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Comparing two enhancing methods for improving kitchen waste anaerobic digestion: bentonite addition and autoclaved de-oiling pretreatment

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Highlights

- Two enhancing methods for KW mono-digestion were comparative studied

- Enhanced 17.7% methane production with adding bentonite at OLR of 1.39 $gVSL^{-1}d^{-1}$

- Two methods showed positive effect on CH_4 production and stability at low OLR

- Showed application potential for a KW biogas plant adding bentonite

Abstract

The effects of different enhancement methods, including adding bentonite (1.25%, w/w, wet substrate) and autoclaved de-oiling pretreatment (121°C, 30 minutes), on the anaerobic digestion of kitchen waste (KW) were comparably studied. Mesophilic continuous stirred tank reactors were used under different organic loading rates (OLRs) of 1.11 to 1.84 gVS (volatile solid)$L^{-1}d^{-1}$ and two different hydraulic retention times (HRTs) (20 d and 25 d). In this study, two enhancement methods and extending HRT could prevent volatile fatty acids (VFA) accumulation and obtain a high methane production at low OLR. Owing to the effect of providing nutrients and buffering capacity, the maximum methane yield was obtained with adding bentonite at OLR of 1.39 $gVSL^{-1}d^{-1}$. However, for high OLR (1.84 $gVSL^{-1}d^{-1}$), a decrease of the methane yield and system breakdown occurred due to the accumulation of VFAs. Engineering design and process evaluation of a CSTR biogas plant treating with KW based on the laboratory experiment was stated.

Keywords: Anaerobic digestion; Kitchen waste; Bentonite; Autoclaved de-oiling

1. Introduction

With the increase of urban populations and changes in consumption patterns in China, more than 30 million tons of kitchen wastes (KW) are produced every year (Li et al., 2016). The increasing large amount of KW will become a big threat to environment if there is no reasonable

treatment. Compared with the traditional landfill and incineration methods, anaerobic digestion (AD) is more attractive because it can produce clean energy (biogas) and digestate that can be used as organic fertilizers (Li et al., 2013; Liu et al., 2009). Furthermore, AD has a significant benefit for reducing greenhouse gas since methane and carbon dioxide both produce in a closed reactor, avoiding its uncontrolled production and release to the atmosphere (Limam et al., 2016).

Co-digestion of KW with other wastes, like press water from organic municipal wastes, sewage sludge and animal manures has been widely studied (Kim et al., 2004; Nayono et al., 2010; Zhang et al., 2013; Tian et al., 2015; Tasnim et al., 2017). However, limited reports can be found on successful performance of single-stage AD system treating KW (Zhang et al., 2012). El-Mashad et al. (El-Mashad et al., 2008) found that a digester treating KW was not stable at the organic loading rate (OLR) of 2.0 gVS(volatile solid)$L^{-1}d^{-1}$ due to the accumulation of volatile fatty acids (VFAs). Although the higher lipid content in KW could improve the methane potential, it is easy to result in an inhibition in AD process (Xu et al., 2009), like long chain fatty acid (LCFA). High concentration of LCFA, which comes from the degradation of KW, can be adsorbed at the surface of microorganism, and then hinder mass transfer and restrain the activity of acid-producing bacteria and methanogen (Palatsi et al., 2009).

Some researchers try to investigate suitable methods to ensure a stable process with KW mono-digestion. Pretreatment of KW was regarded as an effective way to improve the stability and methane yield. Pressure microwave irradiation was successful in obtaining higher soluble COD, protein and sugar concentrations in the supernatant phase (<0.45 μm) as well as in the whole fraction of pretreated KW compared to untreated KW (Marin et al., 2010). Thermo-chemical pretreatment could increase methane yields from fat, oil, grease and synthetic KW co-digestions (Li et al., 2013). Adding additives or trace elements is another way to promote the biogas production. Previous studies showed that inorganic minerals (bentonite, clinoptilolite, coal ash fly) could enhance the gas production of KW, and adding bentonite got the highest biogas production with the optimum dosage of 1.25% (w/w, wet substrate) (Wang et al., 2007; Wang et al., 2006). Supplementation of trace elements could prevent propionic acid accumulation, achieving a stable operation process (Banks et al., 2012). Tampio et al. (Tampio et al., 2014) pointed out that stable digestion of untreated and autoclaved KW were feasible after adding trace elements to the mesophilic reactors at OLRs up to 6 gVS$L^{-1}d^{-1}$ with methane yield of 435 and 393 mLCH$_4$(gVS)$^{-1}$, respectively.

A number of studies have been conducted to improve methane potential of KW, such as adding trace elements, inorganic minerals, pressure microwave pretreatment, etc. However, few studies focused on the effects of hydraulic retention time (HRT), OLR and different enhancing methods on the control of mono-digestion process of KW. The aim of this study was to investigate the effects on methane production and fermentation performance through comparing the difference between the untreated KW and two effective enhancing methods (adding bentonite and autoclaved de-oiling KW). In addition, the influences of HRT and OLR were also discussed.

2. Materials and methods

2.1 KW and inoculum

The KW used in this study was collected from a canteen at China Agricultural University, Beijing, China. It mainly includes residual vegetables, meat, rice and noodles. After picking out paper napkins and plastic bags, KW material was mixed and divided into two portions. One portion was pretreated at 121℃ and 30 min in a vertical pressure steam sterilizer (LT-CPS38C,

LEAD-Tech scientific instrument co. ltd, Shanghai, China) and then was liquefied and homogenized in a mill (JYL-D051, Joyoung, Anhui, China). The other one was directly stirred by a mill (i.e. untreated KW). Both portions were stored at -20ºC until use. The inoculum was taken from an anaerobic reactor treating pig manure. The additive bentonite was obtained from Henan, China. The properties of the untreated KW, autoclaved de-oiling KW and inoculum are shown in Table 1. For autoclaved de-oiling pretreatment, the removal rate of crude fats was 33.3%. Table 2 shows the properties of bentonite.

