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Anaerobic digestion of kitchen wastes in a single-phased anaerobic sequencing batch reactor(ASBR) with gas-phased absorb of CO₂

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Abstract: The performance of the single-stage anaerobic digestion of kitchen wastes was investigated in an anaerobic sequencing batch reactor(ASBR) with gas-phased absorb of CO₂. The ASBR was operated at four chemical oxygen demand(COD) loading rates, 2.8, 5.1, 6.2 and 8.4 g/(L·d) respectively. The COD loading rate was increased with the TS concentration and HRT changing. At maximum COD loading rate of 8.4 g/(L·d), the COD, total solid(TS) removal rate and methane gas yield were 69%, 68% and 2.5 L/(L·d) respectively. The operation of the reactor with gas-phased absorb of CO₂ was stable in spite of the low pH(2.6—3.9) and high concentration of TS(142 g/L) of input mixture. The output volatile fatty acid(VFA) concentration was between 2.7—4.7 g/L and had no inhibition on the methanogenic microorganism. The reactor without gas-phased absorb of CO₂ became acidified when the total COD loading rate was increased to 5.1 g/(L·d). Stoichiometry of the methanogenesis for kitchen wastes showed a considerable amount of alkaline will be required to keep pH in the appropriate range for the methanogenic microorganism based on theoretical calculation. Gas-phased absorb of CO₂ effectively reduced the alkaline consumption, hence avoided excessive cation into the reactor.

Keywords: kitchen wastes; methanogenesis; gas-phased; CO₂

Introduction

There is an ever-increasing quantity of kitchen wastes with the increasing population and living conditions in China. Kitchen wastes have a high proportion of 50%—70% among municipal solid wastes. Taking the city of Shanghai for example, the generation of kitchen wastes amounts to 3000000 tons per year, taking up 58.55% of municipal solid wastes(Fang, 1999; Wang, 2001). Kitchen wastes contain a large amount of volatile organic matter, which is the main source of decay, odor and leachate in collection and transportation(Diggelman, 2003). Incineration is not suitable for kitchen wastes due to its high moisture and low heat value. Currently, most kitchen wastes have been landfilled together with other wastes, resulting in various problems such as stink, toxic gases, and leachate so on. Moreover, with the rapid development of urbanization, the shortage of utilizable land for landfill urges the treatment of kitchen wastes to turn to other methods. Anaerobic digestion is envisaged to be an important addition to the list of options available for managing kitchen wastes(Moody, 2001; Wang, 1997).

Due to the high moisture and high organic matter of kitchen wastes, the wet two-stage anaerobic digestion is usually used to recover methane from food wastes. Most studies have involved a solid waste reactor and a high-rate anaerobic wastewater reactor(Han, 2002a; 2002b; Raynal, 1998; Cho, 1995; Wang, 2002; 2003; Xu, 2002; Rajeshwari, 2001). However, the single-stage anaerobic digestion is rarely used for wastes. In fact, about 90% of the full-scale plants currently in use in Europe for anaerobic digestion of the organic fraction of municipal solid wastes and biowastes rely on one-stage systems from economical

considerations(De Baere, 2000). Moreover, a one-phased system is simpler and can yield at least the same yield biogas(Veturria, 1995).

During the process of single-stage anaerobic digestion for kitchen wastes, it is especially important to realize the balance of acidogenic and methanogenic process because kitchen wastes include high concentration of organic matter that can be rapidly converted to VFA at the initial stage of anaerobic digestion and produce CO₂ as well(Cho, 1995). Low pH usually results from two types of acidity including carbonic acid(H₂CO₃) and volatile organic acids(VFA) that are produced during the biological reaction. The addition of alkalinity is necessary to keep normal pH. Usually normal anaerobic digestion system has low concentration of VFA, and thus requirement of alkalinity is to neutralize high concentration of H₂CO₃ that is caused by high partial pressure of CO₂(Spiece, 2001; Nishimura, 1996). To neutralize H₂CO₃, all kinds of alkaline solution is added into the system, including NaOH, NaHCO₃, Ca(OH)₂ and so on. However alkaline solution brings a large amount of cations (sodium ion) into the system. Higher concentration of sodium ion could readily affect the activity of microbes and interfere with their metabolism(Feijoo, 1995; Chen, 2003). Furthermore, food wastes itself contain high levels of sodium salt. So it is especially necessary to take measures to both buffer pH and bring no cations into the system.

