International Biodeterioration & Biodegradation 129 (2018) 170–178

Contents lists available at ScienceDirect

International Biodeterioration & Biodegradation

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

Evaluation of volatile fatty acids production and dewaterability of waste activated sludge with different thermo-chemical pretreatments

Lei Yu[a], Wenduo Zhang[a], He Liu[a,b,*], Ganghui Wang[a], Hongbo Liu[a,b,**]

[a] Jiangsu Key Laboratory of Anaerobic Biotechnology, School of Environmental and Civil Engineering, Jiangnan University, Wuxi 214122, PR China
[b] Jiangsu Collaborative Innovation Center of Technology and Material of Water Treatment, Suzhou 215011, PR China

ARTICLE INFO

Keywords:
Waste activated sludge
Pretreatment
Fermentation
Volatile fatty acids
Dewaterability
Large-scale project

ABSTRACT

The effects of three kinds of waste activated sludge (WAS) thermo-chemical pretreatments, including thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatments, on volatile fatty acids (VFAs) production and sludge dewaterability were investigated in a large-scale WAS anaerobic fermentation project. Performances of VFAs production of sludge pretreated with thermo-NaOH (7.48 ± 0.64 g VFAs/L) and thermo-CaO_2 (7.91 ± 0.56 g VFAs/L) were proved to be better than that with thermo-mixed alkali (6.93 ± 0.63 g VFAs/L). Sludge pretreated with thermo-CaO_2 presented the best dewaterability and the moisture content of the sludge cake could be reduced to as low as 63.4 ± 4.4% after dewatering by plate-and-frame filter press. Conversely, the dewaterability of sludge pretreated with thermo-NaOH was significantly deteriorated and the VFAs were hard to be recovered. Furthermore, the economic feasibility comparison of thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatments for WAS anaerobic fermentation showed that the net profits were 1.55, 34.44 and 38.69 USD/ton dewatered sludge, respectively. Thermo-mixed alkali and thermo-CaO_2 pretreatments are promising pretreatment methods for the wide application of WAS anaerobic fermentation.

1. Introduction

A large amount of WAS was produced during the operation of wastewater treatment plants (WWTP). The resource recovery is the optimal choice and inevitable trend for WAS treatment and disposal because the WAS still contains a large number of available substances. WAS anaerobic fermentation for VFAs production is a kind of WAS resource recovery technology developed in recent years (Huang et al., 2015b; Li et al., 2016; Xin et al., 2017). The VFAs obtained from WAS anaerobic fermentation can be used as an economical carbon source for enhancing biological nutrient removal (BNR) in WWTP (Elefsiniotis et al., 2004), and they can also be used as raw materials for the production of bioenergy (Choi et al., 2011) and bioplastics (Mengmeng et al., 2009).

Generally, anaerobic digestion is considered to consist of three steps: hydrolysis, acidification and methanogenesis (Li et al., 2018). In the hydrolysis stage, both the solubilization of particle matters and biological decomposition of organic polymers to monomers/dimers occur slowly, thus making it the rate-limiting step of the overall processes (Sun et al., 2016). For purpose of promoting the dissolution of organic particles and the hydrolysis of organic matters, various pretreatment methods have been developed, such as microwave (Gao et al., 2017), ultrasonic (Liu et al., 2015), thermo Liao et al., 2016), alkaline (Ahmadi-Pirlou et al., 2017), thermo-alkaline (Guo et al., 2015; Abudi et al., 2016), oxidation (Pilli et al., 2016) and enzyme (Arun and Palani, 2015; Yin et al., 2016) pretreatments. Because of the simple process and relatively low cost, thermo-alkaline pretreatment has been applied in many studies. For example, Tan et al. (2012) reported that after 6-day fermentation, VFA accumulation was 1.63 times higher than that of untreated sludge when sludge was treated at pH 11 and 60 °C. Ma et al. (2016) reported that in the fermentation with thermo-alkaline pretreated sludge, the VFAs yield (240.14 mg chemical oxygen demand (COD)/g volatile solid (VS)) was much higher than un-pretreated sludge (175.77 mg COD/g VS).

The commonly alkali chemicals used in thermo-alkaline pretreatment are NaOH, KOH, $Ca(OH)_2$ and $Mg(OH)_2$, but they all have some limitations. For instance, although the addition of NaOH and KOH can significantly promote sludge hydrolysis, they also lead to the deterioration of sludge dewaterability due to the release of extracellular polymeric substances (EPS) from the microbial cells of sludge (Zhu et al., 2015). $Ca(OH)_2$ and $Mg(OH)_2$ have no negative effects on sludge dewaterability, but their efficiencies in sludge hydrolysis are lower than

* Corresponding author. School of Environmental and Civil Engineering, Jiangnan University, Wuxi 214122, PR China.
** Corresponding author. School of Environmental and Civil Engineering, Jiangnan University, Wuxi 214122, PR China.
E-mail addresses: liuhe@jiangnan.edu.cn (H. Liu), liuhongbo@jiangnan.edu.cn (H. Liu).

https://doi.org/10.1016/j.ibiod.2018.02.008
Received 1 December 2017; Received in revised form 31 January 2018; Accepted 6 February 2018
Available online 07 March 2018
0964-8305/

those of NaOH and KOH (Jin et al., 2016). Unlike anaerobic digestion for biogas production, anaerobic fermentation for VFAs production requires more attentions to sludge dewaterability since VFAs need to be separated from fermented sludge. Therefore, the mixed alkali was used in this study to investigate whether it is possible to obtain high sludge hydrolysis efficiency without degrading sludge dewaterability. CaO_2 is a classic and efficient oxidant. It slowly degrades in water to produce H_2O_2, O_2 and $Ca(OH)_2$ as shown in equation (1) and equation (2). In recent years, CaO_2 has attracted more attentions due to its high efficiency in promoting sludge hydrolysis and dewatering. For example, Li et al. (2015) found that the total short-chain fatty acids (TSCFAs) production was 3.9 times higher than the control tests and acetic acid comprised 60.2% of TSCFAs after anaerobic fermentation of sludge with the addition of 0.2 g CaO_2/g volatile suspended solid (VSS). Chen et al. (2016) reported that sludge filtration performance was enhanced by CaO_2 with the optimal dosage of 20 mg/g total suspended solid (TSS). CaO_2 seems to have the potential to simultaneously increase acidification performance and dewaterability of WAS. WAS anaerobic digestion for biogas production has been applied for many years. But large-scale application of WAS anaerobic fermentation to produce VFAs has not been reported yet. Until now, most studies about the effects of various pretreatments on WAS anaerobic fermentation were conducted at the laboratory-scale. Unfortunately, these lab-scale studies couldn't provide enough information of technique and economic feasibility, thus limiting the industrial applications of these technologies.

$$CaO_2 + 2H_2O \rightarrow H_2O_2 + Ca(OH)_2 \quad (1)$$

$$2CaO_2 + 2H_2O \rightarrow O_2 + 2Ca(OH)_2 \quad (2)$$

In this study, a large-scale WAS anaerobic fermentation project was constructed, and different WAS pretreatment methods were adopted to obtain a reasonable method for simultaneously enhancing VFAs production by anaerobic fermentation and upgrading the dewaterability of the fermented sludge. The purposes of this study were to investigate (1) the effects of thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatments on sludge hydrolysis performance; (2) the effects of the three pretreatment methods on sludge anaerobic fermentation for VFAs production; (3) the effects of the three WAS pretreatment methods on sludge dewaterability; (4) the technique and economic feasibility of these methods for large-scale WAS anaerobic fermentation to produce VFAs.

