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Co-Digestion Treatment of Municipal Biomass Waste: Effects of Inhibitory Factors on the Reactor

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This paper investigated the co-digestion system stability of municipal biomass waste and the effects of inhibitory factors. It takes the mixed urban biomass of kitchen, fruits and vegetables waste and municipal sludge with the feed ratio of 1:1:1 as the research subject, and studies the influence of organic load and residence time on the stability and biogas production performance of the co-digestion system. Specific methanogenic activity is employed to test the microbial activity of anaerobic system and investigate the inhibition of VFA concentration and ammonia nitrogen concentration on microbial activity. Studies show that within the load range of 3.0-13.0 kg VS·$(m^3 \cdot d)^{-1}$, the concentration of VFA in the discharge material shows an upward trend with the increase of organic load. However, due to the high alkalinity of the reactor, the reactor operates stably in the whole operation process without acidification and other instability phenomena. With the increase of the load, the biogas organic product production rate gradually decreases, indicating that the biomass gas production capacity is inhibited with the increase of the load. The inhibitory factors of the anaerobic digestion process are studied through the activity experiment of producing methane from sludge in the reactor, and the semi-inhibition concentration of organic acid and ammonia nitrogen on the anaerobic digestion process of biomass waste is obtained, among which the value of IC50 for acetic acid to anaerobic digestion is 2150 mg/L, for propionic acid is 1850 mg/L and for ammonia nitrogen is 4500 mg/L. In the actual reactor operation, the control of organic acids is the primary task. The results of this study provide technical supports for the stable operation of urban biomass co-digestion process and the control of inhibitory factors.

1. Introduction

Anaerobic digestion can effectively reduce organic pollutants and realize the transformation of organic resources, providing a new technological choice for the treatment of urban biomass waste (Liu et al., 2018). In the digestion process, co-digestion has become one of the main choices, mainly because of its advantages as follows: significant differences in organic components and element composition of different biomass wastes, for example, the C/N ratio of municipal sludge is about 8-10, while the C/N ratio of kitchen waste is about 15-20. The C/N ratio of municipal sludge digestion alone is low, resulting in instability of the system. Co-digestion can improve the balance of nutrients and water in the whole reaction process, which is conducive to the stability of the system. Secondly, the co-digestion of different substances with significant economic benefits is also conducive to the full use of equipment. Zupančič compared the digestion process of municipal sludge alone and the separation and co-digestion process of municipal sludge and municipal household garbage organic matter, and the results showed that the co-digestion could effectively improve the system's biogas production capacity, which increased by 80% after the co-digestion (Zupančič et al., 2008). Other studies have shown that the co-digestion of municipal sludge and kitchen waste, municipal sludge and municipal biomass waste, livestock excrement and municipal biomass waste have all achieved good digestion efficiency and biogas production capacity (Liu et al., 2012; Silvestre et al., 2011; Sosnowski et al., 2008).
Due to the different anaerobic digestion process and feeding properties, the operating conditions and system efficiency of the anaerobic digestion system are also different. In recent years, studies on the co-digestion process of municipal biomass waste and other solid organic waste have been carried out at home and abroad, which mainly focused on the effects of various technological parameters on digestion efficiency, including

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properties of digested material, total solid (TS), volatile solid (VS), reactor temperature, hydraulic retention time (HRT), organic loading rate (OLR), etc. (Hartmann et al, 2006).

In practical application, when the concentration of organic matter in the feed is constant, the volumetric biogas production rate of the reactor (that is, the biogas production per unit volume of the reactor, which reflects the biogas production capacity of anaerobic digestion of the reactor, is an evaluation index of anaerobic digestion performance of the reactor) increases with the increase of organic load within a certain range. At the same time, as the residence time of the material is shortened, the biogas yield per unit organic matter (that is, the biogas yield per unit organic matter in the feed, which is the evaluation index of the anaerobic digestion performance of the substrate) of the material is reduced, which means the degradation rate of the organic matter is reduced. When the organic load of the reactor is further increased, acid accumulation and free ammonia accumulation will occur, leading to a decrease in the stability of the reactor and even the failure of the reactor operation (Qiao et al., 2010; Mata-Alvarez et al., 2000; Rughoonundun et al., 2010; Wang et al., 2010; Qiao et al, 2011). In the previous studies, there were few studies on the stability of mixed digestion system of typical biomass waste in China, and the influence of inhibitory factors was not systematically reported. Therefore, this study studies the stability of the mixed digestion process of typical biomass wastes in China (including kitchen waste, fruits and vegetables waste, sludge, etc.), and analyzes the methods to maintain the system stability from two aspects of avoiding the accumulation of organic acids and free ammonia.