For the small variation of pH, the methanogenic reactor was usually fed continuously. There is little information for the use of ASBR for the kitchen wastes. Compared to continuous flow reactor, ASBR has many advantages such as relatively easy operation, flexibility, small land occupation, little mechanical equipment, and the fact that it uses the

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same vessel for reacting and settling. ASBR could be used to treat kitchen wastes if appropriate methods were taken to balance the acidogenesis and methanogenesis at relatively high organic loading rate.

In this study, an attempt has been made to use a single-stage ASBR for kitchen wastes. Gas-phased absorb of CO_2 was applied to the digester to reduce the acidity. This article reports the possibility of the single-stage ASBR with gas-phased absorb of CO_2 for kitchen wastes.

1 Materials and methods

1.1 Origin and characteristics of the kitchen wastes

Kitchen wastes were taken from the student restaurant located in Shanghai Jiaotong University. The obtained kitchen wastes mainly contained cooked rice, vegetables, meat, eggs, potatoes and salt. Table 1 shows the major characteristics of the kitchen wastes. The content of TS, VS and TOC was 20%, 19% and 7.2%, respectively, which indicated that the kitchen wastes contained high concentration of organic matter. The ratio of TOC, total nitrogen, and total phosphate was 100:4.61:0.25, and this showed it was necessary to add the nitrogen source and phosphorous source during the anaerobic digestion of the kitchen wastes. The pH in Table 1 represents the mean value of feeding kitchen wastes. It was low and only 3.9 due to the natural acidification. The kitchen wastes contained proteins of 13%, lipids of 10%, and 70% carbohydrates based on COD.

The kitchen wastes were collected once a week. The collected wastes were homogenized in a blender. During smashing, tap water was added to justify the water content in the final mixture in the range of 85.8% to 96.7% based on the feeding requirement. The smashed mixture was kept at 4°C before feeding.

Table 1 Characteristics of the kitchen wastes

TS, %	20
VS, %	19
TOC, %	7.2
VFA(calculated as acetate, g/L)	3.6
Total nitrogen, %	0.33
Total phosphate, %	0.018
C/N/P	100:4.16:0.25
pH	3.9
Proteins(based on COD), %	13
Lipids(based on COD), %	10
Carbohydrates(based on COD), %	70

1.2 Experimental setup

Anaerobic digestion of kitchen wastes was conducted in two parallel-operated SBR reactors. One reactor was designed with CO_2 adsorb in headspace. The other was designed without CO_2 adsorb and served as the control reactor. The two digesters had the same dimensions with working volume of 2 L and operated under the same conditions.

Scheme of the single-stage anaerobic digestion process

with gas-phased absorb of CO_2 is shown as Fig. 1. One part of gas produced in the reactor was introduced into a CO_2 absorb container(A1) containing 5% NaOH, and then was pumped back to the reactor. The other part of the gas passed through another CO_2 absorb container(A2) and to the final methane gas (CH_4) collector. 5% NaOH solution was refreshed when its pH dropped below 10. For the control reactor without gas-phased absorb of CO_2 , gas was directly either recycled back to the digester serving as a mixer or collected in the final CH_4 collector.

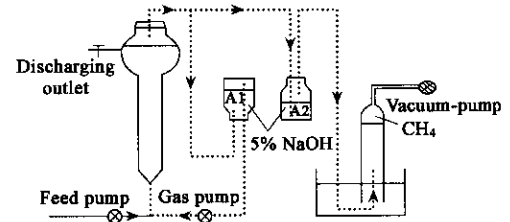


Fig. 1 Scheme of the single-stage anaerobic digestion process with gas-phased absorb of CO_2

1.3 Start-up of the reactor

Activation of obtained anaerobic sludge was performed in one digester. The reactor was inoculated with the mesophilic digester sludge obtained from the sludge digester of Songjiang wastewater treatment plant, located in Shanghai, China. The sludge was firstly cultivated with a synthetic medium with glucose and sodium acetate as carbon source, ammonium chloride as nitrogen source, and dipotassium hydrogen phosphate as phosphorus source. The ratio of COD, N and P was 200:5:1. Fresh synthetic medium with a COD of 25000 mg/L was fed once a day. The HRT was controlled at 5 d. About 2 g NaHCO_3 , and 2 ml mineral solution were added into each liter of medium. The mineral solution contained the following compounds(g/L): EDTA(5), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (2.2), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.6), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (5.0), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (5.0), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (1.1), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (5.5), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1.6), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (5.0), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.1) (Zhang, 2003). The sludge concentration of MLSS (mixed liquor suspended solid) was maintained at 10 g/L. When about 87% of the fed COD was converted to CH_4 at a loading rate of 5 g/(L·d), the start-up period was considered as complete. The active anaerobic sludge was divided into two parts and seeded into the two parallel digesters for sequential experiments.