2. Materials and methods

2.1. Waste activated sludge and seed sludge

2.1.1. Waste activated sludge

The large-scale WAS anaerobic fermentation project was located in a municipal WWTP in Wuxi city, China. The WAS from the WWTP was dewatered by belt filter press and the moisture content was 85.2 ± 1.4%. And it was adjusted to the TSS at 70 g/L with hot water of about 95 °C. After adjusting, the characteristics of the sludge were shown in Table 1.

2.1.2. Seed sludge

The acclimation steps of seed sludge were as follows: Firstly, the WAS from the same WWTP was adjusted to the TSS at 70 g/L and treated at 95 °C for 4 h to kill most of the methanogens that cannot form spores (Park et al., 2005). The total volume of sludge was 2.1 m^3; Secondly, the nutrients were added when the sludge was naturally cooled to about 35 °C; Finally, the sludge was acclimatized at 35 °C and a stirring speed of 50 revolutions per minute (rpm) for 12 days. The concentrations (g/L) of nutrients in sludge were: glucose 14.40, $CaCl_2$ 3.20, yeast extract 3.20, $NaHCO_3$ 0.96, KH_2PO_4 0.56, $MnCl_2{\cdot}4H_2O$ 0.11, $MgSO_4{\cdot}7H_2O$ 0.96, $FeSO_4{\cdot}7H_2O$ 0.12, NH_4Cl 2.40.

Table 1
Characteristics of sludge for pretreatment and anaerobic fermentation.

Parameters	Values
pH	6.82 ± 0.51
TSS (g/L)	71.20 ± 6.65
VSS (g/L)	37.36 ± 4.16
Total protein (g/gVSS)	0.419 ± 0.031
Total carbohydrate (g/gVSS)	0.263 ± 0.019
SCOD (mg/L)	2566.42 ± 411.54
Soluble protein (mg/L)	131.90 ± 38.19
Soluble carbohydrate (mg/L)	256.38 ± 34.18
TN (mg/L)	197.75 ± 28.52
TP (mg/L)	14.44 ± 1.90

2.2. Outline of the project

The flow chart of this project was shown in Fig. 1. The main process units of this project included adjusting tank, pretreatment tank, fermentation tank, conditioning tank, hot water tank, tail gas absorption tank and chemical tank. The effective volumes of these tanks were 1.5, 1.9, 30.0, 2.0, 3.6, 4.6 and 0.25 m^3 respectively. The adjusting tank, pretreatment tank, fermentation tank and conditioning tank were equipped with agitating vanes. Furthermore, the pretreatment tank and fermentation tank were equipped with water jackets to adjust the tank temperature. The chamber volume of the plate and frame filter press was 60 L and the filter area was 5.0 m^3.

The WAS was adjusted by hot water from the hot water tank, then the adjusted sludge was pumped into the pretreatment tank for pretreatment by hot water from the hot water tank and chemicals from the chemical tank. The pretreated sludge was then pumped into the fermentation tank for anaerobic fermentation. After fermentation, the fermented sludge was pumped into the conditioning tank. Finally, it was pumped into the plate and frame filter press for solid-liquid separation to recover VFAs-rich fermentation liquid. The sludge cake derived from this process was transported outside for further disposal. The harmful gas in tail gas generated from the pretreatment tank, fermentation tank and adjusting tank was absorbed by the tail gas absorption tank and then the treated gas was emitted into the atmosphere.

2.3. WAS pretreatment and fermentation

2.3.1. WAS pretreatment

The WAS was adjusted to about 70 g/L at the total volume of 2.1 m^3 by hot water (95 °C), then the adjusted sludge was pumped into the pretreatment tank. The thermo-chemical pretreatments were divided into the following three ways: (1) Thermo-NaOH pretreatment: NaOH solution with a concentration of 5.0 mol/L from the chemical tank was added into the pretreatment tank to adjust the sludge pH to 12 and then the sludge was pretreated at 70 °C for 2 h; (2) Thermo-mixed alkali pretreatment: mixed alkali solution with a concentration of $Ca(OH)_2$ of 4.0 mol/L and a concentration of NaOH of 1.0 mol/L was added into the pretreatment tank to adjust the sludge pH to 12 and then the sludge was pretreated at 70 °C for 2 h; (3) Thermo-CaO_2 pretreatment: 4.0 mol/L of CaO_2 was added to the pretreatment tank at a dosage of 8% (weight/weight) of dry sludge (DS) and then the sludge was pretreated at 70 °C for 2 h. The purity of NaOH, $Ca(OH)_2$ and CaO_2 was all industrial grade.

2.3.2. WAS fermentation

The anaerobic fermentation was operated semi-continuously. The filling rate of fermentation tank was 70%, which meant the total volume of sludge was 21.0 m^3 during fermentation process. Firstly, 2.1 m^3 of seed sludge was pumped into the fermentation tank, and then 2.1 m^3 of pretreated sludge was pumped into the fermentation tank every day until the total sludge volume reached 21.0 m^3. The sludge retention time (SRT) was controlled for 10 days. 2.1 m^3 of fermented sludge was

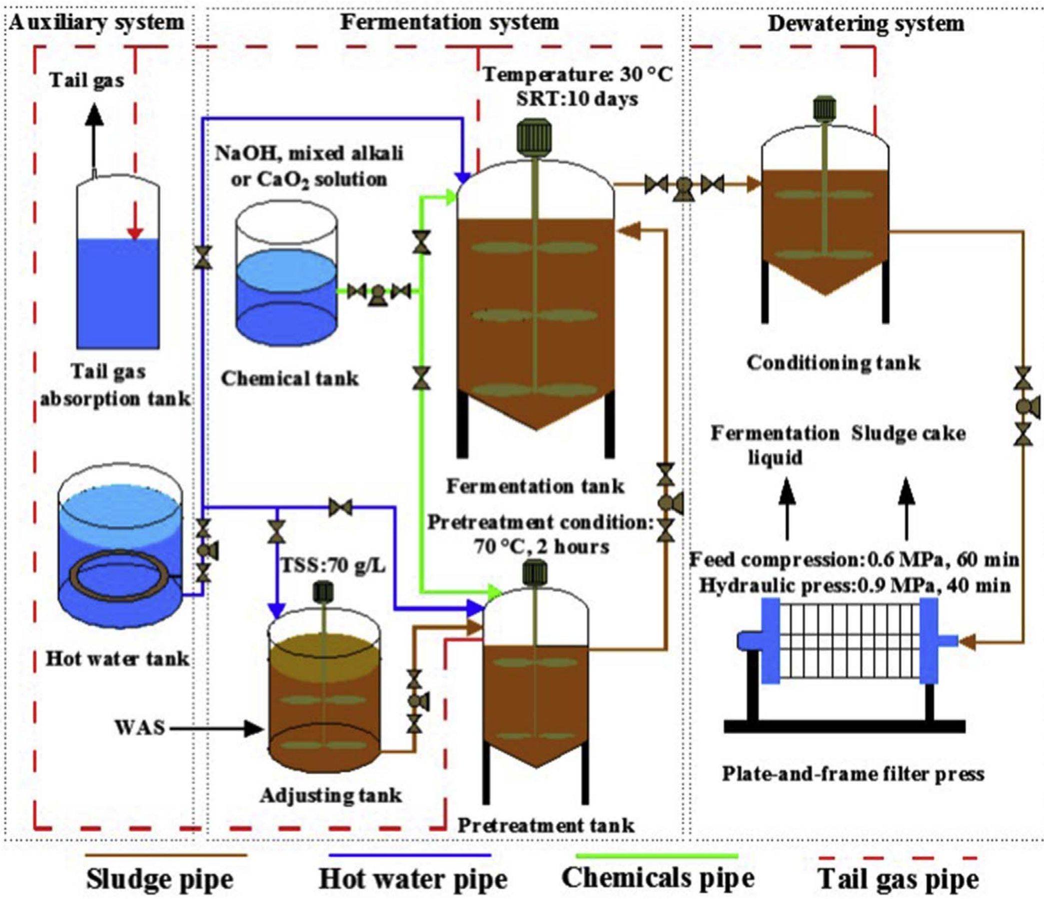

Fig. 1. The flow chart of the WAS anaerobic fermentation project.