In this study, the stability of urban biomass co-digestion process was studied based on a pilot reactor. The stability of the reactor in the process of increasing organic load was mainly investigated. Three inhibitory substances, acetic acid, propionic acid acetate and ammonia nitrogen, were selected to investigate the influence of different concentrations on the stability of the co-digestion system.

2. Materials and methods

2.1 Biomass waste

The municipal biomass waste used in this study included kitchen waste, fruit and vegetable waste and municipal sludge generated from centralized sources. Kitchen waste was taken from the student canteen of Tsinghua University, the main components of which were rice, steamed bread, vegetables, meat and so on. Fruit and vegetable waste was taken from the wholesale market of agricultural products in the north of Huilongguan, Beijing, the main components of which were perishable fruits and vegetables, and fruits and vegetables which were easy to produce garbage. And municipal sludge was from Beijing North Xiaohe river sewage treatment plant. After removing sundries, kitchen, fruit and vegetable waste were broken by hammer crusher to obtain slurry material with particle size less than 1 cm, and then mixed it with sludge. The mixing ratio of the three materials was 1:1:1. The parameters of the crushed and mixed municipal biomass waste were as follows: the moisture content was (85.2±0.7) %, the organic matter content was (115.4 + / - 8.4 g) /kg, protein, fat, cellulose and polysaccharide content were 10.3%, 19.9%, 16.2% and 53.6%, respectively.

2.2 Digestion system

The total volume of the pilot reactor used for anaerobic digestion was 2 m^3, in which the effective volume was 1.6m^3, and the inner diameter was 1 m. Through water bath jacket heating, mechanical stirring and sealing, screw pump was used to feed, and the biogas produced in turn go through the collection pipe, condensate bottle, gas wet flow meter into the biogas collection system.

The inoculated sludge used in the experiment was taken from the sludge anaerobic digestion device of Beijing Xiaohongmen sewage treatment plant. The TS and VS of the inoculated sludge were 25.6 g /kg and 11.2g /kg respectively. The inoculated sludge showed good activity and the maximum methane production rate of the sludge was 0.5g CODCH4 / (g VSS•d). When the reactor start up, 1.6 m^3 of inoculation sludge was pumped into the reactor through screw pump, and the reactor operated under the condition of the medium temperature (35 + 2)°C, with stirring intensity of 100 r/min and stirring for 15 min every 2 h.

2.3 Specific Methanogenic Activity

To determine the digestion sludge activity in the reactor, specific methanogenic activity (SMA) tests were conducted in glass bottles of 250 mL at 35°C. The inoculum sludge was obtained from the digestion reactor. Each bottle was fed with 150 mL of inocula, and the sub-inoculation ratio was 3:1. Distilled water was added to the bottle to obtain 180 mL of inocula and each sample was tested in triplicate. After inoculation, the pH was adjusted to 7.5 by using 1 M sodium hydroxide or 1 M hydrochloric acid. The headspace of each bottle was flushed with nitrogen for 30 s, capped with butyl rubber plugs, and sealed with aluminum ring seals. The absolute methane composition was analyzed by gas chromatography (Shimadzu GC-2010) with a thermal conductivity detector and a Porapak N column. The effects of VFA and NH4+-N were investigated by using this test, and the dosage of these inhibitory components was shown in Table 1 as follows:

