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Volatile fatty acid (VFA) and methane generation from sewage sludge and banana straw: influence of pH and two-phase anaerobic fermentation

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ABSTRACT

Sewage sludge and banana straw were mixed for two-phase anaerobic fermentation while maintaining the pH of the acidogenic phase at 5.5, 6.5, 7.5, 8.5, 9.5, and 10.5. Under these conditions, batch tests were performed to investigate the effects of pH values on the production of volatile fatty acid (VFA) and methane from mixed fermentations. In the fermentation with acidogenic phase, the concentration of VFA in each experimental group reached its highest value on day 2, among which the highest VFA concentration was 7,592 mg L^{-1}. The concentration of VFA in the range of acidity increased with increasing pH, while the range of alkalinity decreased. Cumulative yield and production speed of methane in alkaline experimental group was higher than that of the acid experimental group on day 20, and the maximum methane yield was observed in the 8.5 group, which was 280 mL g^{-1}-VS.

Keywords: Sewage sludge; Banana straw; Two-phase anaerobic fermentation; Volatile fatty acids; pH

1. Introduction

Sludge generated from municipal sewage treatment plants contains a large amount of easily degradable organic matter, odorous substances, heavy metals, and pathogens; therefore, it can easily cause secondary pollution to the environment without reasonable disposal [1]. Sludge treatment in Japan, Europe, and the United States and other developed countries commonly includes application of sludge to farmland, compost [2,3], anaerobic digestion, and incineration [4]. Among these methods, anaerobic digestion offers the potential to recover biogas and achieve resource reuse [5].

Because of the low C/N of sludge, it is easy for the anaerobic digestion alone to be inhibited by ammonia nitrogen; therefore, it is difficult to provide the optimal growth conditions for anaerobic bacteria, which prevents them from becoming the dominant populations [6,7]. As a result, the research direction has shifted to multi-substance collaborative anaerobic digestion [8]. Banana straw contains a high quantity of cellulose and hemicellulose and a high content of C/N and organic matter [9,10]. This material can be mixed and fermented with sludge to adjust the C/N of sludge into appropriate value, which is beneficial to anaerobic fermentation. Substances that have been mixed and fermented with sludge in recent studies include kitchen waste [11], pig manure [12], municipal waste [13], and wheat straw [14]. However, the structure and organic matter content of banana straw are very different from that of other agricultural wastes such as corn stalk and wheat straw, which may have a great influence on the characteristics of methane production [15]. The hydrolysis and acidification efficiency of the acidogenic phase during anaerobic digestion can directly influence the efficiency of the methanogenic phase, and pH has a significant effect on the acid production phase.

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This study was conducted to investigate the effects of pH on production of VFA and methane by sewage sludge and banana straw during two-phase anaerobic fermentation to obtain higher methane yields. The results presented herein will be useful as guidance and references for engineering practices involving use of sewage sludge and banana straw in two-phase anaerobic digestion processes.

2. Materials and methods

2.1. Experimental materials

The sewage sludge taken from a wastewater treatment plant in the city of Nanning was dewatered and stored at 4°C until use. Physical and chemical characteristics of sewage sludge and seeding sludge is shown in Table 1. Banana straw was obtained from a banana plantation of the surrounding area in Nanning, sun dried, and then sealed in plastic bags. Physical and chemical characteristics of banana straw are shown in Table 2.

Potassium hydroxide was used to pretreat the sludge to obtain a high COD dissolution rate [16]. Specifically, sewage sludge was adjusted to pH 12 with potassium hydroxide at 4 mol L^{-1}, then heated in a water bath at 90°C for 104 min. Banana straw was pretreated by passing through a 10 mesh sieve after being crushed. The straw was then treated with 6% TS quality sodium hydroxide and mixed with 9× TS quality water, after which it was heated in a water bath at 30°C for 7 d. The seeding sludge was pretreated by heating in a 100°C water bath with stirring, which was continued for 15 min after the temperature had stabilized to killed the non-sporulating bacteria (including methanogens) and allow the sludge to become acidogenic.

