Full-scale production of VFAs from sewage sludge by anaerobic alkaline fermentation to improve biological nutrients removal in domestic wastewater

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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

A full-scale project of thermal-alkaline pretreatment and alkaline fermentation of sewage sludge was built to produce volatile fatty acids (VFAs) which was then used as external carbon source for improving biological nitrogen and phosphorus removals (BNPR) in wastewater plant. Results showed this project had efficient and stable performances in VFA production, sludge reduce and BNPR. Hydrolysis rate in pretreatment, VFAs yield in fermentation and total VS reduction reached 68.7%, 261.32 mg COD/g VSS and 54.19%, respectively. Moreover, fermentation liquid with VFA presented similar efficiency as acetic acid in enhancing BNPR, obtaining removal efficiencies of nitrogen and phosphorus up to 72.39% and 89.65%, respectively. Finally, the project also presented greater economic advantage than traditional processes, and the net profits for VFAs and biogas productions are 9.12 and 3.71 USD/m^3 sludge, respectively. Long-term operation indicated that anaerobic alkaline fermentation for VFAs production is technically and economically feasible for sludge carbon recovery.

1. Introduction

Volume and mass of waste activated sludge generated in wastewater treatment plants (WWTPs) are expected to increase continuously in the next decades, due to the increasing population connected to sewage networks, the building of new WWTPs and the upgrading of existing plants to fulfill the more stringent local effluent regulations. In China, the annual production of sewage sludge (80% moisture content) has reached almost 4000 million tons, and 80% of it has not obtained necessary stabilization (Duan et al., 2012). Thus, it is essential to find out a technically and economically feasible way to treat the large amount of sludge.

Volatile fatty acids (VFAs) have a wide range of applications, such as in the production of bio-energy (Sawatdeenarunat et al., 2017; Jin et al., 2017; Huang et al., 2016) and the biological removal of nutrients from wastewater as carbon source (Zheng and Chen, 2010; Liu et al., 2016). At present, commercial production of VFAs is mostly accomplished by chemical routes (Chen et al., 2017). However, the use of non-renewable petrochemicals as the raw materials has renewed the interest in biological routes of VFAs production by utilizing organic-rich wastes, such as sludge generated from wastewater treatment plant, food waste, organic fraction of municipal solid waste and industrial wastewater (Kuruti et al., 2017). Such transformation of wastes into VFAs also provides an alternative route to reduce the ever increasing amount of waste (Zhou et al., 2014). A lot of laboratory studies have demonstrated that the fermentative production of VFAs from sewage sludge is feasible and can be significantly improved under alkaline conditions of pH 10 controlled by NaOH (Li et al., 2014; Kurahashi et al., 2017; Liu et al., 2012), and the feasibility of the alkaline fermentation liquid as the carbon source for enhanced biological phosphorus removal has also been verified in the laboratory anaerobic-aerobic sequencing batch reactor (Liu et al., 2016; Tong and Chen, 2009; Li et al., 2011). Li et al. (2011) reported the pilot-scale waste activated sludge alkaline fermentation, fermentation liquid separation and application to improve biological nutrient removal. The study demonstrated the feasibility of the alkaline fermentation liquid as the carbon source of enhanced biological phosphorus removal microbes in pilot scale experiment. Gao et al. (2011) investigated the biological sludge reduction and enhanced nutrient removal in a pilot-scale system with 2-step sludge alkaline fermentation and A^2/O process, and verified that alkaline pH could significantly improve the VFAs yield during the anaerobic hydrolysis and acidification. However, as far as it was known, no papers have been published so far describing full-scale operation of VFAs production and their application for biological nutrients removal process in WWTPs. The economic feasibility is still uncertain of the VFAs production by anaerobic alkaline fermentation of sewage sludge. In addition, except from the laboratory scale of VFAs production, these studies were conducted with the low concentration of solid (TSS < 3%) content, resulting in the large volume of the anaerobic fermenter and the high operation cost, including the energy and land requirement, etc.

In this study, the full-scale VFAs production from alkaline anaerobic fermentation of high-solid waste activated sludge, separation of fermentation liquid from the sludge fermentor and subsequent application of fermentation liquid to improve municipal biological nitrogen and phosphorus removal were investigated. The objectives of the present study were to develop a novel process in full-scale and to provide detailed descriptions of the process, energy consumption and design considerations for VFAs fermentative production and the application for biological nutrient removal in WWTPs.

2. Materials and methods

2.1. Outline of the full-scale sludge fermentation engineering

The full-scale work included the following four parts as shown in Fig. 1, sludge pretreatment system, sludge alkaline fermentation system, fermentation liquid separation system, and municipal wastewater treatment with an anaerobic-anoxic-aerobic (A^2/O) process enhanced by fermentation liquid addition. The sludge fermentation was operated semi-continuously, the sludge pretreatment and the separation of fermentation liquid were operated in batch, but the fermentation liquid was fed into the A^2/O process continuously.

A certain volume of fresh sludge was daily pumped from the thickener to the tank for sludge concentration adjustment ($1.6\,m^3$) (TK1), in which the TSS is adjusted to about 7.0%. Then, the sludge was pumped into the thermal-alkaline pretreatment tank ($1.9\,m^3$) (TK2), which was operated under 70 °C, pH-12 and 2 h for sludge pretreatment. The sludge alkaline fermentation reactor ($30\,m^3$) (TK3) was

mechanically stirred at 48 rpm and controlled temperature at 35 °C by water bath jacket. The separation system was composed of two cylinder tanks and a sludge dewatering machine. One tank was used for receiving the sludge-fermentation mixture (TK4) and another for storing the fermentation liquid (TK5), respectively. Sludge dewatering was conducted by the frame filter press with pressure of 0.6 Mpa.

2.2. Sewage sludge and seeding sludge

The full-scale study was conducted in a municipal wastewater treatment plant in Wuxi city of China. This WWTP was operated with an anaerobic anoxic-aerobic (A^2/O) process. The activated sludge from the WWTP was used as the seeding sludge of the anaerobic fermenter for VFAs production. The sewage sludge used in the anaerobic alkaline fermentation was dewatered sludge with solid concentration of 70 g/L (93% water content).

A tank with the working volume about $1.9\,m^3$ (the same as TK2) was applied to accumulate and acclimate acidogenic microorganisms. The process of the acclimation and re-reactivation of seeding sludge were followed as the previous literature (Wang et al., 2013). When the pH of effluent was stable at 4.5, it means the completion of domestication. The characteristics of dewatered sewage sludge (used for the anaerobic fermentation) and the seeding sludge were shown in Table 1. All measurements were conducted in triplicate with average and standard deviation reported.

