour
Air flow rate	0.03	m^3/hour
Liquid flow rate	1.0	L/hour
Column diameter	0.2	m
Column height	1.5	m
Column volume	0.047	m^3
Packing height	1.0	m
Packing volume	0.031	m^3
Surface area of supporting materials	6.29	m^2
Hydraulic retention time	4.7	min
Biogas Temperature	30 - 32	°C
CH_4 content (gas)	58 - 60	% (v/v)
CO_2 content (gas)	32 - 40	% (v/v)
H_2S content (gas)	≤ 3,000	mg/l
Specific area (packing material)	200	m^2/m^3
Operation temperature	30 - 35	°C

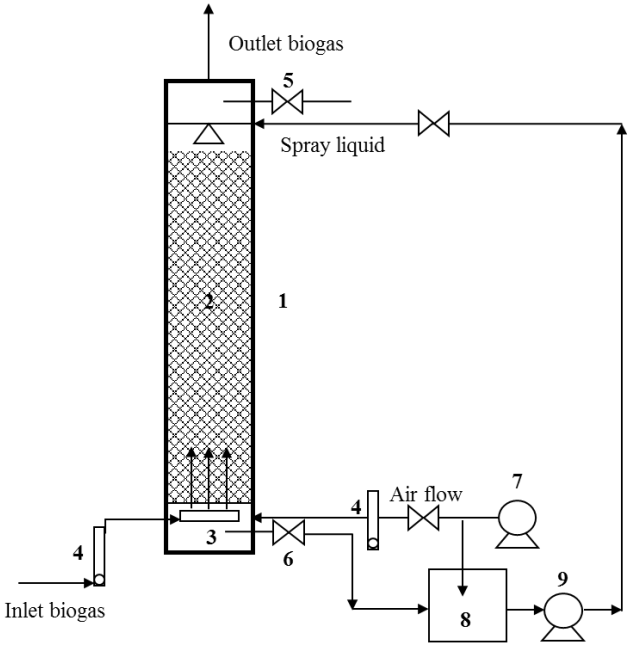

Figure1. Schematic diagram of biofilter system.
1. Biofilter column
2. Packing material (Plastic bio-ball)
3. Air distributor
4. Gas flow meter
5. Gas sampling port
6. Effluent port
7. Air blower
8. Recirculation tank
9. Peristaltic pump

Acclimatized microorganisms were mixed with minerals medium (water with trace element; 50.0 g Na_2-EDTA, 7.34 g $CaCl_2.2H_2O$, 5.0 g $FeSO_4.7H_2O$, 2.5 g $MnCl_2.4H_2O$, 2.2 g $ZnSO_4.7H_2O$, 0.5 g $(NH_4)_6Mo_7O_{24}.4H_2O$, 0.2 g $CaSO_4.5H_2O$ and 11.0 g NaOH dissolved in 1,000 ml of distilled water) in the recirculation tank. The microbial attachment process was initiated by circulating the mixture of microorganisms and minerals medium downflow through the packing materials in the biofilter column at a liquid flow rate of 1 L/hour for 7 days. After that, mineral medium and biogas were continuously supplied to the pilot biofilter. Flow rate of biogas and air were controlled by mass flow meter with 0.60 m^3/hour and 0.03 m^3/hour blow upward from the bottom of packed column, respectively. H_2S inlet/outlet concentration, pH value, forms of hydrogen sulfide (S^{2-}), bisulfide (HS^-) and elemental sulfur were monitored when the biofilm of sulfur oxidizing bacteria was observed on the surface of the plastic bio-ball in pilot biofilter.

Bacteria code F18 from Fang hot-spring was used as inoculum in the first experiment while acclimatized culture from the bio-scrubber effluent of cassava starch wastewater treatment plant and the mixture of bacteria code F18 and acclimatized culture from bio-scrubber effluent were used as an inoculum in the 2nd and 3rd experiment, respectively. The biofilter system was cleaned after each experiment before new seed inoculation.

2.3 Analytical methods

The inlet and outlet H_2S gas flow through pilot biofilter were measured by H_2S gas analyzer (Geotech portable Gas Analyzer, England) (H_2S 0-5,000 ppm).

Sulfate was analyzed by turbidimetric method [7], sulfide in liquid phase was analyzed by iodometric method according to standard methods [7] and elemental sulfur was analyzed by Eschka method [7].