2.2. Experimental devices and methods

The anaerobic fermentation device is composed of a constant temperature water bath, a 500 mL wide-mouth bottle as a fermentation bottle, a 2,500 mL wide-mouth bottle (with 3% sodium hydroxide solution) for gas collection and a 1,000 mL beaker to measure the gas volume. The 500 mL bottle was filled with 43.63 g of pretreated sewage sludge, 70.95 g of pretreated banana straw, and 199.53 g of acidogenic sludge (1:2:1.5 ratio of TS), which were subsequently homogenized. This resulted in a fermentation system with a C/N of 15 and a TS of 6% after water adjustment. The chemical parameters of the pretreated sludge + pretreated banana straw are shown in Table 1. The initial pH of the fermenter was adjusted to 5.5, 6.5, 7.5, 8.5, 9.5, and 10.5 with 2 mol L^{-1} HCl and 2 mol L^{-1} NaOH, after which nitrogen (gas) was passed through the system for 3 min to reach an anaerobic state, and anaerobic fermentation was then conducted in a water bath at 35°C. The pH was adjusted to the initial value every 24 h, after measuring the VFA concentration. After the sample was taken, the fermenter was treated with nitrogen (gas) for 3 min, then sealed with a sealant to maintain the anaerobic state. Stabilization of the VFA concentration was taken to indicate the end of the acidogenic phase. When the acidogenic phase fermentation was finished, the concentrations of ammonia nitrogen, soluble chemical oxygen demand (SCOD), VFA, soluble protein, and total soluble sugar were measured. The pH of all experimental groups was adjusted to be neutral, after which methanogenic sludge 4.62 g (in VS) was directly inoculated into the original fermenter and treated with nitrogen for 3 min, and methane was then collected by the sodium hydroxide solution. Every 7 d, the concentration of ammonia nitrogen, SCOD, VFA, soluble

Table 1
Physical and chemical characteristics of sewage sludge and seeding sludge

	Total solids content /%	Volatile solids content/total solids content/%	C/N	SCOD/ mg·L^{-1}	Soluble protein/mg·L^{-1}	Total soluble sugar /mg·L^{-1}	Volatile fatty acid/mg·L^{-1}
Sewage sludge	18.52	37.10	5.6	–	–	–	–
Pretreated sewage sludge	9.74	38.20	39.33	6,142	2,856	518	–
Seeding sludge	11.3	68	5.3	552.5	201.1	29.5	–
Pretreated sewage sludge + Pretreated banana straw	6	64.43	15	10,931	2,671	1,070	1,155

Table 2
Physical and chemical characteristics of banana straw

	Total solids content /%	Volatile solids content/total solids content/%	C/N	Cellulose content/%	Hemicellulose content/%	Lignin content/%
Banana straw	5.19	84.67	38.98	38.02	22.43	16.88
Pretreated banana straw	87.68	89.33	39.33	31.46	12.87	12.47

protein, and total soluble sugar was measured. Sequential batch experiments were conducted, with two sets of parallel samples for each group.

2.3. Analysis methods

Samples were analyzed for TS, VS, ammonia nitrogen, SCOD, pH, VFA, soluble protein, total soluble sugar, cellulose, hemicellulose, lignin, total carbon, and total nitrogen. The soluble fraction of sludge and straw was detached by hydroextraction at 4,000 rpm for 10 min, after which the supernatant was filtered and analyzed for ammonia nitrogen, SCOD, VFA, soluble protein, and total soluble sugar. The TS, VS, ammonia nitrogen, SCOD, and VFA were determined according to the standard methods [14]. Soluble protein in the liquid phase was analyzed by Lowry's method [17], while total soluble sugar was determined using the Phenol-sulfuric acid method [18] and total carbon and total nitrogen and pH were measured using an EA3000 automatic elemental analyzer and a PHS-3C pH meter, respectively.

