Journal of Integrative Agriculture 2017, 16(6): 1276–1285

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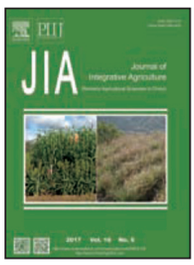

RESEARCH ARTICLE

In-depth observations of fermentative hydrogen production from liquid swine manure using an anaerobic sequencing batch reactor

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Abstract

In this study, experiments were designed to reveal in-depth information of the effect of pH and hydraulic retention time (HRT) on biohydrogen fermentation from liquid swine manure supplemented with glucose using an Anaerobic Sequencing Batch Reactor (ASBR) System. Five values of HRT (8, 12, 16, 20, and 24 h) were first tested and the best HRT determined was further studied at five pH levels (4.4, 4.7, 5.0, 5.3, and 5.6). The results showed that for HRT 24 h, there was a dividing H_2 content (around 37%) related to the total biogas production rate for the ASBR System running at pH 5.0. When the H_2 content went beyond 37%, an appreciable decline in biogas production rate was observed, implying that there might exist an H_2 content limit in the biogas. For other HRTs (8 through 20 h), an average H_2 content of 42% could be achieved. In the second experiment (HRT 12 h), the highest H_2 content (35%) in the biogas was found to be associated with pH 5.0. The upswing of pH from 5.0 to 5.6 had a significantly more impact on biogas H_2 content than the downswing of pH from 5.0 to 4.3. The results also indicated good linear relationships of biogas and H_2 production rates with HRT (r=0.9971 and 0.9967, respectively). Since the optimal ASBR operating conditions were different for the biogas/H_2 production rates and the H_2 yield, a compromised combination of the running parameters was determined to be HRT 12 h and pH 5.0 in order to achieve good biogas/H_2 productions.

Keywords: biohydrogen fermentation, swine manure, hydraulic retention time, pH values, anaerobic sequencing batch reactor

1. Introduction

Currently, hydrogen is produced exclusively from fossil fuels through energy intensive processes, which themselves are not clean technologies from the perspective of sustainability. For being used as a major energy source, hydrogen must be produced *via* sustainable means (Benemann 1996; Dunn 2002), among which biological pathways have come to the center stage due to its low energy needs and environment-friendly nature. Furthermore, biological conversion normally works with waste materials, so it can achieve both waste reduction and energy recovery. In view of these benefits, a considerable amount of research effort has been dedicated to biological production of hydrogen in the last two decades (Chen *et al*. 2008; Bičáková and Straka 2012; Zhao *et al*. 2013; Rai *et al*. 2014), among which fermentative

Received 4 March, 2015 Accepted 3 June, 2015
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doi: 10.1016/S2095-3119(15)61108-X

hydrogen production from organic compounds (especially carbohydrates) by anaerobic bacteria is generating profound interests among researchers due to its unique advantages over other technologies (Liu *et al*. 2013). In this process, high hydrogen production rates can be achieved with an active dark-fermentative consortium without the assistance of a light source (Das and Veziroglu 2001). In addition, the majority of the substrates used for dark fermentation consist of waste materials that otherwise need to be treated before disposal, which incurs extra costs. The investigated waste streams so far for hydrogen fermentation include tofu processing wastewater (Zhu *et al*. 2002), rice winery wastewater (del Campo *et al*. 2012; Yu *et al*. 2002), starch manufacturing wastewater (Yokoi *et al*. 2002), potato processing wastewater (Yokoi *et al*. 2001), beer processing wastewater (Lay *et al*. 2005), sugar refinery wastewater (Won *et al*. 2013), sugarcane bagasse (Rai *et al*. 2014), dairy wastewater (Gadhe *et al*. 2013), cheese whey wastewater (Kargi and Uzunçar 2012), fruit juice wastewaters (Fernández *et al*. 2011), and pineapple wastes (Wang *et al*. 2006). Obviously, the fermentative pathway for hydrogen production can be an ideal vehicle to not only produce hydrogen but also reduce the volume of these wastes, thus saving the treatment costs and paving the way for building a sustainable economy.