2.2 Semi-continuous trial

The semi-continuous trial was carried out using three 22 L continuous stirred tank reactors (CSTR) with the effective volume of 20 L, as shown in Fig.1. Reactors were fed with untreated KW (R1), KW with bentonite (R2) and autoclaved de-oiling KW (R3), respectively. Initial OLR of the three reactors was 1.39 $gVSL^{-1}d^{-1}$ (total solid (TS) content of 3%) and HRT was 20 d. After 60 d (three HRTs), HRT of R1 was extended to 25 d corresponding to a lower OLR of 1.11 $gVSL^{-1}d^{-1}$. Meanwhile, OLR of R2 and R3 was increased to 1.84 $gVSL^{-1}d^{-1}$ (TS content of 4%). Each reactor was fed and discharged once per day. Stir performed after feeding for 3 min at 80-100 rpm. The reactors were operated under mesophilic condition (35 ± 1ºC) by a heated water bath (SY-200, Changfeng Instrument and Apparatus Company, Beijing, China). Produced biogas was collected by a 30 L gas storage bag and gas volume was measured by a gas flowmeter (LML-1, Changchun auto filter co., LTD, Jilin, China). The effluent was sampled for analysis of pH, VFAs, total organic carbon (TOC) and total ammonia nitrogen (TAN).

2.3 Analytical methods

TS and VS were measured according to the standard methods (2005). Crude fat was measured by the Soxhlet extraction method. Crude protein was estimated by multiplying the total Kjeldahl nitrogen by 6.25 and the total Kjeldahl nitrogen was measured by a Kjeldahl apparatus (K1305A, Sonnen Automated Analysis Instrument Co., Ltd., Shanghai, China). Carbohydrate was calculated by subtracting the amount of crude protein and crude fat from VS (Galí et al., 2009).

Methane content was analyzed by a gas chromatograph (1490, Agilent Technologies, USA) equipped with a thermal conductivity detector and a 3 m stainless column packed with Porapak Q (60-80 mesh). The operational temperatures of the injector port, column oven and detector were 120ºC, 150ºC and 120ºC, respectively. Pure nitrogen was used as the carrier gas at a flow rate of 50 mL min^{-1}.

Digestate samples were centrifuged at 4000 rpm for 10 min at room temperature and then used for the chemical analysis. A pH meter (PHS-3C, Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China) was used to determine the pH value. The concentrations of VFAs (including formic, acetic, propionic, butyric, succinic and lactic acid) were measured by a high performance liquid chromatography (LC-10A, Shimadzu Corporation, Kyoto, Japan) equipped with an ultraviolet detector at the wavelength of 210 nm. Before VFAs analysis, the samples were filtered through a 0.22 μm membrane. 5 mM H_2SO_4 was used as mobile phase at a flow rate of 0.8 $mLmin^{-1}$. C18 column (4.6×150 mm) was used as the separation column at 30ºC. Salicylic acid spectrophotometry was used to analyze TAN. TOC was determined by a TOC analyzer (TOC-V, Shimadzu, Japan).

3. Results and discussion

3.1 Biogas and methane yield

Fig. 2A and Fig. 2B show the changes of the daily biogas production and methane content

(v/v) in the entire experiment, respectively. It can be seen that the biogas production increased gradually during the initial 3 d. At OLR of 1.39 gVSL^{-1}d^{-1}, R1 exhibited an unsustainable process in terms of biogas production and methane content dropped rapidly from the 28th d. It didn't recover despite adding NaHCO$_3$ at the 43th d (Fig. 3), which was the same as the result found by Ma et al. (Ma et al., 2011) that mono-digestion system of KW didn't work well. Compared with R1 (untreated KW), R2 (KW with bentonite) and R3 (autoclaved de-oiling KW) maintained a relatively stable level. Table 3 exhibits the average biogas production, methane content and methane yield of each reactor in the stable state at different OLRs, high average biogas production and methane content of 23.5 Ld^{-1} and 66.7%, 20.9 Ld^{-1} and 64.2% were found in R2 and R3, respectively. However, when the OLR increased to 1.84 gVSL^{-1}d^{-1}, biogas production and methane content of R2 and R3 dropped rapidly in the last HRT (101-120 d). It could be concluded that adding bentonite and autoclaved de-oiling pretreatment were effective for obtaining a sustainable AD process of KW at OLR of 1.39 gVSL^{-1}d^{-1}. For R1, when the HRT extended to 25 d (OLR: 1.11 gVSL^{-1}d^{-1}), the process became stable with average biogas production of 18.1 Ld^{-1} and methane content of 63.0%. The result confirmed that the stability of KW mono-digestion system could be improved by extending HRT.

Theoretical methane yields of untreated KW and autoclaved de-oiling KW were 571 and 519 mLCH$_4$(gVS)$^{-1}$ calculated by equation (1) (Yechi, 2014). Base on biogas production, methane content and OLR, actual methane yield was calculated and described in Fig. 2C. The variation of methane yield of all reactors in the whole process was similar to the biogas production. Table 3 illustrates that the methane yield of R1 at OLR of 1.11 gVSL^{-1}d^{-1} was 7.3% higher than that of 1.39 gVSL^{-1}d^{-1}. At OLR of 1.39 gVSL^{-1}d^{-1}, the highest methane yield was obtained in R2, with a prominent increase of 17.7% and 17.0% compared to R1 and R3, respectively. From another point of view, the methane conversion efficiency of R1 with OLR of 1.11 gVSL^{-1}d^{-1}, R2 with OLR of 1.39 gVSL^{-1}d^{-1} and R3 with OLR of 1.39 gVSL^{-1}d^{-1} all over 90.0%, which proved both pretreatments (adding bentonite and autoclaved de-oiling) and extending HRT could improve methane yield in AD process of KW. However, the methane yields of R1 and R3 were almost the same at 1.39 gVSL^{-1}d^{-1}. This phenomenon can be explained by the different chemical compound before and after autoclaving de-oiling. Compared with protein and carbohydrate, lipid has higher methane potential in theory (Yechi, 2014). As shown in Table 1 and equation (1), the percentage of crude fat was reduced after autoclaved de-oiling pretreatment, which resulted in a lower methane yield of R3. When the OLR increase to 1.84 gVSL^{-1}d^{-1}, methane yields decreased by 13.7% and 12.7% in R2 and R3, respectively. LCFA, coming from the degradation of high lipid content of KW, is a well-known inhibitor. It adheres to the surface of microorganism, affecting its transport and protective functions (Demeyer and Henderickx, 1967; Galbraith and Miller, 1973). It can be proved by the similar practical methane yield of R1 and R3 at 1.39 gVSL^{-1}d^{-1}, and R1 should have a higher methane yield due to higher lipid content. Meanwhile, more LCFA was produced when more KW was put into the rectors, causing system collapse in R2 and R3 at 1.84 gVSL^{-1}d^{-1}.