2.3. The operation of the anaerobic fermentor

The operation of fermentation was divided into three stages in which the first stage (1–6 d) was for sludge canning, the second stage (7–15 d) was for inoculation and start-up, the third one (16–102 d) was semi-continuous operation stage. In the first stage, about $12.0\,m^3$ heat-alkaline pretreated sludge was obtained by 6 days operation of the TK2 and was pumped into TK3 in batches, while in the second stage, $1.5\,m^3$ seeding sludge and $7.5\,m^3$ heat-alkaline pretreated sludge were pumped into TK3 in batches by 4 days. In the third stage, every day, $1.5\,m^3/d$ fermented sludge was discharged out from TK3 and then $1.5\,m^3/d$ fresh pretreated sludge was pumped into it from TK2. The organic loading rate (OLR) of the fermenter was about 3.0 kg VS/m^3.d. The sludge was fermented at pH 10–11 with a sludge retention time of 14 d. The NaOH (400 g/L) was used to control the fermentation pH at 10–11.

The A^2/O process consisted of an anaerobic tank, an anoxic tank, an aerobic tank, and a sedimentation tank. Acetic acids and fermentation liquids were added to the A^2/O at the second and third stages, respectively. Detailed operating parameters in different operational stages were shown in Table 2.

2.4. Analytical methods

The concentration of total suspended solid (TSS), volatile suspended solid (VSS), soluble chemical oxygen demand (SCOD) and pH were conducted according to Standard Methods (APHA, 1998). The concentrations of proteins and polysaccharides were measured using the Lowry–Folin (Lowry et al., 1951) and phenol–sulfuric method (Dubois et al., 1956), respectively. To measure SCOD, soluble protein and soluble polysaccharides, the samples were first centrifuged at 10,000 rpm for 10 min, and then were filtered with 0.45 μm syringe filters. All the filtered samples were measured immediately after collection.

The VFAs concentration in the filtrate samples was detected by a gas chromatograph (GC-2010, Japan), equipped with a flame ionization detector (FID) and a fused-silica capillary column (PEG-20 M, 30 m × 0.32 mm × 0.5 lm, China). The column temperature was maintained at 80 °C initially. While, the highest temperature was 210 °C, and then was held for 2 min. Both the injection port and detector temperatures were 250 °C. Before GC measurement, 4-methylvaleric acid (acted as internal standard), 3 M phosphoric acid (acidifier)
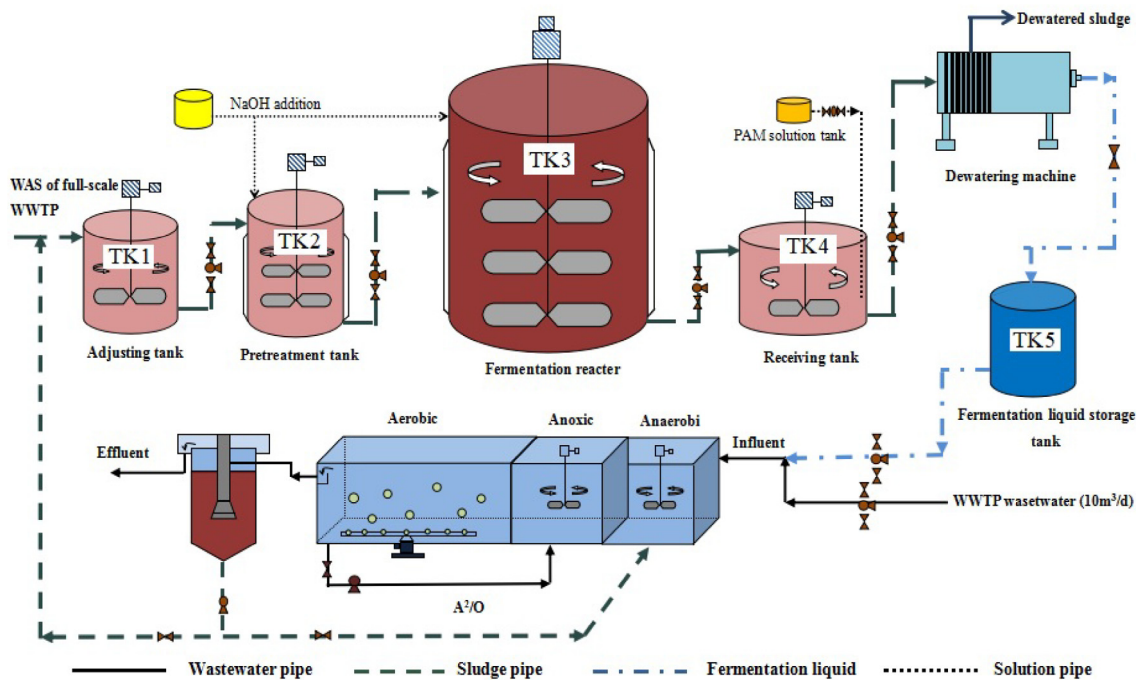
Fig. 1. Outline of the full-scale work for the sludge anaerobic fermentation.

and filtrate sample should be mixed according to the proportion of 1:1:1 (v:v:v). In order to make sure if there was methane produced during the sludge fermentation process, the product spectrum in the headspace, which concluded hydrogen, carbon dioxide and methane, was analyzed by gas chromatography (GC-2010, Japan) outfitted with thermal conductivity detector (TCD) using a stainless steel column.

2.5. Equations

The hydrolysis yield and total VFAs yield of sludge can be calculated according to the following Eqs. (1) and (2):

$$\text{Hydrolysis yield} = \frac{SCOD_{eff} - SCOD_{in}}{TCOD} \times 100\% \tag{1}$$

$$\text{VFAs yield} = \frac{VFA_{eff} - VFA_{in}}{VSS} \tag{2}$$

where $SCOD_{in}$ is the concentration of SCOD in the influent (mg/L), $SCOD_{eff}$ is the concentration of SCOD in the effluent (mg/L), VFA_{eff} is the concentration of VFAs in the fermented sludge, VFA_{in} is the concentration of VFAs in the pretreated sludge.

Table 1
Characteristics of the seeding sludge and dewatered sewage sludge.