1.4 Operation

Smashed kitchen wastes were pumped upwards into the digesters following the successful start-up. The digesters were operated sequentially at a cycle of 24 h, in which 2 h for settling, 15 min for discharging, 15 min for feeding and 22.5 h for reacting. During slurry discharging, nitrogen gas was filled into the headspace of the reactors to avoid the vacuum in the reactors. The amount of feeding wastes was initially

controlled as 0.3 L/d and changed gradually based on the alternation of the loading rate(as indicated in later Table 3). The loading rate was increased with the TS concentration and HRT changing. No buffer solution was added into the digester with the gas-phased absorb after the start-up, while NaHCO₃ was still released into the control reactor to control the pH. The two sets of systems were operated in the 35—37°C room. The whole experiment continued 209 d.

1.5 Analytical methods

pH, TS, VS, alkalinity, COD and total phosphate were analyzed according to the standard method for the examination of water and wastewater(APHA, 1995). Total organic carbon (TOC) was measured with TOC analyzer(a multi N/C 3000 analyzer, German). Total nitrogen was estimated with the Kjeldahl method. Kjeldahl nitrogen was measured based on acid hydrolysis of the insoluble organic nitrogen and total Kjeldahl nitrogen (TKN) titration procedure with nitrogen analyzer(BüCHI, Digestion Unit K-424; BüCHI, distillation Unit B-324) (APHA, 1995). Measured Kjeldahl nitrogen multiplied by 6.25 to give the protein content (APHA, 1995). Lipids concentration was determined gravimetrically after extraction of lipids by petroleum ether according to the Soxhlet extraction method (Nielsen, 2002a; 2002b). Carbohydrates in the wastes were determined according to the

phenol-sulphuric acid method (Nielsen, 2002). The total VFA was titrated according to Anderson and Yang(Anderson, 1992).

2 Results

2.1 Activation of anaerobic sludge

Fig.2 shows the performance of the digester during the activation of anaerobic sludge. The synthetic medium was firstly fed into the digester with the COD loading rate of 5 g/(L·d) (Fig. 2a). However, pH in the reactor decreased quickly from 6.7 to 6.2, as indicated in Fig. 2b. This showed obtained anaerobic sludge could not stand the COD loading rate of 5 g/(L·d). So the COD loading rate was adjusted to 2.5 g/(L·d). Under this loading rate, pH rose again to 6.8 after 3 d and kept in the range of 6.8 to 7.3, 60%—70% of COD was converted into CH₄, and CH₄ yield was stable at about 0.2 L/(L·d)(Fig.2c and Fig.2d). The COD loading rate was increased back to 5 g/(L·d) on day 15 when pH, COD removal rate and CH₄ yield was stable. pH dropped lightly, COD removal rate and CH₄ yield almost increased linearly with the COD loading rate increase and kept stable on day 30. About 87% of COD removal rate and 1.25 L/(L·d) of CH₄ yield was achieved. In addition, no buffer solution was added into the digester after the day 30.