Theoretical methane yields (mLCH$_4$(gVS)$^{-1}$) =

$$415 \text{ (mLCH}_4\text{(gVS)}^{-1}) \times \text{Carbohydrate (\%)} + 527 \text{ (mLCH}_4\text{(gVS)}^{-1}) \times \text{Crude protein (\%)} + 980 \text{ (mLCH}_4\text{(gVS)}^{-1}) \times \text{Crude fats (\%)} \qquad (1)$$

In the study of Guo et al. (Guo et al., 2014), average methane yields were 493.5±44.1 and 381.1±32.2 mLCH$_4$(gVS)$^{-1}$ at OLR of 1.5 and 2.0 gVSL^{-1}d^{-1}, respectively, in AD reactors dealing

with KW with HRT of 40 d. Wei et al. (Wei et al., 2014) found that the semi-continuously fed reactors showed a relatively consistent methane yield (470 $mLCH_4(gVS)^{-1}$) with no apparent deterioration at OLR of 1.0-3.0 $gVSL^{-1}d^{-1}$ with HRT of 40 d. The supplementation of Fe (100 mgL^{-1}), Co (1 mgL^{-1}), Mo (5 mgL^{-1}) and Ni (5 mgL^{-1}) obtained the greatest methane yield of 504 $mLCH_4(gVS)^{-1}$. Furthermore, the supplementation of these metals also resulted in the largest increase (35.5%) in methane production compared to the reactor without supplementing metals (372 $mLCH_4(gVS)^{-1}$) for the AD of KW (Zhang et al., 2015). In this study, the optimal methane yield (564±63 $mLCH_4(gVS)^{-1}$) was obtained in R2 at OLR of 1.39 $gVSL^{-1}d^{-1}$ with HRT of 20 d, with increment of 11.9% compared to the study of supplying Fe, Co, Mo, etc. Besides, it was superior to the previous studies in terms of higher methane yield and shorter HRT. The preferable result attributes to the effect of bentonite. On one hand, bentonite contains many metal ions, such as Fe, Ca, K, Mg and so on, providing necessary elements for the microorganism. On the other hand, Ca and Mg salts can be used as energy supplements to change the cell permeability, promoting microorganism to absorb nutrients selectively (Yadvika et al., 2004).

The average methane yields at OLR of 2.0 $gVSL^{-1}d^{-1}$ corresponding to HRT of 117 d and 94 d for untreated and autoclaved KW were 443±38 and 373±37 $mLCH_4(gVS)^{-1}$, respectively (Tampio et al., 2014). Compared with the autoclaved KW, methane yields of autoclaved de-oiling KW at OLR of 1.39 (482±62 $mLCH_4(gVS)^{-1}$) and 1.84 $gVSL^{-1}d^{-1}$ (421±40 $mLCH_4(gVS)^{-1}$) were higher, respectively, illustrating that de-oiling was important for AD of KW by the decrease of LCFA production. Thus, the results indicated that autoclaved de-oiling pretreatment had superiority for shortening HRT and maintaining system stability at low OLR.

3.2 pH value and VFAs concentration

Many parameters can influence pH value during AD process, such as VFAs concentration, bicarbonate concentration, alkalinity and CO_2 production (Kondusamy and Kalamdhad, 2014). Methanogens work effectively between pH values of 6.5-8.2 (Yechi, 2014). The change of pH value during the entire experiment period is presented in Fig. 3. In the first HRT, the pH value of all reactors dropped slowly from 7.50 to 7.08. In 21-60 d, pH of R2 and R3 was within the suitable range. However, the pH value of R1 dropped rapidly from 6.62 at the 28th d to 4.51 at the 42th d. Thus, R1 was adjusted by adding $NaHCO_3$ at the 43th d, and its pH value slowly returned back to normal, but without obvious biogas production recovery. It might because the amount of $NaHCO_3$ was excessive for the AD system and the excess sodium cations could generate poisonous effect on methanogens (Tada et al., 2005).

After 60 d, R1 was restarted with initial pH of 7.36. Extending HRT from 20 d to 25 d, the OLR was reduced to 1.11 $gVSL^{-1}d^{-1}$. The average pH value of R1 was 6.97±0.34, but it dropped to 5.80 at the 112th d. Result concluded that extending HRT could slow down the acidification rate, but the optimal OLR for dealing with KW was less than 1.11 $gVSL^{-1}d^{-1}$ because of the inapposite pH at the end of the experiment. Therefore, the adaptive enhancing methods for improving the stability and methane production were necessary. At OLR of 1.84 $gVSL^{-1}d^{-1}$, pH value of R2 was in an appropriate range of 6.51-7.04 in 61-100 d and declined under 6.50 after 100 d. Measures including adding $NaHCO_3$ in the 103th d and stopping feedstock from the 103th d were carried out. Even though the pH value recovered after 6 d, the biogas production didn't return. Bentonite can absorb the hydrogen ions in solution. One side, its special flaky texture and internal porosity was conducive to promoting adsorption process of hydrogen ions. On the other side, bentonite could form cohesion compounds such as calcium silicate and aluminum silicate in the AD process, and

then improved the ability of absorbing hydrogen ions (Wang et al., 2007). Thus adding bentonite can offer an effective buffer capacity at lower OLR (1.39 $gVSL^{-1}d^{-1}$) compared untreated KW, but not at higher OLR (1.84 $gVSL^{-1}d^{-1}$). For R3, with OLR of 1.84 $gVSL^{-1}d^{-1}$, the pH value was stable in the whole process except the last 10 d. Based on this result, substrate didn't be putted into the reactor from the 110th d, which caused biogas production decrease.

