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Enhanced methane production from Taihu Lake blue algae by anaerobic co-digestion with corn straw in continuous feed digesters

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HIGHLIGHTS

- ▶ Methane production from Taihu algae succeeded with continuous reactors.
- ▶ Ammonia from algae decay inhibited mainly acetate and propionate degradation.
- ▶ Co-digestion of algae with corn straw enhanced methane productivity and VS removal.
- ▶ Optimal C/N ratio of 20:1 (g/g) was found.
- ▶ Rate limiting step is not hydrolysis but acetate and propionate degradation.

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ABSTRACT

Anaerobic digestion of Taihu blue algae was tested in laboratory scale, continuous feed digesters (hydraulic retention time 10 days) at 35 °C and various organic loading rates (OLR). The methane production and biomass digestion performed well at OLR below 4.00 gVS L^{-1} d^{-1} but deteriorated as OLR increased due to the increased ammonia concentration, causing inhibition mainly to acetate and propionate degradation. Supplementing corn straw as co-feedstock significantly improved the digestion performance. The optimal C/N ratio for the co-digestion was 20:1 at OLR of 6.00 gVS L^{-1} d^{-1}. Methane yield of 234 mL CH_4 gVS^{-1} and methane productivity of 1404 mL CH_4 L^{-1} d^{-1} were achieved with solid removal of 63%. Compared with the algae alone, the methane productivity was increased by 46% with less accumulation of ammonia and fatty acids. The reactor rate-limiting step was acetate and propionate degradation.

1. Introduction

Eutrophication causing the bloom of *Cyanobacteria* in lakes and reservoirs has been major concern for years in China (Xing et al., 2011). Taihu Lake, the third largest lake in China, which provides drinking water for more than 2 million people in Jiangsu Province, had serious water toxicity problems because of an algal bloom by *Microcystis* spp. in the summer of 2007 (Guo, 2007). To reduce the eutrophication of Taihu Lake, refloatation of blue algae after blooming is considered to be the most efficient technical approach to retrieve nitrogen and phosphorus from the lake (Yan et al., 2010). From Taihu Lake, algae biomass collected could amount to about one thousand tons in wet weight per day, but is rarely utilized as resource, becoming long-term concerns of environment (e.g., N, P, S pollution) and nuisances (e.g., bad odors).

The algal biomass, especially oil-producing algal species, has been considered as bioenergy source, especially biofuel, for years (Lü et al., 2011). The algal bloom species are not oil-rich and less attractive for biodiesel. The simplest way for energy recovery from the algal bloom biomass could be anaerobic digestion (AD) to produce biogas or methane. In Taihu Lake area, the process is considered as a potential energy recovery approach and a solution to prevent the environmental pollution from several hundred thousand tons of waste algae refloated annually from Taihu Lake (Aitken and Antizar-Ladislao, 2012; Yuan et al., 2011). Algal biomass consisting of carbohydrates, proteins and lipids can be converted into methane and carbon dioxide. The annual collection of several hundred thousand tons of algal wastes from Taihu Lake is a huge resource for methane production up to several hundred million m^3.

Since 1957, the feasibility of anaerobic digestion of various microalgae has been investigated by many researchers (Golueke et al., 1957; Inglesby and Fisher, 2012; Park and Li, 2012; Ras et al., 2011; Samson and Leduy, 1982; Uziel, 1978; Yen and Brune, 2007;

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Zamalloa et al., 2012). Algal bloom biomass of *Microcystis* spp. was digested under anaerobic conditions to produce methane (Yuan et al., 2011; Zeng et al., 2010). Yuan et al. (2011) demonstrated the feasibility of anaerobic digestion of Taihu Lake algal biomass for methane production and near complete degradation of toxic microcycitin during anaerobic digestion. The algal biomass from Taihu Lake has high protein content (≈47%). Anaerobic digestion of the organic matter with a high nitrogen content (or low C/N ratio) could be susceptible to ammonia inhibition due to accumulation of ammonia from protein degradation, causing reaction failure (Appels et al., 2008; Sukias and Craggs, 2011). Depends on pH, total ammonia-N (TAN) in digester is composed of different fraction of free ammonia (NH_3) and ammonium ions (NH_4^+), NH_3 is the most toxic of both.

$$NH_{3(aq)} + H_2O \leftrightarrow NH_4^+ + OH^- (pK_b = 4.733 \quad \text{at} \quad 35^\circ C) \tag{1}$$

TAN becomes inhibitory to methanogens at concentrations from 15,000 to 3000 mg L^{-1} at pH 7.2–7.6 (Appels et al., 2008; Inglesby and Fisher, 2012; McCarty, 1964). An increase in pH would result in a higher toxicity level due to the shift to a higher fraction of NH_3 (Appels et al., 2008). Studies on co-digestion of algal sludge mainly consisting of *Scenedesmus* spp. and *Chlorella* spp. by supplementing waste paper and food grease, which both have high C/N ratio, showed positive effect on digestion performance and avoided excessive ammonia inhibition (Park and Li, 2012; Yen and Brune, 2007). Therefore, the concern with ammonia inhibition of anaerobic digestion of the Taihu Lake algal biomass could be moderated by using co-digestion with added organic matter containing low nitrogen content. Crop residues, such as corn straw and wheat straw, have high C/N ratio can service for the co-digestion. Recently, we demonstrated the feasibility of anaerobic co-digestion of Taihu algal biomass (mainly *Microcystis* spp.) with corn straw using 150 mL serum bottle as batch reactor at 35 °C (Zhong et al., 2012). The results showed that after anaerobic digestion of mixed feedstocks (initial concentration 20 gVS L^{-1}) with different mass ratio of the algae versus corn straw for 30 days, the best C/N ratio of the feedstock was 20:1 for VS reduction and methane yield. The results suggest that supplementation of high carbon containing co-feedstock can achieve better digestion performance than algae along due to synergistic effect of the co-feedstocks at a proper ratio (Zhong et al., 2012). However, the findings obtained from the batch test cannot provide enough information for reactor design and operation and have to be tested at large scale. In addition, the ammonia inhibition under continuous feeding mode could be different from batch test and the rate-limiting step of the algal degradation has to be characterized.

