Bioresource Technology 175 (2015) 486–493

Contents lists available at ScienceDirect

Bioresource Technology

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

Contribution of precipitates formed in fermentation liquor to the enhanced biogasification of ammonia-rich swine manure by wheat-rice-stone addition

He Huang, Leilei He, Zhongfang Lei, Zhenya Zhang *

Graduate School of Life and Environmental Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8572, Japan

HIGHLIGHTS

- CH_4 yield was increased by 72% after adding WRS at NH_4^+-N = 5145 mg-N/L.
- Effective biogasification period was shortened to 20 days after WRS addition.
- Much faster VFAs utilization rate was detected in WRS addition reactors.
- Struvite and Fe-precipitates might contribute a lot to the decreased ammonia level.

ARTICLE INFO

Article history:
Received 3 September 2014
Received in revised form 25 October 2014
Accepted 28 October 2014
Available online 6 November 2014

Keywords:
Wheat-rice-stone (WRS)
High ammonia concentration
Swine manure
Anaerobic fermentation liquor
Precipitation

ABSTRACT

This study investigated the effect of wheat-rice-stone (WRS) addition on mesophilic anaerobic fermentation for methane production from swine manure under high ammonia nitrogen level (5145 mg-N/L) in addition to exploring its possible mechanisms involved. Results show that addition of WRS could not only effectively increase methane production by 72% from 82.8 (control) to 142.7 ml/g-VS but also remarkably shorten the effective biogasification period from 40 (control) to 20 days. In addition, WRS addition could promote the degradation of *n*-HBu and slow down the accumulation of other volatile fatty acids (VFAs) species, achieving much faster VFAs utilization rate and better pH maintaining capability. More specifically, the existing and released ions especially Ca^{2+}, Mg^{2+}, and $Fe^{3+/2+}$ were supposed to form precipitates (like struvite and Fe-precipitates) with NH_4^+ and PO_4^{3-} rich in the fermentation liquor, probably contributing a lot to the decreased ammonia concentration and enhanced biogasification under WRS addition.

1. Introduction

As an attractive waste treatment method for renewable energy production, anaerobic digestion or fermentation has been received much attention worldwide nowadays. This biotechnology has been successfully applied in the treatment of sewage sludge and other organic wastes. The renewable energy produced from anaerobic digestion, namely biogas, is regarded as a promising candidate for fossil fuels.

Swine manure, an abundant bio-waste in the world, could be used for biogas production via anaerobic digestion. In Japan, annual livestock manure production is about 82.95 million tons, in which swine manure accounts for about 27% (MAFF, 2013). The anaerobic process of swine manure, however, is often limited by slow hydrolysis rate mainly due to the high level of ammonia in fermentation liquor, which is originated from the decomposition of proteins and urea, leading to lower biogas yield (Batstone et al., 2002). Methanogens are reported to be sensitive to ammonia. A concentration of total ammonia nitrogen (TAN) around 1700–1800 mg/L could result in failure of a high rate digester, and partial inhibition has also been detected in anaerobic digestion of swine manure at TAN of 3000 mg/L (Chen et al., 2008; Yenigün and Demirel, 2013). Procházka et al. (2012) claimed that the activity of methanogens ceased when ammonia nitrogen concentration was about 4200 mg/L. Furthermore, it has been pointed out that free ammonia is the main cause of inhibition since it is freely membrane-permeable (Ho and Ho, 2012).

Therefore, numerous trials have been attempted to mitigate ammonia inhibition to anaerobic process, aiming at achieving enhanced biogas production by using such methods as ammonia stripping, zeolite adsorption, membrane, and struvite precipitation

* Corresponding author. Tel./fax: +81 29 853 4712.
E-mail address: zhang.zhenya.fu@u.tsukuba.ac.jp (Z. Zhang).

http://dx.doi.org/10.1016/j.biortech.2014.10.142

(Lauterböck et al., 2012; Lin et al., 2013; Rico et al., 2010; Serna-Maza et al., 2014). Indeed, some of the above-mentioned methods exhibited high efficiency of alleviating ammonia inhibition to anaerobic fermentation. However, these methods are expensive to be applied in practice. Moreover, little research work can be found on the effect of higher level of ammonia (>5000 mg-N/L) on anaerobic process, which will be encountered if further increasing organic loading rate or total solids content so as to achieve high rate or high solids anaerobic fermentation of swine manure. Compared with the above-mentioned methods, a few researchers tried the addition of wheat-rice-stone (WRS), namely porphyritic andesite into anaerobic reactors, to enhance the biogasification performance (Kao et al., 2003; Li et al., 2009; Wang et al., 2012). WRS with porous structure is an abundant material in Asia, possessing excellent adsorption ability and bioactivity by cation dissociation (Kao et al., 2003). Li et al. (2009) reported that WRS could adsorb volatile fatty acids (VFAs), elevate pH level, and accelerate organics degradation during anaerobic digestion of soybean residue. Results from our previous research (Wang et al., 2012) indicated that modified WRS could effectively mitigate ammonium inhibition (3550 mg/L), possibly due to its high adsorption capacity and selectivity for ammonium. Addition of WRS into anaerobic reactors has the following advantages like low cost, non-chemicals addition and handleability. Up to now, however, whether this WRS application is feasible for coping with higher ammonia conditions or not remains unknown. Furthermore, due to the complexity of anaerobic process and variety of feedstocks, the real mechanisms involved in the enhancement of biogasification by WRS addition are still unclear.

