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Anaerobic co-digestion of low chemical oxygen demand concentration sludge mixture by different pretreatment methods

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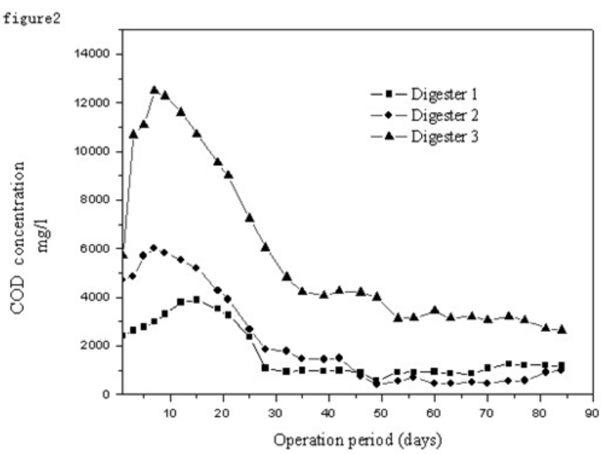
Graphical abstract



Abstract

Three laboratory scale systems were operated to study the anaerobic co-digestion of sewage sludge with the excess activated sludge and cattle manure which contained low Chemical oxygen demand (COD) concentration. The experiments were performed to evaluate the effects of different methods of pretreatment. Since the poor organic substrate, the organic loading rate (OLR) was designed about 1.6kg total solids (TS) $(l\ d)^{-1}$ and the hydraulic retention time was controlled from 78days to 53days throughout the experiment to investigate the effects of the input on overall stability. When the digesters got stabilized, the COD removal efficiencies were 61%, 89% and 54%, respectively, and the pH value fluctuated little in the three digesters. The results indicated that the treatment of 1g volatile solids (VS) of SSEASCM on semi-continuous co-digestion generated more than 200ml of biogas on average. Thus, anaerobic co-digestion of the mixed sludge provided a means for low COD waste treatment and produced renewable energy.

Keywords: Anaerobic digestion, manure, sewage sludge, excess activated sludge, biogas, low cod concentration

1. Introduction

The process of anaerobic digestion has the potential to contribute significantly to the renewable energy budget and also to the reduction of undesirable waste disposal routes (Boopathy, 2003; Hu et al., 2005; vedat. and gokel, 2008; marcia et al., 2007). The wastes are treated either in separate or co-digestion processes (gunaseelan, 1997; claassen et al., 1999; callaghan et al., 2002). The benefits of the co-digestion include: dilution of potential toxic compounds, improved balance of nutrients, synergistic effects of additional advantages include hygienic stabilization and increased digestion rate (Sosnowski et al., 2003). It is well-known that there are a lot of documents on the utilization of co-digestion, such as co-digestion of organic fraction of municipal solid wastes and agricultural residues (Converti et al., 1997; Kuebler et al., 2000; Baris and Mehmet, 2002), and organic solid wastes and sewage sludge (Edelmann et al., 2000). The process of anaerobic digestion could be classified into three steps: hydrolysis, fermentation and methanogenesis (Parkin and Owen, 1986). The rate-limiting step in this process is admitted the hydrolysis of particulate organic matter to soluble substances (Eastman J.A. and Ferguson, 1981). With increasing solubilization of the organic substances, more volatile solids (VS) become biodegradable. Thus, the efficiency of anaerobic digestion is greatly enhanced by improving the rate of the sludge hydrolysis step using physical and/or chemical pretreatment processes. The pretreatment process may include thermal, thermochemical, alkaline, and ultrasonic methods. In this study, alkali treatment and ultrasonic treatment are studied.

