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Zero-valent iron enhanced methanogenic activity in anaerobic digestion of waste activated sludge after heat and alkali pretreatment

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ABSTRACT

Heat or alkali pretreatment is the effective method to improve hydrolysis of waste sludge and then enhance anaerobic sludge digestion. However the pretreatment may inactivate the methanogens in the sludge. In the present work, zero-valent iron (ZVI) was used to enhance the methanogenic activity in anaerobic sludge digester under two methanogens-suppressing conditions, i.e. heat-pretreatment and alkali condition respectively. With the addition of ZVI, the lag time of methane production was shortened, and the methane yield increased by 91.5% compared to the control group. The consumption of VFA was accelerated by ZVI, especially for acetate, indicating that the acetoclastic methanogenesis was enhanced. In the alkali-condition experiment, the hydrogen produced decreased from 27.6 to 18.8 mL when increasing the ZVI dosage from 0 to 10 g/L. Correspondingly, the methane yield increased from 1.9 to 32.2 mL, which meant that the H_2-utilizing methanogenes was enriched. These results suggested that the addition of ZVI into anaerobic digestion of sludge after pretreated by the heat or alkali process could efficiently recover the methanogenic activity and increase the methane production and sludge reduction.

1. Introduction

Waste activated sludge generated from biological wastewater treatment processes has increased continuously in the recent decades due to increasing population and new construction of waste water treatment plants. Large amount of organic compounds containing in the waste sludge presents a potential threat to environment for example leaching of liquid and odor (Lee and Han, 2013). Anaerobic digestion is the most applied technique for waste activated sludge stabilization because of its high abilities to transform organic matters into biogas mixture of methane and carbon dioxide. However, the yield of methane is often limited by slow hydrolysis of sludge. To improve the hydrolysis of waste sludge, chemical, mechanical and biological methods (Lagerkvist and Morgan, 2012; Rani et al., 2012) have been applied to pretreat sludge to disintegrate sludge cells and release intracellular materials into the water phase.

Heat treatment was one of prevalent method to improve the hydrolysis of waste sludge since its simple operation (Oh et al., 2003). Hydrolysis of sludge under alkali condition developed by Zhao et al. (2010) also gained attention in recent years due to its dramatic enhancement of the hydrolysis of sludge. Although improving the hydrolysis–acidification of sludge, the heat and alkali processes are harmful to methanogenesis because methanogens grow only under an appropriate temperature and a narrowly neutral pH range (Dunfield et al., 1993). Three temperature regimes can be used in anaerobic digesters: psychrophilic, mesophilic and thermophilic with varied optimum temperature ranges for the domination of different strains of methane-forming bacteria. Psychrophilic fermentors operate at about 25 °C, mesophilic ones at around 35 °C and thermophilic at around 55 °C. The heat treatment at 102 °C for approximately 30 min could kill most methanogens (Gallert and Winter, 1997). The alkali pH was also a factor in preventing methanogenic activity. Methanogenic bacteria are extremely sensitive to pH and prefer pH around 6.8–7.2 as the growth rate of methanogens is greatly reduced when pH out of this range (Zhang et al., 2013). Thus, after the pretreatment, adding extra seed sludge or inoculum (dosing ratio: 10–30%) into the digester was necessary to maintain the sustainable methane production (Li et al., 2012; Appels et al., 2010), which however not only might increase the operating cost, but also occupied the considerable digestion space to decrease waste sludge load.

Zero-valent iron (ZVI), as a reductive material, has been widely applied in wastewater treatment, groundwater purification and soil remediation (Jiang et al., 2011). In previous study, it was found that ZVI could decline the oxidation–reduction potential (ORP) to

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create a more favorable environment for anaerobic wastewater treatment when it was added into anaerobic systems (Liu et al., 2012). In another previous work, adding ZVI in an anaerobic digestion of waste sludge was confirmed to enhance methane production (Feng et al., 2013). Specifically, the methane production was raised by about 21% at 10 g/L of iron scrap added into the anaerobic sludge digester.

Based on the consideration above, it was assumed that the addition of ZVI in anaerobic digestion was likely to improved the methanogenic activity to make the anaerobic system rapidly recovered from the heat and/or alkali inhibition. If this hypothesis is true, the sludge after the heat and/or alkali treatment might be directly processed for anaerobic digestion with no need of supplementing methanogens or seed sludge. The objectives of this work are (1) to investigate the effects of ZVI on the methanogenesis after the heat pretreatment and/or under alkali condition; and (2) to enhance the methane production from the suppressed sludge by adding ZVI. We expected to provide a new idea in enhancing the digestion of sludge suppressed by heat or alkali pretreatment.

2. Material and methods

2.1. Characteristic of waste sludge

Waste activated sludge used in this study was obtained from the secondary sedimentation tank of a municipal wastewater treatment plant in Dalian, China. The sludge was concentrated by settling for 24 h, and stored at 4 °C before use. It was reported that most methanogens could be killed at 102 °C for 30 min (Gallert and Winter, 1997). Therefore the raw sludge was heated at 102 °C for 30 min to become the heat-treated sludge. The characteristics of the waste activated sludge and heat-treated sludge are listed in Table 1.