Table 1: Dosage of inhibitory components

No.	Acetic acid (mg/L)	Propionic acid(mg/L)	NH_3-N(mg/L)
1	0	0	0
2	300	0	0
3	600	0	0
4	1000	0	0
5	1200	0	0
6	1800	0	0
7	2500	0	0
8	4000	0	0
9	5000	0	0
10	6000	0	0
11	7000	0	0
12	9000	0	0
13	1200	500	0
14	1200	1500	0
15	1200	3300	0
16	1200	4800	0
17	1200	6800	
18	0	0	700
19	0	0	1400
20	0	0	2100
21	0	0	2800
22	0	0	3500
23	0	0	4200
24	0	0	4900
25			7000
26			8000

2.4 Methods of analysis

The analysis of TS, VS, SS, and VSS was based on Standard Analytic Methods (APHA, 2005). The biogas volume was measured with a wet-type gas flow meter. CH4 and CO2 contents of the biogas were monitored by gas chromatography (Shimadzu GC-2010) with a thermal conductivity detector and RT-Q plot column. The VFAs were measured by gas chromatography (Shimadzu GC-2010) with a flame ionization detector and GDX-102 column. The different VFAs included acetic, propionic, iso-butyric, butyric, iso-valeric, and valeric acids.

3. Results and discussion

3.1 Stability of co-digestion system

The single-phase multi-stage CSTR reactor has been running steadily for 200 consecutive days. The operation of the reactor is shown in Table 2. The reactor start-up load was 3.0 kg COD/m3•d, which gradually increased to 13.0 kg COD/m3•d for stable operation. With a maximum load, the reactor stays for 12d and operates in a good state.

The four parameters including pH value, VFA, ammonia nitrogen and alkalinity adopted in this study were used to evaluate the stability of anaerobic digestion process, as shown in Table 2. PH value is one of the evaluation indexes for anaerobic digestion stability, and the pH range suitable for the growth of methanogens in anaerobic digestion is very narrow, generally ranging from 6.5 to 8.2 (Li et al., 2001). It can be seen from the data in Table 2 that during the reactor operation, the discharge pH remains stable, ranging from 7.42 to 7.55, which is suitable for microbial growth.

VFA was an important intermediate product in the anaerobic digestion process, the concentration of which reflected the metabolic process of organic matter. During the reactor operation, with the increase of OLR, the VFA concentration of the reactor discharge increased correspondingly. When the OLR reached 13.0 kg $VS\cdot(m^3\cdot d)^{-1}$, the corresponding VFA was only 1250 $mg\cdot L^{-1}$, however, no acidification or other instability occurred in the reactor with this VFA value.

With the increase of organic load, ammonia nitrogen concentration in the reactor increased to 3123 $mg\cdot L^{-1}$ at the maximum load. Different researchers have found that the anaerobic system's tolerance to ammonia nitrogen varied widely, McCarty noted that ammonia concentration of 100 $mg\cdot L^{-1}$ can inhibit the anaerobic digestive system supplemented with acetic acid salts (Rittmann and McCarty, 2001). Some studies have found that when ammonia nitrogen concentration reached 3000 mg·L^{-1}, the domesticated anaerobic digestion microorganisms can react normally and show no inhibition. In this study, the higher ammonia concentration also did not lead to the instability of the system. It is found that ammonia nitrogen contained in liquid phase system had two forms, free ammonia (NH3) and ammonium ion (NH4+), but it is generally believed that free ammonia is the main inhibitory factor in the anaerobic digestion system. The equilibrium between ammonia and ammonium ions is shown as follows:

$$NH_4^+ = H^+ + NH_3$$

At 30 °C, the reaction equilibrium constant for this reaction is 5.56×10^{-10}, therefore:

$$pH = 9.26 + \lg\frac{[NH_3]}{[NH_4^+]}$$

The calculated concentration of free ammonia in the system under different operating loads of the reactor was shown in Table 2, 27-45 mg·L^{-1}. The concentration of free ammonia was low, so the reactor did not become unstable.

VFA / alkalinity can be used to evaluate the stability of anaerobic digestive system. Studies showed that the system could be determined to be stable when the value of VFA/ alkalinity was less than 0.3 (Callaghan, 2002). During the whole operation, the VFA/ alkalinity of the reactor discharge was far less than 0.3. Although VFA reached 1250 mg·L^{-1} when the reactor was at its highest load, the alkalinity of the system is still high since urban biomass waste, especially kitchen waste, contained a large number of strongly alkaline cations, so that the VFA/ basicity value is relatively small. Therefore, it can be seen that high alkalinity provided a good buffering capacity for the anaerobic digestion system, thus ensuring that the anaerobic digestion system has a good impact resistance capacity.