As most of studies were focused on dealing with the sludge containing high COD concentration, which was about 10000 mg l^{-1} or more than 10000 mg l^{-1} (PARKIN and OWEN, 1986), the treatment of the low Chemical oxygen demand (COD) concentration sludge on anaerobic digestion has seldom been reported. Whereas the most of the agricultural and industrial sludge needed to be treated were in low COD varied from 2000 mgl^{-1} to 3000mgl^{-1}, which was needed more investigation and attention. Recent growth of the amount of excess activated sludge that the by-product of the wastewater treatment plants in China has been given more attention to the safe disposal, including sewage sludge in daily lives with COD concentration below 3000mg l^{-1} and the decomposable animal waste(manure) with COD concentration below 5000mg l^{-1} in the livestock industries. Although the organic substance in these sludges is not high, random emission is still illegal and pollutes the surroundings. Based on what concerted above, anaerobic digestion was employed to degrade the mixed sludge to solve this environmental problem.

In this experiment, sewage sludge with the excess activated sludge and cattle manure (SSEASCM) has been employed to investigate the effect on the anaerobic co-digestion. The effect of different pretreatment methods had been compared in the experiment, and the effluent and input were increased from 40 ml stepwise until the COD concentration above 1000mg l-1 to find the proper HRT of this digester apparatus.

2. Materials and methods

2.1. Material

Anaerobic seed sludge was collected from Shahu wastewater-treatment plant, most capability of which focus on Eastlake water treatment, the famous sight in Wuhan, Hubei, China. The seed sludge had, on average, a total solids (TS) content of 6 % with 38 % of this being VS. Sewage sludge was gathered from the sewer of the Engineering Faculty in Wuhan University Campus, Hubei, China. Excess activated sludge was collected from the Shahu wastewater treatment plant, in the city of Wuhan, Hubei, China. And cattle manure was gathered from the suburb of Wuhan city. The characteristics of the three materials are given in Table 1, showing that the organic matter is not rich, for example, the COD concentrations of the sludge are lower than those reported previously (AMORIM et al., 2005; RIBEIRO et al., 2005; VIDAL and DIEZ, 2005).

Experimental procedure and methods of pretreatment

To deal with SSEASCM, three laboratory-scale digesters (digester 1, digester 2 and digester 3) consisted of glass reactor with a volume of 500 ml, which were sealed with a rubber stopper and operated at a controlled temperature of 35±1℃, were constructed

Figure 1. gave the schematic diagram of digester apparatus.

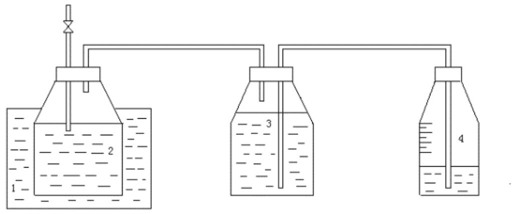


Figure 1. Schematic diagram of digester apparatus.1, water bath;2 digester with SSEASCM;3, gas collector containing a liquid of 2 % (v/v) H2SO4 and 10 % (w/v) NaCl; 4, meter

The digesters were inoculated with 40ml anaerobic seed sludge. The remaining of the working volume was filled with 250 ml sewage sludge, 150 ml excess activated sludge and 50 ml cattle manure. SSEASCM in digester 1 was not pretreated anymore, and was pretreated in digester 2 by ultrasonic in a condition of 100W, 100 kHz, 60min. For the alkali pretreatment, 3.7g sodium hydroxide per100g TS was placed in digester 3 for one week before digestion (MU et al., 2004). The TS and VS of SSEASCM were 7.0% and 36.5%, and the other characteristics are given in Table 2. The mixed substrate was fed from a cooled vessel (-4℃) into the digesters after thawing them in the water-bath at about 70℃.

In this experiment, the effluent and input were increased from 40 ml stepwise until that the COD concentration above 1000mg l^{-1}. The mean organic loading rate (OLR) was 1.6 kg TS m^{-3} d^{-1}, and the initial and last hydraulic retention time (HRT) were 78 days and 53 days.