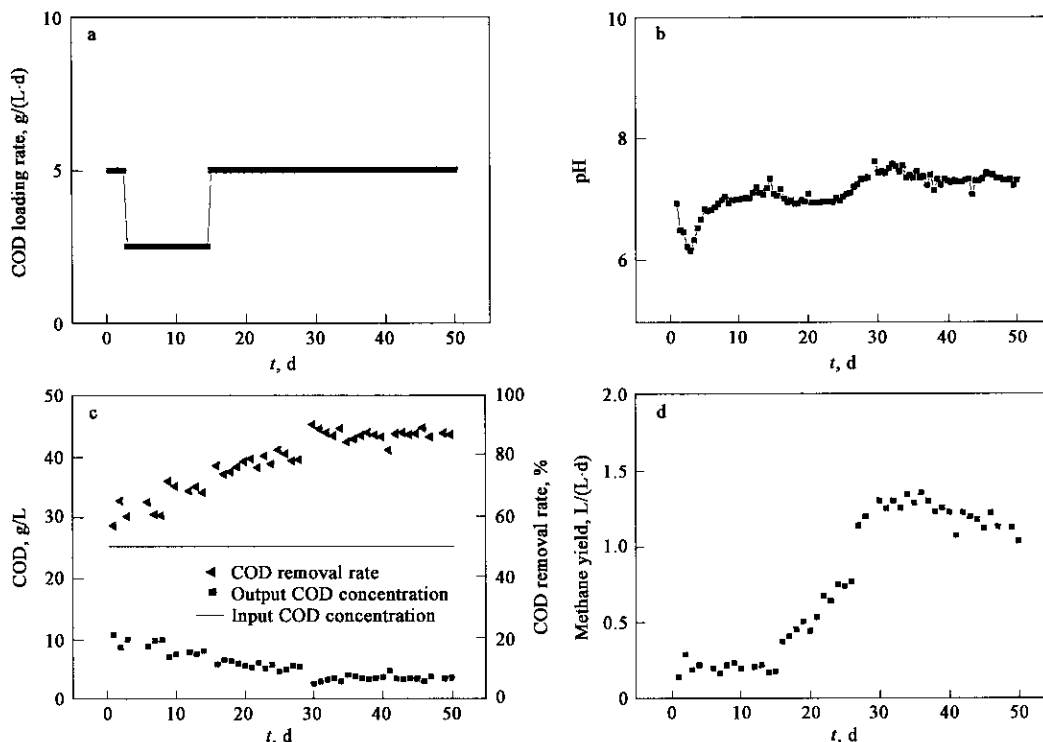


Fig.2 Performance of the reactor during activation of anaerobic sludge

2.2 Performance of two digesters fed with food wastes

2.2.1 Performance of the digester without gas-phased absorb of CO₂

The performance of the digester without gas-phased absorb of CO₂ is shown as Fig. 3. When COD loading rate was between 2.5 to 3.5 g/(L·d) (Fig. 3a) with the average

COD loading rate of 2.8 g/(L·d), the pH (Fig. 3b) and VFA (Fig. 3c) kept stable at about 7.5 and 4—5 g/L, respectively. CH₄ yield (Fig. 3d) increased initially when input material changed from synthetic solution to food waste, and then stabilized at 1.5 L/(L·d) on day 10. However, pH began to decrease, VFA concentration increased sharply to

above 9 g/L with the COD loading rate increased to about 5 g/(L·d). CH₄ yield continued to kept stable for 6 d and later decreased intensely to below 0.4 L/(L·d) at the loading rate

of 5 g/(L·d). When pH began to decreased, 2 g/L NaHCO₃ was added into the digester, however, this could not prevent the failure of the digester operation.