Parameters	Seeding sludge	Dewatered sewage sludge
pH	4.5 ± 0.31	6.71 ± 0.20
TSS (%, w/w)	5.24 ± 0.21	7.07 ± 0.33
VSS/TSS (%, w/w)	68.96% ± 2.4	41.18 ± 1.7
SCOD (mg/L)	28430.81 ± 325.21	3082.11 ± 415.42
Soluble Proteins (mg/L)	124.67 ± 21.6	151.82 ± 73.91
Soluble Carbohydrates (mg/L)	1966.34 ± 59.21	407.24 ± 113.51
TN (mg/L)	1322.54 ± 76.25	142.34 ± 47.82
TP (mg/L)	26.89 ± 5.31	21.72 ± 10.81
TAN (mg/L)	1961.91 ± 84.26	117.52 ± 24.18
TCOD (mg/L)	–	40361.54 ± 3124.23

Table 2
Operating parameters in different operational stage.

Stage	Stage I	Stage II	Stage III
Influent flow (L/d)	10000	5000	7500
MLSS (g/L)	3.92–5.91	4.79–5.07	4.4–5.1
Sludge recycle ratio (%)	100	100	100
Nitrification liquid reflux ratio (%)	200	200	200
HRT (h)	11.2	22.4	14.9
SRT (d)	21	21	21
DO aerobic tank (mg/L)	1.5–3	1.5–3	1.5–3
Temperature (°C)	14–27	17–28	19–25
COD increment (mg/L)	0	50	50
TN increment (mg/L)	0	0	0.96
TP increment (mg/L)	0	0	0.03
Operation time (d)	20	30	52

3. Results

3.1. Performance of the heat-alkaline pretreatment of sewage sludge

Full-scale heat-alkaline pretreatment was confirmed to be reliable for releasing sludge organics into the liquid and providing enough bioavailable substrates for the subsequent acidogenic fermentation. Fig. 2 showed the variations of SCOD, hydrolysis yield, protein and carbohydrates concentrations measured in the heat-alkaline pretreatment tank. As shown in Fig. 2A, a stable hydrolysis reaction was achieved quickly. The average SCOD was below 5000 mg/L before pretreatment, but after the pretreatment, the average concentration of SCOD was about 32800 mg/L, 8.2 times of the initial concentration. The average hydrolysis yields reached as high as 68.7%.

As the main substrates for acidogenic microorganisms, proteins and polysaccharides concentrations were both significantly increased after heat-alkaline pretreatment. As shown in Fig. 2B, the average

concentrations of soluble proteins and polysaccharides were 3893 mg/L and 2471 mg/L, respectively, which indicated that heat-alkaline pretreatment could increase the hydrolysis yield significantly. In addition, the hydrolysis yields and the concentrations of proteins and polysaccharides fluctuated regularly around the average values, indicating the full-scale hydrolysis process could run stably.

3.2. Performance of the VFAs production during fermentation

The long-term performance of the full-scale fermentor for VFAs production was investigated by measuring the VFAs concentrations every two days during the start-up and semi-continuous operation. As shown in Fig. 3, this full-scale system presents high efficiency in VFAs production and good operation stability. The highest value was 376.48 mg COD/g VSS in the 50 days. The average VFAs yield was 261.32 mg COD/g VSS.

Moreover, results indicate alkaline fermentation for VFAs production is feasible for full-scale operation. In this test, pH was adjusted around 10.0–11.0 to prevent methane generation from VFAs. Once pH was above 8.0 (Appels et al., 2008) or below 6.0 (Steinbusch et al., 2009), the growth of methanogens would be inhibited. Adding methanogenic inhibitor and shortening the reaction time could also be used to inhibit methanogens and promote VFAs production (Liu et al., 2012). Thus, for full-scale operation, the former has very high cost and the latter has poor stability.

Furthermore, this full-scale fermentor also realized selective production of acetic acid. As shown in Fig. 3A, there was an obvious difference among the three stages in acidogenic fermentation. The concentration of total VFAs was relatively low during the sludge canning stage, but it sharply increased after inoculation of seed sludge and became stable in the next two stages. The average concentrations of total VFAs were 3.36, 5.42 and 7.53 g/L in three stages, respectively. Despite the total VFAs concentration showed some fluctuations during the stable operation time, it still kept at a high level. Moreover, the total VFAs concentration remained stable after 60 days. The acetic acid was always the main acid product, accounting for 32.21%, 44.63% and 57.69% of the average total VFAs in three stages, respectively. But the propionic acid was relatively low, only accounting for 11.71%, 8.42% and 7.54% of the total VFAs, respectively. The concentration of other acids accounted 56.08%, 46.95% and 34.77% of the total VFAs, respectively. Isobutyrate and isovalerate fluctuated after inoculation, but propionic acid, butyric acid and valerate changed very slightly.

3.3. Reduction of sewage sludge

In this full-scale system, the reduction rate of VSS in sludge reaches as high as 54.19%, which is higher than the traditional sludge
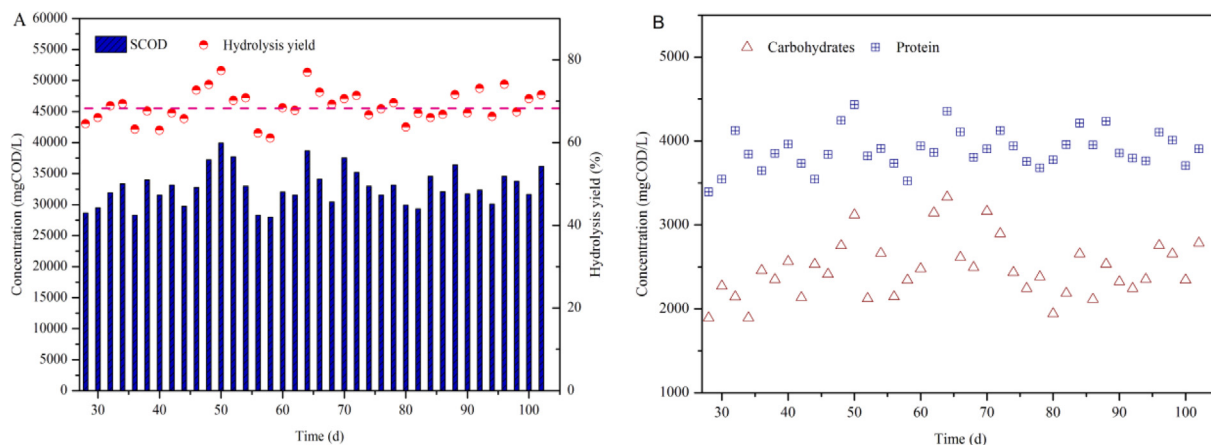