Table 1. Characteristics of sewage sludge, excess activated sludge and cattle manure

	TS （%)	VS （%）	pH	COD mg/l	NH_4-N mg/l	VFA mg/l
Sewage sludge	6.9	13.5	7.27	2305	62.5	1572
Excess activated sludge	5.2	38.1	7.36	2151	185	2194
Cattle manure	10.7	54.5	7.30	5298	137.5	2999

Table 2. Initial characteristics of SSEASCM in digesters1, 2 and 3

Reactors	pH	COD mg/l	NH_4-N mg/l	VFA mg/l
Digester 1	7.53	2413	127	1755
Digester 2	8.01	4725	166	1902
Digester 3	9.25	5725	310	3218

2.2. Analytical methods

The total volume of the biogas generated was measured by a liquid displacement method, passing through a liquid containing 2 % (v/v) H_2SO_4 and 10 % (w/v) NaCl (BEYDILLI et al., 1998) and methane gas was analyzed once a week using a liquid solution containing 20 g l^{-1} of KOH solution (ERGUDER et al., 2000). The TS and VS in feed samples were measured according to the standard procedures (APHA, 1998). COD, volatile fatty acid （VFA）, ammonium-nitrogen（NH_4-N）and pH were measured for effluent samples. Before analysis, samples were centrifuged in 4000prm for 10 min and the supernatant was used for COD, VFA and NH_4-N measurements. The COD and NH_4-N were measured using a COD meter and

NH_4-N meter of the same series, type WT-1. The pH was determined immediately after sampling to avoid any change due to CO_2 stripping, using a pH meter, type pH 211, HANNA. The VFA concentrations in the effluent samples were measured using the combined titration of the alkalinity (Ren et al., 2004) and expressed as g acetic acid (HAc) l^{-1}. Total heavy metals (Cd, Cu, Cr, Ni, Pb, As, Hg and Zn) in the water samples were determined by ICP-OES. The As was 1.03 mg $l^{-1}$and the Hg was 0.1 mg l^{-1} The concentration of the other was below 0.1 mg l^{-1}. Due to the low concentration, the toxic effects were not obvious and could be ignored (ARMANDO et al., 2007).

3. Results and discussions

3.1. COD variations in effluent produced from the anaerobic digesters

COD was monitored as an indicator parameter of the effluent organic strength. Figure 2 showed the daily variation of COD concentration in effluent for the digesters 1, 2 and 3. The initial COD concentration in these three digesters was 2413, 4725, and 5725 mg l^{-1}, respectively. The initial COD value in the digester 2 and digester 3 was much higher than that in the digester 1, because of the effect of the alkali and ultrasonic pretreatment. The COD value of the effluent in the digester 3 increased to 12500 mg l^{-1} on the 7th day, and then decreased sharply. About on the 30th day the decrease became slow and the COD values of the effluent kept steady at about 950, 1500 and 4150 mg l^{-1} in digesters 1, 2 and 3. After the 45th day the COD value in digester 2 was lower than that in digester 1 and the COD values of the effluent in these two digesters all achieved the required effects below 1000mg l^{-1}. From the 56th day the input increased stepwise from 40 ml per week to 50 ml per week, and the digesters were still stable that the COD values of the effluent in three digesters didn't fluctuate so much, which in digester1 and digester 2 was still lower than 1000mg l^{-1}. But when the input increased to 60 ml per week from the 70th day, the COD values in all the three digesters increased, and was already higher than 1000 mg l^{-1} in digester 1, which was beyond the requirement. And only the digester 2 was not overloaded lastly.

The high level of COD concentration of the effluent in digester 3 was attributed to the strong solution function of the sodium hydroxide to SSEASCM. The degradation rate of COD concentration in digester 2 was the highest at about 89% and in the digester 1 and digester 3 it was 61% and 54%. The ultimate value in digester 3 wasn't in accord with the requirement. According to the digestion data of the control (no treatment) group in the previous literature, if no treatment agent is added to the sludge, the COD removal rate is close to 0 (Fan et al., 2009; Kang et al., 2017; Zhang et al., 2011). This study suggested that co-digestion of sewage sludge and excess activated sludge containing the initial COD concentrations below 3000mg l^{-1} was a effective method with the cattle manure in reduction of COD concentration and the pretreatment by ultrasonic had the best result of all. And the digester 1 took second place. The alkali pretreatment process was not proper for disposal of the low COD concentration sludge in this study according to the ultimate high COD value.

