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A hybrid membrane gas absorption and bio-oxidation process for the removal of hydrogen sulfide from biogas

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ABSTRACT

A study was conducted on hydrogen sulfide (H_2S) removal from biogas using a novel hybrid polydimethylsiloxane (PDMS) membrane bioscrubber. The effect of absorption liquid pH, biogas flowrate and DO concentration on H_2S selectivity, removal efficiency and sulfide oxidation were investigated. The process performance at pH 7 was better than pH 8.5 in terms of H_2S removal capacity and selectivity. Desulfurization selectivity of H_2S/CO_2 and H_2S/CH_4 increased along with the increase of gas flowrate (32 l/d) and reached 3.5 and 63, respectively. The calorific value of the biogas significantly increased due to the raising of CH_4 content by 21%. During the long-term operation, air diffusion through the membrane into the biogas was not observed. Almost complete H_2S removal (> 97%) and high conversion ratio to S^o (> 74%) were achieved when volumetric loading rate and DO concentration were kept below 148 g H_2S/m^3d and 1 mg/l, respectively. Partial oxidation of sulfide to S^o (1 mg/l) rather than sulfate (4 mg/l) reduced the caustic consumption by half. Even though S^o and inorganics were detected on membrane surface with SEM-EDS analysis, fouling and wetting problems were not observed. The novel hybrid process developed in this study is a cost-effective and robust alternative to conventional biogas desulfurization.

1. Introduction

Biogas is a renewable and sustainable energy source which is produced by anaerobic digestion of organic substances. The nature of organic substrates and the operational conditions used during anaerobic digestion processes determine the chemical compositions of the biogas. The raw biogas contains mainly, 40–75% of CH_4 and 15–60% of CO_2, 0.1–2%v/v (1000-20,000 ppmv) of H_2S and other impurities (Fortuny et al., 2011; Montebello et al., 2012). The presence of H_2S in biogas needs special attention due to its odor, toxicity and serious corrosion problems and thus limit plant lifetime (Chen et al., 2017; Panza and Belgiorno, 2010; Park et al., 2014). Moreover, during the combustion of biogas it generates sulfur oxides (SOx), which can cause adverse effects on the atmosphere and human health (Chaiprapat et al., 2011; Park et al., 2014). The maximum allowable concentration of H_2S is from 10 to 500 ppmv and below 5 ppmv when biogas is used to produce heat and power and as a fuel for vehicles, respectively (Díaz et al., 2011; Fortuny et al., 2011). Therefore, cleaning of H_2S from the biogas is required prior to use it in any commercial or long-term application. Numerous physicochemical methods of biogas desulfurization were described in the literature, such as absorption, adsorption, chemical oxidation (Table S1, Supplementary materials). However, these processes have high operating costs related with energy and chemicals, and also generate byproduct which needs treatment before discharge (Abatzoglou and Boivin, 2009; Muñoz et al., 2015; Petersson and Wellinger, 2009). To overcome these inconsistencies, biological treatments have been proposed as a convenient alternative for treating H_2S from biogas because of its eco-friendliness, energy savings and low-operating costs (Cline et al., 2003; Syed et al., 2006; Yang et al., 2010). Although these systems have many advantages, there are also problems during operation of these technologies, such as biomass accumulation, clogging, dilution, risk of explosion, difficulty in control of the operational parameters and high capital cost (Table S2, Supplementary materials). Further studies on the biogas desulfurization is required to develop novel technologies, capable of making biogas technically suitable, economically viable, and ecologically appropriate source of energy. Nowadays, membrane processes are considered to be an excellent alternative technology for gas purification. This type of process offers several practical advantages including simplicity and low energy and operating costs. Porous hollow fiber membrane contactors (HFMC) which offer high mass transfer characteristics attracted the attention of researchers for biogas purification (Gabelman and Hwang, 1999).