discharged and 2.1 m^3 of pretreated sludge was fed every day. The fermentation temperature was controlled at 35 ± 2 °C and the pH was maintained at 10 ± 0.2 with the above-mentioned mixed alkali. The sludge in fermentation tank was intermittently stirred (running for 10 min and stopping for 50 min per hour) and the stirring speed was 50 rpm. Each pretreatment condition was run for 50 days, and the data in this study was taken from the last 30 days of the operation, since the operation of the project had been basically stable.

2.4. Sludge dewatering

In order to separate the VFAs-rich fermentation liquid and sludge solids, the fermented sludge was dewatered using the above-mentioned plate and frame filter press. 1.0 m^3 of fermented sludge was pumped into the condition tank. After mixing evenly, the fermented sludge was pumped into the plate and frame filter press using a pneumatic diaphragm pump with the feed pressure of 0.6 MPa and the feed time of 60 min. When the feed compression was completed, the hydraulic press was initiated with the press pressure of 0.9 MPa and the press time of 40 min. The volume of the filtrate was recorded during both feed compression and hydraulic press processes.

2.5. Analytical methods

The sludge moisture content, TSS, VSS, soluble chemical oxygen demand (SCOD) were measured according the standard methods (APHA, 1998). The pH and temperature were measured by online pH meters (PH-8251, Chengci Electronic Co., Ltd., China) and online thermometers (SBWZ, Huangong Automation Instrument Co., Ltd., China). The element content was determined using an inductively Coupled Plasma optical emission spectrometer (Optima 8300, PerkinElmer Co., Ltd., The United States). The concentrations of proteins and carbohydrates were measured using the Lowry–Folin (Lowry et al., 1951) and anthrone methods (Tapia et al., 2009), respectively. The concentrations of total nitrogen (TN), total phosphorus (TP) were measured using Chinese standard methods (SEPA, 2002). Before measuring SCOD, proteins, carbohydrates, TN, TP and NH_4^+–N concentrations, the sludge samples were centrifuged at 7000 rpm for 10 min. After that, the supernatant was filtrated through 0.45 μm filter membranes and the filtrate was collected for measurement. The EPS, including slime-EPS (S-EPS), loosely-bound EPS (LB-EPS) and tightly-bound EPS (TB-EPS), were extracted according to Yuan et al. (2017). The significance test was conducted by Statistical Program for Social Sciences (SPSS).

The VFAs concentration was measured using a gas chromatograph (GC-2010, Shimadzu Co., Ltd., Japan). The fermented sludge was centrifuged at 4 °C and 7000 rpm for 10 min. The collected supernatant was filtrated through 0.45 μm filter membranes. After that, 0.5 mL of 1 mol/L of 4-methylpentanoic acid solution and 0.5 mL of 3 mol/L of phosphoric acid was added in 0.5 mL filtrate. After mixing evenly, the mixture was centrifuged at 10000 rpm for 10 min. After centrifuging, 1 mL of the supernatant was transferred in a vial and tested using the GC. The GC test conditions: AOC-20i autosampler; FID detector; PEG-20 M capillary column; Using the first-order program to heat up, the initial column temperature was 80 °C and held for 3 min, then it was heated up to 210 °C at a rate of 15 °C/min and held for 2 min. The temperature of the injection chamber and the detector was set to 250 °C.

The fermentation liquid recovery rate (R) was calculated by equation (3):

$$R = (W_1 - W_2)/[W_1(1 - W_2)] \times 100\% \quad (3)$$

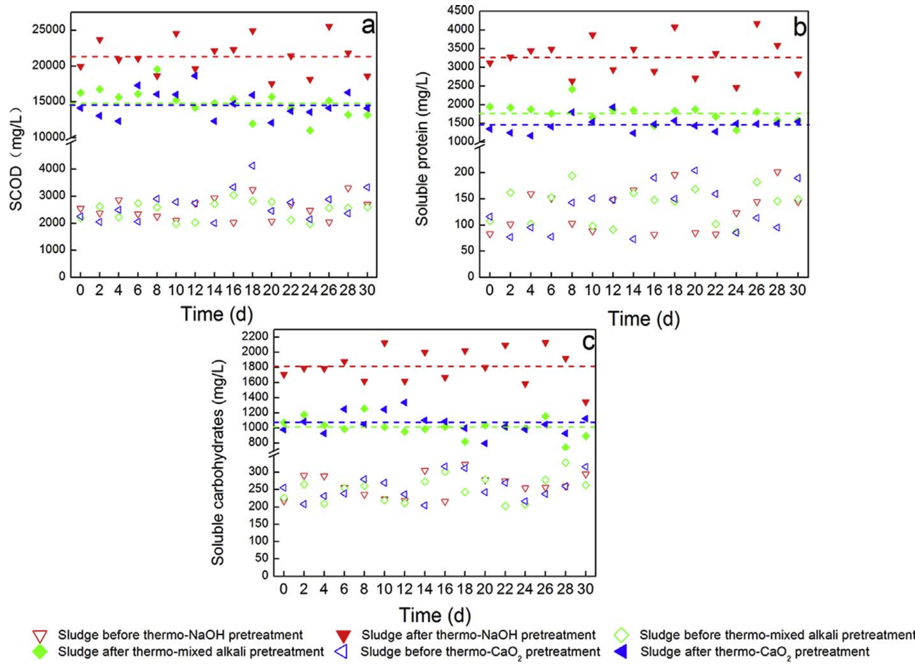

Fig. 2. Variations of SCOD (a), soluble protein (b) and soluble carbohydrates (c) before and after thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatments. The dashed lines represented the average concentration.

where W_1 was the moisture content of the fermented sludge and W_2 was the moisture content of the dewatered sludge after pressing.

The degree of COD solubilization (CS) was calculated by equation (4):

$$CS = (SCOD_a\text{-}SCOD_b)/TCOD \times 100\% \quad (4)$$

where $SCOD_a$ and $SCOD_b$ were the SCOD of the sludge after and before pretreatments. TCOD was the total COD of the sludge before pretreatments.

3. Results and discussion

3.1. Effects of pretreatments on organic matters releases

The efficiencies of pretreatments in sludge hydrolysis could be expressed by the changes of SCOD concentration (Su et al., 2013). After thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatments, the average concentrations of SCOD in sludge were 21317.52 ± 2414.33, 14911.48 ± 1947.55 and 14662.04 ± 1845.03 mg/L, respectively (Fig. 2a). The efficiency of thermo-NaOH pretreatment in sludge hydrolysis was much higher than those of thermo-mixed alkali and thermo-CaO_2 pretreatments ($P < 0.01$). The degree of COD solubilization after thermo-NaOH pretreatment in this study reached 63.82%, which was similar to or even higher than previous laboratory-scale studies (Cho et al., 2013; Xu et al., 2014). Although the efficiencies of these pretreatment methods in sludge hydrolysis were different, the concentrations of SCOD from pretreated sludge were all significantly increased compared with un-pretreated sludge (2566.42 ± 411.54 mg/L). These results proved that thermo-chemical pretreatments were equally efficient and stable in sludge solubilization under large-scale operation.

