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Bio-desulfurization of biogas using acidic biotrickling filter with dissolved oxygen in step feed recirculation

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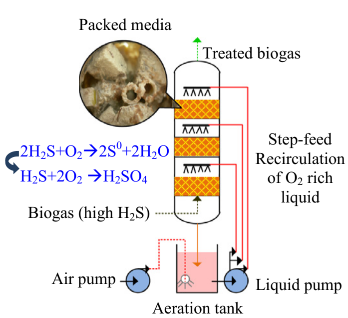
HIGHLIGHTS

- Triple stage biotrickling filter was superior to single stage biotrickling filter.
- H_2S removal efficiency was enhanced by step feeding O_2 rich liquid recirculation.
- 1st order removal rate coefficient of T-BTF was 47% higher than S-BTF.
- Larger liquid recirculation shifted O_2/H_2S balance system to complete oxidation.
- Sulfuric acid production improved with an increasing liquid recirculation velocity.

GRAPHICAL ABSTRACT



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ABSTRACT

Triple stage and single stage biotrickling filters (T-BTF and S-BTF) were operated with oxygenated liquid recirculation to enhance bio-desulfurization of biogas. Empty bed retention time (*EBRT* 100–180 s) and liquid recirculation velocity (q 2.4–7.1 m/h) were applied. H_2S removal and sulfuric acid recovery increased with higher *EBRT* and q. But the highest q at 7.1 m/h induced large amount of liquid through the media, causing a reduction in bed porosity in S-BTF and H_2S removal. Equivalent performance of S-BTF and T-BTF was obtained under the lowest loading of 165 $gH_2S/m^3/h$. In the subsequent continuous operation test, it was found that T-BTF could maintain higher H_2S elimination capacity and removal efficiency at 175.6 ± 41.6 $gH_2S/m^3/h$ and $89.0 \pm 6.8\%$ versus S-BTF at 159.9 ± 42.8 $gH_2S/m^3/h$ and $80.1 \pm 10.2\%$, respectively. Finally, the relationship between outlet concentration and bed height was modeled. Step feeding of oxygenated liquid recirculation in multiple stages clearly demonstrated an advantage for sulfide oxidation.

1. Introduction

Waste to energy approach is now becoming a standard practice, where various waste material feedstocks are converted to different forms of energy. Biogas from waste is among the most economical methods to transform liquid or semi-solid wastes through anaerobic digestion to methane (CH_4), which can be used as fuel to substitute conventional sources such as natural gas and oil. Hydrogen sulfide (H_2S) is an odorous and corrosive gas that is inevitably formed with the biogas when sulfur is present in the feedstock. It has detrimental effects in environment. At 1000–3000 ppm, human exposure to H_2S can cause instantaneous death (Wang et al., 2005). Combustion of the biogas containing H_2S

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generates SO_2 which is an acid rain precursor leading to damages to vegetation, architecture and building structure. For suitable biogas utilization in power generation, H_2S level below 500 ppm is generally a recommended upper limit while the ideal H_2S-free biogas is desired in order to avoid corrosion of biogas engines and fast degradation of engine lube oil.

Since the governmental subsidy from Thailand Ministry of Energy for small renewable power generation was put in place in 1995, anaerobic digestion for industrial wastewaters had flourished due to the maturation of technology and environmental benefit it provided. So far, factories in Thailand have installed over 1145 biogas systems across various sectors (Thailand Energy Policy and Planning Office, 2012). Among, the concentrated latex and ethanol industries have shown little interest in biogas technology although their wastewaters have a potential. Their high sulfate wastewaters are often problematic through the offensive odor of H_2S emitted from waste storage ponds to surrounding communities. If anaerobic digester is used, there will be an intense H_2S production with the biogas, reaching as high as 13,000–26,000 ppm for concentrated latex industry (Chaiprapat et al., 2011; Saelee et al., 2009) and 30,000 ppm for ethanol industry (Frankel, 1986). In addition, some specific factories have also produced the biogas with high H_2S such as some seafood processing plants whose biogas containing 5000–8000 ppm as a result of alum use in the process.

