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Dosing time of ferric chloride to disinhibit the excessive volatile fatty acids in sludge thermophilic anaerobic digestion system

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HIGHLIGHTS

- Supplementation of $FeCl_3$ could accelerate the hydrolysis–acidification process.
- The optimum dosing time of $FeCl_3$ is 72nd hour after startup.
- Acetic acid was the main inhibitor in the thermophilic AD system.
- $FeCl_3$ contributes to build a favorable condition, except to remove acetic acid.

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ABSTRACT

An investigation into the effect of ferric chloride ($FeCl_3$) on the disinhibition of excessive volatile fatty acids (VFAs) in sludge thermophilic anaerobic digestion (AD) system was performed. The optimum dosing time of $FeCl_3$ was tested with the time interval of 0 h, 36 h, 72 h, 108 h and 144 h. The maximum biogas production was obtained in the case of 72nd hour dosing group, and the biogas production potential was 293.13 ± 11.38 mL/gVS based on modified Gompertz predicted model with the maximum rate of 8.55 ± 0.38 mL/(gVS day), which was triple as that in the control group. More biodegradable organic matters were generated from sludge with $FeCl_3$ additive and then consumed efficiently according to excitation–emission matrix (EEM) fluorescence spectra analysis in the dissolved organic matter (DOM). Acetic acid was the main inhibitor and synthetic effects occurred for the disinhibition of excessive VFAs with the additive of $FeCl_3$, except to direct removal of acetic acid in the system.

1. Introduction

The amount of waste activated sludge (WAS) is growing extremely fast each year in China, and up to 11.2 million tons annually, due to the stricter discharge requirements for the biological wastewater treatment in municipal wastewater treatment plants (WWTPs) (Feng et al., 2015; Sun et al., 2015). At present, many conventional ways have been attempted to treat WAS, including landfill, combustion, and composting for farmland use (Zhang et al., 2014a). Anaerobic digestion (AD), for its ability to harness the energy embedded in WAS and transform organic matters into biogas, has been considered as one of the most attractive options to realize the sludge stabilization and reduction (Xu et al., 2014). Compared to mesophilic AD, thermophilic AD has additional benefits including a high degree of waste stabilization, better pathogen inactivation and improved post-treatment sludge dewatering (Vrieze et al., 2013). However, process instability still prevents AD from being widely commercialized, which attributed to the reaction rate imbalance between the two groups of microorganisms, acidogens and methanogens, in terms of the different physiology, nutritional needs, growth kinetics, and sensitivity to environmental conditions (Siegert and Banks, 2005). The non-desirable consequence is the accumulation of inhibitory substances, and a wide variety of substances have been reported to be the leading cause of anaerobic system upset. Specially, the excessive volatile fat acids (VFAs) often occurred in thermophilic AD of WAS due to the fast hydrolysis and acidification rate, which inhibits the activity of methanogens and potentially decreases the biogas production (Li et al., 2015).

The stable operation in thermophilic AD system is the guarantee for improving the biogas generation, and some approaches were applied, including controlling the feedstock to inoculum (F/I) ratio and carbon to nitrogen (C/N) ratio, providing proper

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pH buffering, employing a two-stage digestion system to separate methanogenesis stage from other stages of hydrolysis–acidification, and the adding of trace element (TEs) to accelerate the growth of methanogens (Sheets et al., 2015). TEs addition seems to be a convenient and practical way for the AD system adjustment, and TEs have been proven to be serving as the essential co-factors of enzymes (such as methyl-coenzyme M, carbon monoxide dehydrogenase (CODH) and coenzyme M methyl-transferase) for the growth of methanogens (Zhang et al., 2015). Several trace metals, such as Co, Ni and Fe have been tested in different AD systems to accelerate the anaerobic microorganisms, and all of them were found to be positive contribution for biogas generation due to their vital role in the metabolic machinery of a wide range of anaerobic microorganisms active in the conversion of complex organic substrates to biogas (Yekta et al., 2014). Besides, due to the outstanding performance in sulfur control, Fe is largely supplemented to biogas reactors to participate in an array of reactions (Firer et al., 2008; Fermoso et al., 2010).

Three types of methane metabolic pathways, including the aceticlastic methanogenesis pathway, the hydrogenotrophic methanogenesis pathway and the methyl compound utilizing pathway were presented in the AD system, and all the pathways will produce methane from the methyl coenzyme M by the methyl CoM reductase (Xu et al., 2014). It has been reported that there are different sensitivities to the inhibitors in the methanogenic pathways, and excessive VFAs is the main factor for the thermophilic AD system through the different effects on these three pathways (Xu et al., 2010). Excessive VFAs inhibition could be alleviated by chemical precipitation, and ferric nitrate was applied in autothermal thermophilic aerobic digestion (ATAD) system for improving the sludge stabilization rate (Jin et al., 2015); Zhang et al. (2013) also found that the addition of waste iron scrap could reduce the VFAs concentration during anaerobic digestion of excess sludge by iron salts precipitation. In our previous work, it was found that the addition of ferric chloride ($FeCl_3$) could enhance the biogas production by enriching *Coprothermobacter* for proteins fermentation and *Methanosarcina* for methanogenesis from the perspective of microorganisms (Yu et al., 2015). It is proposed that the introduction of $FeCl_3$ might contribute to the reduction of VFAs content. Thus the dosing time of $FeCl_3$ will be very important influence factor for the methanogenesis process.