Fig. 2. (A) SCOD production and hydrolysis yield, (B) concentrations of protein and polysaccharides after heat-alkaline pretreatment.
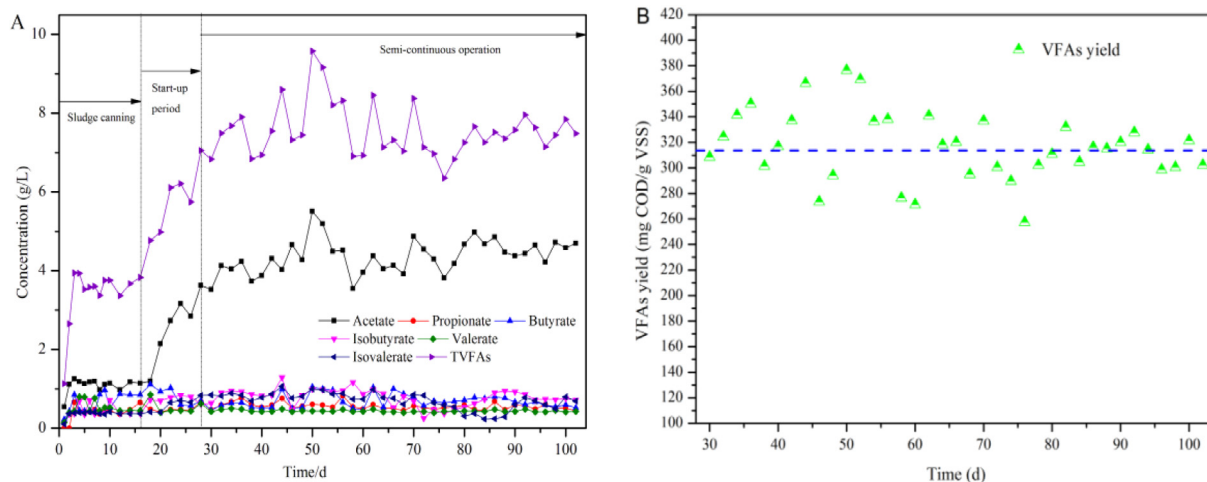
Fig. 3. (A) VFAs accumulation during the operation, (B) VFAs yield during the fermentation of sewage sludge.
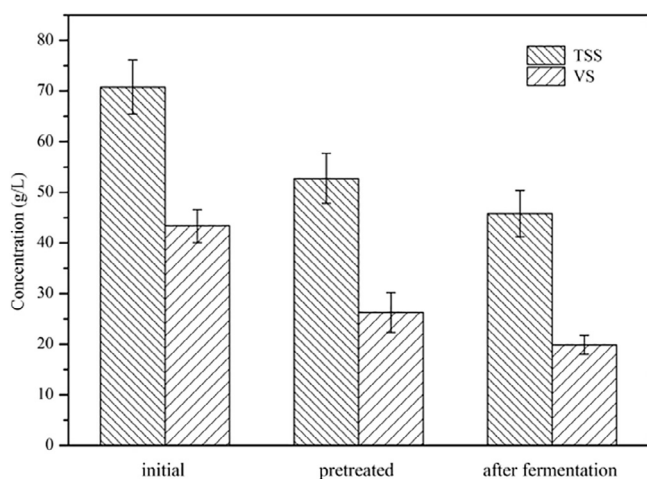

Fig. 4. TSS and VSS changes of initial, pretreated and fermented sludge.

anaerobic digestion (Maspolim et al., 2015). As shown in Fig. 4, both processes of hydrolysis and acidification contribute to the reduction of sewage sludge, which mainly happen in the pretreatment and anaerobic fermentation stages, respectively, including organics disintegration, solids solubilization and the subsequent biodegradation and bioconversion into VFAs.

Fig. 4 showed the changes in the TSS and VSS content at different stages. The initial TSS and VSS are 70.79 g/L and 52.75 g/L, respectively. When the fermentation process was in stable stage, TSS and VSS content in the fermented sludge were 45.78 g/L and 19.8 g/L, respectively, with the VSS reduction at 54.19%. Therefore, such a relatively high sludge reduction indicates that the hydrolysis and biodegradation of refractory organic materials are improved by heat-alkaline pretreatment and acidogenic fermentation.

3.4. Characteristics of fermented liquid

Applying the sludge fermentation liquid as additional carbon source to improve the nutrients removal in BNPR systems was one of the purposes of this study. Although high-solid sewage sludge with heat-alkaline pretreatment can release large amounts of organic matters which enhanced the subsequent acidogenic fermentation significantly, nitrogen and phosphorus were also released simultaneously during the pretreatment. However, they are undesirable for the BNPR systems due to the load increase of nitrogen and phosphorus in the wastewater treatment.

In this study, the sludge fermentation liquid was submitted to the dewatering process by diaphragm filter press to obtain the liquid with VFAs. Due to the application of the chemical polymeric flocculants in the dewatering process, it leads to VFAs loss and change of individual VFA composition. However, the more important thing is that a large part of nitrogen and phosphorous released in the process of pretreatment and fermentation could also be removed. Therefore, it is necessary to analyze the characteristics of fermentation liquid before and after dewatering. Table 3 showed the average concentrations of different components and the ratios of SCOD/TN and SCOD/TP in fermentation liquid. The concentration of SCOD, VFAs, TN, NH_4^+-N and TP are 327800, 7630, 1300, 274 and 114 mg/L, respectively. After the dewatering, the removal rates of TP, TN and NH_4^+-N can be 82.99%, 56.34% and 20.12%, respectively. The loss of SCOD and VFAs is not high. Before and after dewatering, the ratios of SCOD/TN and SCOD/TP can reach 25.2, 288.9 and 51.9, 1515.4, respectively, suggesting the ratios of SCOD to TN and TP increase significantly because of the nutrients removal in the fermentation liquid by the use of chemical coagulants.

The compositions of separated fermentation liquid were measured in this study. After dewatering, the VFAs, proteins and carbohydrates were still the main components of SCOD, accounting for 57.91%, 9.82% and 5.46% of the total SCOD in separated fermentation liquid, respectively. Acetic acid was always the predominant product and accounted for 55.72% of the total VFAs. Besides, propionic acid, butyric acid, isobutyric acid, valeric acid and isovaleric acid accounted for 7.46%, 9.78%, 10.53%, 5.68% and 10.83%, respectively.