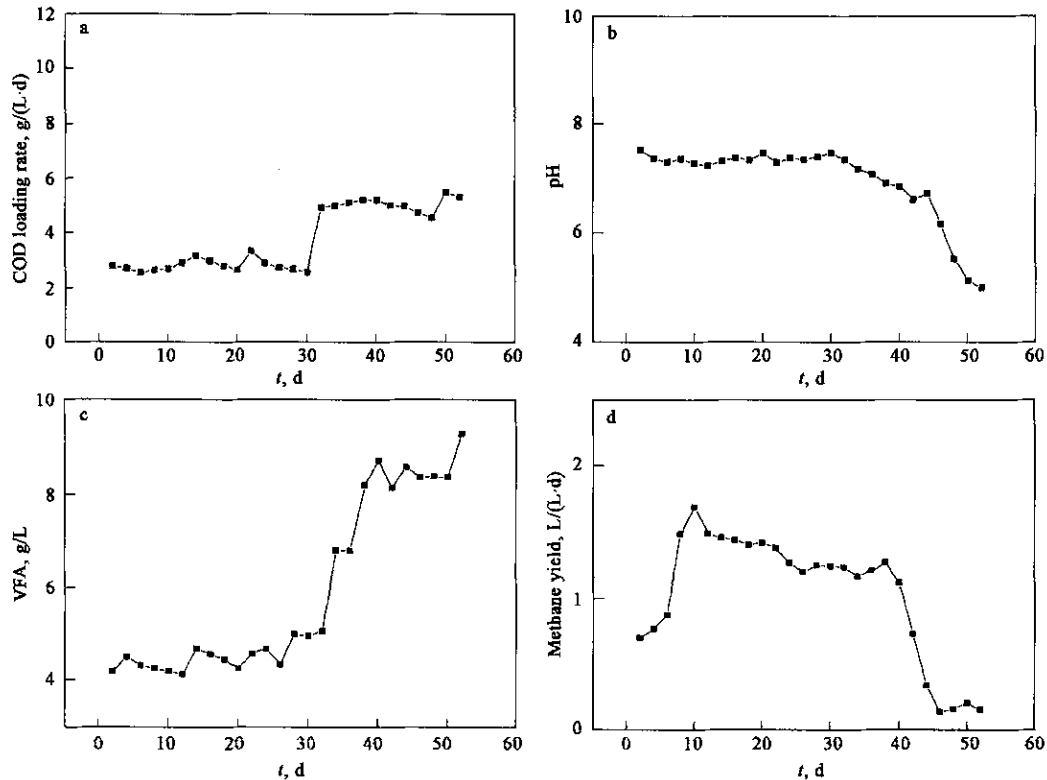


Fig.3 Performance of the digester without gas-phased absorb of CO₂

2.2.2 Performance of the digester with gas-phased absorb of CO₂

The performance of the digester with gas-phased absorb of CO₂ is shown as Fig.4. It can be seen from Fig.4a that COD loading rate was stepwise increased with four periods. Corresponding to COD loading rate change, variation of pH, VFA, alkalinity, output COD concentration and methane yield are shown in Fig.4b, 4c, 4d, 4e and 4f, respectively. Table 2 summarized the average results of four periods corresponding to Fig.4. The COD loading rate was increased step by step from 2.8 g/(L·d) to 5.1, 6.2 and 8.4 g/(L·d). During the whole COD loading rate increase, pH in the digester with gas-phased absorb of CO₂ ranged from 7.2 to 8.7 although input wastes had become acidified and the minimal pH attained 2.6. The output VFA began to decrease to below 2 g/L at the first period due to the COD loading was less than that at the stage of activation. With the COD loading rate increase, VFA concentration lifted to 3–4.5 g/L with the mean value of 3.6 g/L. VFA continued to increase at the third and fourth period, however, VFA had no obvious change at the two periods, and kept at 4.5 and 4.7 g/L respectively. Output alkalinity kept stable with the average 3.2 g/L at the first period. But at the beginning of the second period, the alkalinity rose abruptly to 6.8 g/L, and then dropped gradually with the COD loading rate

increase, generally. As indicated from Table 2, the output alkalinity was 5.2, 4.5 and 3.8 g/L respectively at period 2, 3 and 4. Input COD concentration was lifted with input TS concentration of wastes increase. The inlet COD concentration was increased stepwise from 20 to 51, 82 and 114 g/L with the TS concentration increasing from 33 to 73, 104 and 142 g/L. Output COD concentration increased lightly corresponding to the input COD. However, as shown from Table 2, the COD removal rate kept similar at the later three stages. Methane gas yield increased with the enhanced COD loading rate with the mean value of 1, 1.5, 2.0 and 2.5 g/(L·d). Variation of methane gas yield at every period was caused by the fluctuation of input COD concentration. About 56%–69% of COD was converted into CH₄ at different COD loading rates.

Table 2 Variations of characteristics of the digester with gas-phased absorb of CO₂ at different organic loading rates

Organic loading rate, g/(L·d)	2.8 ± 0.2	5.1 ± 0.3	6.2 ± 0.2	8.4 ± 0.6
Input total COD, g/L	20 ± 5	51 ± 3	82 ± 3	114 ± 12
HRT, d	6.7	10	13.3	13.3
COD removal rate, %	56 ± 5	68 ± 8	66 ± 4	69 ± 4
Output VFA, g/L	2.7 ± 0.7	3.6 ± 0.5	4.5 ± 0.4	4.7 ± 0.3
Input TS, g/L	33 ± 5	73 ± 3	104 ± 4	142 ± 13
TS removal rate, %	48 ± 3	63 ± 5	63 ± 6	68 ± 4
Methane gas yield, L/(L·d)	1 ± 0.1	1.5 ± 0.3	2.0 ± 0.2	2.5 ± 0.3
Alkalinity, g/L	3.2 ± 0.3	5.2 ± 0.6	4.5 ± 0.6	3.8 ± 0.3
Input pH	3.9 ± 0.3	3.3 ± 0.3	3 ± 0.3	2.9 ± 0.1
Output pH	8.1 ± 0.2	8 ± 0.3	7.8 ± 0.2	7.7 ± 0.3