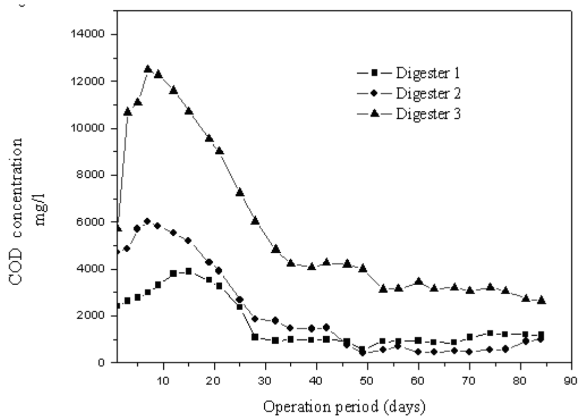


Figure 2. Daily variation of COD concentrations in effluent from digester 1, digester 2 and digester 3

3.2. VFA variations in effluent produced from the anaerobic digesters

The concentration of VFA is an important parameter for the stability of the anaerobic process. VFAs are important intermediate compounds in the metabolic pathway of methane fermentation and cause microbial stress if present in high concentrations. This results in a decrease of pH and ultimately led to failure of the digesters.

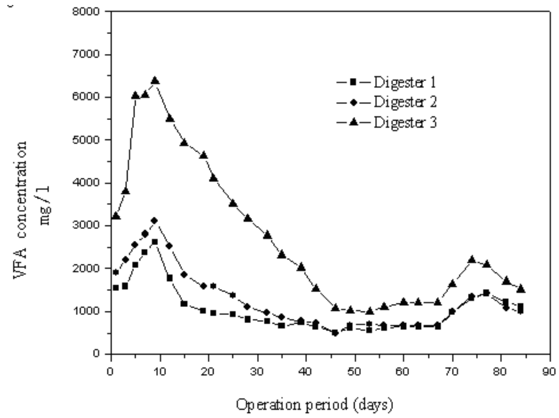


Figure 3. *Daily variation of VFA concentrations in effluent from d digester 1, digester 2 and digester 3*

The initial VFA concentrations in effluent sample were 1536, 1902, 3218 mg l^{-1} in digesters 1, 2 and 3. (Figure. 3). The VFA values in the three digesters reached the highest on the 9th day which were 2621, 3106, and 6363 mg l^{-1}, and then decreased. Organic matter degradation in the initial phase of the fermentation caused high VFA concentration (Oaman and Delia, 2005). The VFA value in digester 3 did not decrease on the 45th day and stayed at about 1100 mg l^{-1}. Before the 45th day the VFA value in digester 3 was much larger than that in digester1 and 2 owing to the pretreatment of alkali. The VFA value in digesters 1 and 2 did not decrease so quickly from the 32nd day and then stayed at about 600 mg l^{-1} on the 45th day. On the 56th day the input increased stepwise from 40 ml per week to 50 ml per week, and the digesters were still stable. But when the input increased to 60 ml per week on the 70th day, the VFA values in all of the three digesters increased due to the accumulation of the VFA, similar with COD variation. The high level of VFA concentration in digester 3 was ascribed to the effect of the alkali pretreatment that hydrolyzed and decomposed lipids, hydrocarbon, and protein into smaller soluble substances.