3. Results and discussion

3.1. VFA

Variations in VFA concentration among pH groups with time are shown in Fig. 1. The VFA concentration of every group rose rapidly with the fermentation time, peaked after 2 d, and then decreased to a stable state. At the end of the acidogenic phase, the VFA of every experimental group was between 3,283 and 4,749 mg COD L^{-1}. Chen et al. [19] found that the VFA concentration of sewage sludge fermented alone basically stabilized after 8 d. However, VFA produced by mixing with sewage sludge and banana straw began to stabilize on day 4. In comparison, the mixed fermentation of sludge and stalks required shorter periods for VFA production. This was because sewage sludge and banana straw all had great effects on pretreatment under alkaline conditions, with a large amount of SCOD being dissolved, providing more organic materials for acidogenic microorganisms. Furthermore, straw added to the sludge regulated the C/N of the fermentation system, which maintained the nutrient balance and promoted the anaerobic fermentation of the acidogenic phase. On the second day of fermentation, the VFA concentration in the pH = 6.5 group was 7,592 mg COD L^{-1}. This value was the highest concentration among all groups and was also much higher than that of 2,600 mg COD L^{-1} reported by Wu et al. [20] in an investigation of VFA production by sewage sludge fermented alone. This was because, during the pure fermentation of acidogenic microorganisms, neutral conditions were more conducive to their growth [21]. This led to a large number of acidogenic microorganisms and production of more VFAs through metabolism. Moreover, the maximum concentration of VFA in the alkaline groups decreased as pH increased, except for the pH = 7.5 group being slightly lower than the pH = 8.5 group. Because the seeding sludge was pretreated by heating, there was a very small amount of methanogen residues. The pH 7.5 experimental group was very close to the optimum pH of methanogens [22]; therefore, the VFA of the experimental group was consumed in small amounts. The VFA concentration during each stage of fermentation is shown in Fig. 2. After metabolism of acidogenic bacteria in the acidogenic phase, a large amount of VFA was produced, which could be used as raw material for methanogens. In the subsequent methanogenic phase, VFA was consumed rapidly and the concentration gradually decreased. There was still a small amount of VFA remaining at the end of the methanogenic phase, with the maximum and minimum residue of 353 and 140 mg COD L^{-1} being found in the pH 7.5 group and the pH 8.5 group, respectively. The types of substrates that can be used directly by methanogens are limited, consisting of only acetic acid, methyl mercuric compounds, hydrogen, and carbon dioxide [23].

3.2. Soluble chemical oxygen demand

Fig. 3 shows the SCOD concentration at each stage of fermentation. When the acidogenic phase ended, the SCOD showed a substantial increase in all experimental groups except the pH 5.5 and 6.5 groups, which showed slight decreases. Among these groups, the SCOD of the pH = 5.5 group showed the greatest decrease of 32% compared with the initial value. In the pH 10.5 group, the SCOD showed

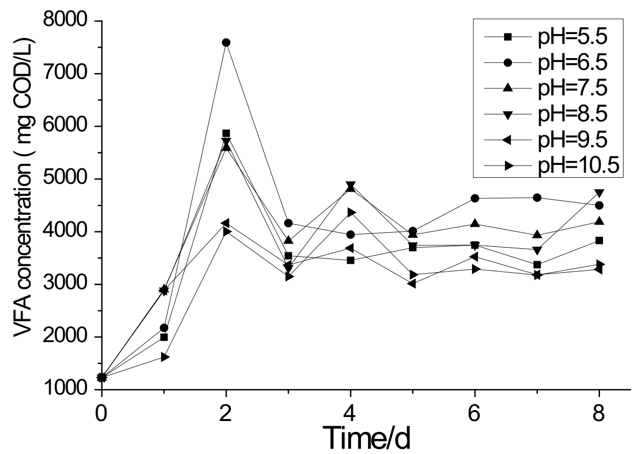

Fig. 1. Changes in VFA concentration over time at different pH values.

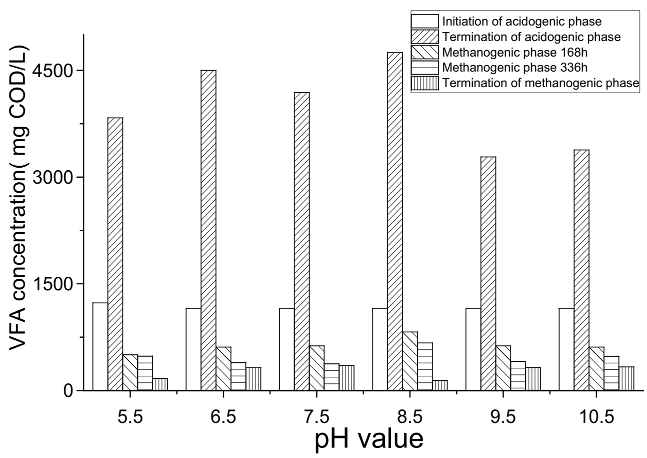

Fig. 2. VFA concentration during fermentation.