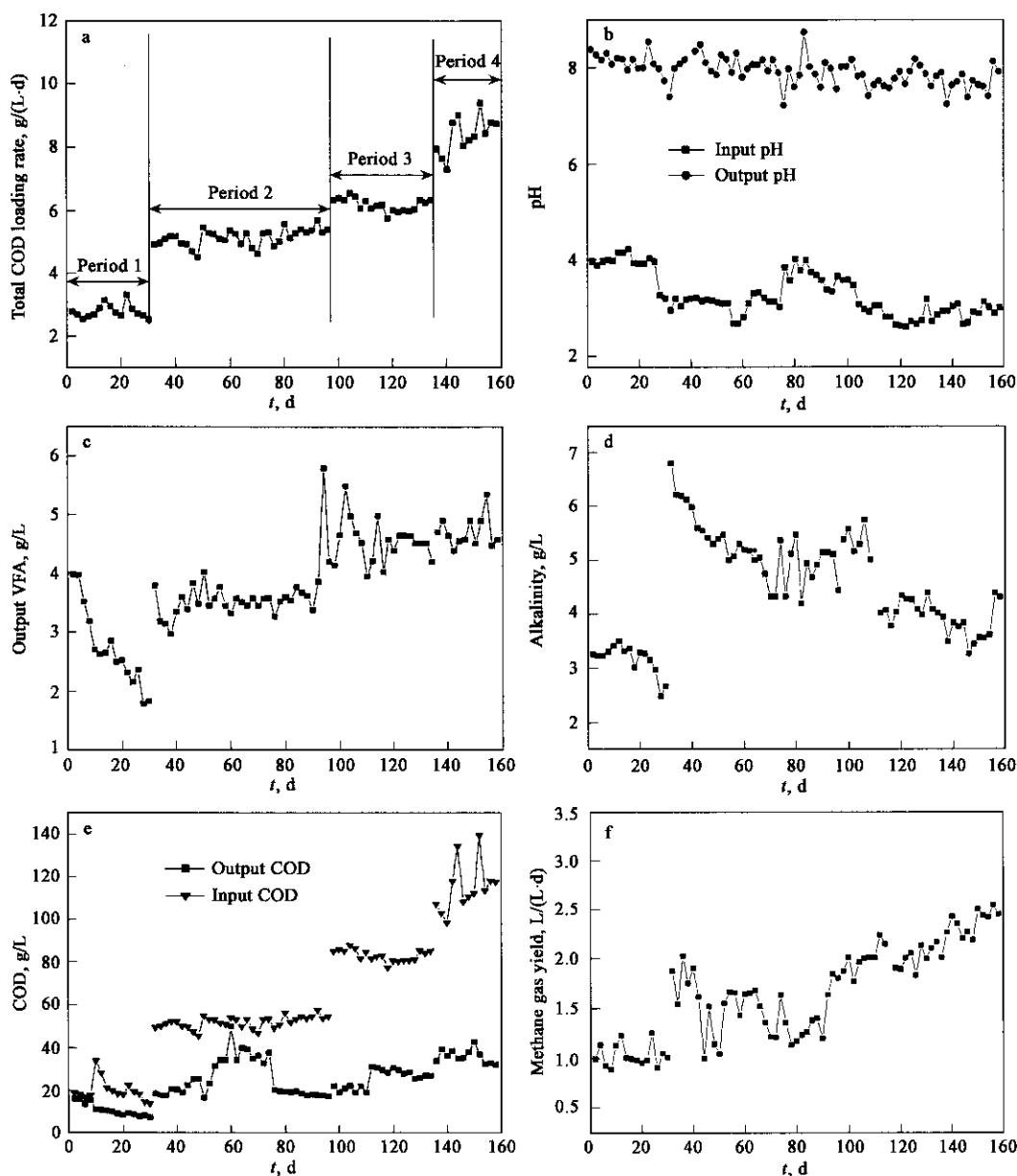


Fig. 4 Performance of the methanogenic reactor with gas-phased absorb of CO₂

3 Discussion

3.1 Effect of CO₂ absorb on stable performance of the digester

The study showed that the gas-phased absorb of CO₂ considerably improved the performance of anaerobic digestion for kitchen wastes.