3.5. Enhanced nitrogen and phosphorus removals in A^2/O process

In order to explore the efficiency of fermentation liquid as external carbon source for nitrogen and phosphorus removals, the separated fermentation liquid were added into the anoxic tank of the A^2/O wastewater treatment process, and commercial acetic acid was used as the

Table 3

Average concentrations of different components in the fermentation liquid and dewater fermentation liquid.

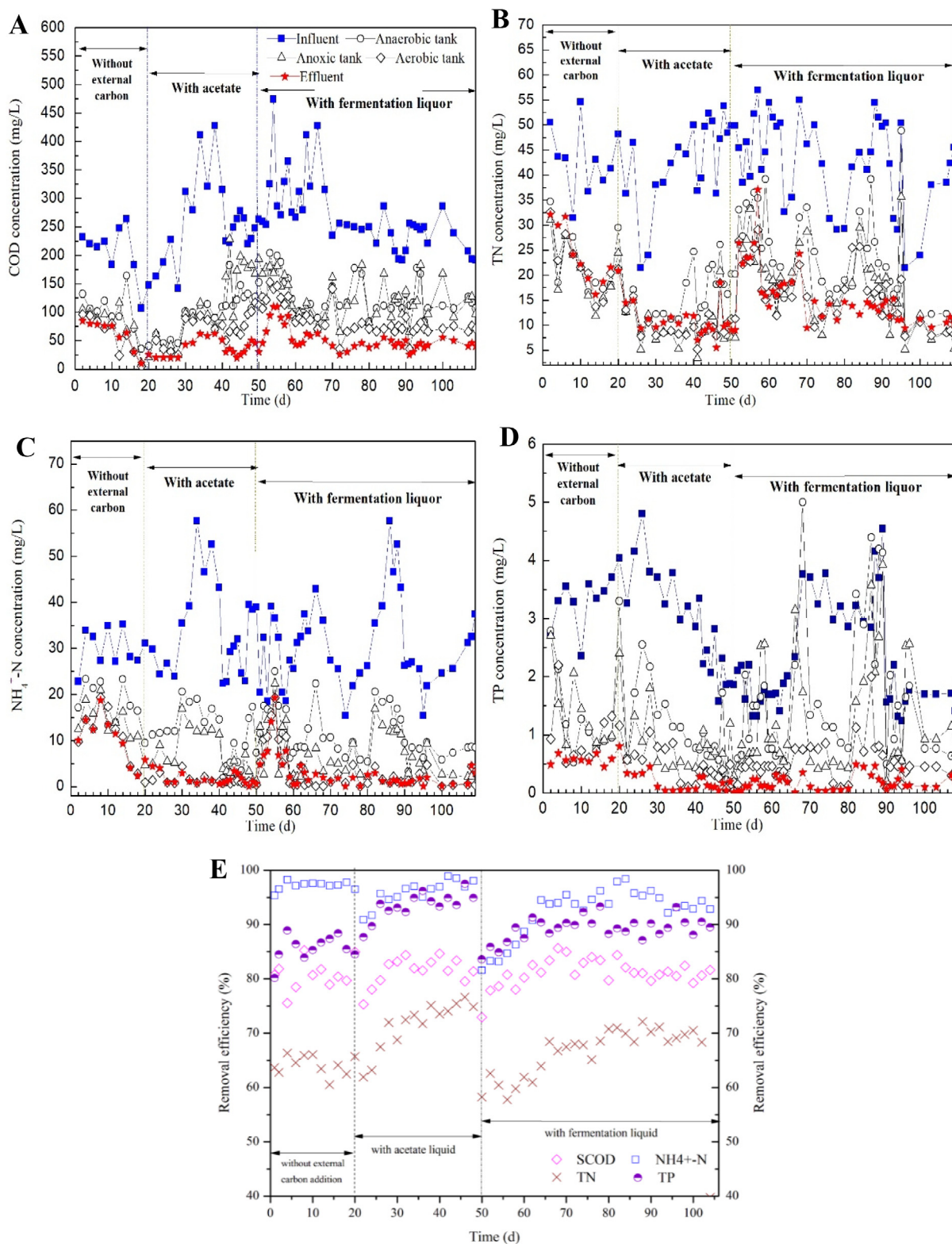| Parameters	Before dewatering	After dewatering	Removal rate
SCOD (mg/L)	32799.81	29444.39	10.23%
Total VFAs (mg/L)	7630	5020	8.11%
NH_4^+-N (mg/L)	274.21	219.04	20.12%
TN (mg/L)	1299.94	567.55	56.34%
TP (mg/L)	113.54	19.43	82.99%
SCOD/TN (mg/L)	25.2	51.9	–
SCOD/TP (mg/L)	288.9	1515.4	–

Fig. 5. Concentrations of SCOD (A), TN (B), ammonia (C), TP (D) and their removal efficiencies (E) at different tanks.

control. Fig. 5 shows the concentrations and removal efficiencies of SCOD, TN, ammonia and TP at different stages and Table 4 exhibits the average concentrations of SCOD, TN, ammonia and TP in the A^2/O process at different seasons.

As shown in Fig. 5, acetic acids (50 mg/L, calculated as COD) was continuously feed into the anoxic tank and the A^2/O process was under stable operation. Before adding the acetic acids, the average removal

efficiencies of nitrogen and phosphorus were 65.25% and 86.83%, respectively. The A^2/O process become more stable after adding the acetic acids. The average removal efficiencies of nitrogen and phosphorus were up to 75.88% and 96.06%, respectively. When fermentation liquids (50 mg/L, calculated as COD) was added into the A^2/O process to replace acetic acid after 50 d, the effluent began to deteriorate slightly. However, the effluent concentration of nitrogen and

Table 4
Nutrients concentrations at different units of the A^2/O process in the project.