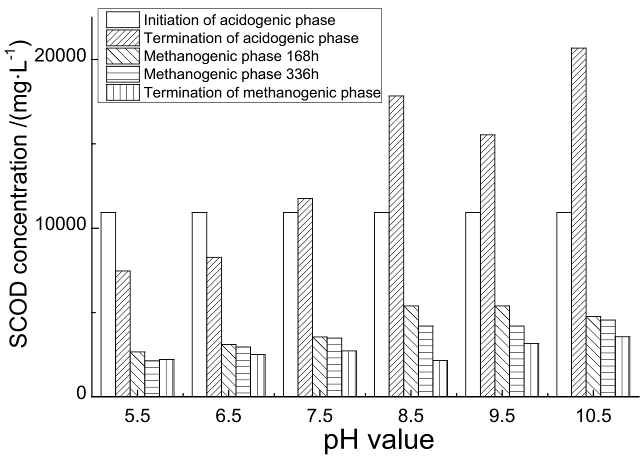

Fig. 3. SCOD concentration during fermentation.

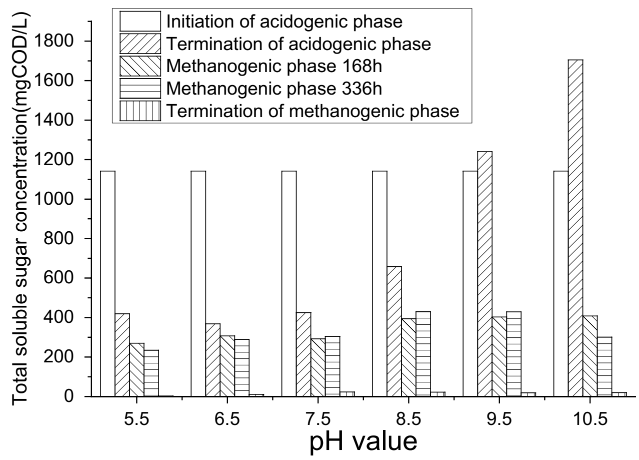

Fig. 4. Concentration of soluble total sugar during fermentation.

the greatest increase of 89% over the initial value. The SCOD continued to dissolve under alkaline conditions, resulting in a generally higher concentration of SCOD under acidic conditions in the acidogenic phase. Even though the highest concentration of SCOD was found in the pH 10.5 group, the production rate of VFA was basically the lowest because the pH was too high. This restrained the microbial enzyme activity under extremely alkaline conditions, which further inhibited the microbial metabolic efficiency, resulting in low VFA yield. Because of the static phase separation, the acidogenic phase provided the material foundation for the post-stage fermentation. After the methanogenic phase began, the methanogens consumed a large amount of SCOD, resulting in a continuous decrease in the concentration of SCOD during subsequent methanogenic fermentation. However, at the end of the methanogenic phase, there was a higher concentration of SCOD (2,215–3,566 mg L^{-1}) retention in the experimental group. Because the initial ratio of sewage sludge and banana straw is 2:1 (based on the TS), 16.88% of the lignin contained in banana straw was difficult to degrade, resulting in a large concentration of SCOD conservation at the end of the methanogenic phase. In addition, the residual concentration of SCOD increased with increasing pH. Overall, the amount of SCOD consumed by the pH 8.5 group was the largest, and this group contained the lowest residual SCOD.

3.3. Total soluble sugar

The changes in total soluble sugar concentration in experimental groups with different pH values are shown in Fig. 4. The saccharides (cellulose, hemicellulose) in the fermentation system were converted into VFAs after fermentation, providing the raw materials for the metabolism of methanogens during the methanogenic phase. The concentrations of total soluble sugars in the pH 5.5, 6.5, 7.5, and 8.5 groups decreased significantly at the end of the acidogenic phase, with that in the pH 6.5 group showing the greatest decrease of 68% from the initial value. The high concentration of VFA in the pH 6.5 group might have been a result of consumption of a large quantity of carbohydrates. The concentration in the pH 9.5 and 10.5 groups all increased, with the greatest increase of 49% being observed in the pH 10.5 group. Because VFAs production by this group was lower than that of others, fewer carbohydrates were consumed. VFAs consumption by methanogens promoted degradation of saccharides by bacteria that hydrolyze and acidogenic matter, causing the concentration of saccharides to decrease significantly. At the end of the methanogenic phase, the sugars were almost completely consumed, and the remaining sugar concentration in each group was 3–23 mg COD L^{-1}.