Total VFAs and individual VFA concentrations of different reactors in the whole period are shown in Fig. 4. VFAs are intermediate metabolite in methanogenesis process, as well as inhibitors when excessive accumulation occurs (Li et al., 2013). Horiuchi et al. (Horiuchi et al., 2002) found that AD process was slightly inhibited when the VFAs concentration was above 4 gL^{-1} and the biogas composition changed obviously with the VFAs concentrations over 6 gL^{-1}. The degradation rate of propionic acid is the slowest in all kinds of VFAs and microbes are sensitive to it (Demirel et al., 2002; Wang et al., 2009; Izumi et al., 2010). Hanaki et al. (Hanaki et al., 1994) pointed out that the limited propionate concentration for methanogens was less than 1.0 gL^{-1}, and lactic acid was the direct substrate for propionic acid production (Li et al., 2014). Its optimal pH value for conversion process is 5-6 (Fu et al., 1999).

From Fig. 4A, at OLR of 1.39 $gVSL^{-1}d^{-1}$, VFAs in R1 remained around 1.0 gL^{-1} throughout the 1-24 d. With the addition of KW sequentially, the VFAs concentration increased from 1.77 gL^{-1} at 25 d to 11.54 gL^{-1} at 43 d and over 6 gL^{-1} in 34-43 d. It can be seen that the biogas production and methane content significantly changed. The percentage of lactic acid reached 66.5% of total VFAs in the ascent stage. What's more, the propionic acid concentration exceeded 1.0 gL^{-1} during the 34-43 d. Refer to pH value (4.50-6.0) of 34-43 d, it's consistent with the results of Fu et al (Fu et al., 1999). In order to alleviate the toxicity from VFAs, feeding was stopped on the 43-50 d and 55-60 d. And then HRT of R1 was extended to 25 d after three HRTs corresponding to the OLR of 1.11 $gVSL^{-1}d^{-1}$. At the lower OLR, VFAs concentration was under 2.69 gL^{-1} and the biogas production was stable, which meant that prolonging HRT could be a method to get a stable AD process of KW.

Average VFAs concentration of R2 at OLR of 1.39 $gVSL^{-1}d^{-1}$ was 0.82 gL^{-1}. Compared with the high VFAs concentration and low biogas production of R1, the stable performance of R2 at the same OLR level could be explained by the flocculating capacity of bentonite that can precipitate LCFA. Another explanation was the cations found in bentonite. Fe is the most effective substance for stabilizing AD process of KW (Zhang et al., 2012), and Ca has been shown to limit the concentration of dissolved LCFA (Roy et al., 1985). From Fig. 4B, while increasing OLR to 1.84 $gVSL^{-1}d^{-1}$ at 61 d, VFAs concentration gradually increased and ranged from 3.23 gL^{-1} to 5.66 gL^{-1} during 103-120 d, resulting in an unstable biogas production. From the result, adding bentonite could keep a stable AD process of KW at a lower OLR with HRT of 20 d.

At OLR of 1.39 $gVSL^{-1}d^{-1}$, average VFAs concentration of R3 was 0.71 gL^{-1}. Similar to R2, there was no obvious fluctuation until OLR increased to 1.84 $gVSL^{-1}d^{-1}$ (Fig. 4C), and the largest VFAs concentration reached 2.50 gL^{-1} on 97 d. Its biogas production was not affected by VFAs.

3.3 TOC concentration

Fig. 5 reflects the TOC concentration of digestate of all reactors at different OLRs and HRTs. It's obvious that TOC concentration of R1 increased significantly from the 28th d and grew persistently until the third HRT finished. During this time, there was less organic matter translated into methane and carbon dioxide, so that much organic matter was remained in digestate. This maybe influenced by pH and VFAs concentration. What's more, the variation tendency of TOC

concentration was corresponding to that of the VFAs, pH and biogas production in all reactors. For R2 and R3, TOC concentration kept a lower value and relatively stable. TOC removal rates of R1, R2 and R3 are shown in Table 3, which are more than 80% except for R1 (53.41%) at OLR of 1.39 $gVSL^{-1}d^{-1}$ with HRT of 20 d.

3.4 TAN concentration

Even though ammonia is an essential nutrient for bacterial growth, ammonia inhibition potentially encounters during AD process of protein-rich feedstock, such as KW, pig manure (Sung and Liu, 2003). TAN consists of ammonium ion (NH_4^+) and free ammonia (NH_3). Both forms can directly and indirectly cause inhibition in an AD system (Yenigün and Demirel, 2013). TAN concentration of 1700-1800 mgL^{-1} was completely inhibitory with unacclimated inoculum under mesophilic conditions (Kroeker et al., 1979). The advised value of free ammonia was below 150 mgL^{-1} (McCarty et al., 1961). The free ammonia concentration could also be calculated by fermentation temperature (T), TAN concentration and pH, showing in the following equation (Anthonisen et al., 1976):

$$N - NH_3 = \frac{TAN \times 10^{pH}}{e^{\frac{6344}{273.15+T}} + 10^{pH}} \qquad (2)$$

Fig. 6 shows the variation of TAN concentration in different reactors. In the startup stage, TAN concentration of all reactors was the highest (1232±24 mgL^{-1}). This is because TAN concentration of inoculums is higher than KW. In the third HRT, TAN concentration of all reactors reached a stable level. TAN concentrations of R1, R2 and R3 were 360, 313, 389 mgL^{-1}, respectively. The higher TAN concentration in R3 attributed to higher protein content in autoclaved de-oiling KW. Compared with R1, adding bentonite could indirectly influence TAN concentration through enhancing methanogen growth and controlling VFAs accumulation.