The aim of this study is to identify the main VFA inhibition type during the thermophilic AD process, to evaluate the effects of different dosing time on hydrolysis–acidification and biogas production through analyzing variation of soluble chemical oxygen demand (SCOD), VFAs and the composition of organic matters in the supernatant. Excitation–emission matrix (EEM) and fluorescence regional integration (FRI) technique were used to examine the distribution of the dissolved organic matter (DOM) species and content of the substrate environment, which have the advantages of high sensitivity, high selectivity and rich fluorescent information. Aside from the bioavailability assessment of iron ion, kinetic analysis for describing the performance of biological treatment system was applied to clearly explain the effects of $FeCl_3$ with different dosing time.

2. Methods

2.1. Characteristics of sludge and inoculum

WAS applied was obtained from the secondary sedimentation tank of a municipal wastewater treatment plant (MWWTP) in Shanghai, China, where wastewater was treated by the anaerobic–anoxic–aerobic process with a capacity of 50,000 m^3/d. The sludge obtained was screened with a 1.0-mm mesh to eliminate large particles and hair before thickening to required solid concentrations. Then the pretreated samples were stored at 4 °C for further analyses. The inoculum (seed sludge) was collected directly from a long-term continuous lab-scale anaerobic bioreactor in our lab (Yu et al., 2015). The main characteristics of WAS and seed sludge are given in Table 1.

2.2. Batch experiments

Batch experiments were carried out in double-walled cylindrical vessels, and each group had three parallel reactors with 6 L working volume. Oxygen was removed from the headspace by exchanging it with nitrogen gas (99.99%) for 5 min after loading 5 L mixture of inoculum and raw sludge with a ratio of 1:9 (volume:volume). All the reactors maintained at a thermophilic digestion temperature of 55 ± 2 °C by water circulation, equipped with stainless-steel stirrers for mixing the contents. During the digestion, the biogas produced from each reactor was collected into gasbag for analysis, and then the volume was measured using a calibrated sampling syringe. All samples from the reactors were analyzed in triplicate, and one-way analysis of variance (ANOVA) at 0.05 level was used to analyze the data.

In our previous study, it was found that the introduction of $Fe(NO_3)_3$ and $Fe_2(SO_4)_3$ was adverse to the methanogenesis process, while $FeCl_3$ could create a favorable anaerobic environment; thus $FeCl_3$ was chosen as the additive (Yu et al., 2015). Since the serious unbalance of hydrolysis–acidification and methanogenesis often occurred in the initial stage of thermophilic AD, a dosing time gradient of 0 h, 36 h, 72 h, 108 h and 144 h was adopted after the experimental startup (referred to as R2, R3, R4, R5 and R6, respectively). The control group (R1) was also carried out under the same operation conditions without $FeCl_3$. The whole cycle of digestion process occupied 43 days and samples were taken from each reactor at particular intervals (initial, 3rd, 6th, 9th, 12th, 15th, 18th, 23rd, 28th, 33rd, 38th and 43rd day) for analysis intermittently. Aim to investigate the effects of different dosing times on the biogas production kinetics during the thermophilic AD process of WAS, a fixed dosage of 200 mg/L $FeCl_3$ was applied, which based on the concentration of iron ion, as reported in our previous study (Yu et al., 2015). No alkalinity or buffering agent was added into the system, and the pH value was not adjusted during the entire process.

2.3. Analytical methods

Total solids (TS) and volatile solids (VS) were measured according to the Standard Methods (APHA et al., 2005), and the values were subtracted with TS and VS that chemicals engendered by itself. The pH and oxidation reduction potential (ORP) of the sludge samples were determined by a pH meter (pHs-3C, Leici Co. Ltd., Shanghai) and an ORP meter (ORP-502, Ruosull Technology Co.,

Table 1
Characteristics of WAS and seed sludge used in experiments.[a]

Parameters	WAS	Seed sludge
pH	6.64–6.70	6.87–6.90
TS (mg/L)	39,500–40,100	68,700–69,200
VS (mg/L)	30,200–30,800	49,600–52,200
TCOD (mg/L)	31,630–36,480	81,040–85,960
SCOD (mg/L)	836–980	14,620–17,860
Soluble proteins (mg/L)	2.2–2.4	398.2–466.2
Soluble carbohydrates (mg/L)	92.4–98.2	237.6–258.3
Fe (%)	1.46–1.54	1.73–1.85

SCOD: soluble chemical oxygen demand; the content (%) of Fe was in dry sludge solid.
[a] TS: total solid; VS: volatile solid; TCOD: total chemical oxygen demand.