Parameters	NH$_4^+$-N (mg/L)			TN (mg/L)			TP (mg/L)		
	Anaerobic	Anoxic	Aerobic	Anaerobic	Anoxic	Aerobic	Anaerobic	Anoxic	Aerobic
Summer season									
Wastewater	13.24 ± 0.93	5.86 ± 1.51	**0.94 ± 0.03**	14.08 ± 1.46	11.24 ± 0.71	**13.75 ± 0.63**	1.24 ± 0.88	0.73 ± 0.31	0.34 ± 0.11
Addition of acetic acid	15.54 ± 2.41	6.31 ± 1.61	**1.04 ± 0.21**	17.54 ± 2.91	6.34 ± 2.21	**10.32 ± 1.51**	0.58 ± 0.31	0.46 ± 0.21	0.08 ± 0.05
Addition of fermentation liquids	8.46 ± 1.14	5.59 ± 1.84	**1.54 ± 0.17**	16.94 ± 2.34	8.36 ± 1.38	**11.54 ± 1.02**	1.34 ± 0.34	0.66 ± 0.18	**0.21 ± 0.11**
Winter season									
Wastewater	18.24 ± 2.91	15.04 ± 1.23	**11.79 ± 2.19**	28.42 ± 4.67	24.04 ± 2.39	**23.95 ± 3.63**	4.35 ± 3.64	1.74 ± 0.78	0.59 ± 0.21
Addition of acetic acid	11.42 ± 1.05	6.74 ± 1.57	**5.25 ± 1.93**	25.36 ± 3.71	17.24 ± 3.16	**11.13 ± 2.52**	1.24 ± 0.47	0.64 ± 0.13	0.34 ± 0.15
Addition of fermentation liquids	12.64 ± 1.73	11.35 ± 1.43	**6.35 ± 1.33**	22.31 ± 2.42	20.97 ± 2.86	**11.78 ± 2.43**	1.32 ± 0.36	0.86 ± 0.21	**0.29 ± 0.08**

phosphorus were still bellow 11.57 and 1.0 mg/L, respectively, indicating that the addition of sludge fermentation liquid did not cause overloading at stable operation stage. Finally, the average removal efficiencies of nitrogen and phosphorus were up to 72.39% and 89.65%, respectively. In the effluent, 70.37% of TN and 85.12% of SCOD were removed. The purpose of enhanced nitrogen and phosphorus removal was achieved. Table 4 showed the nutrients removal efficiencies at different process units in summer season (temperature: 19–23 °C) and winter season (temperature: 5–11 °C).

4. Discussion

4.1. Pretreatment and acidogenic fermentation

Since the hydrolysis is usually the limiting step for the anaerobic digestion of the organic solid wastes, the pretreatment become very important and necessary for the sewage sludge fermentation. At the lab-scale, a lot of different methods, such as physical, chemical or biological methods, etc. have been reported (Appels et al., 2013; Bougrier et al., 2006; Bayr et al., 2013). Among the above methods, heat-alkaline pretreatment was reported as a high efficient and cost-effective method for improving the hydrolysis of the sewage sludge (Wang et al., 2016; Tan et al., 2012). In this study, heat-alkaline pretreatment was applied at full scale (30 m^3) and the average hydrolysis yield reached to 68.7%, which was similar to the results of previous lab experiments (Kang et al., 2012; Liu et al., 2016). Under the effect of heat combined with alkaline, the extracellular polymeric substances (EPS) adhered outside of the sludge floc could be rapidly dissolved and the structure of sludge microorganisms would be destroyed, which could promote sludge microbial cells to release soluble proteins and polysaccharides, and provide a lot of organic matters for the subsequent acidogenic fermentation (Liu et al., 2016). In Fig. 2, the average concentrations of SCOD, proteins and polysaccharides after pretreatment reached around 32800 mg/L, 3892 mg/L and 2471 mg/L, respectively. The stable hydrolysis yields achieved in the pretreatment provided good premium for the subsequent acidogenic fermentation. Finally, it should be noted that although the heat-alkaline pretreatment increased the hydrolysis yield significantly, a large amount of organic matters which are not proteins and polysaccharides was also released from the sludge(Yin et al., 2016).

Alkaline fermentation at above pH 10.0 is the key factor for VFAs production from sewage sludge, in which the methane generation was blocked in a largely extent (Lee et al., 2014). In this study, a fed batch fermentation with the organic loading rate at 5 kg VSS/m^3·d was carried out in one year operation. Due to the complete pre-treatment and good control of process conditions, a total VFAs yield reached 261.32 mg COD/g VSS in a full-scale project, which is slightly lower than the result (360 mg VFAs/g VSS) reported by Liu et al. (2016) in a pilot-scale WAS fermentation. The composition of fermentation liquid will influence the impact of nitrogen and phosphorus removal. Acetic acid and propionic acid are usually the preferred carbons to BNPR process (Tayà et al.,

2015; Elefsiniotis and Wareham, 2007). In this study, the acetic acid was always the main VFA product (5.51 g/L), accounting for 57.69% of the total VFAs in the stable operation stage. In most studies, the acetic acid is always the dominant VFA in the alkaline fermentation liquid. Compared to the acetic acid, the fermentation liquid as additional carbon source will finally reach the same nutrients removal efficiency although the initial specific denitrification rate is lower than the acetic acid (Zheng et al., 2009).

Since the pretreatment and fermentation also lead large amount of nitrogen and phosphorus release in the liquid, the nutrients should be removed before the fermentation liquid was used as external carbon source in A^2/O system. Fortunately, the nutrients can be removed during the dewatering step of fermented sludge because of the chemical coagulants (Tong and Chen, 2009; Li et al., 2011). After dewatering, the nitrogen and phosphorus removal rate were 56.34% and 82.99%, respectively. Meantime, the loss of SCOD and VFAs is very low. The average ratios of SCOD/TN and SCOD/TP in the separated fermentation liquid were 51.9 and 1515.4 (Table 3). According to Grady (2011), the minimal requirement ratios for biological nitrogen and phosphorus removal should be in the range of 5–10 mg COD/mg N and 7.5–10.7 mg COD/mg P. Therefore, it is feasible that the fermentation liquid can be used as external carbon source to enhance BNPR system which has been verified in some previous lab scale studies (Zheng et al., 2009; Gao et al., 2011; Ji and Chen, 2010).

Finally, it should be noted that the VFAs fermentation has an obvious advantage over the biogas fermentation from sewage sludge due to the short SRT and revenue of the products. In this study, the SRT for VFAs production is only one third of the biogas fermentation, indicating that the smaller volume of anaerobic fermenter and space requirement for VFAs production compared to biogas fermentation. This is an obvious merit over the traditional anaerobic digestion of sludge for biogas production.

4.2. BNPR system operated by fermentation liquid as external carbon source

Due to the increasing strict discharge standards of nutrients, fermentative VFAs from waste activated sludge attracted more and more interests as external carbon sources to improve nitrogen and phosphorus removal in WWTPs (Tong and Chen, 2009; Gao et al., 2011). Although several lab scale studies have demonstrated the feasibility of VFAs from WAS fermentation in the application for improving the nitrogen and phosphorus removal efficiencies (Zheng and Chen, 2010), until now, there is no report on the full scale and practical application of acidogenic fermentation liquid as external carbon sources in WWTPs. In this study, the feasibility of using fermentation liquid to enhance nutrients removals was verified in a A^2/O domestic wastewater treatment process by comparing with acetic acid, which was usually used in the research and practical WWTPs (Tong and Chen, 2009).