From 61 d, the acidulating digestate of R1 was replaced by fresh inoculum. As a result, its TAN concentration reached 1267 mgL^{-1} again. There was a small increase of TAN concentration in R2 and R3 at 60-64 d due to the increase of OLR. Obviously, TAN concentration in all reactors presented a declining trend at the fourth HRT. At 80-120 d, the TAN concentrations of R1, R2 and R3 were 434, 429 and 419 mgL^{-1}, respectively. In terms of TAN, there is no obvious inhibition.

Based on the equation (2), free ammonia in this study was calculated, and it can be found that the maximum free ammonia values of R1, R2 and R3 in the whole process were 42, 43 and 42 mgL^{-1}, respectively, which can be accepted by microorganism.

4. Practical application

The results of the semi-continuous experiment can be helpful to establish optimal design parameters for a biogas plant treating KW. Assuming a biogas plant with CSTR of 500 m^3, the basic operation parameters are listed in Table 4. Based on the above test, HRT is 25 d with OLR of 1.11 $gVSL^{-1}d^{-1}$ for untreated KW and HRT is 20 d with OLR of 1.39 $gVSL^{-1}d^{-1}$ for KW with bentonite. Thus the annual biogas and methane production of untreated KW and KW with bentonite are 148774 m^3 and 93732 m^3, 192756.5 m^3 and 128553 m^3, respectively. So we can see that firstly in a stable mono-digestion process, TS conversion rates of the two treatment are both more than 88.0%(Fig. 7), however, more KW (about 273.0 t) will be dealt with by adding bentonite per year, simultaneously obtaining more biogas (43982.5 m^3) and methane (34821 m^3). Secondly, the heat value of biogas is 23000kJ/m^3, approximately 31.4 t standard coals can be saved per year. Finally, the manure cost is not considered in this study. It was known that the price of 1 m^3 biogas and 1 t bentonite are 1.5 CNY and 200 CNY, respectively. Thus, the annual

addition amount and cost of bentonite is 17.0 t and 3400 CNY. The application of bentonite could not only improve AD process of KW, but also earn economic benefits (about 62573.8 CNY). Mass flow balance diagram of the biogas plant.

5. Conclusion

In conclusion, at OLR of 1.39 $gVSL^{-1}d^{-1}$, the AD of untreated KW failed due to the accumulation of VFAs. This problem could be alleviated by increasing HRT, bentonite addition or autoclaved de-oiling pretreatment. Moreover, adding bentonite to the reactors or autoclaved de-oiling pretreatment not only resulted in enhanced AD stability, it also increased the methane yield and reduced the concentration of VFAs at HRT of 20 d. However, the total VFAs accumulated when the OLR increased to 1.84 $gVSL^{-1}d^{-1}$, illustrating that the two enhancing methods were limited to keep the system stability.

Acknowledgments

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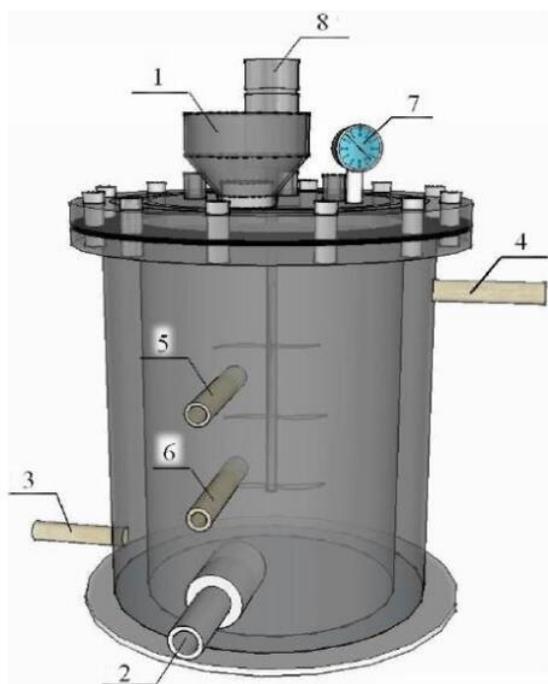
1. Feeding inlet   2. Feeding outlet   3. Circulating water inlet   4. Circulating water outlet
      5. Sample pipe A   6. Sample pipe B   7. Temperature sensor   8. Motor and stirrer