The pH value was analyzed by pH meter (Metler).

2.4 Calculation

Efficiency of H_2S Removal

Removal Efficiency (%) = (Inlet H_2S gas – Outlet H_2S gas) x 100 / Inlet H_2S gas

Efficiency of H_2S Removal

Hydraulic retention time (min.) = Column volume / Biogas flow rate

3. Results and Discussion

In each experiment, the packing materials were randomly added in the pilot biofilter with the height of 1.0 m in the column. Biogas flow rate was fixed at 0.60 m^3/hour and inlet H_2S concentration was about 2,000 to 3,000 mg/L. The temperature of biogas varied between 30 to 35°C. Hydrogen sulfide concentration from biogas inlet and outlet were monitored every 4 hours in 3 days in each experiment and used to calculate the removal efficiency (%). The operating parameters of the pilot biofilter during this study are shown in Table 1.

The H_2S removal efficiency of F18 (Fang hot-spring) bacterial biofilter was over 75% (76.62 ± 3.43%) throughout 72 hours (Figure 2) when the recirculation liquid flow rate and air flow rate were set at 1 L/hour and 0.03 m^3/hour, respectively. The pH value of the effluent dropped from 7.0 (at the beginning of the experiment) to lower than 3.0 after 1 day and retained at pH 2.5 to 3.0 until the end of the experiment. The amount of sulfate about 300 mg/l was detected in the recirculation tank.

H_2S may be degraded by microorganisms in 3 different ways: assimilation, mineralization, and sulfur oxidation [8]. The pathway for microorganisms to degrade H_2S by oxidation results in the release of energy and produces sulfuric acid. In oxygen-limited environments, oxidation may proceed only to elemental sulfur which produces less energy.

$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2\,H^+ \ (\Delta G^0 = -798.2 \text{ kJ/rxn}) \text{ ---------- (1)}$$

$$HS^- + ½\,O_2 + H^+ \rightarrow S_0 + H_2O \ (\Delta G^0 = -209.4 \text{ kJ/rxn}) \text{ --------- (2)}$$

$$S_0 + H_2O + 1½\,O_2 \rightarrow SO_4^{2-} + 2H^+ \ (\Delta G^0 = -587.1 \text{ kJ/rxn}) \text{ ---- (3)}$$

$$½S_2O_3^{2-} + ½\,H_2O + O_2 \rightarrow SO_4^{2-} + H^+ \ (\Delta G^0 = -409.1 \text{ kJ/rxn}) \quad (4)$$

Under the same operating conditions as in the first experiment, the average H_2S removal efficiency of acclimatized

bacteria from bio-scrubber effluent was 82.77±3.11% (Figure 3). The produced sulfate concentration in the recirculation tank was 300 mg/l and the pH of the effluent was also dropped from 7.0 to 2.5-3.0. Sulfide and Elemental sulfur were found a little in the recirculation liquid suggesting that oxygen in the biofilter may have been limited during the 2nd experiment. The highest hydrogen sulfide removal efficiency of 88.13±2.17% was achieved when the mixture of two bacterial sources (F 18 and acclimatized bacteria from bio-scrubber effluent) was used as inoculum in the pilot biofilter system (Figure 4). This indicated that cultures in biofilter can remove H_2S (sulfide loading rate) better than a single culture.

Biofilter is a promising method for removal of hydrogen sulfide in the biogas process. The results in this study indicate that the use of bacterial biofilm immobilized on plastic bio-balls can guarantee the effectiveness of hydrogen sulfide removal. As a next step to this work, the removal of hydrogen sulfide in a large scale biofilter system is planned, targetting a removal efficiency of more than 95%.