3.4. Soluble protein

Soluble protein was also an important part of SCOD. Volatile fatty acids can be produced through hydrolysis and acidification by microorganisms. The soluble protein concentration of various stages in each experimental group is shown in Fig. 5. The protein concentrations in the pH 5.5 and 6.5 groups decreased, with the greatest decrease of 58% being observed in the former group. Conversely, the protein concentrations of the alkaline test groups increased, with the greatest increase of 128% being observed in the pH 10.5 group. At the end of the methanogenic phase, the remaining concentration of proteins in each group ranged

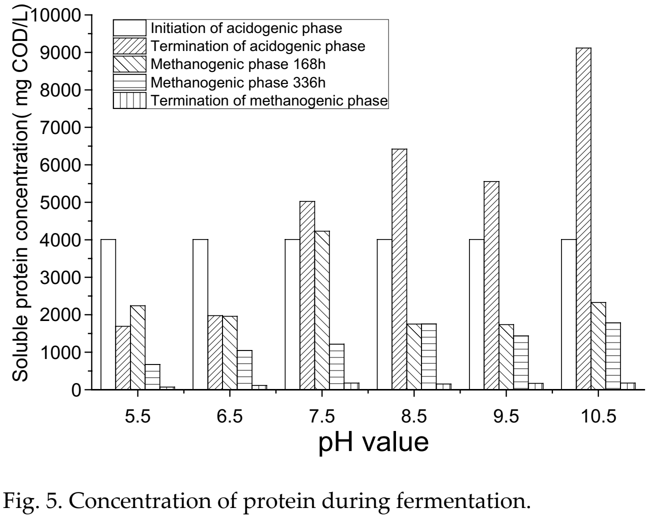

Fig. 5. Concentration of protein during fermentation.

from 107 to 266 mg COD L^{-1}, which was greater than the concentration of carbohydrates, indicating that the degree of carbohydrates utilization by microorganisms was greater than that of proteins.

3.5. Ammonia nitrogen

Nitrogen balance is a very important factor in anaerobic digestion that has the potential to vary the pH during methanogenic phase. The ammonia nitrogen concentration in each experimental group is shown in Fig. 6. As the reaction proceeds, the ammonia nitrogen increases from the acidogenic phase to the methanogenic phase. Because of the nitrogen produced by disintegrating the protein in the fermentation system, part of the nitrogen was converted into nitrogen (gas) by the metabolism of bacteria, those nitrogen (gas) was present in the biogas. A portion of the nitrogen was also used by the bacteria for cell proliferation, while most was converted to ammonia nitrogen.

3.6. Methane production rate

The 20 d methane production rate in the methanogenic phase is shown in Fig. 7. The methane production rate during the two-phase anaerobic fermentation of sludge and banana straw in each experimental group was 227–280 mL g^{-1}·VS, and there was a general increase than single-phase system in the methane production rate. The highest methane yield in the pH 8.5 group was 280 mL g^{-1}·VS, which was 1.53 times greater than that in the single-phase fermentation system that contained mixed sludge and banana straw. Since the concentration of VFA was highest in the pH 8.5 group at the end of the acidogenic phase, this group provided a large number of substances that can be directly used by methane-producing bacteria for metabolization. This group also had a high level of efficiency of hydrolysis, with a large amount SCOD of 17,837 mg L^{-1} (Fig. 3). A great quantity of SCOD can provide a material basis for the generated VFA, which rapidly and continuously provides more materials for subsequent metabolization of methanogens to produce methane. These substances, which can be directly used by microorganisms, boosted the methane production rate. The methane yield in

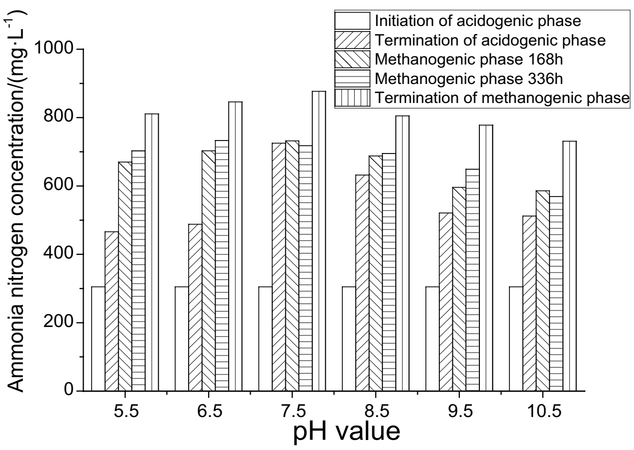

Fig. 6. Concentration of ammonia nitrogen during fermentation.

