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Enhanced anaerobic digestion of waste activated sludge digestion by the addition of zero valent iron

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ABSTRACT

Anaerobic digestion is promising technology to recover energy from waste activated sludge. However, the sludge digestion is limited by its low efficiency of hydrolysis–acidification. Zero valent iron (ZVI) as a reducing material is expected to enhance anaerobic process including the hydrolysis–acidification process. Considering that, ZVI was added into an anaerobic sludge digestion system to accelerate the sludge digestion in this study. The results indicated that ZVI effectively enhanced the decomposition of protein and cellulose, the two main components of the sludge. Compared to the control test without ZVI, the degradation of protein increased 21.9% and the volatile fatty acids production increased 37.3% with adding ZVI. More acetate and less propionate are found during the hydrolysis–acidification with ZVI. The activities of several key enzymes in the hydrolysis and acidification increased 0.6–1 time. ZVI made the methane production raise 43.5% and sludge reduction ratio increase 12.2 percent points. Fluorescence in situ hybridization analysis showed that the abundances of hydrogen-consuming microorganisms including homoacetogens and hydrogenotrophic methanogens with ZVI were higher than the control, which reduced the H_2 accumulation to create a beneficial condition for the sludge digestion in thermodynamics.

1. Introduction

Waste activated sludge (WAS) produced from municipal wastewater treatment plant is a problem with growing importance because of its huge production, potentially environmental risk and high cost for disposal. Anaerobic digestion is considered to be the most energy efficient method for destroying and stabilizing waste sludge and methane byproduct as a form of fuel may reduce treatment cost (Wang et al., 2013). Three stages are involved in the anaerobic digestion of sludge, e.g. (i) hydrolysis of biological polymers with subsequent production of H_2, acetate and other VFAs, (ii) conversion of these VFAs to H_2 and acetate by syntrophic bacteria under a low hydrogen partial pressure and (iii) conversion of acetate and H_2 to methane (Lv et al., 2010). Of them, hydrolysis is recognized as the rate-limiting step in the anaerobic sludge digestion (Tiehm et al., 2001; Bougrier et al., 2006). To accelerate the sludge digestion, various pre-treatments have been used to improve the hydrolysis of the sludge, including thermal (Imbierowicz and Chacuk, 2012), chemical (Chiu et al., 1997; Ibeid et al., 2013) and mechanical methods (Nah et al., 2000).

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On the other hand, the microbiology of anaerobic digestion is complicated and each microbial stage has their optimal functioning conditions. They are sensitive to and possibly inhibited by operational parameters such as pH, hydrogen, volatile fatty acids and others. H_2, a byproduct during acidification of organics, is considered as a thermodynamically unfavorable intermediate during anaerobic methanogenesis because it may impede the decomposition of organic acids (Fukuzaki et al., 1990). For example, propionic acid and butyric acid, two main VFA forms in acidification, can be decomposed into acetate only when pH_2 is less than 10^{-4} for n-butyric acid and 10^{-5} atm for propionic acid (Siriwongrungson et al., 2007). However the partial pressure of hydrogen in practice usually exceeds this range especially as the substrates are rich in carbohydrate such as WAS (Hawkes et al., 2002). Until now, very few publications are focused on accelerating the anaerobic digestion of sludge by reducing the accumulation of hydrogen.

Zero-valent iron (ZVI), a reductive material, has been widely applied in wastewater treatment, groundwater purification and soil remediation (Jiang et al., 2011). ZVI may decline the oxidation-reduction potential (ORP) when added into anaerobic systems, enabling to create a more favorable environment for anaerobic biological processes (Liu et al., 2012a). It could significantly improve conversion of complex organics into volatile fatty acids (VFAs) and methanogenesis. It was found that propionate production dropped with addition of ZVI because propionic-type fermentation did not prefer low ORP (Alkaya and Demirer, 2011; Ren et al., 2007). Although the effects of ZVI on anaerobic degradation of sucrose were primarily investigated in our previous work, the functions of ZVI in the anaerobic sludge digestion still remain unknown. As mentioned above, the sludge digestion is different with the digestion of simple organics in terms of the limiting step and H_2 production rate. In this study, ZVI was added into an anaerobic digestion system for accelerating the sludge digestion. To our best knowledge, it is the first time to enhance the anaerobic digestion of sludge through adding ZVI. The effects of ZVI on hydrolysis–acidification and methanogenesis of the sludge were investigated, with the aim to provide a simple and effective method to accelerate the anaerobic digestion of sludge.

2. Materials and methods

2.1. Sludge pretreatment

WAS used in this study was obtained from the secondary sedimentation tank of municipal wastewater treatment plant in Dalian, China. The sludge was concentrated by settling at 24 h, and storage at 4 °C before use. To enhance the hydrolysis, the sludge was pretreated using alkaline-method before the anaerobic fermentation according to the reference (Chu et al., 2009). The pH of sludge was adjusted to 12 using 4 mol/L of sodium hydroxide, and then the sludge was stirred at 80 rpm for 6 h. After pretreatment, the pH of sludge was adjusted to 7 for anaerobic digestion. The characteristics of raw sludge and alkaline-pretreated sludge are compared in Table 1.

Table 1 – Characteristics of the raw sludge and alkaline-pretreated sludge.

Parameters	Raw WAS	Alkaline-pretreated WAS
pH	7.16 ± 0.1	7.06 ± 0.1
TSS (total suspended solids)	13.4 ± 0.954	11.7 ± 0.412
VSS (volatile suspended solids)	8.57 ± 0.104	6.54 ± 0.142
TCOD (total chemical oxygen demand)	12875 ± 784	10829 ± 697
SCOD (soluble chemical oxygen demand)	634 ± 75	4336 ± 324
Total protein (as COD)	7725 ± 575	6820 ± 543
Total polysaccharide (as COD)	1545 ± 215	1332 ± 148
Soluble protein (as COD)	348 ± 76	2454 ± 286
Soluble polysaccharide (as COD)	81 ± 47	516 ± 176

All values are expressed in mg/L except pH.
Average data and standard deviation obtained from three tests.

2.2. Operation

The seed sludge was collected from a UASB reactor in our laboratory. The alkaline-pretreated sludge and seed sludge was mixed with a ratio of 9:1 for the anaerobic digestion. To investigate the effects of ZVI on hydrolysis and methanogenesis, respectively, the experiments were divided into the two stages. The first experiment was lasted only for 3 d to explore the effect of ZVI on hydrolysis–acidification, and the second experiment was conducted for 20 d to investigate the effect on whole anaerobic digestion of sludge including hydrolysis–acidification and methanogenesis.

2.2.1. Effects of ZVI dosage on hydrolysis–acidification

The VFAs produced tended to be consumed by methanogens, and then it was necessary to eliminate its interference in the experiment of this first stage. Heat treatment and BESA (2-bromoethanesulfonic acid) addition have been reported to efficiently get rid of methanogens from anaerobic fermentation system (Oh et al., 2003; Basu et al., 2005). Therefore, in the experiment of the first stage, the mixture sludge including alkaline-pretreated sludge and seed sludge was heated at 102 °C for 30 min. After the mixture was cooled down to room temperature, BESA with a concentration of 50 mM was mixed in for use. 250 mL of the mixed sludge above was added into four serum bottles with working volume of 250 mL, respectively. Afterwards, 0, 1, 4 and 20 g/L of ZVI powder (diameter of 0.2 mm, BET surface area of 0.05 m^2/g, purity >98%) were added into the four bottles, respectively. All 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 72 h. 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.