Bioresource Technology 231 (2017) 124–128

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Short Communication

Elimination of methane in exhaust gas from biogas upgrading process by immobilized methane-oxidizing bacteria

Ya-Min Wu [a,b,1], Jing Yang [a,1], Xiao-Lei Fan [b], Shan-Fei Fu [b,c], Meng-Ting Sun [b,c], Rong-Bo Guo [b,*]

[a] State Key Laboratory of Mining Disaster Prevention and Control Co-founded by Shandong Province and the Ministry of Science and Technology, Shandong University of Science and Technology, Qingdao, Shandong Province 266510, PR China
[b] Shandong Industrial Engineering Laboratory of Biogas Production & Utilization, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, Shandong Province 266101, PR China
[c] University of Chinese Academy of Sciences, Beijing 100049, PR China

HIGHLIGHTS

- Porous active carbon was successfully made from biogas digestate.
- Active carbon was used as immobilized material for MOB.
- Biofilter with immobilized MOB showed higher methane-oxidizing efficiency.
- Low concentration of methane can be efficiently disposed by immobilized MOB.

ARTICLE INFO

Article history:
Received 24 October 2016
Received in revised form 8 January 2017
Accepted 11 January 2017
Available online 13 January 2017

Keywords:
Methane oxidation
Biogas digestate
Immobilization
Biofilter

ABSTRACT

Biogas upgrading is essential for the comprehensive utilization of biogas as substitute of natural gas. However, the methane in the biogas can be fully recovered during the upgrading process of biogas, and the exhaust gas produced during biogas upgrading may contain a very low concentration of methane. If the exhaust gas with low concentration methane releases to atmosphere, it will be harmful to environment. In addition, the utilization of large amounts of digestate produced from biogas plant is another important issue for the development of biogas industry. In this study, solid digestate was used to produce active carbon, which was subsequently used as immobilized material for methane-oxidizing bacteria (MOB) in biofilter. Biofilter with MOB immobilized on active carbon was used to eliminate the methane in exhaust gas from biogas upgrading process. Results showed porous active carbon was successfully made from solid digestate. The final methane elimination capacity of immobilized MOB reached about 13 mol h^{-1} m^{-3}, which was more 4 times higher than that of MOB without immobilization.

1. Introduction

As one of the most important biofuels, biomethane production from organic substrate according to anaerobic digestion receives increasing attentions (Monlau et al., 2014). Large numbers of biogas plants are built all over the world, particularly Germany, where the people are implementing assistance measures and legal regulations for renewable energy sources to promote the progress of biogas technology. At the end of 2008, there were approximately 4000 agricultural biogas plants operating on German farms, and the number of biogas plants grows continuously and exceeded 7000 plants by the end of 2011(Hans et al., 2012). In china, government has set a goal to built 60 million household-scale anaerobic digesters in rural areas by 2020 (You et al., 2014).

Biogas is a mixture, which contains about 60% CH_4, 40% CO_2 and small amounts of H_2S, H_2, and NH_3 (van der Ha et al., 2012). Raw biogas can be directly used to generate power, but the large volume of CO_2 reduces the heating value of biogas and limits economic feasibility to use (Andriani et al., 2014). Raw biogas has a calorific value of 22,000–25,000 kJ·m^{-3}, however, after removing CO_2, the calorific value of the methane gas goes up to 39,000 kJ·m^{-3} (Xiao et al., 2014; Yin et al., 2009). Purifying biogas to methane content above 96%, it will obtain similar property as natural gas, which can be used as a transport vehicle fuel, or as a substitute for natural gas. However, the methane in the biogas

* Corresponding author at: Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, No. 189 Songling Road, Qingdao, Shandong Province 266101, PR China.
E-mail address: guorb@qibebt.ac.cn (R.-B. Guo).
[1] These author contributes to this study.

http://dx.doi.org/10.1016/j.biortech.2017.01.020
0960-8524/

can be fully recovered during the purification process of biogas, and the exhaust gas produced during biogas upgrading may contain a very low concentration of methane. When the exhaust gas releases to environment, the remaining methane will contribute to the global warming. The disposal of exhaust gas produced during biogas upgrading is an important aspect in biogas upgrading system. Compared with other treatment methods, biotechnological applications using methane-oxidizing bacteria (MOB) are economically beneficial and environmentally friendly, which had been used for ruminants' gas effluent and atmospheric methane (Ganendra et al., 2015, 2014). However, methane-oxidizing bacteria have not been reported to be used for methane removal in exhaust gas from biogas upgrading process.

Meanwhile, the fast developing of biogas plants will also produce a large amount of solid digestate that cannot be utilized by microbes in the anaerobic process (Cai et al., 2011). Only a little biogas residue has been used as fertilizer, because the amount of lignin in anaerobically digested residue is higher than in conventional slurry, especially for anaerobic digestion of agricultural by-products, such as dairy manure, straw and energy crops (Arthurson, 2009). More of the biogas residue was deposited in biogas plants or on arable land around the plants, then it would have a negative effect on the environmental protection. In our previous study, solid digestate presented to be an ideal substrate to prepare active carbon, which can be used as immobilized material for methane-oxidizing bacteria to increase the methane-oxidizing efficiency (Yuan et al., 2011).

In this study, the solid digestate was used to prepare active carbon, which was subsequently used as the immobilized material for methane-oxidizing bacteria. And the biofilter with methane-oxidizing bacteria immobilized on active carbon from solid digestate were investigated to deal with exhaust gas produced during biogas upgrading.