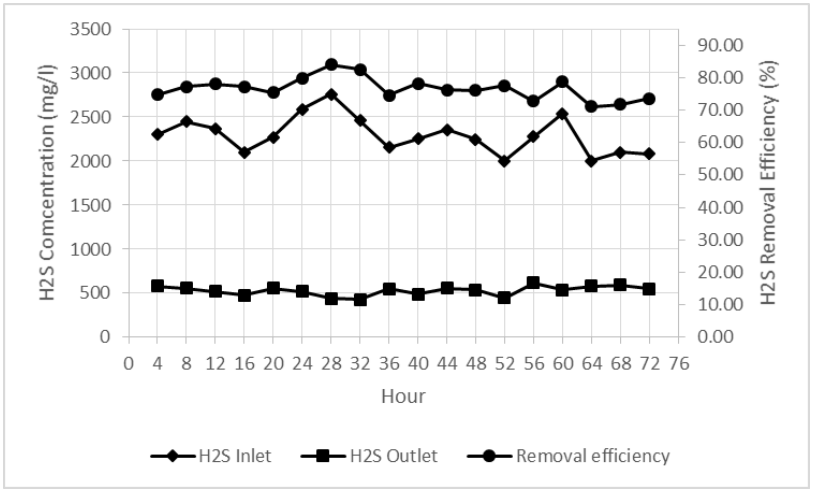

Figure 2. The hydrogen sulfide removal efficiency of F18 (Fang hot-spring) bacterial biofilter.

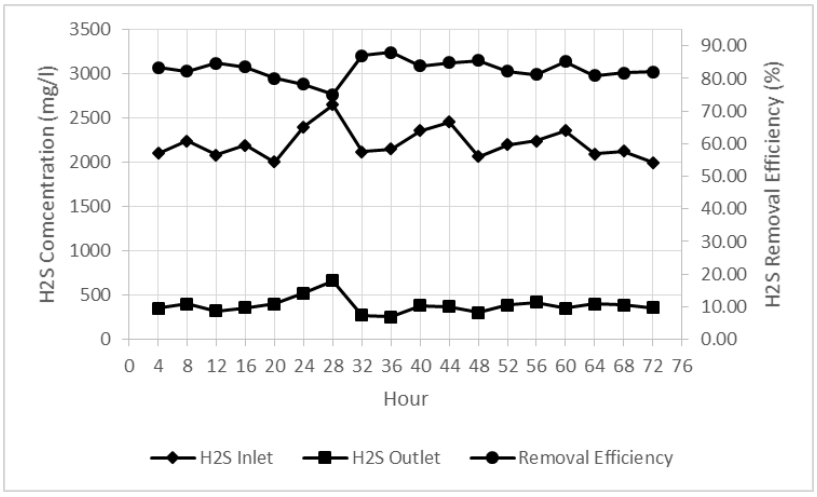

Figure 3. The hydrogen sulfide removal efficiency of bio-scrubber effluent bacterial biofilter.

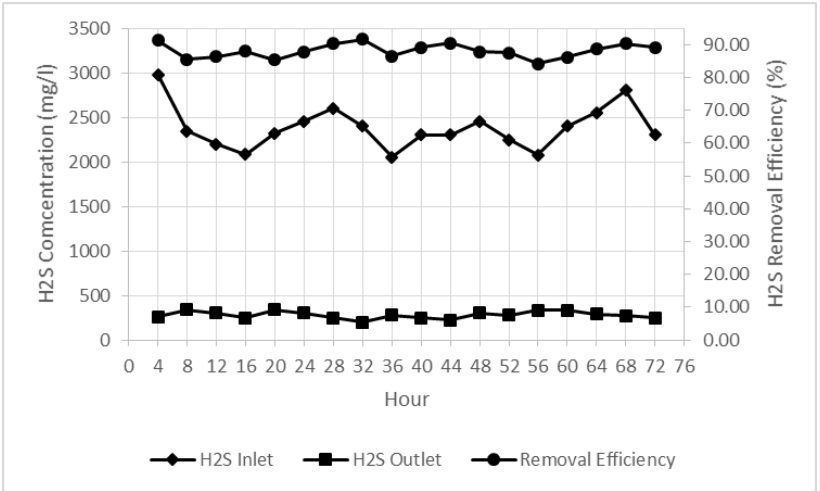

Figure 4. The hydrogen sulfide removal efficiency of F18 (Fang hot-spring) mixed with bio-scrubber effluent bacterial biofilter.

4. Conclusions

The removal of high H_2S concentration (about 2,000 - 3,000 mg/l) by bacterial biofilm from different sources in a biofilter system was investigated. The results showed that biofilter inoculated with hot-spring bacterial biofilm and bio-scrubber effluent biofilm had hydrogen sulfide removal efficiency more than 75 and 80 %, respectively. While the hydrogen sulfide removal efficiency more than 85% was achieved when mixture of two bacterial sources was used.

5. References

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