Chemical Engineering Journal 294 (2016) 105–110

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

H_2S in-situ removal from biogas using a tubular zeolite/TiO_2 photocatalytic reactor and the improvement on methane production

Xiaoyan Hao [1], Guangying Hou [1], Peixue Zheng, Rutao Liu, Chunguang Liu *

School of Environmental Science and Engineering, Shandong University, Jinan, Shandong Province 250100, China

HIGHLIGHTS

- A zeolite/TiO_2 photocatalytic reactor was developed for H_2S in-situ removal.
- The reactor exhibited excellent H_2S removal rate and lower SO_2 selectivity.
- Bio-methane production was enhanced following H_2S in-situ removal.
- The cost-effectiveness of the photocatalytic removal of H_2S from biogas was studied.

ARTICLE INFO

Article history:
Received 22 November 2015
Received in revised form 20 February 2016
Accepted 22 February 2016
Available online 27 February 2016

Keywords:
Anaerobic digestion
Desulfurization
Swine manure
TiO_2
Waste sludge

ABSTRACT

A tubular photocatalytic reactor filled with zeolite/TiO_2 was developed with the objective of H_2S selective removal from synthetic gas as well as in-situ removal from raw biogas and its improvement of methane production via anaerobic digestion of waste sludge with 25% addition of swine manure. For the H_2S selective removal from synthetic gas, reactor C (containing zeolite/TiO_2) is better than reactor D (containing zeolite/TiO_2 and TiO_2 film), reactor A (containing zeolite) and B (containing TiO_2 film). For H_2S in-situ removal experiment using reactor C, H_2S removal rate reached 98.1% and no SO_2 was detected. Furthermore, H_2S in-situ removal enhanced biogas production of 4.5% and bio-methane production of 16.1%, compared to the blank control. Considering the excellent H_2S removal rate, lower SO_2 selectivity and improvement for bio-methane production, H_2S in-situ removal using zeolite/TiO_2 proved to have promising applications in biogas purification.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

With the strengthening of environmental protection and legal system, more and more wastes (agricultural waste, industrial waste and organic municipal wastes) are used as substrate for biogas production by anaerobic digestion [1], and the biogas can be used as renewable and sustainable energy source in households and industry or as a vehicle fuel [2]. However, the hydrogen sulfide (H_2S), as a malodorous and sour impurity gas in biogas, which is spanning from 100 to 2400 ppm in biogas depending on the fermentation substrate [3], can cause much environmental and economic concerns, e.g. corroding the engine, combustor and metal parts via emission of SO_2 from combustion [4]. Therefore, H_2S must be economically and effectively removed to increase the practical use of biogas.

The common techniques to remove these sulfur compounds include adsorption method (such as zeolite) [5–7], biological processes (such as bio-scrubbing, bio-filter) [2,8] and chemical oxidation/scrubbing technologies (such as hydrogen peroxide, chlorine, hypochlorite, and ozone oxidation) [9,10]. However, the adsorption method needs to replace and dispose adsorbent, which would result in secondary waste and high initial cost [8]. Biological processes take time and also produce organic wastes as by-product needing to be disposed of eventually [11]. Alternatively, photocatalytic methods have been successfully tested for H_2S removal at ambient temperature, with the advantages of low cost, energy saving, minimal waste and environmental protection [12]. However, several problems appeared during H_2S photocatalytic reaction process, (i) low recovery efficiency of TiO_2 fine particles, (ii) SO_2 emission, (iii) deactivation of photocatalyst [13,14]. Many researches were carried to solve these problems, e.g. development of suitable catalyst support.

Many kinds of suitable materials were studied for the support of nano TiO_2 in order to solve the above problems [15]. Of various

* Corresponding author. Tel.: +86 150541873869; fax: +86 053188364868.
E-mail address: chunguangliu2013@sdu.edu.cn (C. Liu).
[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.cej.2016.02.098
1385-8947/© 2016 Elsevier B.V. All rights reserved.

materials, zeolites have been an alternative supporting material for nano TiO_2, due to their unique structures, uniform pores and channels and high selectivity and compatibility towards polar compounds (e.g. H_2S and NOx) [16–18]. On the other hand, synergistic effect can be obtained by combining the photocatalytic activity of TiO_2 with the adsorption properties of zeolite, not only resulting in the enhancement of photocatalytic efficiency but also reducing the emission of SO_2 due to zeolite adsorption [19]. At present, a few of researchers have studied the removal of H_2S by zeolite or by TiO_2 ex-situ [6,20]), which is generally costly and requires various process applications due to various composition of the biogas. On contrary, the development of an in-situ removal technique would be an attractive alternative in the perspective of economic and environmental advantages [21], but very few studies focused on the H_2S in-situ removal [22], as well as its effect on bio-methane production. Therefore, further research is necessary before this technology goes into practical applications.

Thus, in this study, a zeolite/TiO_2 photocatalytic reactor was developed to enhance H_2S removal and to reduce SO_2 selectivity with the synergetic effect of zeolite and TiO_2 during biogas purity. Furthermore, the performance of the photocatalytic reactor was assessed with the H_2S in-situ removal and its positive effect on bio-methane yield and the content in biogas from the anaerobic digestion of waste sludge with 25% addition of swine manure. This research provides a new route not only to reduce H_2S limitation for bio-methane production, but also alleviate the downstream challenges of the centralized treatment of the impurity gas (e.g. carbon dioxide, hydrogen sulfide, water vapor) in biogas [4,23].