Protein and carbohydrates are main constituents of organic matters in WAS, and they are the main substrates for VFAs production (Feng et al., 2009). Similar to the variations of SCOD, the average concentrations of soluble protein and carbohydrates after thermo-NaOH pretreatment were also much higher than those after thermo-mixed alkali and thermo-CaO_2 pretreatments ($P < 0.01$) (Fig. 2b and c). The reason for this result might be that the Ca^{2+} released from $Ca(OH)_2$ and CaO_2 enhanced the re-flocculation of fragments, so the solubilized organic matters could be transformed into sludge flocs again (Li et al., 2008). Strong alkali, such as NaOH and $Ca(OH)_2$ could change cell osmotic pressure and led to saponification and hydrolysis reactions of lipids and proteins on the cell membrane, thereby promoting cell rupture and lysis of intracellular material. Moreover, the use of heat could further promote sludge hydrolysis because thermo-pretreatment could enlarge the pore size of the cell wall and cell membrane to facilitate the dissolution of intracellular substances and promote the degradation of organic macromolecules. Unlike NaOH and $Ca(OH)_2$, the mechanism of CaO_2 action relied on the release of active oxygen (H_2O_2, ·OH), which could destroy proteins, liquids and nucleic acids (Zawieja et al., 2017). Although the degree of hydrolysis increased with the pretreatment time and CaO_2 dosage (Fig. S1), the pretreatment time was set to 2 h in this study as most of the organic matters were released from sludge in the first 2 h when heat and CaO_2 were used in combination. Furthermore, the CaO_2 dosage was set to 8% of DS as CaO_2 had a high efficiency in sludge hydrolysis at this dosage. Fig. 2a–c clearly showed that as an oxidant, the efficiency of CaO_2 in sludge hydrolysis was close to that of mixed alkali. The average concentrations of SCOD and soluble carbohydrates from sludge after these two kinds of pretreatments showed no statistical differences ($P > 0.05$). The average concentration of soluble protein in sludge after thermo-mixed alkali pretreatment (1775.65 ± 239.10 mg/L) was only slightly higher than that after thermo-CaO_2 pretreatment (1467.32 ± 192.92 mg/L). Moreover, although the solubility of CaO_2 was low and the dosage was high, there was no pipeline blockage in this project, suggesting that thermo-CaO_2 pretreatment was technically feasible.

3.2. Effects of pretreatments on nitrogen and phosphorus releases

Obviously, the releases of organic matters were accompanied by the releases of nitrogen and phosphorus. As shown in Fig. 3a, the concentrations of dissolved TN in sludge were all significantly increased after thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatments, reaching 1583.92 ± 202.08,1094.78 ± 136.25 and 1028.83 ± 109.59 mg/L, respectively, which were accordance with the increase of soluble protein (Fig. 2b). As shown in Fig. 3b, unlike the variation of TN, the concentrations of TP after thermo-mixed alkali and thermo-CaO_2 pretreatments were only 83.21 ± 13.68 and 37.27 ± 5.58 mg/L, respectively, which were

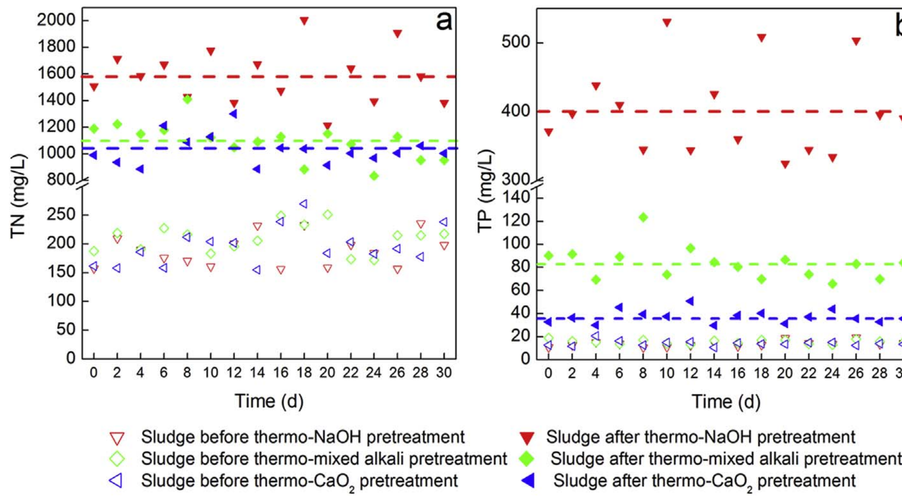

Fig. 3. Releases of nitrogen (a) and phosphorus (b) after thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatments. The dashed lines represented the average concentration.

significantly lower than that after thermo-NaOH pretreatment (401.54 ± 63.07 mg/L) ($P < 0.01$) since the Ca^{2+} from $Ca(OH)_2$ and CaO_2 reacted with PO_4^{3-} to form the precipitation of $Ca_3(PO_4)_2$ (Li et al., 2011). High concentration of TP in sludge fermentation liquid was a big burden on BNR process when the fermentation liquid was used as an additional carbon source. Therefore, the removal of TP is conducive to the use of fermentation liquid.

3.3. Effects of pretreatments on VFAs production

The production and proportion of VFAs in fermented sludge were depicted in Fig. 4. It was interesting that although the concentrations of dissolved organic matters in thermo-NaOH pretreated sludge were much higher than that in thermo-CaO_2 pretreated sludge, the concentrations of VFAs in fermented sludge by thermo-NaOH and thermo-CaO_2 pretreatments showed no significant difference ($P > 0.05$), the VFAs concentrations were 7.48 ± 0.64 and 7.91 ± 0.56 g/L, respectively. The results suggested that microbial communities might also be an important factor affecting VFAs production. In general, the phyla Firmicutes, Chloroflexi and Proteobacteria were recognized as common fermentative phyla (Regueiro et al., 2014). In addition to hydrolysis efficiency, the type of chemicals also affected microbial communities of sludge (Li et al., 2017). Li et al. (2015) found that the addition of CaO_2 increased the relative abundance of Firmicutes. Firmicutes phylum, e.g. Clostridium and Bacillus, was correlated with propionate and acetate production through propionate pathway (Huang et al., 2016a). This result might explain why the concentration of VFAs in fermented sludge

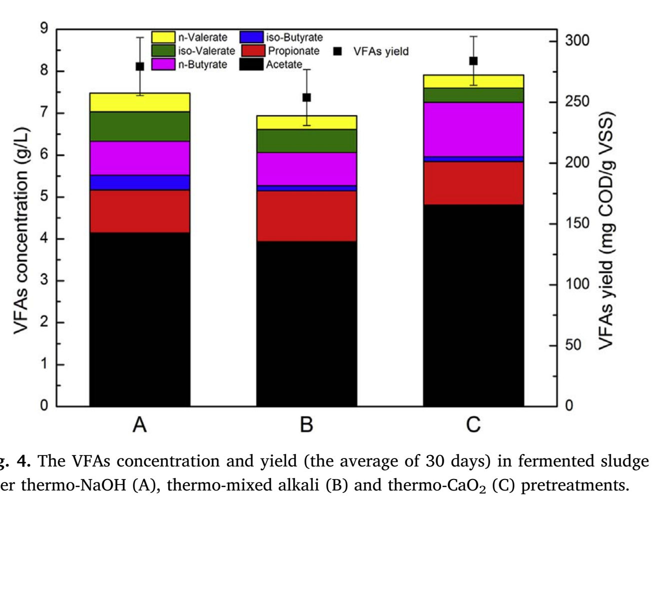

Fig. 4. The VFAs concentration and yield (the average of 30 days) in fermented sludge after thermo-NaOH (A), thermo-mixed alkali (B) and thermo-CaO_2 (C) pretreatments.