2. Methods and materials

2.1. Preparation and chemical characterization of activated carbons

Solid digestate in this study was obtained from a 500 m^3 size of biogas plant (Qingdao, Shandong province, China), which used corn straw as feedstock and running at 35 °C with Hydraulic Retention Time (HRT) of 35 d. The solid waste were washed with little water and then used for active carbon preparation. The process of active carbon preparation followed previous study (Yuan et al., 2011).

Methylene blue (MB) adsorption was used to evaluate the adsorption ability of produced active carbon. 0.1 g active carbon was added into 500 mL conical flasks with stopper containing 300 mL MB solution of 20 mg L^{-1}, 40 mg L^{-1} and 60 mg L^{-1} at pH 7.0, respectively. The flasks were agitated mechanically for predetermined time intervals at 140 rpm using a rotary orbital shaker, and maintained at 25 °C. The progress of the adsorption process was determined by measuring the absorbance of the solution after filtration using a UV/visible spectrometer (Cary 50, Varian, USA) at a wavelength of 665 nm at different time intervals. This experiment was carried out in duplicate, and the results expressed as a mean. The MB uptake by the adsorbent was calculated using the Eq. (1).

$$q_t = V(C_0 - C_t)/w \quad (1)$$

where q_t (mg g^{-1}) is the amount of MB adsorbed and C_t (mg L^{-1}) was the concentration of MB solution at time t (Lonappan et al., 2016).

2.2. Separation and enrichment of methane-oxidizing bacteria

Paddy soil with total solid (TS) of 62.82% and volatile solid (VS) of 3.79% (% of TS) collected from Sanya, Hainan province was used as source for methane-oxidizing bacteria separation. The separation and enrichment of methane-oxidizing bacteria were conducted in 250-mL serum bottles, during which the Nitrate Mineral Salt (NMS) medium described as Sheets, et al. was used as nutrient solution. It contained $MgSO_4{\cdot}7H_2O$ (1.0 g L^{-1}), KNO_3 (1.0 g L^{-1}), KH_2PO_4 (0.272 g L^{-1}), Na_2HPO_4 (0.284 g L^{-1}), $CaCl_2{\cdot}2H_2O$ (0.134 g L^{-1}), chelated Fe solution (0.2% (v/v)), and a trace element solution (0.05% (v/v)). The chelated Fe solution contained ferric (III) ammonium citrate (1.0 g L^{-1}), EDTA (2.0 g L^{-1}), and concentrated HCl (0.3% (v/v)) in deionized (DI) water. The trace element solution contained EDTA (500 mg L^{-1}), $FeSO_4{\cdot}7H_2O$ (200 mg L^{-1}), $ZnSO_4{\cdot}7H_2O$ (10 mg L^{-1}), $MnCl_2{\cdot}4H_2O$ (3.0 mg L^{-1}), H_3BO_3 (30 mg L^{-1}), $CoCl_2{\cdot}6H_2O$ (20 mg L^{-1}), $CaCl_2{\cdot}2H_2O$ (1.0 mg L^{-1}), $NiCl_2{\cdot}6H_2O$ (2.0 mg L^{-1}), and $Na_2MoO_4{\cdot}2H_2O$ (3.0 mg L^{-1}) in DI water. The initial pH of the NMS medium was 6.6–6.8 (Sheets et al., 2016). During the separation process, 5 mL supernatant of paddy soil and 45 mL NMS medium were mixed in serum bottle, and then the bottle was sealed with a rubber stopper. Methane at atmospheric pressure was used to replace the air of bottle to reach a CH_4:air ratio of 1:4 (v/v). Then all the bottles were placed in a shaking air bath at 30 °C with 160 rpm. The methane concentration in the headspace of bottle was measured daily and the gas in the bottle was also replaced with a mixture of methane and air at the ratio of 1:4 daily. After three days, 5 mL sample of each enriched culture was transferred into a new bottle that contained 45 mL of fresh NMS medium and the same mixture ratio of CH_4 and air. This process was repeated every 3 days.

2.3. Elimination of methane in exhaust gas from biogas upgrading process by biofiltration with immobilized methane-oxidizing bacteria

In this study, a gas mixture of methane, carbon dioxide and air at the ratio of 0.9:15:84.1 was used to simulate the exhaust gas produced during biogas upgrading. Biofilter with a diameter of 6 cm and height of 50 cm was used to investigate the biofiltration performance of methane-oxidizing bacteria. One biofilter was filled with NMS solution to a height of 40 cm as control. Another biofilter was filled with active carbon, which was soaked in NMS solution for one day, and the height was also adjusted to 40 cm. 150 mL enriched MOB was added to each biofilter as source of methane-oxidizing bacteria. During the methane-oxidization process, the flow rate of gas mixture was kept at 10 mL/min.

2.4. Analytical methods

During this study, the TS and VS of paddy soil were tested by standard method (APHA, 2006).

The microbial community structure analysis of the enriched methane-oxidizing bacteria system was conducted at GENEWIZ, Inc. (Beijing, China). FastDNA® Spin Kit for Soil (CWBIO) was used for DNA extraction followed with the manufacture's protocols. 0.8% agarose gel and Qubit 2.0 Fluorometer (Invitrogen, Carlsbad, CA) were used to check the quality of DNA samples and quantify, respectively. 5–50 ng DNA was used to generate amp icons using a MetaVx™ Library Preparation kit (GENEWIZ, Inc., South Plainfield, NJ, USA). A panel of proprietary primers was designed to anneal to the relatively conserved regions bordering V3 (variable V3 region of 16S rRNA), V4 (variable V4 region of 16S rRNA), and V5 (variable V5 region of 16S rRNA) hypervariable regions. The forward primers containing the sequence "CCTACGGRRBGCASCAGKVRVGAAT" and reverse primers containing the sequence "GGACTACNVGGGTWTC