Water Research 139 (2018) 363–371

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Pre-separation of ammonium content during high solid thermal-alkaline pretreatment to mitigate ammonia inhibition: Kinetics and feasibility analysis

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ARTICLE INFO

Article history:
Received 15 January 2018
Received in revised form
23 March 2018
Accepted 26 March 2018
Available online 27 March 2018

Keywords:
Waste activated sludge
Thermal-alkaline pretreatment
High solid anaerobic digestion
Hydrolysis kinetics
Ammonia pre-separation

ABSTRACT

The feasibility of ammonia pre-separation during the thermal-alkaline pretreatment (TAP) of waste activated sludge was evaluated to mitigate ammonia inhibition during high solid anaerobic digestion (HSAD). The results showed that the TAP increased the organics hydrolysis rate as much as 77% compared to the thermal hydrolysis pretreatment (THP). The production and separation of the ammonia during the TAP exhibited a linear relationship with the hydrolysis of organics and the Emerson model. The pre-separation ratio of the free ammonia nitrogen exceeded 98.00% at a lime dosage exceeding 0.021 g CaO/g TS. However, the separation ratio of the total ammonia nitrogen (TAN) was hindered by its production ratio. Compared to the THP, the TAP increased the methane production rate under similar production yield. A mass flow analysis indicated that the TAP-HSAD process reduced the volume of the digester compared to the THP-HSAD process and the recirculated HSAD-TAP process recovered 45% of the nitrogen in the waste activated sludge.

1. Introduction

Waste activated sludge (WAS) is a by-product of wastewater treatment in wastewater treatment plants (WWTP) and has to be treated sufficiently to prevent environmental pollution. The production of WAS reached 55 million tons (80% water content) in 2014 and is still increasing (Liu et al., 2017). However, approximately 80% of WAS is not anaerobically digested in China (Dai et al., 2013). Anaerobic digestion (AD), which is the biochemical process to remove organic components in sludge and produces methane, has been widely applied in WWTP to stabilize the WAS (Jiang et al., 2014). High solid AD (HSAD), in which the solids content of the raw sludge exceeds 10% to decrease the volume of digester and energy consumption significantly, is a promising process for improving the conventional AD (Dai et al., 2014; Zhang et al., 2018). As the solids content of the WAS increases, the anaerobic biodegradation process is hindered by the hydrolysis of organics and ammonia inhibition (Appels et al., 2008; Rajagopal et al., 2013). A thermal hydrolysis pretreatment (THP) is the most widespread technology for AD pretreatment because it degrades the cell walls effectively and renders the sludge more amenable to AD (Barber, 2016; Li and Noike, 1992; Ometto et al., 2014; Zhen et al., 2017). However, the concentration of free ammonia nitrogen (FAN), which is the main inhibitor (Wang et al., 2016) during HSAD, can easily exceed a threshold (0.6 gFAN/L) (Duan et al., 2012; Li et al., 2017b). FAN is influenced by temperature, total ammonia nitrogen (TAN) concentration, and pH and those factors tend to be fixed values under stable AD operating conditions. Therefore, it is difficult to control the FAN concentration during HSAD.

In light of the concerns regarding ammonia inhibition during THP-HSAD, various attempts have been proposed to mitigate the ammonia inhibition by controlling the TAN concentration. Horttanainen et al. (2017) evaluated the potential for ammonia recovery from dewatered sludge during thermal drying. Yao et al. (2017) investigated simultaneous ammonia-stripping and AD for treating dairy manure at high solids concentration. These studies indicated that the conversion of the TAN to ammonia gas might be a promising approach to reduce the TAN concentration. The Emerson model (Emerson et al., 1975) states that the TAN tends to consist of

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https://doi.org/10.1016/j.watres.2018.03.064
0043-1354/

FAN at high temperatures and high pH. Therefore, due to the requirements of high pH and temperature, the thermal-alkaline pretreatment (TAP) of the WAS provides the opportunity to control the FAN concentration with ammonia pre-separation via the release of the exhaust gas. The conventional TAP of sludge is a closed system, in which the produced FAN is dissolved in the sludge after cooling down. By releasing the exhaust gas and opening the vessel after heating is completed, the cooling process of the TAP has been modified to an evaporation system or ammonia-stripping process. Thus, the FAN produced by the TAP cannot dissolve in the sludge, which means the pre-separation of the FAN during the HSAD can be achieved. As a result, the TAP provides the conditions required to convert the TAN to ammonia gas.

The characteristics of the TAP of WAS have been widely investigated in recent years. Li et al. (2016) reported that a TAP reduced the energy consumption and increased the methane yields. Carrère et al. (2010) determined that the temperature was lower for the TAP (120–130 °C) than for the THP (170 °C) at similar methane production performance. Xiang et al. (2017) explained the relationships among the hydrolysis rate constant, the temperature, and the pH during the TAP of WAS. Li et al. (2017a) reported that the TAP-AD process achieved self-sufficiency of energy with proper lime dosage. In summary, the hydrolysis of organics in sludge using a TAP has been widely investigated. However, the process of the production and phase conversion of the TAN during the TAP has not been described to date and the feasibility of the TAN separation by the TAP is unknown.