Fig. 1 –Schematics of the reactor.
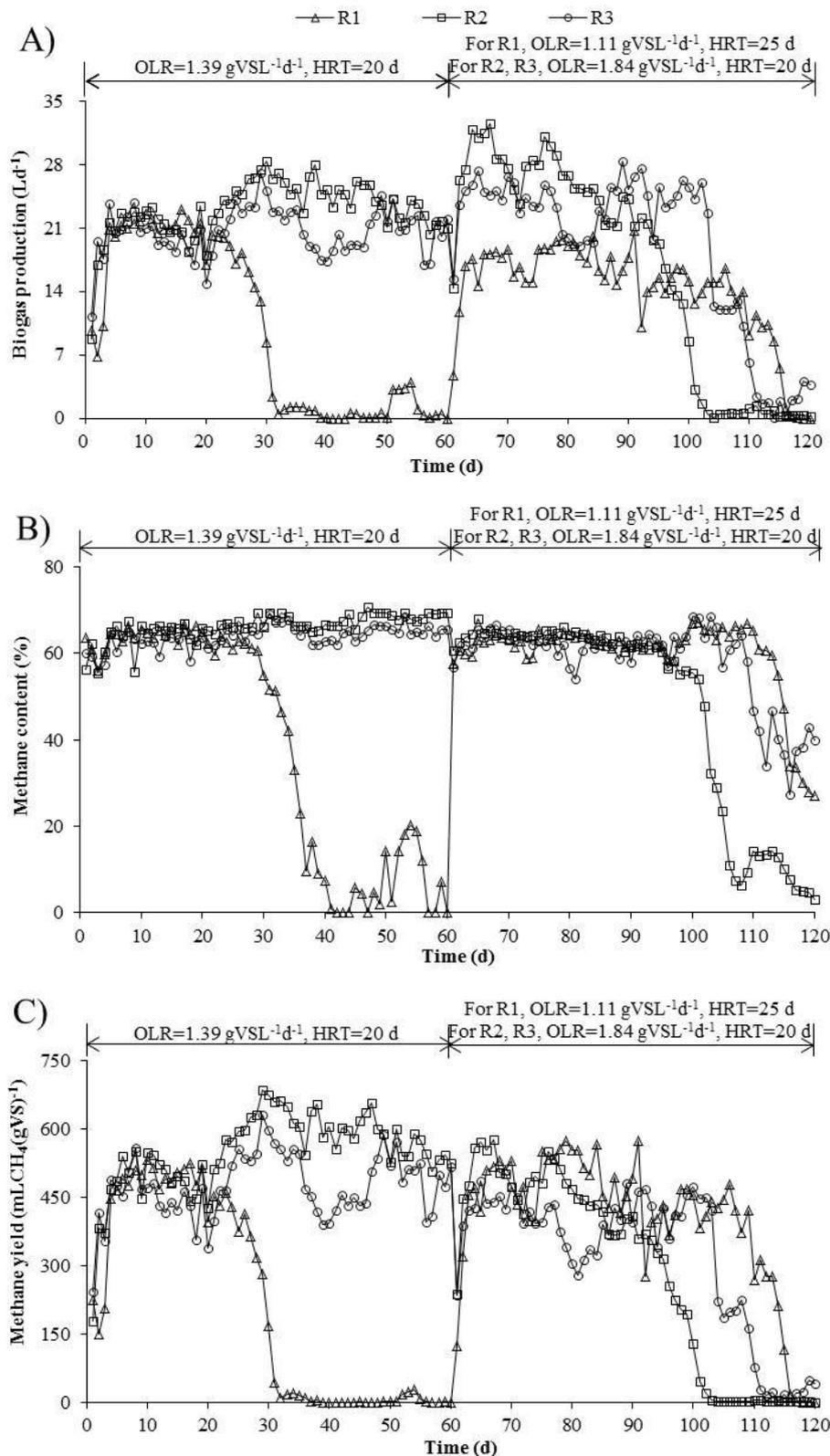
Fig. 2 - The daily biogas production, methane content and methane yield of R1, R2 and R3 at different OLRs and HRTs.

Fig. 3 - The variation of pH value of R1, R2 and R3 at different OLRs and HRTs.

Fig. 4 - Total VFAs and individual VFA concentration of R1, R2 and R3 at different OLRs and HRTs.