by thermo-CaO_2 pretreatment (7.91 ± 0.56 g/L) was higher than that by thermo-mixed alkali pretreatment (6.93 ± 0.63 g/L) ($P < 0.01$) although their efficiencies in sludge hydrolysis were similar. In addition, due to the slow decomposition characteristics of CaO_2 (Zhang et al., 2015), the $Ca(OH)_2$ and H_2O_2 released during the fermentation process could further promote sludge hydrolysis. The concentration of SCOD in fermented sludge by thermo-CaO_2 pretreatment (18320.96 ± 1688.90 mg/L) was higher than that by thermo-mixed alkali pretreatment (15540.72 ± 1723.42 mg/L). This result might also cause the increase of VFAs production in thermo-CaO_2 pretreated sludge. In general, methanogens were inhibited under alkaline conditions (Liu et al., 2012), while acidogenic microbes could be enriched under alkaline conditions (Ma et al., 2017). So the fermentation pH was regulated to 10 in this study to promote VFAs production. The VFAs production capacity of sludge could be directly described by VFAs yield. As could be seen in Fig. 4, the VFAs yields were 279.33, 253.82 and 283.96 mg COD/g VSS by thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatments, which were lower than some published studies (292–712 mg COD/g VSS) (Huang et al., 2015a, 2016b, 2015b; Zhou et al., 2014). In general, low sludge concentration is beneficial for increasing the VFAs yield during fermentation. Considering that the concentration of sludge in this study (TSS was about 70 g/L) was much higher than that in those published studies (TSS was 15–30 g/L), the VFAs yields in this study could be considered within the normal range.

The proportions of VFAs were different among different pretreatment conditions. In each pretreatment, acetate was the dominant VFAs due to the extensive distribution of acetate-producing bacteria and their various metabolic pathways (Ma et al., 2017). And the three most common VFAs were acetate, propionate and n-butyrate. The sum of these three VFAs in fermented sludge reached 79.94%, 85.70% and 90.31% of the total VFAs by the pretreatments of thermo-NaOH, thermo-mixed alkali and thermo-CaO_2, respectively. In addition, the proportion of acetate in fermented sludge by thermo-CaO_2 pretreatment was 60.81%, and it was higher than those by thermo-NaOH and thermo-mixed alkali pretreatment ($P < 0.01$). Since acetate is a kind of carbon source with high quality (Chen et al., 2015), high proportion of acetate is beneficial for the fermentation liquid to be used as carbon source for enhancing BNR process. The higher proportion of acetate in fermented sludge by thermo-CaO_2 pretreatment might be ascribed to the transformation of the microbial communities in the fermentation system, and the mechanism of which deserves further investigation.

3.4. Dewaterability of fermented sludge

At the beginning of this study, several flocculants were selected to

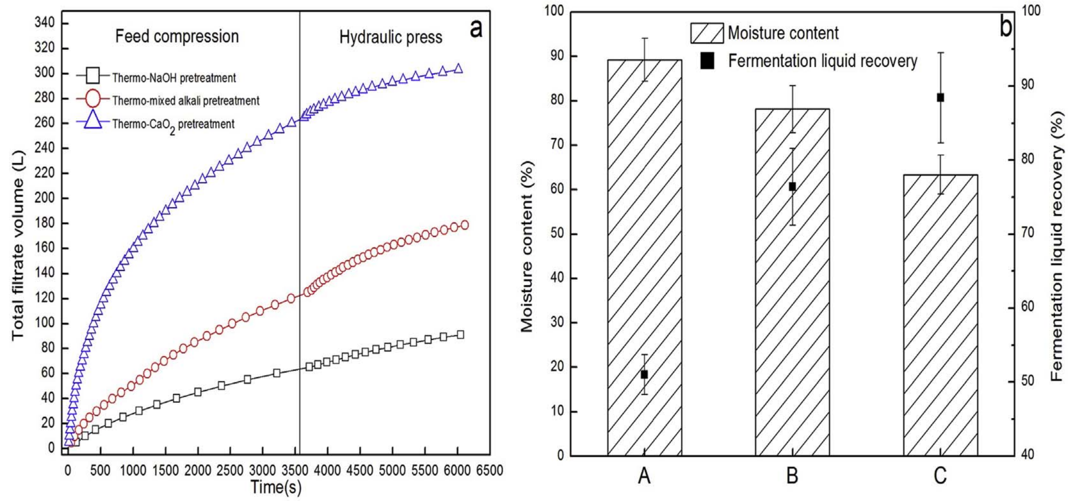

Fig. 5. The total filtrate volume (a) and dewatered sludge cake moisture content (b) of fermented sludge after thermo-NaOH (A), thermo-mixed alkali (B) and thermo-CaO_2 (C) pretreatments.

be added to the fermented sludge for sludge dewatering. However, these flocculants have no obvious effect on improving sludge dewaterability, possibly due to the high concentration of fermented sludge. In the study, the fermented sludge was dewatered directly without adding any flocculants for saving costs and reducing environmental hazards. As shown in Fig. 5a, the fermented sludge pretreated by thermo-CaO_2 and thermo-mixed alkali showed higher dewatering rates than that by thermo-NaOH, and the sludge dewatering rate by thermo-CaO_2 pretreatment was the highest ($P < 0.01$). In the whole dewatering process, the average sludge dewatering rates (as well as the filtrate volume) by thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatment were 0.90 L/min (91 L), 1.76 L/min (179 L) and 3.02 L/min (303 L), respectively. High dewatering rate could shorten the dewatering time and reduce the dewatering cost. The dewatered sludge cakes were shown in Fig. S2 and the moisture contents of sludge cakes were shown in Fig. 5b. The moisture contents of the sludge cakes were 89.2 ± 4.8%, 78.1 ± 5.3% and 63.4 ± 4.4% with the pretreatments of thermo-NaOH, thermo-mixed alkali and thermo-CaO_2, respectively, and corresponded with the fermentation liquid recoveries of 51.0 ± 2.7%, 76.4 ± 5.2% and 88.4 ± 6.1%, respectively, calculated according to formula (1). Generally, sludge dewaterability would deteriorate after pretreatment. However, after dewatering, the moisture content of fermented sludge by thermo-CaO_2 pretreatment was even lower than un-pretreated sludge (the moisture content was about 74.5% after dewatering). The low moisture content of sludge cake and high fermentation liquid recovery were beneficial to reduce the transportation and disposal costs of sludge cake, and reduce the waste of VFAs, thus increasing the economic benefits.

