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New method for enhancement of bioenergy production from municipal organic wastes via regulation of anaerobic fermentation process

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HIGHLIGHTS

- A new method for increasing bioenergy production from municipal organic wastes was reported.
- The increases in hydrogen production and remarkably high VFA accumulation were achieved.
- The methane yield was improved by using the VFA-enriched fermentation liquid.
- The enzymatic activities of hydrolysis, acidification, and hydrogen production were enhanced.

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ABSTRACT

Although biological recovery of energy (such as hydrogen and methane) from municipal organic wastes (MOW) is a hot topic, the bio-energy production yield is usually unsatisfied due to the low efficiency of anaerobic fermentation process regulation. In this paper, a new method for increasing the production yields of hydrogen and methane from MOW via efficiently regulating the anaerobic fermentation process was reported. It was found that by firstly fermenting the MOW under alkaline conditions to produce hydrogen and volatile fatty acids (VFA)-enriched fermentation liquid (stage I), and then anaerobically treating the fermentation liquid at neutral pH value for methane production (stage II), the yields of both hydrogen and methane were significantly increased. The highest yields of H_2 and VFAs were obtained at C/N of 25.2 and pH of 8 in stage I, and the corresponding fermentation liquid generated the highest CH_4 yield in stage II. The overall energy gain of this method was estimated as 4.54 kW h/kg-COD. The mechanism study showed that the enzymatic activities with MOW hydrolysis (protease and amylase), acidification (phosphotransacetylase, phosphotransbutyrylase, acetate kinase, butyrate kinase, oxaloacetate transcarboxylase, and CoA transferase) and hydrogen generation (pyruvate-ferredoxin oxidoreductase) exhibited the greatest at alkaline pH, which resulted in the increase of hydrogen production together with remarkably high VFA (especially acetic acid) accumulation. When this VFA-enriched fermentation liquid was used to produce methane, the enhancement of methane yield was therefore observed.

1. Introduction

China has a population of nearly 1.3 billion, and the municipal waste has reached more than 150 million tons each year. With the rapid economic development, the level of urbanization and the improvement of people's living standards, the amount of municipal solid waste in China is increasing greatly with a rate of around 8%. It is an urgent task faced by China's environmental protection to develop an effective management of municipal organic wastes (MOW) with low environmental pollution. As there are large numbers of organic compounds, such as protein and polysaccharide, in MOW, it is attractive to recover valuable bio-products from municipal organic wastes [1].

Anaerobic treatment of organic wastes is a highly sustainable process because it can reduce the environmental pollution of wastes and simultaneously generate energy (such as hydrogen and methane) [2–4]. During anaerobic treatment the organic compounds usually undergo the stages of hydrolysis (i.e., carbohydrates and proteins in wastes are hydrolyzed to their soluble monomers), acidification (the hydrolyzed soluble monomers are bio-converted to volatile fatty acids (VFA), especially acetic acid, and carbon dioxide and hydrogen), and methanogenesis (methane

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is produced from acetic acid and hydrogen) [5]. As hydrolysis is generally the rate-limited step during anaerobic treatment of MOW, in order to increase the energy recovery efficiency physical or chemical pretreatment methods have been applied to accelerate the hydrolysis process [6–9]. Nevertheless, very few publications reported the simultaneous increase of hydrogen and methane production from municipal organic wastes by improving the hydrolysis, acidification and methanogenesis steps.

It is well known that acetic acid is a preferred substrate for methane production. It has been reported that acetic acid and hydrogen are produced in the acidification step, and higher acetic acid generation is usually accompanied with greater hydrogen production [10]. However, few studies considered that the simultaneous improvement of both hydrogen and methane yields could be achieved during wastes anaerobic treatment by firstly increasing the acetic acid accumulation, and then using the acetic acid as the substrate to produce methane. The purpose of this paper was therefore to report a new strategy for increasing both hydrogen and methane production from municipal organic wastes by regulating the anaerobic fermentation process, especially the hydrolysis and acidification steps. Unlike the traditional method, in this study, municipal organic waste was firstly fermented under alkaline conditions (i.e. stage-I) to produce hydrogen and VFA-enriched fermentation liquid, and then the fermentation liquid was treated at neutral pH value for methane productions (stage-II). As the yields of both hydrogen and methane were significantly increased by the use of this new method, the fundamental microbial mechanisms were then investigated in detail.

