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Disinhibition of excessive volatile fatty acids to improve the efficiency of autothermal thermophilic aerobic sludge digestion by chemical approach

Ningben Jin [a], Bo Jin [b], Nanwen Zhu [a,*], Haiping Yuan [a], Jianbo Ruan [a]

[a] School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
[b] School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

HIGHLIGHTS

- Ferric nitrate was introduced to remove excessive volatile fatty acids in ATAD.
- Ferric nitrate dosed digester achieved stabilization 9 days earlier than the control.
- Total VFAs and acetic acid in ferric nitrate dosed digester were lowest.
- The lower Total VFAs favored removal of NH_4^+-N, SCOD and TP.
- The lower Total VFAs improved the microbial activity.

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ABSTRACT

In this study, we explored a chemical approach to eliminate inhibition of excessive volatile fatty acids (VFAs) in autothermal thermophilic aerobic digestion (ATAD). Ferric nitrate, ferric chloride, potassium nitrate and potassium chloride were employed to demonstrate the combined action of ferric ion and nitrate ion. Supplementation of ferric nitrate in the sludge digestion system resulted in reducing the concentration of Total VFAs (TVFA) by round 5000 mg/L and more than 2000 mg/L of acetic acid at the end of digestion. Lower TVFA concentration contributed to faster sludge stabilization rate and the VS removal of ferric nitrate dosed digester achieved 38.18% after 12 days digestion which was 9 days in advance compared with the stabilization time of sludge in digester without chemicals addition. Lower concentrations of NH_4^+-N and SCOD in supernatant while higher content of TP in digestion sludge were obtained in digester with ferric nitrate added.

1. Introduction

Sewage sludge containing numerous organic compounds and pathogens could deliver potential risks for environment and human health. The treatment and disposal of sewage sludge is a costly practice and challenge in wastewater treatment plants (WWTPs), due to rapid increase of sludge and gradually strict standards implemented (Liu et al., 2011a). Stabilization treatment of sludge is needed prior to its landfilling and land use application. Thus a number of methods, especially the biological processes with low costs have been devoted to stabilization of sludge (Yuan et al., 2011). Aerobic digestion is a commonly used biological process for stabilizing sludge in medium- and small-sized WWTPs due to its economic advantages (Liu et al., 2010). Autothermal thermophilic aerobic digestion (ATAD) is considered as an advanced aerobic process for the treatment of sludge, as it has efficient pathogen inactivation, and high volatile solids (VS) reduction capability, and low energy consumption and simple control requirements (Lloret et al., 2012). To date, ATAD system has undergone two generation (Staton et al., 2001) and one-stage ATAD process, as the second generation of ATAD system, has received much more attention for its simple units and small area-occupation while achieving the same stabilization effect (Liu et al., 2012a). In Europe and North America, the ATAD process has been proposed to be put into use in small- and medium-sized WWTPs since 1970s and become more widely used later (Kelly and Mavinic, 2003) while there appears to be no ATAD process in service so far in China (Cheng et al., 2005).

ATAD process can be operated at a high sludge digestion rate with 45.0% VS removal at 55 °C for 552 h, for the reason that

* Corresponding author. Tel./fax: +86 021 54743170.
E-mail address: nwzhu@sjtu.edu.cn (N. Zhu).

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thermophilic temperature promotes the microbial metabolism in the ATAD system (Liu et al., 2012a). In fact, the ATAD system is operated under oxygen-deficiency condition due to reduction in aeration and the oxidation reduction potential(ORP) in the system is in a low range between −335 and −245 mV (Liu et al., 2013), leading to the accumulation of volatile fatty acids (VFAs) (Fothergill and Mavinic, 2000; Mavinic et al., 2001; Liu et al., 2011b). In one-stage ATAD system, VFAs production will be increased during the initial stage of the digestion process, on account of the micro-oxygen environment which makes oxygen, as terminal electron acceptor of biochemical reactions, transfer along the respiratory chain be hindered (Liu et al., 2012b). Once the electron transport chain is impeded, biochemical metabolic process starts through a synthetic pathway to produce acetic acid, propionic acid and other VFAs for the digestive system to meet the demand of nicotinamide adenine dinucleotide oxidation state (NAD^+) and achieve the maximum of ATP synthesis (Angus et al., 1996). Meanwhile propionic acid has an ongoing generation, result from over high concentration of acetic acid which restrains the transformation from propionic acid to acetic acid and its capability that more conducive to the oxidation of NADH-H than butyrate acid (Liu et al., 2012b). It was found that the concentration of TVFA can reach about 8000 mg/L while the total concentration of acetic acid and propionic acid reached about 3000 mg/L in one-stage ATAD process (Liu et al., 2011b, 2012b). A high concentration of TVFA at 5000 mg/L and propionic acid of to 1000 mg/L resulted in inactivation of some species of microorganisms, especially Gram-positive bacteria (Chen et al., 2008). It has been proved that the dominant bacteria in ATAD system are almost Gram-positive bacteria (Hayes et al., 2011), which makes the high concentration of VFAs toxic to the microbial metabolism in the ATAD system. However, no researches in seeking for methods to relieve inhibition caused by superfluous VFAs have been reported in the literature.