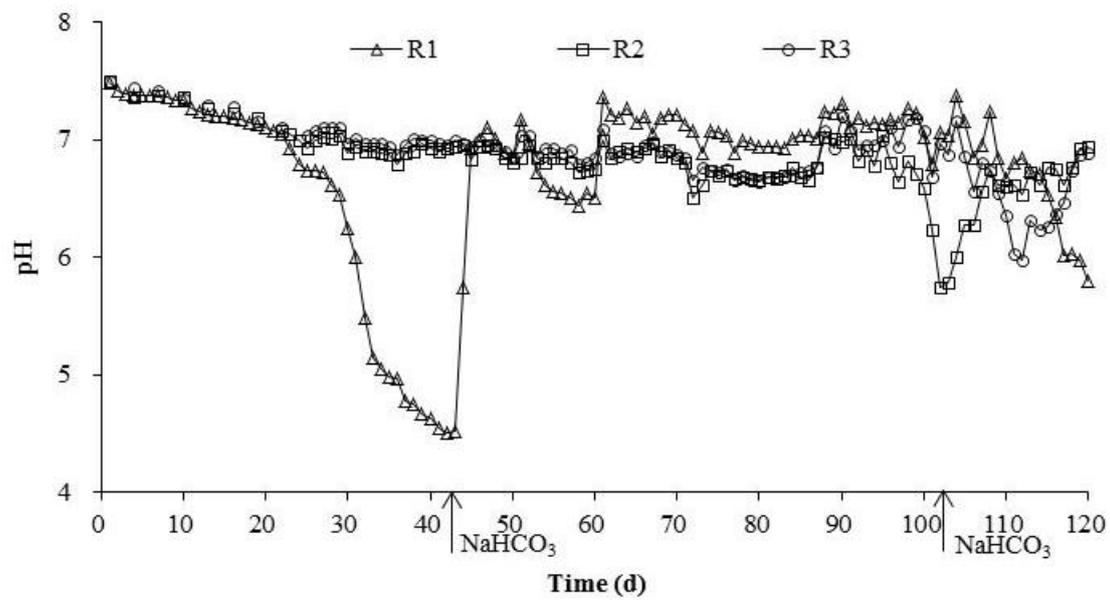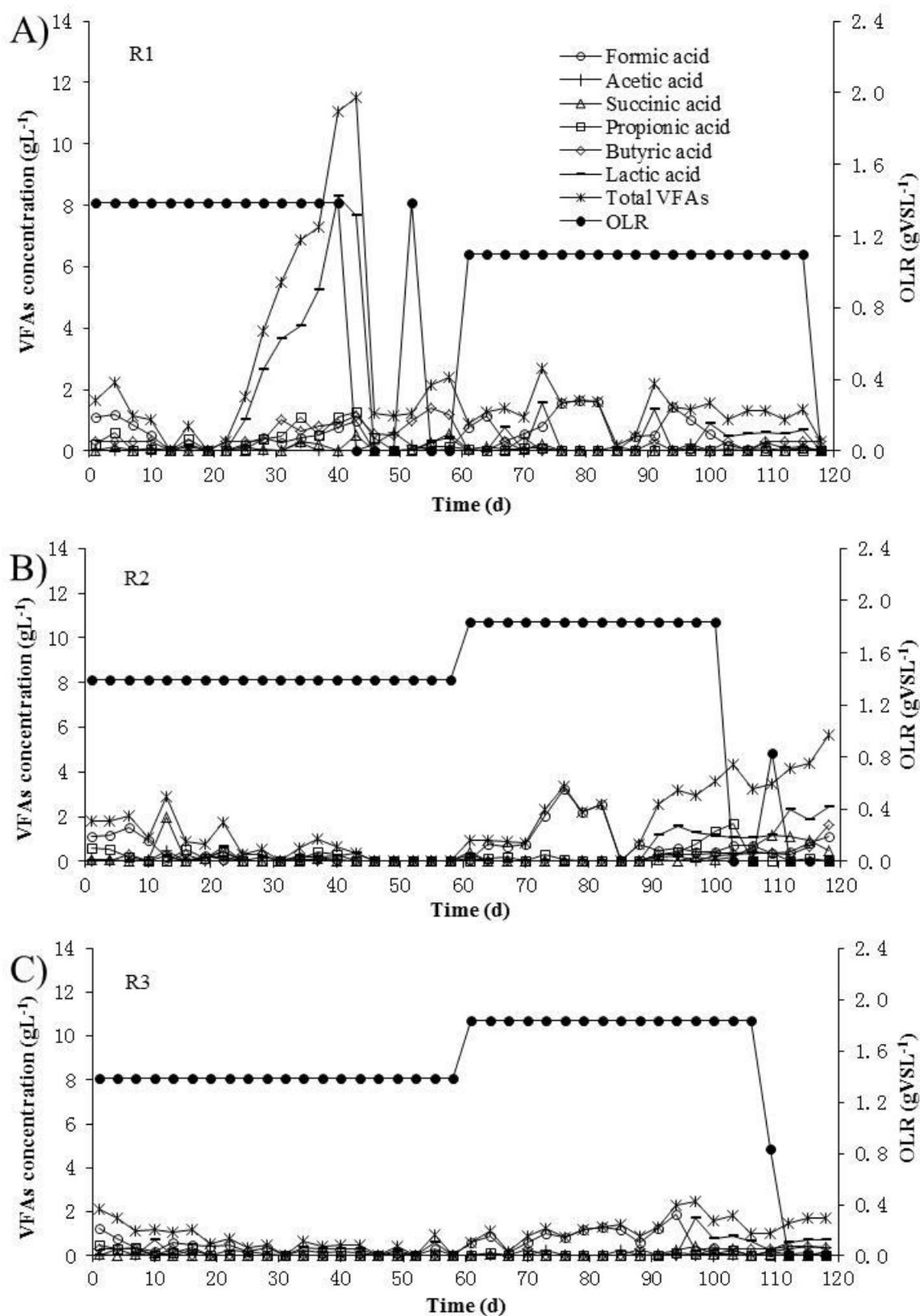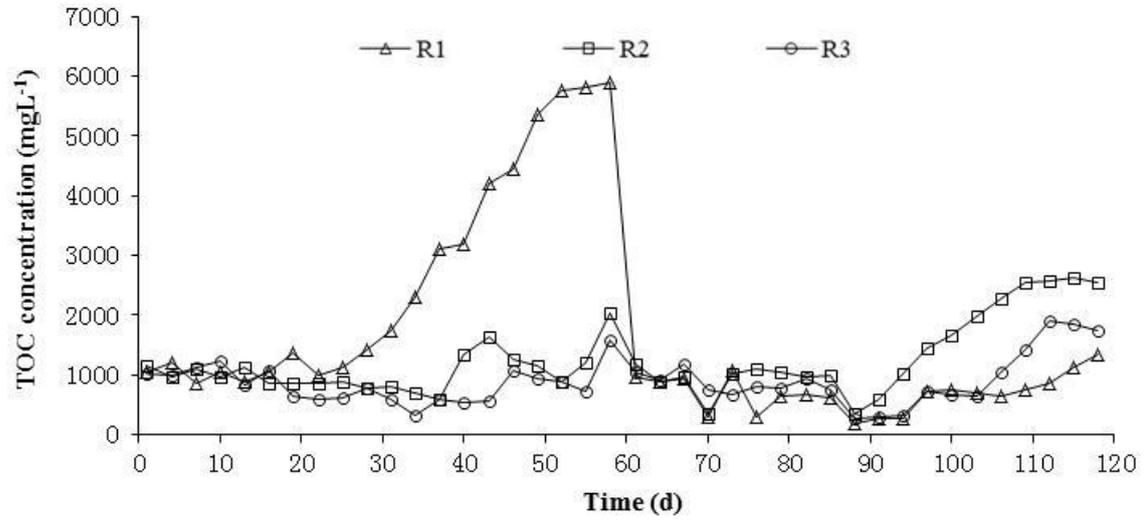**Fig. 5 - The variation of TOC concentration of R1, R2 and R3 at different OLRs and HRTs.**

Fig. 6 - The variation of TAN concentration of R1, R2 and R3 at different OLRs and HRTs.

Biogas	
Mass flow	477 kgTSd^{-1}
Volume	408 m³d^{-1}
Methane content	63.0%

KW	
Total feeding amount	18000 kgd^{-1}
Total KW	2992 kgd^{-1}
Total TS of KW	540 kgTSd^{-1}

Anaerobic digestion system

Biogas residues	
Mass flow	17523 kgd^{-1}
Total TS of digestate	63 kgTSd^{-1}

Untreated KW

Biogas	
Mass flow	597 kgTSd^{-1}
Volume	528 m³d^{-1}
Methane content	66.7%

KW	
Total feeding amount	22500 kgd^{-1}
Total KW	3740 kgd^{-1}
Total TS of KW	675 kgTSd^{-1}

Anaerobic digestion system

Biogas residues	
Mass flow	21903 kgd^{-1}
Total TS of digestate	78 kgTSd^{-1}

KW with bentonite

Fig. 7 - Mass flow balance diagram of the KW biogas plant.