In order to explain the differences of sludge dewaterability under three pretreatment conditions, the concentrations of EPS and ions were measured. Firstly, as shown in Fig. S3a, the concentration of S-EPS in fermented sludge by thermo-NaOH pretreatment (50.89 mg/g TSS) was much higher than those by thermo-mixed alkali pretreatment (28.22 mg/g TSS) and thermo-CaO_2 pretreatment (30.76 mg/g TSS) due to the high efficiency of NaOH in sludge hydrolysis, thus causing deterioration of sludge dewaterability (Wang et al., 2015; Yu et al., 2010). Secondly, the high concentration of sodium ions in fermented sludge by thermo-NaOH pretreatment and the high concentration of calcium ions in fermented sludge by thermo-mixed alkali and thermo-CaO_2 pretreatment (Fig. S3b) could also explain their distinction of dewaterability of fermented sludge among three pretreatments. According to the divalent bridging model, calcium and other divalentions could bridge the negatively charged sites on EPS, thereby causing to form a matrix of EPS and single cells. But when the concentrations of monovalent ions (such as sodium) were high, the divalentions in the floc matrix would be ion exchanged by monovalent ions, (Christensen et al., 2015), thus weakening floc structure and leading to the deterioration of sludge dewaterability.

3.5. Mass balance analysis

The mass balance was calculated in the forms of VFAs and COD to further assess the system performance and efficiency under different thermo-chemical pretreatment conditions. As shown in Fig. 6 and 1107 kg/d of water was added into 993 kg/d of WAS to adjust the moisture content of the sludge to about 93.0%. So the total mass of input was 2100 kg/d (including 60.1 kg/d of TCOD). The mass of COD in liquid of pretreated sludge revealed the efficiencies of different pretreatment methods in sludge hydrolysis. After pretreatment and fermentation processes, 43.7, 30.6 and 36.2 kg/d of COD were dissolved in liquid of fermented sludge in thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatment systems, respectively. In addition, the mass of VFAs in the output was 14.8, 13.7 and 15.6 kg/d in thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatment systems, respectively. Due to differences of sludge dewaterability in different pretreatment conditions, the mass of VFAs (as well as COD) that could be recovered from fermented sludge was also different. The highest VFAs recovery was obtained in thermo-CaO_2 pretreatment system, 13.8 kg/d of VFAs were recovered from fermented sludge and only 1.8 kg/d of VFAs were left in dewatered sludge. Conversely, about half of VFAs were recovered from fermented sludge in thermo-NaOH pretreatment system, and half of VFAs left in dewatered sludge. Although the VFAs recovery by thermo-mixed alkali pretreatment was lower than that by thermo-CaO_2 pretreatment, 10.4 kg/d of VFAs could be recovered. The results of mass balance evaluation suggested that the thermo-CaO_2 pretreatment had the highest efficiency in sludge volume reduction and VFAs recovery although thermo-NaOH pretreatment had the highest efficiency in sludge hydrolysis.

3.6. Economic feasibility comparison

In order to evaluate the economic benefits of WAS anaerobic fermentation under three different pretreatment conditions, the engineering economic feasibility comparison (Project scale: was assumed to be 100 tons of dewatered sludge/day and he moisture content of the dewatered sludge was 80%.) was conducted according to the various parameters obtained from this study. As shown in Table 2, the cost differences under the three pretreatment conditions mainly resulted

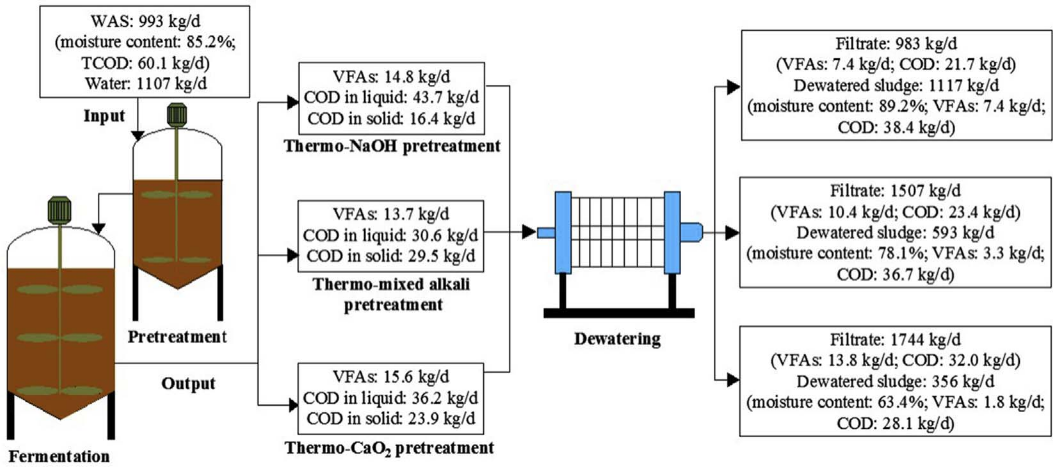

Fig. 6. Mass balance of VFAs and COD in different thermo-chemical pretreatment systems.

Table 2
Economic feasibility comparison of thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatments for WAS anaerobic fermentation to produce VFAs.

Items	Thermo-NaOH	Thermo-mixed alkali	Thermo-CaO_2
Cost of electric power (USD/ton WAS[a])	1.3	1.3	1.3
Cost of tap water (USD/ton WAS)	0.04	0.04	0.04
Cost of chemicals[b] (USD/ton WAS)	2.14	2.49	16.32
Depreciation of equipment[c] (USD/ton WAS)	12.09	12.09	12.09
Wages for workers[d] (USD/ton WAS)	0.44	0.44	0.44
Income of VFAs[e] (USD/ton WAS)	9.39	12.95	17.05
Income of sludge reduction[f] (USD/ton WAS)	−21.24	8.44	22.42
Policy subsidy (USD/ton WAS)	29.41	29.41	29.41
Net profit (USD/ton WAS)	1.55	34.44	38.69

[a] The WAS here represents dewatered sludge with a moisture content of 80%.
[b] The dosage of NaOH in thermo-NaOH pretreatment was 4.86 kg/ton WAS. The dosage of NaOH was 1.6 kg/ton WAS and the dosage of $Ca(OH)_2$ was 11.9 kg/ton WAS in thermo-mixed alkali pretreatment. The dosage of CaO_2 in thermo-CaO_2 pretreatment was 16.0 kg/ton WAS.
[c] The cost of equipment was 4411765 USD and the service life of the equipment was 10 years.
[d] The project required three workers, each with a monthly salary of 441USD.
[e] The price of VFAs was 912 USD/ton and the total weight of VFAs was calculated by the fermentation liquid recovery and VFAs concentration.
[f] The disposal fee for dewatered sludge was 44 USD/ton.

from the different costs of chemicals. The cost of the thermo-CaO_2 pretreatment was the highest (16.32 USD/ton). The result was caused by two reasons. On the one hand, the price of CaO_2 was relatively high (1020.0 USD/ton) while the prices of NaOH and $Ca(OH)_2$ was as low as 440 and 150 USD/ton, respectively. On the other hand, since the addition amount of CaO_2 in this project was 8% DS, the consumption of chemicals was higher than those of the thermo-NaOH and the thermo-mixed alkali pretreatments.