2.2. Effects of ZVI on methane production from heat pretreated sludge

Adding inoculum sludge into waste sludge is a common method to proceed a sludge digestion (the inoculum seed ratio ranges from 10% to 30%). This model had been operated in our previous works to investigate the effects of ZVI (Feng et al., 2013). In the present study, in order to more directly observe the function of ZVI in recovering the methanogenic activity from the pretreatment, the sludge digestion was operated under no addition of inoculums but with whole pretreated sludge. After the sludge was heated and cooled down to the room temperature, 200 mL of the sludge was added into five 250 mL serum bottles, respectively. Five dosage levels of ZVI powder (0, 1, 2, 5 and 10 g/L, 0.2 mm diameter, 0.05 m^2/g BET surface area, purity >98%) were added into the five serum bottles above, respectively. All serum bottles were capped with rubber stoppers and flushed with nitrogen gas to remove oxygen before the anaerobic digestion. The bottles were placed in an air-bath shaker (120 rpm) at 35 ± 1 °C for 20 d. During the digestion, the biogas produced from each bottle was collected into gasbag for analysis. After the digestion, the mixture was poured out, and their supernatant and remainder sludge were analyzed, respectively.

Table 1
Characteristics of the raw sludge and heat-treated sludge.

Parameters	Raw sludge	Heat-treated sludge
pH	7.0 ± 0.2	7.0 ± 0.2
TSS (total suspended solids, mg/L)	11,832 ± 749	10,885 ± 868
VSS (volatile suspended solids, mg/L)	7219 ± 401	6497 ± 286
TCOD (total chemical oxygen demand, mg/L)	12,194 ± 1345	10,730 ± 1171
SCOD (soluble chemical oxygen demand, mg/L)	384 ± 34	662 ± 61
Total protein (mg/L)	3511 ± 212	3230 ± 335
Total polysaccharide (mg/L)	868 ± 39	781 ± 71

Standard deviation obtained from triplicate tests.

2.3. Influence of ZVI on methane production from sludge under alkali condition

Another experiment was operated under alkali condition to compare the methane production from the sludge digestion with four dosage levels of ZVI (0, 1, 5, 10 g/L). Zhao et al. (2010) found that anaerobic fermentation under pH 10 could significantly enhance the hydrolysis–acidification and decrease the methanogenic activity. Although ZVI could alleviate the anaerobic acidity to help the system kept at a neutral pH through the reaction of $Fe + 2H^+ = Fe^{2+} + H_2$, it had no capacity to make the pH of digestion system up to 10. Therefore, 4 M NaOH was added to maintain the pH of all serum bottles at 10 during the digestion no matter how much ZVI was dosed. The digestion was lasted for 8 d. Other experimental conditions were the same as the sludge digestion with the heat-treated sludge. All the experiments were repeated twice, and their mean values were used as the experimental results.

2.4. Analysis

Sludge samples from the reactors were analyzed for total suspended solid (TSS), volatile suspended solids (VSS), total protein and total polysaccharide. Then the samples were centrifuged at 8000 rpm for 10 min and immediately filtered through a cellulose membrane with a pore size of 0.45 μm for analysis of soluble COD (SCOD), soluble protein, soluble polysaccharide and VFAs. TSS, VSS and SCOD were determined according to Standard Methods for the Examination of Water and Wastewater (APHA., 1998). Proteins were measured with Lowry's method using bovine serum albumin as a standard solution (Fr et al., 1995). Polysaccharide was measured with phenol–sulfuric acid method using glucose as a standard solution (Masuko et al., 2005). The equivalent relationships between COD and substrates were as follows: 1.5 g-COD/g protein, 1.06 g-COD/g carbohydrate, 1.07 g-COD/g acetate, 1.51 g-COD/g propionate, 1.82 g-COD/g butyrate, and 2.04 g-COD/g valerate (Lu et al., 2012). The ORP was measured using an ORP combination glass-body redox electrode (Sartorius PY-R01, Germany). The components of biogas (including methane, hydrogen and carbon dioxide) were analyzed with a gas chromatograph (Shimadzu, GC-14C) equipped with a thermal conductivity detector and a 1.5 m stainless-steel column (Molecular Sieve, 80/100 mesh). The temperatures of injector, detector and column were kept at 100 °C, 105 °C and 60 °C according to Zhao and Yu (2008). Nitrogen was used as the carrier gas at a flow rate of 30 ml/min. VFAs (acetate, propionate, butyrate and valerate) were measured in another gas chromatograph (Shimadzu, GC2010) with GC-flame ionization detector, FID (Shimadzu, Model 14B) and a 30 m × 0.25 mm × 0.25 μm fused-silica capillary column (DB-FFAP). The operating temperatures for the injection port and the FID were 170 °C. The temperature in the oven was gradually increased from 100 to 130 °C at a rate of 5 °C/min according to Fan et al. (2006).

3. Results and discussion

3.1. Effects of ZVI on methane production from heat-pretreated sludge

3.1.1. Biogas production

It was reported that heat pretreatment could ruptures the cell wall and cell membranes of bacteria in the waste sludge (Carrère et al., 2010). It caused the complex organic molecules such as