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Biogas desulfurization under anoxic conditions using synthetic wastewater and biogas slurry

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ABSTRACT

A feasibility study was conducted to determine whether aerated biogas slurry is a suitable nutrient solution for biogas desulfurization systems with a biotrickling filter. At a loading rate of 36.20 g-H_2S $m^{-3}h^{-1}$, the H_2S and NO_x^--N removal efficiencies were 84.7% (average elimination capacity of 30.67 g-H_2S $m^{-3}h^{-1}$) and 60.9%, respectively, when utilizing synthetic wastewater in a simultaneous biogas desulfurization and wastewater denitrification system. However, these efficiencies were just 61.9% (average elimination capacity of 22.42 g-H_2S $m^{-3}h^{-1}$) and 49.2%, respectively, when biogas slurry was used. High-throughput sequencing revealed that the *Thiobacillus* and *Sulfurimonas* genera were the main functional bacteria. Alpha- and beta-diversity analyses showed that the H_2S loading rate significantly affected the microbial community structure, especially in the system utilizing aerated biogas slurry. Finally, based on the results, we describe a feasible approach to using biogas slurry for biogas desulfurization.

1. Introduction

Biogas, which comprises a mixture of different gases, is produced by anaerobic digestion (Lastella et al., 2002). Manure from livestock and poultry is the main raw material for the production of biogas in China (Li et al., 2009a). Manure contains large quantities of proteins and other sulfur-containing compounds. As a consequence, the biogas produced by anaerobic digestion will contain hydrogen sulfide (H_2S) (Pokorna et al., 2015; Potumarthi et al., 2009), which is a toxic gas with a strong corrosive effect on combustion power equipment and metal pipes (Vikromvarasiri et al., 2017). Furthermore, during the combustion of biogas, H_2S is converted into sulfur oxides, which are released into the atmosphere, causing air pollution (Watsuntorn et al., 2017; Zhou et al., 2015). Therefore, the H_2S in biogas must be removed before used.

Currently, physicochemical and biological methods are typically adopted for the removal of H_2S from biogas (Kao et al., 2012). However, physicochemical methods such as chemical oxidation, physical adsorption, and cryogenic separation require large quantities of chemical agents and adsorbents, and they consume significant amounts of energy (Zhang et al., 2016). Moreover, these adsorbents are expensive to dispose of and may cause secondary pollution (Chaiprapat et al., 2011). Hence, the most popular method for removing H_2S from biogas is biological desulfurization (Pokorna et al., 2015; Rattanapan et al., 2010), of which there are two main types: aerobic desulfurization and anoxic desulfurization. Aerobic desulfurization technology has been studied extensively (Rattanapan et al., 2010). With this method, however, oxygen is used as the electron acceptor, and mixing oxygen with biogas can dilute the biogas and lead to an increased risk of explosion. Anoxic desulfurization has lower limitations on the mass transfer for

Abbreviations: H_2S, hydrogen sulfide; BTF, biotrickling filter; WWTP, Wastewater Treatment Plants; SDD, simultaneous biogas desulfurization and wastewater denitrification system; LR, loading rate; RE, removal efficiency; EC, elimination capability; HRT, hydraulic retention time; EBRT, empty bed residence time

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nitrate compared to oxygen absorption in aerobic biotrickling filters (BTFs). However, the cost and the need for large quantities of nitrate can limit the application of anoxic desulfurization (Almenglo et al., 2016b). The anoxic method utilizes NO_x^- as the electron acceptor, whereby H_2S is oxidized to elemental sulfur or sulfates (Almenglo et al., 2016a). The reaction conditions are mild and require little energy, and simultaneous desulfurization of biogas and denitrification of wastewater can be achieved by exploiting the principle of treating waste with waste (Mahmood et al., 2007a). The main reactions in the systems are as follows (Li et al., 2009b):

$$5S^{2-} + 2NO_3^- + 12H^+ \rightarrow 5S + N_2 + 6H_2O\ \Delta G^\theta = -955\ \text{kJ/reaction} \quad (1)$$

$$5S + 6NO_3^- + 2H_2O \rightarrow 5SO_4^{2-} + 3N_2 + 4H^+\ \Delta G^\theta = -2738\ \text{kJ/reaction} \quad (2)$$

$$3S^{2-} + 2NO_2^- + 8H^+ \rightarrow 3S + N_2 + 4H_2O\ \Delta G^\theta = -917\ \text{kJ/reaction} \quad (3)$$

$$3S + 6NO_2^- \rightarrow 3SO_4^{2-} + 3N_2\ \Delta G^\theta = -2027\ \text{kJ/reaction} \quad (4)$$

Unfortunately, biogas plants are typically located in remote locations, where there are no available wastewater resources containing NOx^- ions, such as a domestic wastewater or swine wastewater (Pirolli et al., 2016). The use of synthetic wastewater is uneconomical, and it increases operational and maintenance complexity (Arespacochaga et al., 2014). As is known, ammonia nitrogen can be converted into nitrate/nitrite nitrogen by a nitrification reaction, and this reaction has been widely employed for removing ammonia from Wastewater Treatment Plants (WWTPs) (Deng et al., 2009). Therefore, if biogas slurry could be used for biogas desulfurization plant, it would greatly reduce construction costs and simplify the operational process. However, because the composition of biogas slurry is complex, there have been few reports of its use in desulfurization procedures (Almenglo et al., 2016b; Deng et al., 2009). Moreover, even fewer studies have compared synthetic wastewater and biogas slurry as a nutrient solution in a simultaneous biogas desulfurization and wastewater denitrification system (SDD).