The full-scale digester for anaerobic digestion of algae is mainly considered to be continuously stirred tank reactor (CSTR) (Yen and Brune, 2007). The digester can be fed continuously or semi-continuously, similar to the high rate digester for sewage sludge treatment with organic loading rate (OLR) of 1.6–3.2 g L^{-1} d^{-1} and hydraulic retention time (HRT) of 10–15 days. The parameters for the co-digestion of algae has yet be identified since little research has been done on the effect of OLR and the influence of ammonia on the performance of the digestion of the algal biomass, which are essential for the scale-up of digestion process and engineering design.

In this study, we investigated the feasibility of digestion of the *Microcystis* dominated Taihu Lake algal biomass at various OLR and the co-digestion of the algal biomass together with corn straw in laboratory scale-digesters with continuous feed mode. The results demonstrated the loading rate limitation of anaerobic digestion of Taihu Lake algal biomass due to ammonia accumulation and synergistic effect of the co-digestion on reactor performance. The optimal mass ratio of algal biomass versus corn straw and rate-limiting step were identified for further application and reactor configuration modification.

2. Methods

2.1. Feedstock

Blue algal biomass was freshly collected from a blue algae refloating site near Taihu Lake, Wuxi City, Jiangsu Province, China at the end of July, 2011. The biomass was dominated with *Microcystis* spp. (>99%) based on microscopic observation. The algal biomass was kept frozen at −4 °C prior to use. The frozen biomass was thawed at room temperature and then diluted with medium to a desired volatile solid concentration prior to being fed to the reactors. The corn straw was collected from Nanshao Town, Beijing, China. The straw was air-dried to final moisture contents of 7–8%, and then chopped with a paper chopper (PC500, Staida Co., Tianjin, China) to a particle size of approximately 3 cm and then ground into 5–10 mm particles by a hammer mill (YBS-200, YiBo Co., Guangzhou, China). Then they were packed in plastic bags and placed under 62 ± 1% relative humidity and 4 ± 0.5 °C until use. The characteristics of the algal biomass and corn straw are listed in Table 1.

2.2. Reactor and operational procedures

Two identically sized CSTR digesters utilized this study with working volume of 4 L (14 cm ID × 38 cm height) were fabricated with double wall Perspex cylinder (15 mm thickness) (Fig. 1). The temperature was maintained at 35 °C by recirculating temperature-controlled water through the water jacket of the reactor. The reactors were sealed with a Perspex cover which had three ports on the top. One port was for substrate feeding. The second port was connected to a wet gas flow meter (BSD 0.5, Krom Watch Industry Co., Shanghai, China). Gas sample was taken via a silicone tube by a 250 μL pressure-tight gas syringe (VICI, Precision Sampling Inc., USA). The third port was inserted with a high-power magnetic stirrer (JJ1-200 W, Jintan Medical Instrument Factory, China) for intermittent mixing at 150 rpm for 24 min every 2 h. The daily biogas production was recorded using the gas flow meter (Fig. 1). The inoculum of the anaerobic reactor was anaerobic sludge from a mesophilic laboratory scale upflow anaerobic sludge blanket reactor (50 L) treating dining hall wastewater at the Department of Environmental Engineering, Tsinghua University, Beijing, China. The sludge contained 63.26 g L^{-1} total solids (TS) and 38.09 g L^{-1} (VS) volatile solids. The two CSTR reactors were filled with 3 L of sludge and 1 L of glucose plus trace element solution to obtain 1.0 g glucose L^{-1}, and then incubated at 35 °C for five days. Subsequently, a long-term fed batch operation was conducted in order to develop algae-degrading anaerobic microbial

Table 1
Characteristics of Taihu Lake algae, corn straw and inoculum.[a]

Constituent	Algae	Corn straw	Inoculum
TS (%)	10.63 (0.86)	94.72 (5.83)	6.43 (0.68)
VS (%-TS)	82.32 (6.35)	91.20 (3.74)	60.21 (2.43)
pH	5.70	NA	7.47
TC (mg g^{-1} TS)	592.53 (17.83)	468.57 (3.21)	484.67 (12.25)
TNK (mg g^{-1} TS)	96.78 (4.29)	6.61 (0.69)	15.87 (0.77)
C/N ratios	6.1	70.9	30.5
Lipids (%-TS)	4.12 (0.62)	5.28 (0.62)	NA
Protein (%-TS)	47.62 (2.11)	4.13 (0.35)	NA
Carbohydrate (%-TS)	30.58 (3.27)	81.79 (3.26)	NA

[a] NA = no analysis. Data are the means of three measurements, and numbers in parentheses are the standard deviations. The protein content of algae and straw were calculated by multiplying respective TNK value by 4.92 and 6.25, respectively (Lourenço et al., 2002).