Traditional technologies of gas decontamination are based on physical, chemical and thermal principles that normally incur high operating cost and generate waste to be disposed. Biological treatments are economically advantageous especially when the gas stream contains biodegradable or bio-convertible compounds (Devinny et al., 1999; Gabriel and Deshusses, 2003; Tomàs et al., 2009). In biotrickling filtration system, a subgroup of biofiltration, active microbes are immobilized onto bed material while the liquid moves downward typically in countercurrent with the gas stream. The mixture of gaseous H_2S and O_2 coming from air injection is absorbed to liquid phase then dispersed to the attached biofilm. That H_2S is biochemically oxidized to the metabolic products of elemental sulfur (S^0) or sulfuric acid (H_2SO_4) depending on whether partial or complete oxidation is taking place (Devinny et al., 1999; Maier et al., 2009; Yamanaka, 2008). Although both reactions are carried out by sulfide oxidizing bacteria (SOB), to what degree each reaction proceeds depends on the reactor configuration and operating condition that will dictate the micro environment interphase within the filter bed. However, previous studies have mostly focused on the biodesulfurization at low concentrations (Jin et al., 2005; Tang et al., 2009). Only a few works on biofiltration were conducted at elevated H_2S concentrations, i.e. above 4000 ppmv (Fortuny et al., 2008, 2011; Rattanapan et al., 2009), but even fewer were done using real biogas with high H_2S as inlet (Chaiprapat et al., 2011; Rodriguez et al., 2014; Tomàs et al., 2009).pH of recirculating liquid, liquid recirculation rate and empty bed retention time are among the key operating parameters in biotrickling filtration influencing the biochemical H_2S oxidation performance. Because sulfuric acid is a product of H_2S oxidation, acidic biofiltration was considered suitable. Although some alkaline biotrickling filtration was proposed (González-Sánchez et al., 2008), higher operating cost to maintain pH against the acidifying state becomes a big obstacle for industrial biogas cleanup. Some sulfide oxidizing bacteria (SOB) such as *Acidithiobacillus* sp. are capable of living in extreme pH due to their ability for adaptations that involve changes to the cytoplasmic membrane controlling ion transport (McArthur, 2006). In this work, extreme acidic condition was employed since the recovery of sulfuric acid by microbial activity was aimed as a byproduct from the process.

Oxygen availability and mass transfer could become a limiting factor for biological H_2S oxidation because of its low solubility in water, only 8.24 mg/L at 25 °C (Colt, 1984). Over supply of air, which composed of only 21% oxygen, through air mix with biogas to biotrickling filter will cause dilution of methane (Chaiprapat et al., 2011). Duangmanee et al. (2009) succeeded in control of O_2 at lower than 5% in off gas by micro-aeration for removing H_2S with partial oxidation although it was strictly chemical reaction. O_2 could be delivered in other means to avoid over injecting of air. In biofiltration, O_2 could be delivered in dissolved form (dissolved oxygen, DO) through the recirculating liquid coming in contact with the biogas stream (Rodriguez et al., 2014). The liquid recirculation velocity (q, m/h), defined as the amount of recirculating liquid applied per unit surface area of a packed bed, could play an important role in regulating such O_2 supply to the system. This method not only reduced CH_4 dilution in biogas but also supplied moisture and nutrients to the microorganisms inside the reactor, and wash the microbial metabolic products off the biofilm (Charnnok et al., 2011). However, a long travel path of biogas and recirculating liquid with single inlet point from the opposite ends cause uneven distribution of the reactants. By dividing the bioreactor into multiple stages with different reactant injection points, the biochemical reactions can be distributed more evenly (Metcalf and Eddy, 2004). In this case, it may shift the reaction toward complete H_2S oxidation by mitigating mass transfer limitation. This bed division or staging configuration also benefited from the lower weight of media pressing down to the lower level that can prevent compaction of the material and clogging of microbial mass leading to lower pressure drop (Elías et al., 2000).

EBRT represents a ratio of empty bed volume of a biotrickling filter to its gas inflow rate. It was reported by many researchers that longer resident time of the H_2S stream within a bioreactor gave higher removal efficiency (Chaiprapat et al., 2011; Charnnok et al., 2013; Montebello et al., 2014). It is worth noticing that the range of *EBRT* in those studies varied greatly from a few seconds to around 5 min. This was depending mainly on the loading to their systems and concentration of H_2S inlet, oxygen availability, and other operating regimes. Although longer *EBRT* could benefit the removal of H_2S, excessively large reactor volume typically resulted in higher construction costs. Effects of EBRT as a base parametric variable in interaction with staging and flow pattern on biotrickling filter system performance are of interest in this study.

The aim of this research was to investigate the effects of *EBRT* and liquid recirculation velocity (q) on H_2S removal efficiency of the triple stage step-feed biotrickling filter in light of a better oxygen distribution through reactor staging configuration. In depth comparison to the single stage biotrickling filter was conducted to identify the degree of improvement in terms of sulfate–sulfide speciation from the proposed multi stage step-feed liquid recirculating system. Finally, a simplified equation with minimal variable to predict H_2S removal was developed and used to compare the single and triple stages biotrickling filters.

2. Method

2.1. Biotrickling filter system and operation

A laboratory single stage biotrickling filter (S-BTF) and triple stage step-feed biotrickling filter (T-BTF) (Fig. 1) were made of cylindrical acrylic with an inner diameter of 4.4 cm and 90 cm in height. The total packed bed media depth was 30 cm equivalent to 456.3 cm^3 empty bed volume. The packed bed of T-BTF was divided into 3 stages (lower, middle and upper) at 10 cm high in each stage, to improve dissolved O_2 distribution to the bed. S-BTF with equal size of total packed bed volume was operated for comparison to T-BTF. Coconut husk (the outer layer of the coconut fruit, consisting of long fibers and sponge-like pith particles) was chosen