3.3. pH variations in effluent produced from the anaerobic digesters

The pH of the effluent samples was in accord with the concentration of VFA measured in all digesters. The variation of pH profiles of the whole time was provided in Figure 4. The initial pH values of the effluent from digesters 1, 2 and 3 were 7.48, 7.32, and 8.53. The pH value of digester 3 was higher than that in the digesters 1 and 2 throughout the experiment due to the sodium hydroxide added during the pretreatment and the low organic matter in the materials. The lowest pH values were 6.72, 6.65, and 7.40 on the 7th day in the three digesters, according with the variation of VFA. The pH value in digester 3 was always lower than the initial value, and was between 8.53 and 7.40 during the experiment. The distinction of pH values in the digesters 1 and 2 was not great and at the most and last time of the experiment the pH value in digester 2 was lower than that in the digester 1. It revealed that the increase of the input didn't have big effect on the pH value of the three digesters, due to the buffering capacity of SSEASCM.

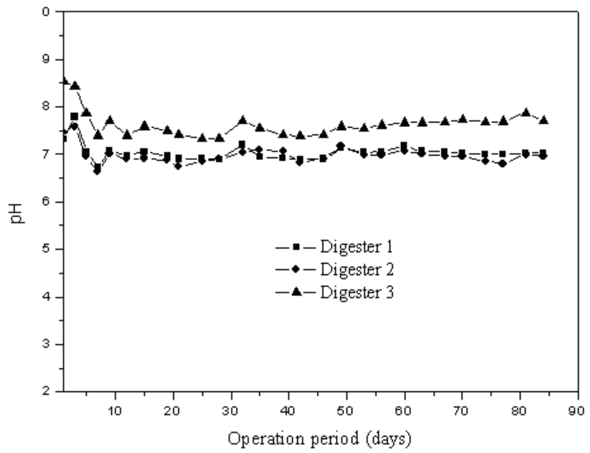


Figure 4. *Daily variation of pH concentrations in effluent from digester 1, digester 2 and digester 3*

3.4. NH_4-N variations in effluent produced from the anaerobic digesters

The results of the NH_4-N concentrations measured in effluent samples throughout the experiment from the three digesters were given in Figure 5. The initial NH_4-N concentrations measured in effluent were 127, 166, and 310 mg l^{-1} in digesters 1, 2 and 3. The highest NH_4-N concentrations were 396, 335 and 522 mg l^{-1} through mineralization of organic compounds. The result turned out that the NH_4-N concentrations in digester 3 was higher than that in digesters 1 and 2 since digester 3 had the high organic matter attributed to the addition of alkali which was in favor of the degradation of the compound in SSEASCM. In addition, the NH_4-N concentration in digester 2 was lower than that in digester 1 after the 7th day, similar with pH value.

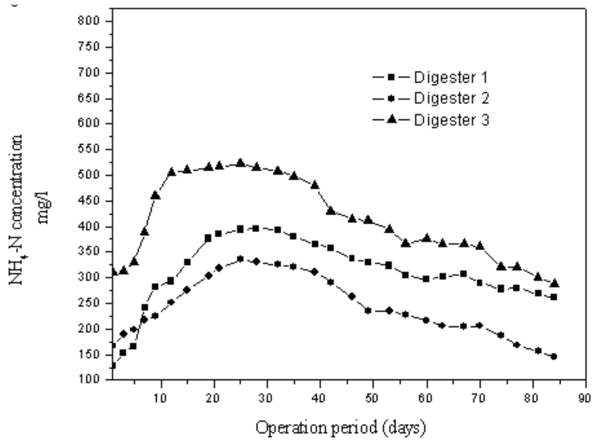


Figure 5. Daily variation of NH4-N concentrations in effluent from digester 1, digester 2 and digester 3