The differences in incomes under the three pretreatment conditions were mainly reflected in the benefits of VFAs and the reduction of sludge. It could be seen that the VFAs income by thermo-CaO_2 pretreatment was the highest, reaching 17.05 USD/ton. This was due to its high VFAs production and fermentation liquid recovery. Furthermore, since thermo-CaO_2 pretreatment had the highest efficiency in enhancing sludge dewaterability, the daily sludge cake yield was only 49.2 tons and the moisture content was only 63.4%, which greatly reduced the follow-up transportation and disposal costs, so the sludge reduction income reached 22.42 USD/ton. In addition, the daily sludge cake yield reached 148.1 tons after filter pressing when sludge was pretreated by thermo-NaOH. Compared with the initial sludge volume, the total sludge volume even increased, and the subsequent disposal would be very difficult. So the sludge reduction income was negative (−21.24 USD/ton). Therefore, taking the various costs and incomes of WAS fermentation into account, the net profits of thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatments were 1.55, 34.44 and 38.69 USD/ton, respectively. It could be seen that the thermo-mixed alkali and thermo-CaO_2 pretreatments could achieve higher profits than thermo-NaOH pretreatment, which made them economically feasible in wide application. Although the cost of thermo-CaO_2 pretreatment was higher, the net profit was still higher than that of the thermo-mixed alkali pretreatment due to its advantages in VFAs production and sludge reduction.

It could be seen that although NaOH were used in many studies due to its low cost and high efficiency in sludge hydrolysis. Most of these studies did not pay enough attention to the deterioration of sludge dewaterability when NaOH was added. This study showed that sludge pretreated with thermo-NaOH was almost unable to obtain solid sludge cake after dewatering, which limited the recovery of fermentation liquid and increased the cost of subsequent sludge disposal unless there was an effective technique for promoting sludge dewatering.

4. Conclusions

Thermo-NaOH, thermo-mixed alkali and thermo-CaO_2 pretreatments could significantly promote sludge hydrolysis, and thermo-NaOH pretreatment had the highest efficiency. The sludge pretreated with thermo-NaOH and thermo-CaO_2 showed better VFAs production capacity than the sludge pretreated with thermo-mixed alkali, reaching 7.48 ± 0.64 and 7.91 ± 0.56 g/L respectively. Compared with thermo-mixed alkali and thermo-CaO_2 pretreatment, the dewaterability of fermented sludge by thermo-NaOH pretreatment was significantly deteriorated, which limited the recovery of fermentation liquid. The fermented sludge by thermo-CaO_2 pretreatment obtained the best dewaterability and the moisture content of the dewatered sludge cake was

63.4 ± 4.4%. Engineering economic feasibility comparison showed that thermo-mixed alkali and thermo-CaO_2 pretreatments were economically feasible pretreatment methods for WAS anaerobic fermentation.

Conflicts of interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, "Evaluation of volatile fatty acids production and dewaterability of waste activated sludge with different thermo-chemical pretreatments".

Acknowledgements

This research was financially supported by the National Natural Science Foundation of China (51678280), the National Key Technology R&D Program of the Ministry of Science and Technology (2014BAD24B03-02), the Fundamental Research Funds for the Central Universities (JUSRP51633B) and the Postgraduate Research & Practice Innovation Program of Jiangsu Province (SJCX17-0499). The authors stated that the manuscript had no conflict of interest to declare.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ibiod.2018.02.008.