The feasibility of the TAN pre-separation during the TAP was determined with the goal of mitigating the ammonia inhibition in a THP-HSAD process. The hydrolysis of organics, as well as the TAN production and separation during the TAP, which are chemical domination processes, are described by kinetic analyses and by investigating different duration times and lime dosages. In addition, the ability to pre-separate the TAN by the TAP was evaluated. Furthermore, the combination of the TAP (ammonia pre-separation) and the HSAD is investigated using mass flow calculations.

2. Materials and methods

2.1. Sludge sampling and characterization

The high solid WAS was obtained from the 4th WWTP in Xi'an, which uses an anaerobic-anoxic-oxic (A^2/O) process. The solids content of the WAS was adjusted to 12.5% by dewatering and it was stored at 4 °C in the laboratory prior to analysis. The characteristics of the high solid WAS are listed in Table 1.

2.2. TAP device

The TAP device was a vertical heating pressure steam sterilizer (Shanghai Shenan Medical Instrument Factory, LDZX-30KBS). The pretreatment of the high solid sludge was conducted as follows. The sample (WAS, 12.5% solid content) was mixed with lime (0.00 gCaO/gTS, 0.05 gCaO/gTS, 0.10 gCaO/gTS, 0.15 gCaO/gTS and 0.20 gCaO/gTS). The sample container of the steam sterilizer was filled with the sludge (about 25 mL per container) and placed into the steam sterilizer. The level of pure water beneath the container was checked and the steam sterilizer was sealed. The steam sterilizer was heated to the desired temperature (120 °C) and the duration time (30 min, 60 min, 90 min, 120 min and 150 min) to reach the temperature was recorded. When the duration time was reached the set value, the exhausted gas was released and the heating was stopped. Finally, the steam sterilizer was allowed to cool naturally with the vessel being open and the sludge was stored at 4 °C.

2.3. Batch test of AD

Biochemical methane potential (BMP) tests were conducted to evaluate the influence of the pretreatment on the AD of the sludge. The BMP reactors consisted of a shaking incubator (maintained at 35 ± 1 °C, 120 rpm) and 100 mL detest oxygen bottles. The inoculum sludge was obtained from a lab-scale mesophilic AD reactor (10.0% solid content, hydraulic retention time (HRT) of 20 d, stable for over 200 days), and the inoculum to substrate ratio of BMP test was 3 gVS/gVS. The methane concentration in the biogas was measured and converted to methane production yield. The duration of BMP test was 20 d. The pH wasn't neutralized prior to the BMP test.

2.4. Analytical methods

The analyses to characterize the sludge and biogas included pH, volatile suspended solids (VSS), chemical oxygen demand (COD), soluble COD (SCOD), TAN, total nitrogen (TN), dissolved TN (STN), and phosphate (PO_4^{3-}). The particulate COD (PCOD) was calculated as COD - SCOD.

VSS, TN, STN, TAN, PO_4^{3-}, COD and SCOD were analyzed according to standard methods for the examination of water and wastewater (APHA, 2005). pH was determined using a model PHS-3c pH meter (Shanghai Jingke Corp. China). Methane content was measured by gas chromatograph (3420A, BEIFEN Corp., China) with a thermal conductivity detector (TCD) and a packed column (TDX-01, 3 mm × 2 m) (Wu et al., 2016).

For statistical analysis, two-way Analysis of Variance (ANOVA) at the 0.05 significance level was used. Microsoft Excel and IBM SPSS Statistics 24 were used to determine the p-value and Pearson correlation coefficient, respectively.

2.5. Kinetic analysis

The separation of TAN during TAP could be described as following steps: influence of lime on pH, hydrolysis of organics, production of TAN, conversion of TAN to FAN, and separation of FAN. The kinetic analysis of organic hydrolysis and TAN pre-separation was carried out basing on following principles: a custom equation was used to describe the effect of lime on OH^- concentration; first-order relationship could be used to describe the hydrolysis of organics during thermal pretreatment (Luo et al., 2012; Xiang et al., 2017); an Arrhenius-type equation was used to describe the effect of pH on the hydrolysis of organics with regard to the influence of the temperature on the thermal hydrolysis (Farno et al., 2014, 2015); liner relationship between the production of TAN and hydrolysis of VSS; Emerson model was used to describe the conversion of TAN to FAN (Emerson et al., 1975); liner relationship between the production of FAN and separation of FAN. Kinetic analysis of results was performed using Matlab 2016b (9.1.0.441655). The coefficients in the equations were determined by curve or surface fitting of data.

3. Results and discussion

3.1. Overall performance of TAP

The optimization of the TAP conditions was essential to determine the effects of the TAP on the organic hydrolysis and TAN pre-separation. After the TAP, a portion of the particulate organics in the sludge was converted into the liquor, resulting in the acceleration of the AD process. The characteristics of the sludge are listed in Table 1.

The TAP had a significant effect on the organic hydrolysis. The VSS reduction ratio (1-VSS/VSS_{raw}) and the PCOD reduction ratio