Considering the application potential of anaerobic digestion of wastes would be mainly for small-scale communities or even for single family, the digester should be designed as batch feeding and the single reactor for minimizing labor and economic requirement. ASBR can achieve solids capture and removal of organics in one vessel and especially appropriate for small-scale communities. One possible disadvantage of the ASBR, however, was loading rate. The highest loading rate reported by Angenent with ASBR treating sucrose was 19 gCOD/(L·d) (Angenent,

1995), much less than the 100 gCOD/(L·d) reported for an upflow anaerobic sludge blanket(UASB) fed milk powder and sucrose (Fang, 1993). The average COD loading rate for ASBR was generally below 10 gCOD/(L·d). Timur *et al.* used an ASBR to treat landfill leachate and the volumetric loading rate was achieved to 9.4 g/(L·d) (Timur, 1999). Dugda and Zhang compared the thermophilic-mesophilic ASBR system to the mesophilic-mesophilic ASBR system for the dairy wastewater (Dugda, 1999). And the maximal VS loading rate was in the range of 2—4 g/(L·d). The low achievable maximum loading was mainly due to the operating strategy of ASBR. The operating strategy provides high initial substrate concentration and easily led to an acid formation problem (Shizas, 2002). This is the reason that the control reactor without gas-phased absorb of CO₂ became acidified with input COD loading rate increasing. The acidification problem could be solved to some extent by reducing the CO₂

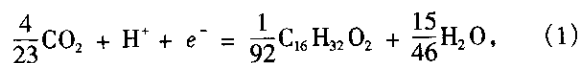
acidity in the reactor. In this study, compared to the digester without gas-phased absorb of CO₂, gas-phased absorb of CO₂ improved the COD loading rate of ASBR. About 8.4 g/(L·d) of the maximal COD loading rate was achieved in this experiment.

Gas-phased absorb of CO₂ also improved the input TS concentration of the digester. In this study, the maximal input TS concentration was achieved to 142 g/L (equal to 14.2% (w/v)) without any buffer addition and the system still had a stable performance. Cho *et al.* reported that the methanogenic reactor of municipal food wastes having higher than 5% (w/v) TS was found to be difficult without buffer addition and dilution rate control (Cho, 1995). Veturtia *et al.* diluted the fruit and vegetable wastes to a TS content of around 4% in a single-stage system (Veturtia, 1995). Bouallagui *et al.* showed there was a significant decrease in conversion of the substrate to biogas when the feed TS concentration increased from 6% to 8% (Bouallagui, 2003). Muroyama *et al.* found that excessive accumulation of unconverted solids would prevent substrate loading rate from increasing (Muroyama, 2001). Especially, for ASBR, at present, researchers selected the low-strength wastewater and the high alkalinity of dairy wastewater as the substrate (Udeme, 1997; Gouranga, 1997; Rodrigues, 2003; Massé, 2002). Higher input TS concentration was mainly attributed to the timely release of CO₂ from the anaerobic reactor because pH will decrease 0.3 unit if the partial pressure of CO₂ doubles (Spiece, 2001). Proper pH guaranteed the normal growth of hydrolytic-acidogenic and methanogenic microorganism.

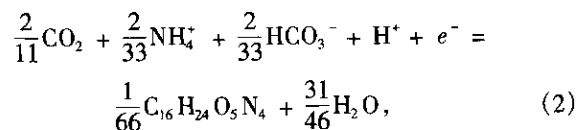
3.2 Stoichiometry of the methanogenesis for kitchen wastes