References

Abudi, Z.N., Hu, Z., Xiao, B., Abood, A.R., Rajaa, N., Laghari, M., 2016. Effects of pretreatments on thickened waste activated sludge and rice straw co-digestion: experimental and modeling study. J. Environ. Manag. 177, 213–222.
Ahmadi-Pirlou, M., Ebrahimi-Nik, M., Khojastehpour, M., Ebrahimi, S.H., 2017. Mesophilic co-digestion of municipal solid waste and sewage sludge: effect of mixing ratio, total solids, and alkaline pretreatment. Int. Biodeterior. Biodegrad. 125, 97–104.
APHA, 1998. twentieth ed. Standard Methods for the Examination of Water and Wastewater American Public Health Assosiation, Washington, DC.
Arun, C., Palani, S., 2015. Solubilization of waste activated sludge using a garbage enzyme produced from different pre-consumer organic waste. RSC Adv. 5, 51421–51427.
Chen, H.B., Wang, D.B., Li, X.M., Yang, Q., Zeng, G.M., 2015. Enhancement of post-anoxic denitrification for biological nutrient removal: effect of different carbon sources. Environ. Sci. Pollut. Res. 22, 5887–5894.
Chen, Z., Zhang, W., Wang, D., Ma, T., Bai, R., Yu, D., 2016. Enhancement of waste activated sludge dewaterability using calcium peroxide pre-oxidation and chemical re-flocculation. Water Res. 103, 170–181.
Cho, H.U., Park, S.K., Ha, J.H., Park, J.M., 2013. An innovative sewage sludge reduction by using a combined mesophilic anaerobic and thermophilic aerobic process with thermal-alkaline treatment and sludge recirculation. J. Environ. Manag. 129, 274–282.
Choi, J.D., Chang, H.N., Han, J.I., 2011. Performance of microbial fuel cell with volatile fatty acids from food wastes. Biotechnol. Lett. 33, 705–714.
Christensen, M.L., Keiding, K., Nielsen, P.H., Jorgensen, M.K., 2015. Dewatering in biological wastewater treatment: a review. Water Res. 82, 14–24.
Elefsiniotis, P., Wareham, D.G., Smith, M.O., 2004. Use of volatile fatty acids from an acid-phase digester for denitrification. J. Biotechnol. 114, 289–297.
Feng, L., Chen, Y., Zheng, X., 2009. Enhancement of waste activated sludge protein conversion and volatile fatty acids accumulation during waste activated sludge anaerobic fermentation by carbohydrate substrate addition: the effect of pH. Environ. Sci. Technol. 43, 4373–4380.
Gao, F., Xia, Z., Wang, W., 2017. Enhancing anaerobic biodegradability and dewaterability of sewage sludge by microwave irradiation. Int. J. Agric. Biol. Eng. 10, 224–232.
Guo, H., Zhang, S., Du, L., Liang, J., Zhi, S., Yu, J., Lu, X., Zhang, K., 2015. Effects of thermal-alkaline pretreatment on solubilisation and high-solid anaerobic digestion of dewatered activated sludge. Bioresources 11, 1280–1295.
Huang, C., Liu, C., Sun, X., Sun, Y., Li, R., Li, J., Shen, J., Han, W., Liu, X., Wang, L., 2015a. Hydrolysis and volatile fatty acids accumulation of waste activated sludge enhanced by the combined use of nitrite and alkaline pH. Environ. Sci. Pollut. Res. 22, 18793–18800.
Huang, X., Shen, C., Liu, J., Lu, L., 2015b. Improved volatile fatty acid production during waste activated sludge anaerobic fermentation by different bio-surfactants. Chem. Eng. J. 264, 280–290.
Huang, C., Lai, J., Sun, X., Li, J., Shen, J., Han, W., Wang, L., 2016a. Enhancing anaerobic digestion of waste activated sludge by the combined use of NaOH and Mg(OH)2: performance evaluation and mechanism study. Bioresour. Technol. 220, 601–608.
Huang, X., Mu, T., Shen, C., Lu, L., Liu, J., 2016b. Effects of bio-surfactants combined with alkaline conditions on volatile fatty acid production and microbial community in the anaerobic fermentation of waste activated sludge. Int. Biodeterior. Biodegrad. 114, 24–30.
Jin, B., Wang, S., Xing, L., Li, B., Peng, Y., 2016. Long term effect of alkali types on waste activated sludge hydrolytic acidification and microbial community at low temperature. Bioresour. Technol. 200, 587–597.
Li, H., Jin, Y., Mahar, R., Wang, Z., Nie, Y., 2008. Effects and model of alkaline waste activated sludge treatment. Bioresour. Technol. 99, 5140–5144.
Li, X., Chen, H., Hu, L., Yu, L., Chen, Y., Gu, G., 2011. Pilot-scale waste activated sludge alkaline fermentation, fermentation liquid separation, and application of fermentation liquid to improve biological nutrient removal. Environ. Sci. Technol. 45, 1834–1839.
Li, Y., Wang, J., Zhang, A., Wang, L., 2015. Enhancing the quantity and quality of short-chain fatty acids production from waste activated sludge using CaO_2 as an additive. Water Res. 83, 84–93.
Li, G., Zhang, P., Wang, Y., Sheng, Y., Lv, X., Yin, J., 2016. Enhancing biological denitrification with adding sludge liquor of hydrolytic acidification pretreated by high-pressure homogenization. Int. Biodeterior. Biodegrad. 113, 222–227.
Li, X., Peng, Y., Li, B., Wu, C., Zhang, L., Zhao, Y., 2017. Effects of alkali types on waste activated sludge (WAS) fermentation and microbial communities. Chemosphere 186, 864–872.
Li, L., He, J., Xin, X., Wang, M., Xu, J., Zhang, J., 2018. Enhanced bioproduction of short-chain fatty acids from waste activated sludge by potassium ferrate pretreatment. Chem. Eng. J. 332, 456–463.
Liao, X., Li, H., Zhang, Y., Liu, C., Chen, Q., 2016. Accelerated high-solids anaerobic digestion of sewage sludge using low-temperature thermal pretreatment. Int.Biodeterior. Biodegrad. 106, 141–149.
Liu, H., Wang, J., Liu, X., Fu, B., Chen, J., Yu, H.Q., 2012. Acidogenic fermentation of proteinaceous sewage sludge: effect of pH. Water Res. 46, 799–807.
Liu, Y., Li, X., Kang, X., Yuan, Y., Jiao, M., Zhan, J., Du, M., 2015. Effect of extracellular polymeric substances disintegration by ultrasonic pretreatment on waste activated sludge acidification. Int. Biodeterior. Biodegrad. 102, 131–136.
Lowry, O.H., Rosebrough, N.J., Farr, A.L., Randall, R.J., 1951. Protein measurement with the Folin phenol reagent. J. Biol. Chem. 193, 265–275.
Ma, H., Chen, X., Liu, H., Liu, H., Fu, B., 2016. Improved volatile fatty acids anaerobic production from waste activated sludge by pH regulation: alkaline or neutral pH? Waste Manag. 48, 397–403.
Ma, H., Liu, H., Zhang, L., Yang, M., Fu, B., Liu, H., 2017. Novel insight into the relationship between organic substrate composition and volatile fatty acids distribution in acidogenic co-fermentation. Biotechnol. Biofuels 10, 137.
Mengmeng, C., Hong, C., Qingliang, Z., Shirley, S.N., Jie, R., 2009. Optimal production of polyhydroxyalkanoates (PHA) in activated sludge fed by volatile fatty acids (VFAs) generated from alkaline excess sludge fermentation. Bioresour. Technol. 100, 1399–1405.
Park, W., Hyun, S.H., Oh, S.E., Logan, B.E., Kim, I.S., 2005. Removal of headspace CO_2 increases biological hydrogen production. Environ. Sci. Technol. 39, 4416–4420.
Pilli, S.T.T., More, S.Y., Tyagi, R.D., Surampalli, R.Y., 2016. Fenton pre-treatment of secondary sludge to enhance anaerobic digestion: energy balance and greenhouse gas emissions. Chem. Eng. J. 283, 285–292.
Regueiro, L., Veiga, P., Figueroa, M., Lema, J.M., Carballa, M., 2014. Influence of transitional states on the microbial ecology of anaerobic digesters treating solid wastes. Appl. Microbiol. Biotechnol. 98, 2015–2027.
SEPA, 2002. fourth ed. Water and Wastewater Monitoring Methods Chinese Environmental Science Publishing House, Beijing.
Su, G., Huo, M., Yuan, Z., Wang, S., Peng, Y., 2013. Hydrolysis, acidification and dewaterability of waste activated sludge under alkaline conditions: combined effects of NaOH and $Ca(OH)_2$. Bioresour. Technol. 136, 237–243.
Sun, J., Guo, L., Li, Q., Zhao, Y., Gao, M., She, Z., Wang, G., 2016. Structural and functional properties of organic matters in extracellular polymeric substances (EPS) and dissolved organic matters (DOM) after heat pretreatment with waste sludge. Bioresour. Technol. 219, 614–623.
Tan, R., Miyanaga, K., Uy, D., Tanji, Y., 2012. Effect of heat-alkaline treatment as a pretreatment method on volatile fatty acid production and protein degradation in excess sludge, pure proteins and pure cultures. Bioresour. Technol. 118, 390–398.
Tapia, J.M., Munoz, J.A., Gonzalez, F., Blazquez, M.L., Malki, M., Ballester, A., 2009. Extraction of extracellular polymeric substances from the acidophilic bacterium Acidiphilium 3.2Sup(5). Water Sci. Technol. 59, 1959–1967.
Wang, Z., Zheng, G., Zhou, L., 2015. Degradation of slime extracellular polymeric substances and inhibited sludge flocs destruction contribute to sludge dewaterability enhancement during fungal treatment of sludge using filamentous fungus Mucor sp. GY-1. Bioresour. Technol. 192, 514–521.
Xin, X., He, J., Qiu, W., 2017. Performance and microbial community evolutions in anaerobic fermentation process of waste activated sludge affected by solids retention time. Water Air Soil Pollut. 228, 194.
Xu, J., Yuan, H., Lin, J., Yuan, W., 2014. Evaluation of thermal, thermal-alkaline, alkaline and electrochemical pretreatments on sludge to enhance anaerobic biogas production. J. Taiwan Inst. Chem. E 45, 2531–2536.
Yin, Y., Liu, Y., Meng, S., Kiran, E.U., Liu, Y., 2016. Enzymatic pretreatment of activated sludge, food waste and their mixture for enhanced bioenergy recovery and waste

volume reduction via anaerobic digestion. Appl. Energy 179, 1131–1137.
Yu, G.H., He, P.J., Shao, L.M., 2010. Novel insights into sludge dewaterability by fluorescence excitation-emission matrix combined with parallel factor analysis. Water Res. 44, 797–806.
Yuan, D., Wang, Y., Qian, X., 2017. Variations of internal structure and moisture distribution in activated sludge with stratified extracellular polymeric substances extraction. Int. Biodeterior. Biodegrad. 116, 1–9.
Zawieja, I., Lidia, W., Marta, P., 2017. Impact of the excess sludge modification with selected chemical reagents on the increase of dissolved organic substances concentration compounds transformations in activated sludge. Environ. Res. 156, 652–656.
Zhang, X., Gu, X., Lu, S., Miao, Z., Xu, M., Fu, X., Qiu, Z., Sui, Q., 2015. Degradation of trichloroethylene in aqueous solution by calcium peroxide activated with ferrous ion. J. Hazard Mater. 284, 253–260.
Zhou, A., Du, J., Varrone, C., Wang, Y., Wang, A., Liu, W., 2014. VFAs bioproduction from waste activated sludge by coupling pretreatments with Agaricus bisporus substrates conditioning. Process Biochem. 49, 283–289.
Zhu, Y.F., Liu, H.B., Liu, H., Huang, S., Ma, H.J., Tian, Y., 2015. Filtration characteristics of anaerobic fermented sewage sludge for fatty acids production. Sep. Purif. Technol 142, 8–13.