One of the waste materials that have not been studied extensively in hydrogen fermentation is liquid swine manure, despite a few publications existing in the literature, almost all of which, however, were coming from the work conducted by the authors (Wu *et al*. 2009; Zhu *et al*. 2009). The results from these reports, in general, evidenced the feasibility of using swine manure as substrate for hydrogen fermentation, but without elaborating on some intrinsic characteristics of the fermentation process. Given the fact that swine manure contains all the necessary components for hydrogen fermentation by microorganisms such as *Clostridia* and the tremendous volume generated in the world every year, it is worthwhile to further our understanding of the process by providing in-depth information on the characteristics of the process for biogas/hydrogen production. Therefore, in this study, new information that had not been reported before related to fermenting swine manure supplemented with glucose to produce hydrogen was collected and reported using an Anaerobic Sequencing Batch Reactor (ASBR) System running on different hydraulic retention time (HRT) and pH values. Such information might provide insight on improving the hydrogen fermentation efficiency of liquid swine manure.

2. Materials and methods

2.1. Seed sludge and pretreatment

A running anaerobic digester treating dairy manure, located in St. Peter, Minnesota, USA, was the source for the seed sludge for this study. After collection, the sludge was pretreated using a prepared nutrient medium under room temperature for 24 h. The nutrient medium (1 L) contained 10 g glucose, 1.5 g KH_2PO_4, 0.5 g NH_4Cl, 0.18 g $MgCl_2 \cdot 6H_2O$, 0.05 g $FeSO_4$, 5 g polypeptone and 2 g yeast extract (Fang *et al*. 2006). The pH of the medium was also lowered from 7.1 to 5.0 with hydrochloric acid. After incubation, the sludge was boiled at 100°C for 30 min to inactivate non-H_2-producing bacterial species in the sludge.

2.2. Liquid swine manure source and preparation

The main substrate, liquid swine manure, was collected from a finishing building at the University of Minnesota Southern Research and Outreach Center at Waseca, USA. Preliminary treatments of the collected manure included dilution with tap water to a solid content of 0.5% followed by freezing in a freezer, if not placed immediately in the feeding tank. According to our preliminary trials (data not shown), swine manure alone was found to be ineffective in H_2 fermentation, and a sugar source, such as glucose, was needed in the culture media due to the lack of sufficient carbohydrates in the manure for the fermentative bacteria. To that end, to assist the growth of H_2 producing bacteria with sufficient carbohydrates, the manure in the feeding tank was supplemented with 10 g L^{-1} glucose, 500 mg L^{-1} KH_2PO_4, and 400 mg L^{-1} peptone. The characteristics of the raw liquid swine manure and the prepared substrate were presented in Table 1. The adjusted pH, which was slightly higher than 5.0, took into account the potential pH drop caused by the fresh influent fed into the reactor at the beginning of each ASBR cycle that would normally reduce the liquid pH as a result of quick production of organic acid.

2.3. Reactor setup and operation

The lab-scale ASBR System was presented in Fig. 1. A polyethylene jar, 20.3 cm in diameter and 45.0 cm in height, was employed as the bioreactor, which had a total volume of 8 L with a working volume of 4 L. The reactor was heated by a hot plate stirrer to maintain the mixed liquor temperature inside the reactor. Complete mixing of the reactor was obtained using a centrifugal water pump circulating the liquid through an outside loop where a T connector was installed with a pH probe (Cole-Parmer, USA) connected to it to simultaneously record the real-time pH. A pH controller (Cole-Parmer, USA) was used to take feedback from the probe, based on which two microtube-pumps were operated to add either base (1.0 mol L^{-1} NaOH) or acid (1.0 N HCl) to the reactor for pH adjustment. The feeding tank was a 20-L water bottle equipped with a mixer that ran for 10 s to

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