This study utilizes synthetic wastewater and aerated biogas slurry as a nutrient solution to investigate the influence of the biogas loading rate (LR) on the H_2S removal efficiency (RE), and on the structure of the key microbial communities during the reaction process. We also compare the effectiveness of two types of nutrient solutions, synthetic wastewater and aerated biogas slurry. Based on the results, some suggestions for how biogas slurry can be used for biogas desulfurization are provided.

2. Materials and methods

2.1. Experimental reactors of biogas desulfurization

The experimental reactors, packed with pall rings (r × H = 12.5 mm × 25 mm), were constructed from poly(methyl methacrylate), with a total volume of 7.0 L and a working volume of 5.0 L. Clear poly(methyl methacrylate) tubes, located at the top and bottom of the reactor, were respectively used as the inlet and outlet for the biogas (Fig. 1 (6)). The nutrient solution was circulated using a peristaltic pump (LongerPump BT 300-2J), and the precise biogas flow was controlled using a glass rotor flowmeter (LZB-4, China). A centrifuge pump (MP-10RN, China) was used to mix the nutrient solution in the reactor before sampling. The operations were carried out at a constant temperature of 30 ± 1 °C.

2.2. Inoculum sources and biofilm culture

The inoculants were a mixture of an aerobic activated sludge from a WWTP and anaerobic digestion slurry (Wang et al., 2015). In the biomass immobilization stage, the mineral medium was used to cultivate and enrich functional microorganisms. The mineral medium was replaced every day. Once the NO_3^- removal rate was stable, the raw biogas was added into the reactor through the inlet (biogas flow rate = 0.5 L/min). When the H_2S RE reached stable values above 90%, this operation was stopped.

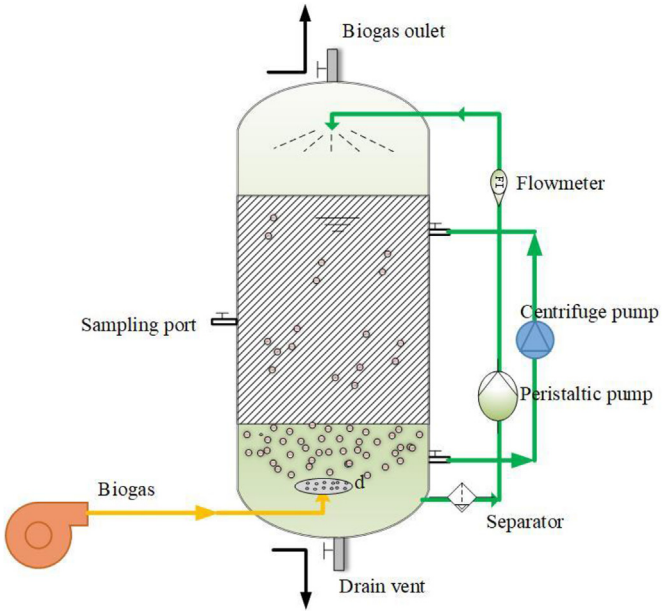

Fig. 1. Schematic diagram of the experimental reactor.

The composition of the mineral medium was: $Na_2S_2O_3{\cdot}5H_2O$ (5.0 g/L), KNO_3 (4.0 g/L), KH_2PO_4 (2.0 g/L), $NaHCO_3$ (1.0 g/L), $MgCl_2{\cdot}6H_2O$ (0.5 g/L), $FeSO_4{\cdot}7H_2O$ (0.01), and trace element solution (1 mL) (Xu et al., 2016). The pH of the medium was adjusted to 7.0 using aqueous solutions of NaOH (1 mol/L) and HCl (1 mol/L) before the overall volume was increased to 1 L using tap water (Wang et al., 2015).

The composition of the trace element concentrate was as follows: EDTA (0.5 g/L), $FeSO4{\cdot}7H_2O$ (0.2 g/L), and 100 ml/L of trace element solution SL-6. The trace element solution SL-6 was composed of the following (g/L): $ZnSO_4{\cdot}7H_2O$ (0.1 g/L), $MnCl_2{\cdot}4H_2O$ (0.03 g/L), H_3BO_3 (0.3 g/L), $CoCl_2{\cdot}6H_2O$ (0.2 g/L), $CuCl_2{\cdot}2H_2O$ (0.01 g/L), $NiCl_2{\cdot}6H_2O$ (0.02 g/L), and $Na_2MoO_4{\cdot}H_2O$ (0.03 g/L) (Almenglo et al., 2016b).

2.3. Experimental setup

In this study, two reactors were set up, A0 (without inoculum) and A (with inoculum). The inoculum of the BTF A0 was 5 L of tap water, and the BTF A was inoculated with a mixture of anoxic sludge and tap water. The study was divided into two stages. In stage I, the influent was synthetic wastewater, and 1 L synthetic wastewater was exchanged every day. In stage II, the influent was aerated biogas slurry, and 0.5 L aerated biogas slurry was exchanged every day. The second stage was initiated based on the promising results obtained from stage I. The operating parameters for the two stages are shown in Table 1.

The biogas used in this study was obtained from an anaerobic digester with a volume of 200 m^3, which contained 66–69% (*v/v*) methane, 25–30% carbon dioxide, and 0.2% H_2S. The compositions of the synthetic wastewater, aerated biogas slurry, and raw biogas slurry are shown in Table 2.

2.4. Influence of the main operational variables

The LR, hydraulic retention time (HRT), elimination capability (EC), empty bed residence time (EBRT), and RE are respectively derived using Equations (5)–(9):