2. Materials and methods

2.1. Municipal organic wastes and anaerobic granular sludge

Polysaccharide (or carbohydrate) and protein were the main organic components of MOW, and the variations of their ratio were observed to affect both hydrogen and methane yields. In this study, the food waste and municipal waste sludge were mixed, and then used as the MOW. The food waste came from a dining hall in Shanghai, China, which was milled to slurry state and diluted with tap water to final total COD (TCOD) of 142.3 ± 15.1 g/L before experiments. The data showed it had total carbohydrate of 84.1 ± 5.3 g COD/L, total protein of 21.4 ± 3.2 g COD/L, total solids (TS) of 80.6 ± 4.2 g/L and volatile solids (VS) of 76.8 ± 3.8 g/L, respectively. The municipal waste sludge was withdrawn from a municipal wastewater treatment plant. After concentrated by settling at 4 °C for 24 h, its main characteristics were TCOD 17.5 ± 1.1 g/L, total carbohydrate 1.7 ± 0.2 g COD/L, total protein 9.5 ± 1.1 g COD/L, TS 17.4 ± 2.6 g/L, and VS 12.2 ± 1.3 g/L. The anaerobic granular sludge (AGS), obtained from an upward-flow anaerobic sludge blanket (UASB) reactor of a food wastewater treatment plant in Wuxi (Jiangsu province, China), was used as the inoculums for methane production from the VFA-enriched fermentation liquid of MOW. In order to eliminate the possible influences of methanogens, which might appear in different content in the fermentation substrate (food waste and municipal waste sludge), on the experiments, the MOW was pretreated at 102 °C for 30 min to kill methanogens [11], and then cooled down to room temperature for the tests.

2.2. Tests of bio-hydrogen production and VFA generation from municipal organic wastes

The experiments were conducted in serum bottles with working volume 600 mL each. The initial TCOD of MOW in all tests maintained almost identical (5143 ± 204 mg/L), and the changes of carbon to nitrogen ratio of MOW were achieved by mixing different fraction of food waste and sludge. At each carbon to nitrogen ratio six pH values (5.0, 6.0, 7.0, 8.0, 9.0 and 10.0) were studied. Every two hours the fermentation pH was adjusted by 4 M hydrochloric acid or 4 M sodium hydroxide to their initial one. The serum bottles were flushed with nitrogen gas, capped with rubber stoppers, and then placed in an air-bath shaker (120 rpm, 35 °C). Samples were obtained at different fermentation time for chemical analyses, such as VFA and hydrogen. For the assays of enzymatic activity, samples were withdrawn from the continuous fermentation serum bottles. The serum bottles were operated almost the same as described above with minor modifications. The fermentation mixture was wasted every day to maintain the hydrolytic retention time (HRT) to be approximately 8 d in each bottle, and the same amount of fresh food waste and waste sludge were supplemented. It took 86 days' culture before the generations of H_2 and VFA in all reactors reached relatively stable, and then the activities of key enzymes were determined.

2.3. Experiments of producing methane from the fermentation liquid of MOW

Our previous study indicated that the expanded granular sludge bed (EGSB) showed a much higher methane production yield from the fermentation liquid of waste activated sludge than the up-flow anaerobic sludge bed (UASB) and anaerobic sequencing batch reactor (ASBR) [12]. Therefore, in this study, the methane production from three fermentation liquids (i.e., the fermentation liquid of carbon to nitrogen ratio = 7.2 and pH = 10, the fermentation liquid of carbon to nitrogen ratio = 25.2 and pH = 8, and the fermentation liquid of carbon to nitrogen ratio = 40.1 and pH = 5) was studied and compared in three identical EGSB reactors. Each reactor had a working volume of 4.5 L with the internal diameter of 60 mm and height of 1400 mm, and was maintained at a constant temperature room (35 ± 2 °C). The operation of EGSB and the culture of anaerobic granular sludge were the same as that described by Zhang et al. [12]. The pH values of all fermentation liquids were adjusted to pH 7 before experiments. The final organic loading rate (OLR) was controlled at 40 kg-COD/m^3/d. After the methane production in all reactors did not change significantly with time, the data were reported.

2.4. Analytical methods

The content of ATP and the activities of protease, mylase, pyruvate-ferredoxin oxidoreductase (POR) and H_2-uptake hydrogenase were measured according to Refs. [13–16]. The gas components, such as methane and hydrogen, were determined via a gas chromatograph (6890N, Agilent, Santa Clara, CA, USA) equipped with a thermal conductivity detector using nitrogen as a carrier gas [10]. The energy gain of anaerobic treatment was calculated according the literature [17]. Other enzymes (including phosphotransacetylase (PTA), phosphotransbutyrylase (PTB), acetate kinase (AK), butyrate kinase (BK), oxaloacetate transcarboxylase (OAATC), CoA transferase, pyruvate-ferredoxin oxidoreductase (POR), formate dehydrogenase (FDH) and formyltetrahydrofolate synthetase (FTHFS)), VFA, protein and carbohydrate were assayed as described in our previous publications [18–20]. In this study the sum of measured acetic, propionic, *n*-butyric, iso-butyric, *n*-valeric, and iso-valeric acids was recorded as the concentration of total VFA with proper COD conversion (i.e. 1 g acetic acid = 1.07 g-COD, 1 g propionic acid = 1.51 g-COD, 1 g butyric acid = 1.82 g-COD, and 1 g valeric acid = 2.04 g-COD [21]).