2. Experiment

2.1. Materials

Zeolite used in this research was obtained from Makino Store, Kiyosu, Japan and was used as supporter for TiO_2. The TiO_2 used as photocatalyst in this study was TiO_2 slurry (Ishihara Sangyo Kaisha, Ltd., Japan). The characteristics of the TiO_2 slurry were as follows: 20 nm, Anatase 40%, pH 8.3, Absorbance 0.43, Viscosity 42.2 mP s. the other characteristics (X-ray powder diffraction, Field emission scanning electron microscopy, specific surface area and pore volume distributions) of zeolite/TiO_2 were shown in our previous studies [23]. Waste sludge and anaerobic digested sludge were obtained from a sewage treatment plant in Jinan, China. The swine manure was obtained from a pig farm in Jinan, China. The characteristics of the substrate (waste sludge with 25% addition of swine manure) and inoculation sludge (anaerobic digested sludge) were shown as Table 1.

2.2. Experimental setup

The photocatalytic tests were carried out in a photocatalytic reactor including single-pass cylinder columns, a UV-light lamp, light concentrators, control valves, flow-meters, pump, pipes, and so on. The glass tube was 450 mm in length and 6 mm in diameter, filled with zeolite, zeolite/TiO_2 granules, through which the biogas or H_2S was passed. The reactor was sealed to avoid the leak of gas.

Table 1
Characteristics of the substrate and inoculation sludge.

Parameter	Substrate	Inoculation sludge
COD (mg/L)	26830 ± 50	19086 ± 50
SCOD (mg/L)	3678 ± 20	2016 ± 20
Sulfate (mg/L)	3162 ± 20	2088 ± 20
Sulfide (mg/L)	365 ± 5	186 ± 5
pH	6.8 ± 0.01	7.5 ± 0.01

The UV-light source is a 40 W black light tube (Philips TL 40 W) with a spectral peak centered at 365 nm and surrounded by the cylinder Quartz glass tubes. The irradiance received by the TiO_2 coating was 5 mW/cm^2. Details of the test apparatus are shown in Fig. 1.

2.3. Evaluation of zeolite/TiO_2 activity

In this part, four reactors (A, B, C and D) filled with different material were used to evaluate the activities of four materials according to H_2S removal and SO_2 selectivity. The glass columns of reactor A, B, C and D is filled with raw zeolite, coated withTiO_2 film without filler, filled with zeolite/TiO_2, coated with TiO_2 film and filled with zeolite/TiO_2, respectively. A synthetic gas (35% CO_2, 65% CH_4 with 40% moisture) containing 1000 ppm of H_2S was used for the evaluation of the zeolite/TiO_2 activity. The gas velocity was 20 ml/min. The contents of H_2S and SO_2 in the outlet gas were monitored with a Draeger (Pac III) electrochemical sensor at an interval of 30 min. For each sample, the test was repeated for three times. Regeneration ability experiment was carried out (180 min per circle, 5 circles) using the synthetic gas, and zeolite/TiO_2 was washed after one circle with a NaOH solution (pH = 10) and calcined in a muffle furnace (400 °C, 2 h). Selective production rate to SO_2 (S_{SO2}) was calculated according to the following equation: $S_{SO2} = (SO_2)_{outlet}/((H_2S)_{inlet} - (H_2S)_{outlet}) \times 100\%$.

2.4. In-situ experiments

Reactor C was used for H_2S in-situ removal in biogas from the anaerobic digestion of waste sludge with 25% addition of swine manure in a 500 ml fermenter. Anaerobic digestion was conducted at 37 °C and with an initial pH of 7 for 30 days. Inoculation rate was 15% with inoculation sludge. Biogas was on-site collected then entered the fermenter again after desulphurizing using the zeolite/TiO_2 reactor. Considering the yield of biogas, H_2S content and the performance of the reactors, in-situ desulfuration of biogas was carried out 24 h interval and for 120 min every time. The control experiment was performed by using the same fermenter under the same conditions without any treatment for the biogas.

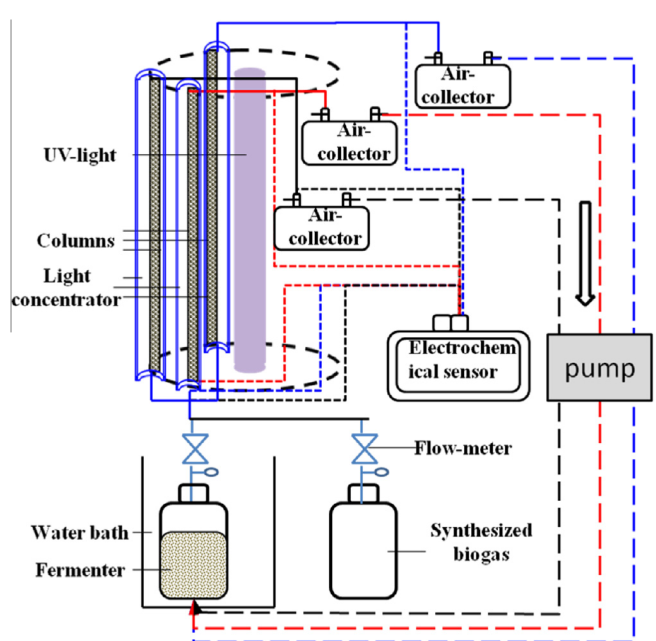

Fig. 1. Schematic diagram of experimental setup for H_2S in-situ removal.

Download English Version:

https://daneshyari.com/en/article/145703

Download Persian Version:

https://daneshyari.com/article/145703

Daneshyari.com