Mass transfer of CO₂ has an important impact on the overall process of anaerobic digestion (Merkel, 1999). Transport of CO₂ out of the liquid phase strongly influences pH-value and buffer capability of the carbonate-system. pH governed the thermodynamic and kinetics of biological reactions. Ghaly studied the effect of controlling the pH of acid cheese of the second chamber of a two-stage reactor (Ghaly, 1999). The results indicated that operating the digester without pH control resulted in a low pH(3.3), which inhibited the methanogenic bacteria. In order to show the effect of gas-phased absorb of CO₂ on pH and alkalinity in the digester, stoichiometry of the methanogenesis for kitchen wastes need be established. The kitchen wastes in this study consisted of 10 percent fatty acids, 13 percent protein and 70 percent carbohydrate based on COD (Table 1). Kitchen wastes were treated with SRT (solid retention time) of 20 d. A typical empirical formula for protein is C₁₆H₂₄O₅N₄, for fatty acids is C₁₆H₃₂O₂ and for carbohydrate is C₆H₁₀O₅ (Rittmann, 2001). Firstly, the electron-donor equation was devised.

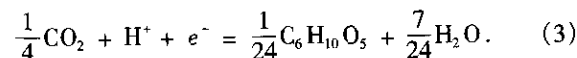
Fatty acids:



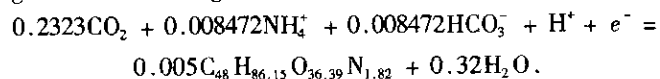
Protein:



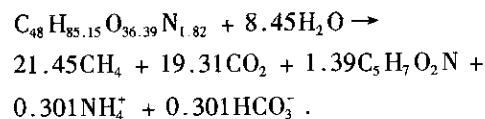
Carbohydrate:



From this, taking 10 percent of the Equation (1) and 13 percent of the Equation (2) and 70 percent of the Equation (3) and adding the respective results together can generate a following donor half-reaction:



According to the method of Rittmann and McCarty (Rittmann, 2001), an overall equation for kitchen wastes was obtained as follows:



From above equation, COD removal rate, CH₄ production, the partial pressure of CO₂, alkalinity and pH in the methanogenic reactor can be calculated theoretically as Table 3. It can be seen from Table 3 that if CO₂ was not absorbed, alkalinity in every stage was much less than VFA produced in the reaction that would inevitably inhibit the growth of the methanogenic microorganism. And pH in the reactor was low and not appropriate for the growth of methanogenic microorganism if no buffer solution was added. When gas-phased absorb of CO₂ was applied, however, mean pH was kept at 7.9 (Table 2). Moreover, according to the balance equation of carbonate system (CO₂-HCO₃⁻-H₂CO₃), with ionic strength assumed to be 0.0 and the temperature at 35°C, the required amount of alkalinity was 8.2 g/L when pH was increased from 6.3 to 7.5. If sodium bicarbonate was selected for the 2 L reactor, about 26.9 g sodium bicarbonate was required to meet the need of alkalinity of 8.2 g/L. Thus 6.8 g of sodium ion were remained in the reactor every day. So more and more sodium ion would be accumulated and have a destructive effect on the performance of the methanogenic reactor. Gas-phased absorb of CO₂ effectively reduced the alkaline consumption, and thus precautioned the sodium ion inhibition.

4 Conclusions

The kitchen wastes can be effectively treated by single-stage ASBR with the gas-phased absorb of CO₂.

The methanogenic reactor with gas-phased absorb of CO₂ can effectively improve pH from 6.4 to 7.9 at the maximum organic loading rate of 8.4 g/(L·d). Hence alkalinity could

be saved and cation inhibition could be precautioned.

Table 3 The characteristics of the methanogenic reactor without gas-phased absorb in theory

Input COD, g/(L·d)	2.8	5.1	6.2	8.4
Flow rate, L/d	0.3	0.2	0.15	0.15
COD removal rate, %	56	68	66	69
COD removal rate, g/d	3.3	7	8.2	11.8
CH ₄ production, L/d	1	2.4	2.8	4
Partial pressure of CO ₂ , atm	47	47	47	47
Alkalinity, mg/L	57	320	469	743
pH	5.3	6.0	6.2	6.4

About 2.5 L/(L·d) of methane yield, 69% of the total COD removal rate, and 68% of TS removal rate were achieved at maximum organic loading rate. Compared to other ASBR treating other wastewater, the digester with gas-phased absorb of CO₂ showed better performance for the feeding mixture of solid and liquid.

The principal advantages of this process are: (1) the enhanced performance of TS removal and stability of the digester due to the gas-phased absorb of CO₂ of the process; (2) the simple and economical operation by using batch and single-stage reactor.

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