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However, the performance of HFMC declines when it is used for long operational periods, owing to penetration of solvent through the pores of wetted membranes (Table S1, Supplementary materials). By selecting non-porous dense polymeric membranes, these problems can be eliminated.

Accordingly, in this study a PDMS membrane gas purification and bio-oxidation processes were combined. During the process, H_2S is first dissolved in an aqueous absorption liquid according to reaction 1, followed by two dissociation reactions 2 and 3. In order to maintain a high H_2S diffusion rate, mildly alkaline solution is generally used. Then, bio-oxidation of H_2S occurs in the bioreactor according to reactions 4 and 5. The route of H_2S oxidation is dependent on the concentration of oxygen, i.e., it is oxidized to elemental sulfur (S^o) or sulfate under oxygen limiting and non-limiting conditions, respectively.

$$H_2S_{gas} \leftrightarrow H_2S_{aq} \quad (1)$$

$$H_2S_{aq} + OH^- - \leftrightarrow HS^- + H^+ \quad (pKa = 7.0) \quad (2)$$

$$HS^- + OH^- \leftrightarrow S^{2-} + H_2O \quad (pKa = 12.9) \quad (3)$$

$$HS^- + 0.5O_2 \leftrightarrow S^o + OH^- \quad (\Delta G^o = -169.35\ kJ.mol^{-1}) \quad (4)$$

$$HS^- + 2O_2 \leftrightarrow SO_4^{-2} + H^+ \quad (\Delta G^o = -732.58\ kJ.mol^{-1}) \quad (5)$$

It is clear that the concentration of CO_2 in biogas is much higher than H_2S, and both have similar acidic behavior. CO_2 and H_2S can both be absorbed in an alkaline solution (Miltner et al., 2017; Ryckebosch et al., 2011). Absorption, hydrolysis and dissociation of CO_2 in alkaline solutions are indicated in reactions 6–9. Hence the removal of CO_2 generates additional H^+, which can decrease the pH of the absorption liquid according to reactions 8 and 9. In order to maintain a high H_2S removal efficiency, pH of the absorption liquid needs to be high; therefore, extra alkali should be supplemented, which increases the operational costs.

$$CO_{2gas} \leftrightarrow CO_{2aq} \quad (6)$$

$$CO_{2aq} + H_2O \leftrightarrow H_2CO_{3aq} \quad (7)$$

$$H_2CO_{3aq} \leftrightarrow HCO_3^- + H^+ \quad (pKa = 6.4) \quad (8)$$

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \quad (pKa = 10.3) \quad (9)$$

The CO_2 removal should be minimized to reduce the alkali chemical consumption, which can be achieved by using non-porous dense PDMS membranes due to its higher selectivity towards H_2S compared to CO_2 (Montoya, 2010; Tilahun et al., 2017). The objective of this study was to evaluate the performance of a novel hybrid membrane bio-scrubber (MBS) process for selective H_2S removal from a simulated biogas. In addition, the effects of the absorption liquid pH, gas flowrate (loading) and DO concentration on biogas desulfurization performance were discussed.