According to the operation manual of the WWTP, the target of

Table 5
Average concentration of different parameters.

Parameters	SCOD (mg/L)			NH$_4^+$-N (mg/L)			TN (mg/L)			TP (mg/L)		
	Influent	Effluent	Removal (%)	Influent	Effluent	Removal (%)	Influent	Effluent	Removal (%)	Influent	Effluent	Removal (%)
Wastewater	234.29	**45.29**	80.67	34.18	**0.94**	97.25	38.81	**13.75**	64.57	2.58	**0.34**	86.83
Acetate acids	245.50	**44.28**	81.96	31.06	**1.28**	95.88	30.86	**7.73**	74.95	2.03	**0.08**	96.06
Fermentation liquids	283.46	**42.18**	85.12	27.45	**1.54**	94.39	38.95	**11.54**	70.37	1.84	**0.19**	89.65
Discharging standard	–	**50.00**	–	–	**8.00**	–	–	**12.00**	–	–	**0.50**	–

acetic acid or fermentation liquid addition into the influent was to elevate the COD of 50 mg/L in the anaerobic zone of the plant. As shown in Table 5, the addition of external carbon source improved the nitrogen and phosphorous removal efficiencies. When using acetic acid, the average removal efficiencies of nitrogen and phosphorus increased to 95.88% and 96.06%, respectively. By adding fermentation liquid, the average removal efficiencies of nitrogen and phosphorus were 94.39% and 89.65%, respectively, very close to that by using acetic acid. In the effluent, the concentration of TN and TP were 11.54 mg/L and 0.19 mg/L, respectively, meeting the requirements of current standards of China. The data in Table 4 showed the long term effect of acetic acid or fermentation liquid addition on the BNPR system. The results indicated that the acetate addition will improve the denitrification and biological phosphorus removal significantly. Moreover, the addition of fermentation liquid can obtain the equal or similar effect as the acetate does for the nutrients removal. Especially in the winter season, the nutrients cannot meet the discharge standard without the additional carbon source. However, the addition of acetate and fermentation liquid with the increase of COD at 50 mg/L or 100 mg/L can improve the BNPR system greatly.

4.3. Mass balance analysis of VFAs production and carbon source requirement for nutrient removal

Inadequate influent carbon source in domestic wastewater is a major limiting factor for the low efficiency of denitrifying reaction, resulting in that the nitrogen and phosphorus in effluent can not meet the state standards. Application of VFAs from sludge acidogenic fermentation as external carbon source provide a feasible solution to this problem. However, to make this technology commercial, it is also necessary to analyze mass balance between the VFAs production from the sewage sludge and carbon source requirement for the nutrient removal in WWTPs. In this study, a WWTP with an anaerobic-anoxic-aerobic (A^2/O) process is taken as an example, which has the treatment capacity of 40000 m^3/d (Fig. 6).

According to the data from the WWTP, the daily sludge (80% water content) amount is 32000 kg and the daily VSS amount is 3840 kg. When acidogenic fermentation with the VFAs yield in this study, the VFAs production is 1216 kg/d, the total nitrogen and phosphorus production are 118.84 kg/d and 10.38 kg/d, respectively. After dewatering, the amount of organic carbon is 1152 kg/d (calculated as COD), and the total nitrogen and phosphorus are 23.77 and 2.08 kg/d, respectively, because of the chemical precipitation by use of coagulants (Tong and Chen, 2009). On the other hand, after the state effluent discharge standard was upgraded from first order B to A, the extra amount of TN and TP removals of the WWTP with treatment scale of 40000 m^3/d increased by 223.77 kg/d (plus the nitrogen from the fermentation liquid) and 22.08 kg/d (plus the phosphorus from the fermentation liquid), respectively.

According to the minimal carbon requirement from Grady (2011), the total carbon demand for the effluent upgrade is 1224.79 kg/d (calculated as COD). Compared with the VFAs yield (1152 kg/d), it is obvious that the carbon source from the acidogenic fermentation with sewage sludge can almost meet the carbon demand (1224.79 kg/d). Because the COD represented by the VFAs only accounts 57.90% of

total COD in the fermentation liquid, so the carbon source provided by the fermentation can completely meet the carbon requirement, suggesting that the sludge from the domestic wastewater treatment can provide enough carbon supply by the acidogenic fermentation to fulfill the carbon demand for the nutrients upgrade in effluent.

4.4. Economic evaluation

In order to investigate the economic potential of VFAs production by acidogenic fermentation from sewage sludge and its application in the BNPR of WWTPs, the cost and income of the process were calculated and compared with the widely applied biogas production process based on the experimental results and literature data. The amount of treated sewage sludge is 3.0 m^3/d with the TSS concentration of 70 g/L (93% water content) and the VSS content is 60.0% of TSS in sludge. The SRT of VFAs fermentation is 7.0 d, but 25 d for biogas fermentation (Duan et al., 2012). For VFAs production, the sludge was pretreated at pH 11.0 and 70 °C for 2 h, but the pH for conventional biogas fermentation is around 7.0 and no pretreatment. The VFAs yield was 0.261 g COD/g VSS and methane yield was 0.35 L/g VSS (Duan et al., 2012). Finally, there is no purification step for the recovery of VFAs but only dewatering to separate solid and fermentation liquid containing VFAs and other SCOD.

When the project in this study was used as the scenario for the calculation, and only pretreatment and fermentation steps of the whole process were considered while the dewatering step and disposal of the sludge residuals were not considered as them were not referred in this study. Table 6 listed the cost and income of VFAs production and biogas production according to the above parameters. The fermenter for VFAs production is 30.0 m^3 but the biogas process is 85.7 m^3 because of the longer SRT. The cost of the pretreatment comes from the NaOH for pH adjustment and electricity consumption for heating. The operation cost of fermentation mainly comes from electricity consumption which is based on the kilo-watt-hour meter of the project. According to the economic analysis, the net profits for VFAs and biogas productions are 9.12 and 3.71 USD/m^3 sludge, respectively, suggesting that the revenue from VFAs is obviously much higher that of biogas.