Table 2: Parameters of reactor operation

No.	I	II	III	IV	V	VI
Organic loading rate /kg VS(m3·d)$^{-1}$	3.0	5.0	7.0	9.0	11.0	13.0
HRT/d	52	31	22	17	14	12
Volumetric biogas production / m3·(m3·d)$^{-1}$	2.17	3.53	4.70	5.68	6.45	7.13
Biogas yield / m3·kgVS^{-1}	0.72	0.71	0.67	0.63	0.59	0.55
pH	7.42 ±0.03	7.51 ±0.05	7.34 ±0.04	7.55 ±0.08	7.5 ±0.04	7.42 ±0.03
VFA / mg·L^{-1}	241 ±41	280 ±69	605 ±79	882 ±118	954 ±154	1250 ±173
NH4+-N / mg·L^{-1}	2012 ±126	1839 ±98	2199 ±202	2284 ±224	2321 ±197	2766 ±224
Alkalinity / gCaCO3·L^{-1}	10.9 ±0.4	11.4 ±0.4	12.1 ±0.8	12.8 ±1.0	14.7 ±0.6	15.3 ±0.4
VFA / alkalinity	0.02	0.02	0.05	0.07	0.06	0.08
Free ammonia / mg·L^{-1}	27	33	26	45	40	40

3.2 Inhibitory effect

As shown in Table 2, when the load increased to 13.0 kg COD/m3•d, the reactor did not experience instability such as acidification. However, as the load increased, it can be seen that organic product yield of biogas gradually decreased, indicating that with the increase of load, although the reactor did not become unstable, its gas generation capacity was inhibited. Therefore, this paper studies the inhibitory factors and conducts an experimental analysis on the effects of acetic acid, compound acid of acetic acid / propionic acid, and ammonia nitrogen on the activity of methanogenic generated from sludge. Experimental parameters are shown in Table 1.

The activity results of methanogens (determined by Specific Methanogenic Activity, and represented by methane production rate) under different inhibitory conditions are shown in Figure 1 and Figure 2. The inhibitory effect of organic acids and ammonia nitrogen on methanogens is biological equilibrium inhibition, that is, the inhibitory process is non-reactive toxic and reversible. This inhibition process conforms to the law of indirect competition and can be simulated by dose-effect curve, as shown in Figure 1 and Figure 2. The equation parameters of the simulated curve are shown in Table 3.

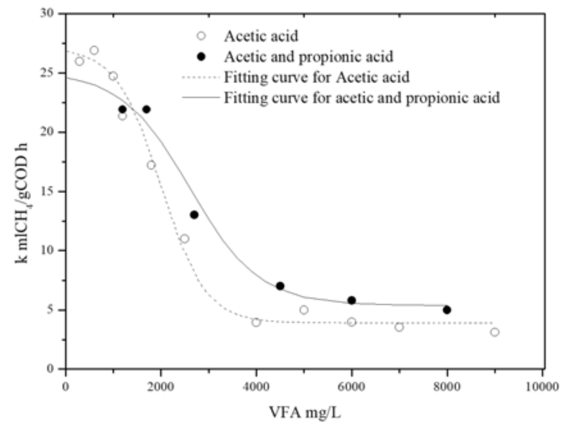

Figure 1: Acetic acid inhibition and synergistic inhibition of acetic acid / propionic acid