Table 1 - Main properties of untreated KW, autoclaved de-oiling KW and inoculum

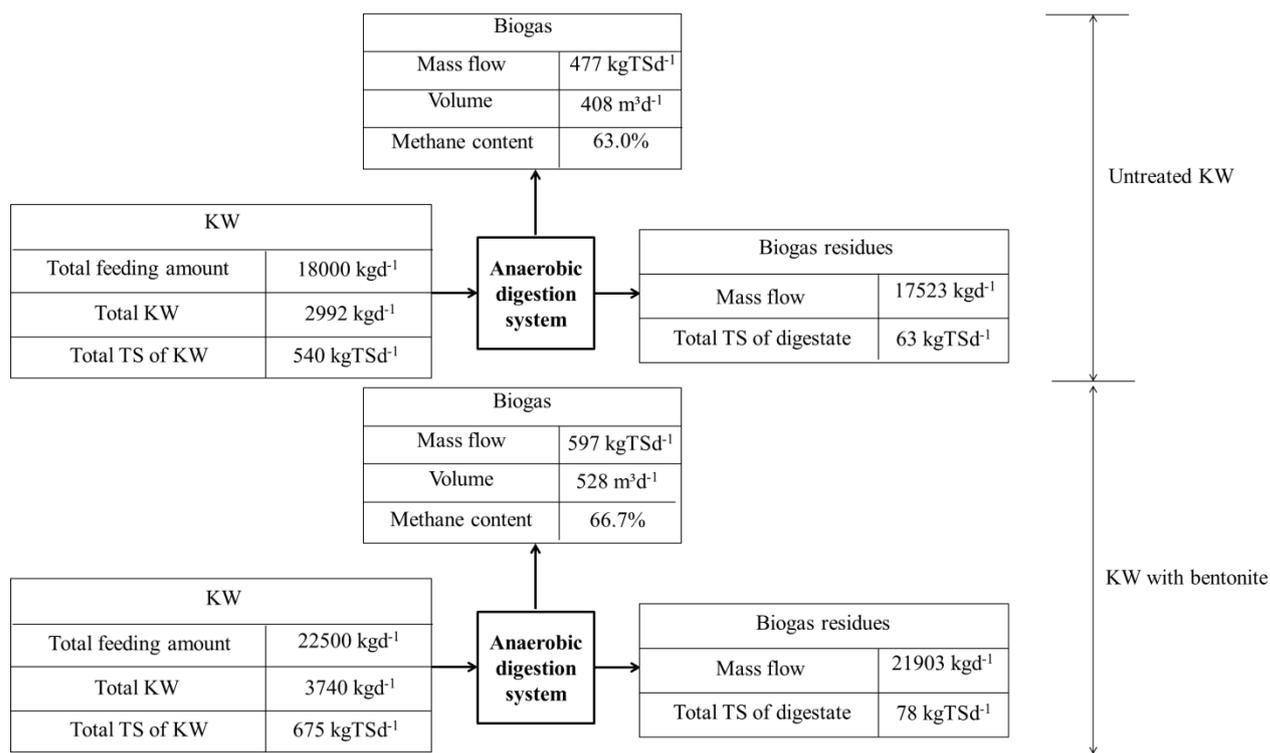| Properties	Untreated KW	Autoclaved de-oiling KW	Inoculum
Total solid (TS)(%w)	18.05±1.35	17.69±2.08	1.71±0.45
Volatile solid (VS)(%w)	16.70±1.25	16.41±2.10	0.78±0.04
pH	—	—	7.50
Crude protein (%TS)	14.32±0.47	15.76±0.65	—
Crude fats (%TS)	30.30±8.14	20.64±5.15	—
Carbohydrate (%TS)	47.87±7.93	56.27±5.01	—

—: no analysis, w: wet base.

Table 2 - Main properties of bentonite

Properties	Values	Properties	Values
Color	Grey white	Expansion times	30
Component	Montmorillonite (≥85%)	Metal ion	Fe, Ca, Si, Mg, Al
pH	6-8	Stiffiness	20
Density	60 gcm$^{3-1}$	Viscosity	50 mPa·s

Table 3 - The average value of methane potential and process parameters with different OLRs

Reactors	R1		R2		R3	
Feed concentration of TS (%)	3	3	3	4	3	4
OLR (gVSL^{-1}d^{-1})	1.39	1.11	1.39	1.84	1.39	1.84
HRT (d)	20	25	20	20	20	20
Biogas production (Ld^{-1})	20.8±1.3	18.1±1.7	23.5±2.4	27.8±2.5	20.9±2.4	24.7±2.0
Methane content (%)	64.0±1.9	63.0±1.3	66.7±2.5	64.5±1.1	64.2±2.3	63.1±3.3
Methane yield (mLCH$_4$(gVS)$^{-1}$)	479±36	514±52	564±63	487±49	482±62	421±40
Methane conversion efficiency/%	83.9	90.0	98.8	85.3	92.9	81.1
pH	6.27±0.96	6.97±0.34	6.96±0.18	6.70±0.27	7.03±0.17	6.78±0.27
Effluent TAN (mgL^{-1})	349±84	415±118	356±63	431±48	442±65	418±47
Effluent TOC (mgL^{-1})	2638	699	1056	1403	833	936
TOC removal rate (%)	53.42	86.97	81.48	80.28	81.07	83.56

Table 4 - The technical parameters of the KW biogas plant

Name	Value and unit (untreated KW)	Value and unit (KW with bentonite)
Total volume of reactor	500 m^3	500 m^3
Effective volume of reactor	450 m^3	450 m^3
OLR	1.11 gVSL^{-1}d^{-1}	1.39 gVSL^{-1}d^{-1}
HRT	25 d	20 d
Digestion temperature	35±1℃	35±1℃
Total KW	2991.7 kgd^{-1}	3739.6 kgd^{-1}
Bentonite addition	0	46.7 kgd^{-1}
Methane content	63.0%	66.7%
Methane yield	514 mLCH$_4$(gVS)$^{-1}$	564 mLCH$_4$(gVS)$^{-1}$
Total biogas production	407.6 m^{3}d^{-1}	528.1 m^{3}d^{-1}
Total methane production	256.8 m^3 CH$_4$d^{-1}	352.2 m^3 CH$_4$d^{-1}