Therefore, the lucrative superiorities of sludge fermentation for VFAs production than that for biogas production could be mainly summarized into several aspects. 1) The former needs much lower investment and operation cost, because the reaction time of sludge for VFAs production is only about 6.0–7.0 days, just one fourth of that for biogas production. 2) VFAs has higher added-value than that of biogas. 3) The machines for the purification and energy conversion of biogas need a lot of money while VFAs from sludge fermentation almost could be directly used as the external carbon for BNPR. 4) Sludge for VFA production is more operable. In most of wastewater treatment in China, the content of organics in sewage sludge is often as low as less than 50%, which results that the energy from the produced biogas is not enough to support the digestion process.

5. Conclusion

A full-scale of sewage sludge anaerobic alkaline fermentation for VFAs production was built and applied in wastewater treatment plant.
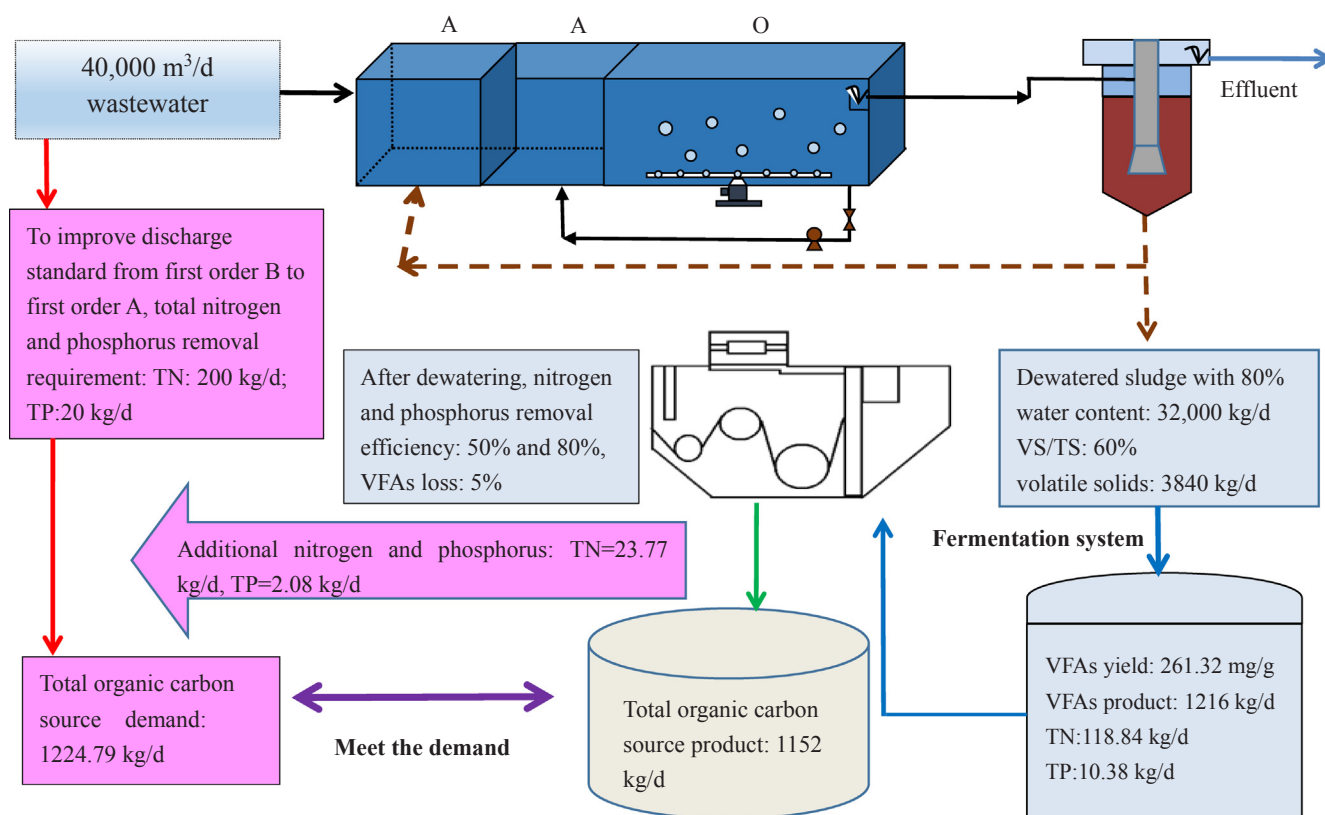
Fig. 6. Mass balances of VFAs yield and carbon requirement for nutrients removal in the WWTP.

Table 6
Economic comparison of VFAs and biogas production processes from sludge by anaerobic digestion.

Items	VFAs production	Biogas production
Volume of digester (m³)	30	85.7
Volume or VS mass of treated sludge (m³/d or kg/d)	3.0(180)	3.0(180)
Cost of pretreatment (USD/m³ sludge)[a]	8.19	–
Cost of dewatering (USD/m³ sludge)[b]	0.12	0.12
Cost of biogas purification (USD/m³ biogas)[c]	–	0.15
Cost for digester operation (USD/m³ sludge)[d]	1.39	4.96
Total cost (USD/m³ sludge)	9.70	5.53
Yield (g COD/g VS or L/g VS)	0.32	0.35
Amount of VFAs or biogas (kg/m³ or m³/m³ sludge)	19.20	21.00
Price of products (USD/kg VFAs or USD/m³ biogas)	0.98	0.44
Income (USD/m³ sludge)	18.82	9.24
Net profit (USD/m³)	9.12	3.71

a: The dosage of sodium hydroxide is 0.19 kg/kg TS and the price for sodium hydroxide 0.15 USD/kg; the electricity consumption is the energy demand of sludge heated from 20 to 70 °C and the heat recovery rate is 70%. b: The PAM used for dewatering of sludge is 1.5 g/kg TS and its price is 0.82 USD/kg. c:The cost of the purification of biogas is 0.15 USD/m³. d: The electricity for the fermenter operation based on the electricity meter is 1.39 USD/m³ sludge.

Long-term operation indicated the adoption of this system could simultaneously realize sludge reduction, carbon source recovery and nutrient removal enhancement. About 54% of sludge could be reduced, average VFAs yield reached 261.32 mg COD/g VSS, and removal efficiencies of TN and phosphorus were increased to 73.37% and 89.65% in wastewater treatment, respectively. Moreover, theoretically, VFA production and demand reached balance which then could make it

stable. Finally, this system also showed much greater economic advantages than that of biogas production process.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.biortech.2018.03.105.

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