2. Materials and methods

2.1. Experimental set-up and operation

The laboratory scale hybrid membrane bio-scrubber contactor setup used in this study was shown in Fig. 1. It was consisted of a cylindrical glass reactor with 120 mm of diameter and 200 mm of depth and a working volume of 1.5 l. The glass reactor was filled completely with tap water to minimize the volatilization of the sulfur compounds. Besides, it was operated by feeding with a simulated biogas (Hat Industrial Gases PLC, Kocaeli, Turkey) containing 60% (v/v) CH_4, 39% (v/v) CO_2, and 1% (v/v) (10,000 ppmv) H_2S through the PDMS tubular membrane. The membrane was folded and fully submerged into the absorption liquid. The flowrate of the biogas was adjusted and controlled by using mass flow controller at outlet of the gas cylinder and measured by gas counters (MGC, Ritter) both in the influent and effluent of the membrane contactor. The commercial tubular PDMS membrane (EUROFLEX GmbH, Germany) had an internal diameter of 7.0 mm, wall thickness of 1.0 mm and length of 3.25 m, corresponding to a total surface area of 9.2 dm^2. The reactor was inoculated with the sludge taken from a laboratory scale aerobic membrane bioreactor treating sulfide containing textile wastewater. The inoculum consisted of two dominating sulfide oxidizing bacteria, *Thiobacillus* spp. and *Thioalkalivibrio sulfidiphilus* (Yurtsever et al., 2017). The liquid medium was composed of (g/l): K_2HPO_4 2.0, NH_4Cl 0.4, $MgCl_2{\cdot}6H_2O$ 0.2 and tap water. Due to low cost and its effectiveness, NaOH was used as alkaline chemical (Jegatheesan et al., 2015). Conductivity of the absorption liquid in the bioreactor increased during the operation due to NaOH addition and sulfate generation. Hence, around 2/3 of the absorption liquid was periodically removed from the bioreactor not to disturb the bacterial activity when conductivity raised over 7 mS/cm. During the operation, the absorption liquid was aerated to supply oxygen to sulfide oxidizing bacteria as electron acceptor. The reactor content was continuously stirred with a magnetic stirrer at 550 rpm to achieve complete mixing and to control the attachment of biomass on the membrane surface. The pH of the absorption liquid was controlled automatically by addition of NaOH (1N) with a pH transmitter and a dosing pump (Seko, PR 40/Q). The temperature was kept at 30 ± 1 °C using an electric heating pad wrapped around the bioreactor. During the experiments, conductivity, oxidation reduction potential (ORP) and dissolved oxygen (DO) were monitored online using a digital multimeter (Multi 9430, WTW GmbH, Germany). The hybrid membrane bio-scrubber (MBS) operating parameters were shown in Table 1.

2.2. Analytical methods

The CO_2, H_2S and CH_4 compositions in the inlet and outlet of the membrane contactor were measured using a gas chromatograph (Shimadzu GC-2014, Japan) equipped with thermal conductivity detector (TCD) (Reddy et al., 2016). Sulfide concentrations in the absorption liquid were determined spectrometrically (DR/2800, HACH, USA) following the methylene blue method described by Standard Methods (APHA/AWWA/WEF, 2012). In the MBS liquor samples, following 0.45 μm filtration, sulfate, thiosulfate and sulfite concentrations were analyzed daily using an ion chromatography. Biomass concentration in the bioreactor was estimated by measuring Total Kjeldahl (TKN) according to standard methods (APHA/AWWA/WEF, 2012). Before analyzing TKN, the liquid sample was centrifuged and the biomass was washed 3 times with deionized water to remove dissolved nitrogen compounds. The presence and crystal structure of elemental sulfur (S^o) and other byproducts from the suspended biofilms of the MBS reactor was examined using X-Ray diffraction (XRD). The morphology of clean and used membrane surface at the end of the experiment period was examined using an optical microscope and scanning electron microscopy (SEM) images. In addition, SEM coupled with Energy Dispersive X-ray Spectroscopy (EDS) analyses were conducted to determine the inorganic content of the biofilm attached on the external surface area of the membrane.

2.3. Calculations

In this study, the CO_2 or H_2S gas phase removal efficiencies (R) and CH_4 loss were calculated according to Eq. (10).

$$R\ (\%) = \frac{(Q_g in * C_g in) - (Q_g out * C_g out)}{(Q_g in * C_g in)} * 100 \quad (10)$$

where, R-gas phase removal efficiencies, Q_g^{in} – inlet biogas flowrate (m^3/d), Q_g^{out} – outlet biogas flowrate (m^3/d), C_g^{in} - inlet gas concentrations (mg/l), C_g^{out} - outlet gas concentrations (mg/l). In gas purification processes the performance of the system can be indicated also by computing the selectivity factor. Selectivity of the gas-liquid-