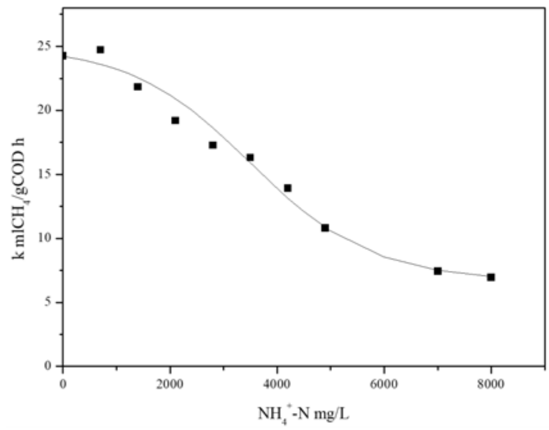

Figure 2: Fitting diagram of ammonia nitrogen inhibition curve

Table 3: Inhibition curve fitting results

Fitting formula: y=A2 + (A1-A2)/(1 + exp((x-x0)/dx))						
	Acetic acid		Acetic and propionic acid		NH_4^+-N	
R2	0.921		0.936		0.901	
	values	standard deviation	values	standard deviation	values	standard deviation
A1	27.1	3.1	25.1	1.5	25	0.5
A2	3.9	0.6	5.4	1	6.7	0.9
x0	1997	192	2614	693	3512	719
dx	461	99	721	102	1132	210

The curve fitting results in Table 3 show that the fitting correlation coefficient is relatively high. In the dose-effect curve, the inhibitory effect of the inhibitor can be characterized by the semi-inhibitory concentration IC50, which refers to the drug dose that can cause the inhibitory effect on 50% of the subjects. For methanogens, the higher the IC50, the higher the inhibitory threshold for such inhibitors.

As shown in Figure.1, when acetic acid concentration was less than 1200 mg/L, it had little influence on methane-producing activity of microorganisms. When acetic acid concentration was greater than 1200 mg/L, methanogenic activity of microorganisms decreased sharply. When acetic acid concentration was more than 4000 mg/L, methanogenic activity of microorganisms was basically completely inhibited. The semi-inhibitory concentration of acetic acid on methanogens in the reactor was 2150 mg/L. When the concentration of acetic acid was set at 1200mg/L, the synergistic inhibitory effect of propionic acid was as follows: when the concentration of propionic acid was less than 500 mg/L, the methanogenic activity of microorganisms was less affected. When propionic acid concentration was greater than 500 mg/L, methanogenic activity of microorganisms decreased sharply until completely inhibited. When acetic acid concentration was 1200 mg/L, the semi-inhibitory concentration of propionic acid on methanogens in the reactor was 1850 mg/L. By comparing the inhibition of acetic acid and the co-inhibition of acetic acid / propionic acid (see Figure 1), it can be found that, in the low concentration range, acetic acid / propionic acid has a synergistic inhibition on the anaerobic digestion process, so it is of great significance to control the production of propionic acid in the anaerobic digestion process.

Figure 2 shows that when ammonia nitrogen concentration was less than 1400 mg/L, it had little influence on methanogenic activity of microorganisms. When the concentration of ammonia nitrogen was greater than 2100 mg/L, the methanogenic activity of microorganisms dropped sharply and had obvious inhibitory effect. The semi-inhibitory concentration of ammonia nitrogen on methanogens in the reactor was 4500 mg/L. As the C/N of mixed biomass waste in this study was relatively high, the actual ammonia nitrogen concentration in the reactor measured in the field was between 1839 mg/L and 2766 mg/L, far lower than this concentration. Therefore, in the actual reactor operation, the control of organic acids is the primary task.

4. Conclusions

According to the study on the co-digestion of the mixed urban biomass of kitchen, fruits and vegetables waste and municipal sludge with the feed ratio of 1:1:1 based on a pilot reactor, it can be found that within the load range of 3.0-13.0 kg VS·$(m^3 \cdot d)^{-1}$, the effect of organic load on ammonia concentration and alkalinity was not obvious. With the increase of organic load, the concentration of VFA in the reactor discharge showed an upward trend. However, due to the high alkalinity and strong buffering capacity of the reactor, all the indicators of the reactor discharge remained stable and within the normal range during the whole operation, and the reactor operation was stable.

Although the system is in a stable state, the methane-producing rate of organic product of the system is affected by these inhibitory factors. By studying the inhibitory factors, the semi-inhibition concentration of organic acid and ammonia nitrogen on the anaerobic digestion process of biomass waste was obtained, among which the value of IC50 for acetic acid to anaerobic digestion is 2150 mg/L, for propionic acid is 1850 mg/L and for ammonia nitrogen is 4500 mg/L. All provides guidance for the operation control and inhibition recovery of the reactor.

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