This study tested the effect of WRS addition on biogasification of swine manure at ammonia nitrogen >5000 mg/L (5145 mg-N/L) by using batch experiments. The variations of biogas production, pH, ammonia concentration, soluble chemical oxygen demand (SCOD), and VFAs were monitored during the whole anaerobic process. In addition, the major cations and anions were determined in order to estimate the possibility of precipitation reactions between/among them. Due to the fact that many cations could be released from WRS during anaerobic process (Wang et al., 2012), batch anaerobic fermentation experiments with addition of WRS soaked water (WRS-water) was also conducted in parallel with WRS addition condition. Compared to previous research works, much attention was paid in this study to the precipitates possibly formed in the fermentation liquor, with expectation of shedding light on the mechanisms of enhanced biogasification involved in the complex anaerobic process brought about by WRS addition.

2. Methods

2.1. Swine manure and seed sludge

Swine manure and seed sludge (anaerobically digested sludge) in this study were collected from a pig farm located in Tokyo and Shimodate wastewater treatment plant (Ibaraki, Japan), respectively. The main physicochemical characteristics are listed in Table 1. In order to elevate the ammonia nitrogen level higher than 5000 mg-N/L after dilution of the swine manure in the following fermentation experiments, a certain amount of NH_4Cl was added into the raw swine manure. After being mixed thoroughly, the prepared swine manure and the seed sludge were stored at 4 °C and used within 1 month.

2.2. WRS and WRS-water

WRS were obtained from Henan Province, China. The WRS particles with size between 3 and 4 mm were used in this study. 50 g of WRS were immersed in 1000 ml distilled water at 35 °C for 60 days and the resultant supernatant was labeled as WRS-water in this study. The WRS-water mainly contained mineral elements (mg/L) including Na (4.7 ± 0.3), K (3.2 ± 0.7), Ca (50.7 ± 6.9), Mg (10.6 ± 2.2), Fe (33.1 ± 0.4), Ni (0.5 ± 0.1), and Co (0.1 ± 0.0).

2.3. Experimental conditions for batch anaerobic fermentation

Batch anaerobic fermentation trials were conducted in 500 ml glass bottles with working volume of 400 ml. The effect of WRS addition on biogasification was assessed under high ammonia nitrogen level (>5000 mg-N/L in this study). These reactors were grouped into three kinds, namely Control, Reactor 1 (R1) and Reactor 2 (R2), respectively. The difference among the three group reactors was as follows: (1) only swine manure (diluted with distilled water) in the Control reactors, (2) swine manure thoroughly mixed with the designated amount of WRS (50 g/L) and diluted with distilled water in R1, and (3) swine manure diluted with WRS-water in R2 reactors, respectively. All the fermentation tests started from the same initial conditions of total solids (TS), volatile solids (VS), total ammonia nitrogen (TAN), and chemical oxygen demand (COD), soluble COD (SCOD) and VFAs concentrations by diluting the swine manure with distilled water or WRS-water, around 2.1%, 1.8%, 5145 mg-N/L, 35,945 mg/L, 18,684 mg/L and 3800 mg-COD/L, respectively. Each reactor was inoculated with 20% (v/v) of the seed sludge, and the initial pH values in the reactors were adjusted to 7.0 with 1 M HCl or NaOH. All these reactors were

Table 1
Physicochemical characteristics of raw swine manure and seed sludge used in the experiment.

Items	Unit	Swine manure	Seed sludge
Total solid (TS)	%	18.9 ± 0.1	1.15 ± 0.01
Volatile solid/Total solid (VS/TS)	%	76.4 ± 0.1	70.05 ± 0.02
Chemical oxygen demand (COD)	g/L	210.0 ± 48.0	6.7 ± 0.4
Total ammonia nitrogen (TAN)	mg/L	22506.0 ± 1052.1	1806.0 ± 16.2
Total phosphorus (TP)	mg/L	2758.6 ± 87.2	534.5 ± 2.8
Orthophosphate phosphorus (Ortho-P)	mg/L	1525.0 ± 59.8	335.3 ± 4.0
Main metals in the swine manure and seed sludge			
Na	mg/L	1414.8 ± 21.6	41.3 ± 0.3
K	mg/L	3808.0 ± 41.0	166.2 ± 3.5
Mg	mg/L	376.0 ± 8.0	23.9 ± 0.1
Ca	mg/L	2032.0 ± 9.0	68.5 ± 2.2
Fe	mg/L	106.0 ± 3.9	45.0 ± 2.8
Co	mg/L	0.4 ± 0.1	N.D.
Ni	mg/L	1.6 ± 0.1	N.D.

N.D., non-detectable.