The purpose of this study was to testify the chemical approach using ferric nitrate on removing the inhibition of excessive VFAs in ATAD process, by mean of decreasing the available content of acetic acid so as to improve the sludge stabilization. In the meantime, comparison experiments were also conducted using ferric chloride, potassium nitrate and potassium chloride to clarify mechanisms of the function of ferric nitrate with sludge. The effects of all chemicals on eliminating the inhibition of excessive VFAs were evaluated with respect to the variations in sludge properties before and after treatments by chemical approach.

2. Methods

2.1. Sewage sludge sample

Sewage sludge used in this study was sampled from the secondary sedimentation tank of a municipal wastewater treatment plant in Shanghai, China. The collected sludge was immediately sieved to remove substances of particle size greater than 0.5 mm before centrifuged at 3000 rpm for 3 min to acquire concentration of total solid (TS) between 5% and 6% (Staton et al., 2001; Xu et al., 2013). The properties of initial sludge were shown in Table 1.

2.2. Startup of the digestion process

Five simulated autothermal thermophilic aerobic digesters were utilized to conduct experiments (Fig. 1). The digester was constructed with a tempered glass cylinder with available capacity of 5 L while the working volume was 4 L. Operating temperature of the cylinder was controlled by a heating water jacket connected to a water bath. The temperature of digestion reaction rose from 35 to 55 °C, controlled by water bath at rate of 5 °C one day, and then stayed at 55 °C for 17 days subsequently. Aeration was provided by pumping compressed air via a gas device associated with mass flowmeter at air flow rate of 0.13 L/min to provide a micro-aerobic condition (Chu et al., 1997), along with a constant stirring rate of 100 resolutions. A thermometer and an oxidation reduction potential (ORP) meter were installed in each digester while pH in the digestion system was not regulated.

The whole digestion process took 21 days and all indicators excepted pH were measured after samples taken on 1st, 2nd, 4th, 6th, 9th, 12th, 15th, 18th, 21st day as well as at the beginning of digestion. As the VFAs could be generated fast to achieve a peak level on the 6th day in ATAD process (Liu et al., 2012b), the chemical reagents were dosed separately on the 6th day with designed dosages. On 6th day, all of the chemical reagents were dosed separately into digesters 6 h before sampling, for the sake of adequate reactions between chemical reagents and sludge. The dosage of $Fe(NO_3)_3{\cdot}9H_2O$ was 3.16 g/L sludge, which was calculated based on the ideal molar ratio of Fe^{3+}:CH_3COO^- equaling to 1:3 to reduce acetic acid of 1500 mg/L with the decreased amount of sludge by sampling before 6th day counted. The dosage of other chemical reagents like $FeCl_3{\cdot}9H_2O$, KNO_3 and KCl was set up as 2.12, 2.38 and 1.75 g/L sludge, respectively, which were calculated on the basis of equal molar weight of Fe^{3+} between $Fe(NO_3)_3{\cdot}9H_2O$ and $FeCl_3{\cdot}9H_2O$, NO_3^- between $Fe(NO_3)_3{\cdot}9H_2O$ and KNO_3, Cl^- between $FeCl_3{\cdot}9H_2O$ and KCl or K^+ between KNO_3 and KCl. Moreover, defined amounts of sodium hydroxide were added into digesters which were added with chemical reagents of ferric nitrate and ferric chloride, respectively, in order to maintain the digestion system neutral. The operating conditions of the different reactors were designated as those showed in Table 2.

2.3. Analytical methods

The pH was measured by a pH meter (pHs-3C, Leici Co. Ltd., Shanghai). VS and TS were determined according to the Standard Methods (APHA et al., 2005) with values of influence caused by chemical reagents subtracted.

The measurement of adenosine triphosphate (ATP) content in sludge was based on the following reaction (1) (Roche, 1999):

$$\text{ATP} + D\text{-luciferin} + O_2 \rightarrow \text{oxyluciferin} + \text{PPi} + \text{AMP} + CO_2 + \text{light} \quad (1)$$

The sludge sample was undertaken a reaction with luciferase (Bac Titer-Glo microbial cell viability assay, Promega Corp.), which was measured as a Relative Luminescence Unit (RLU) in a Spectra Max L microplate luminometer (Varioskan Flash, Thermo Corp.)

Table 1
Properties of initial sludge employed in simulated one-stage ATAD process.[a]

Parameter	pH	TS (g/L)	VS (g/L)	SCOD (mg/L)	TN (mg/L)	NH_4^+-N (mg/L)	TP (mg/L)
Value	6.46	53.2 ± 0.3	39.8 ± 0.2	4195 ± 40	109 ± 5	88 ± 3	334 ± 8

[a] SCOD, soluble chemical oxidation demand; TN, total nitrogen in supernatant; TP, total phosphate in supernatant.