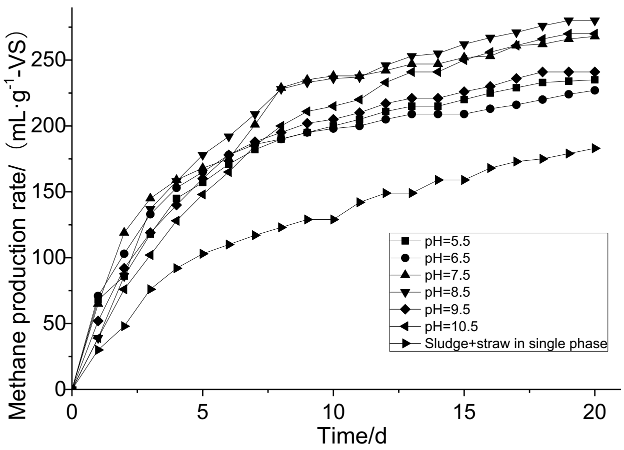

Fig. 7. 20 d methane production rate in methanogenic phase.

the pH 7.5 group was 268 mL g^{-1}·VS, which was 1.46 times that of the single-phase system and only 4.29% lower than that of the pH 8.5 group. The lowest methane production rate of the experimental group was 227 mL g^{-1}·VS in the pH 6.5 group, which was still 1.24 times greater than that of the single-phase system with mixed sewage sludge and banana straw. When the acid production phase was over, the concentration of VFA was still at a high level. In addition, the SCOD of the group was at a level far lower than that of the alkaline test group (Fig. 3). The methane production rate of the pH 10.5 group also reached as high as 270 mL g^{-1}·VS, which was followed by that of the pH 8.5 group. Keeping the pH of the acidogenic phase close to the neutral state in engineering practice of the two-phase anaerobic reactor with sewage sludge and banana straw can reduce consumption of alkaline substances during actual operation, which will lead to economic advantages.

The cumulative methane production rate of 20 d for the single-phase fermentation system of mixed sludge and banana straw accounted for 90.44% of the total methane production rate. However, for each experimental group in the two-phase fermentation system, the cumulative yield of methane of 20 d accounted for 91.00%–97.19% of the total methane production rate. The speed of methane production was generally higher than that of the single-phase system. Among treatments, the proportion of methane produced by the pH 7.5 group over 20 d was largest, accounting for 97.19% of the total methane production rate, which was also the fastest methane production in all experimental groups. The methane production speed of the test groups in the range of alkaline pH values was generally faster than that of the test groups in the range of acidic pH values. This was especially evident for the pH 9.5 group and the pH 10.5 group, when the cumulative methane yield ratio for 20 d was 96.14% and 96.7%, respectively (slightly lower than the pH 7.5 group). Although the pH 9.5 and pH 10.5 groups did not have high concentration of VFA at the end of the acidogenic phase, they did show remarkable efficiency for hydrolysis as indicated by dissolution of a large amount of SCOD (Fig. 3). This SCOD then provided the material basis for the subsequent fermentation process and ensured the speed of methane production.

4. Conclusions

The methane production rate of the two phase anaerobic fermentation system with sludge and banana straw was 227–280 mL g^{-1}·VS, generally increased than the single-phase anaerobic fermentation system. In the acidogenic phase, the concentration of VFA generally reached the peak value on day 2 in the six experimental groups with different pH values. The highest VFA concentration, which was observed in the pH 6.5 group, was 7,592 mg L^{-1}. Furthermore, as the pH became acidic, the maximum VFA concentration increased slightly. Conversely, the maximum VFA concentration decreased with increasing alkalinity. In the methanogenic phase, the rates of methane production in the alkaline experimental group were higher than those in the acidic experimental group. The highest methane production rate of 280 mL g^{-1}·VS was observed in the pH 8.5 group; however, the methane production rate in the pH 7.5 group was 4.29% lower than in the pH 8.5 group, indicating that the speed of methane production was higher than that of the pH 8.5 group. Overall, the optimum operation of the two-phase fermentation occurred at a pH of 7.5 based on the efficiency, rate and cost of methane production.

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