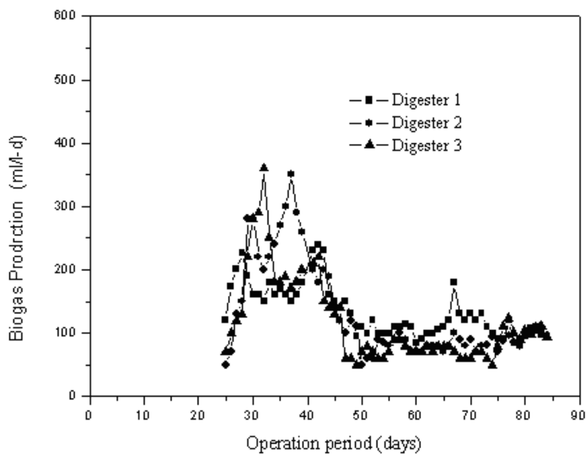


Figure 6. Daily variation of biogas production during the experiment in digester 1, digester 2 and digester 3

3.5. Biogas production in the anaerobic digesters

The quantity of biogas in digesters 1, 2 and 3 were provided in Figure 6. It showed that there were two peak values in all digesters. In digester 1 the first peak value appeared on the 28th day at 226 ml $(l\text{-}d)^{-1}$ and the second appeared on the 42nd day at 240 ml $(l\text{-}d)^{-1}$; in digester 2 the first peak value appeared on the 30th day at 280 ml $(l\text{-}d)^{-1}$ and the second appeared on the 37th day at 350 ml $(l\text{-}d)^{-1}$; in digester 3 the first peak value appeared on the 32nd day at 360 ml $(l\text{-}d)^{-}$ and the second appeared on the 42nd day at 220 ml $(l\text{-}d)^{-1}$. The difference time when the peak value appeared in the three digesters was attributed to the different pretreatment methods. On the 45th day the biogas productions were steady and digester 1 had the highest yield (more than 100 ml $(l\text{-}d)^{-1}$). When the input increased on the 56th day, the biogas production also increased in digester 1, but not in evidence. The yields of the gas were stably in all digesters at the residual experiment

Totally, biogas production in digester 1 was correspondingly smooth and generated relatively more methane compared with digester 2 and 3.

4. Conclusions

The results of this study showed that co-digestion of the pretreated SSEASCM was an effective method in COD removal, VFA reduction and pH adjustment in a condition of the low initial COD concentration.

Compared with the sludge containing high organic matter, SSEASCM was more difficult to dispose. The maximum COD removal rate was about 89% in digester 2 and 61%, 59% in digesters 1 and 3. The VFA reduction rate was the highest in digester 3, no difference between in digesters 1 and 2, because of the low initial VFA concentration in these two digesters. The pH values were always smooth in three digesters due to the strong buffering capacity and the variation of the NH_4-N concentrations could be tolerated by every digester.

As a result, the alkali pretreatment process in this study was not proper for disposal of SSEASCM according to the ultimate COD value; the ultrasonic pretreatment process was most effective on the COD removal; as all factors were concerned, the digester 1 had the best effect that the ultimate COD decreased to the required degree, the rate of biogas production was stable and the biogas productivity was the highest. In the condition of the low COD concentration, the pretreatment process for SSEASCM used in this study had effect on some extent and co-digestion of SSEASCM can achieve the expectant requirement.

As a whole, the pretreatment process, especially the alkali pretreatment process, had no significant influence on the degradation of low COD sludge in the whole experiments under different conditions. Owing to strong solution function of the sodium hydroxide and ultrasonic to SSEASCM, the dissolved COD in digester 2 and 3 was higher than it before pretreated compared with it in digester 1. It could be found that the yield of biogas in these two digesters was not larger than it in digester 1 and the time of CH4 production was not earlier from figure 6 So it can be deduced that the rate-limiting step of the co-digestion in low COD in this experiment was methanogenesis not the hydrolysis as most documents described in high COD containing processing and the sequent study in this domain should focus on the step of methanogenesis to improve the processing.

Appendix A. Nomenclature

COD	dissolved chemical oxygen demand
HAc	acetic acid
HRT	hydraulic retention time
NH_4-N	ammonium-nitrogen
OLR	organic loading rate
SSEASCM	sewage sludge with the excess activated sludge and cattle manure
TS	total solids
VFA	volatile fatty acid
VS	volatile solids

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