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Acidification of waste activated sludge during thermophilic anaerobic digestion

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Abstract

The effects of pH value, temperature, adding ratio of waste activated sludge (WAS) and hydraulic retention time (HRT) on WAS acidification in thermophilic anaerobic digestion system were investigated by batch experiments. The results indicated that the WAS acidification at pH 9.0 was the greatest (VFAs content was about 148mg/L), followed by the pH uncontrolled (105mg/L) and the neutral pH (87mg/L). Compared to the conditions of pH uncontrolled, the VFAs accumulation was retarded at acidic (pH 3.0 and pH 5.0), neutral (pH 7.0) or strong alkaline pH values (pH 11.0). Optimal temperature of thermophilic anaerobic digestion on VFAs accumulation was shown to be 60℃ (VFAs content was 148mg/L), better than lower temperature 50℃ (79mg/L) or higher temperature 70℃ (75mg/L). Each adding ratio has its own optimal HRT to producing maximum VFAs. The VFAs accumulation was attained peak value at dosing 12.5% and HRT 8d (about 184mg/L). In conclusion, in order to maximize the accumulation of VFAs for providing more carbon, the optimal operating conditions for WAS thermophilic anaerobic digestion observed in this study was pH 9.0, 60℃, adding ratio 12.5% and HRT 8d, revealing that the performance of WAS acidification was sensitive to operating conditions.

Keywords: waste activated sludge; anaerobic digestion; thermophilic; VFAs

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1. Introduction

With the acceleration of urbanization, urban sewage treatment rate of domestic sewage increases year by year, the sludge production in sewage treatment plant rises dramatically, this is becoming one of the most important and complex problem needed to be dealed with urgently in the years ahead.

Recently, as readily biodegradable carbon source is required more and more for biological denitrification process and the biological phosphorus removal (BPR) process in municipal domestic waste water treatment field (Tong and Chen, 2009; Zheng et al., 2010), the shortage of soluble organic compounds is becoming another increasingly common problem (Feng et al., 2009).

Thus, more and more efforts have been made to obtain soluble carbon source from the sewage sludge rich in organic substance (Wilson and Novak, 2009). Recently, much attention has been paid to the fermentation of sewage sludge for Volatile fatty acids VFAs (Guo et al., 2008; Zhang et al., 2010) which have been demonstrated to be the most suitable substrates to support denitrification (Elefsiniotis et al., 2004) and BPR (Chanona et al., 2006; Tong and Chen, 2007), avoiding costly external carbon source addition (Thomas et al., 2003). So, how to enhance the VFAs production from the sludge is worthy to be researched.

Two strategies have been applied by researchers to enhance the VFAs production in scientific ways. Optimization of system surroundings, such as pH, Temperature and so on, is one method which had been investigated. Chen et al. (2007) studied the influence of pHs on the acidification of waste activated sludge (WAS) at ambient temperature, finding that the VFAs production was significantly improved under alkaline. Under pH uncontrolled conditions, Kim et al. (2002) and Song et al. (2004) compared the mesophilic (35℃) and thermophilic (55℃) anaerobic fermentation, showing that the latter produced more VFAs than the former. Zhang et al. (2009) investigated the effect of pHs (4.0-11.0) on WAS short-chain fatty acids accumulation under mesophilic (35℃) and thermophilic (55℃) conditions, indicating that no matter in mesophilic or thermophilic fermentation, the accumulation of VFAs at alkaline pHs was greater than at acidic or uncontrolled pHs.

The development and improvement of treatment technology is the other way to enhance the VFAs production. Guo et al.(2008) adopt a novel anaerobic fermentation process—multistage countercurrent fermentation to improve the bio-production of VFAs from excess municipal sludge, showing that the VFAs concentration increased by 31% when compared with the conventional anaerobic fermentation. Besides, other treatment technologies, such as thermal treatment (Bougrier et al., 2008), sonication (Naddeo et al., 2009; Shao et al., 2010), microwave (Dogan and Sanin, 2009), and so on, were applied to enhance the efficiency of anaerobic digestion to improve VFAs production.

Thermophilic anaerobic digestion of sludge (the temperature range is from 40 to 70℃) has been investigated regularly linking with mesophilic anaerobic digestion (Riau et al., 2010; Ge et al., 2011). Fewer studies researched on thermophilic anaerobic digestion independently, especially on its production of VFAs. Furthermore, the optimal operating conditions for maximizing VFAs production from such process remain undetermined, particularly the optimum temperature of thermophilic anaerobic digestion.

This study researched on thermophilic anaerobic digestion of waste activated sludge independently, focusing on its production of volatile fatty acids, which not only provided a sustained supply of carbon, but also realized sludge reduction. In order to produce maximal VFAs from sewage sludge by thermophilic anaerobic digestion, this paper focused on the effects of pH (3.0-11.0), thermophilic temperature (50-70℃), and adding ratio of sludge(12.5%, 25%, 50%, 75%) on WAS solubilization and acidification during thermophilic anaerobic digestion. Efficiency of thermophilic anaerobic digestion process in this study was evaluated by soluble chemical oxygen demand (SCOD), Soluble protein, Soluble carbohydrate and VFAs.

2. Methods

2.1. WAS source

The WAS samples used in this study were taken from the secondary sedimentation tank of a municipal sewage plant in Nanjing, China. The sludge was concentrated by settling at 4℃ for 24h. The main characteristics of the concentrated WAS are presented in Table 1.

Table 1. Characteristics of the concentrated WAS

▪Parameter	Value
▪pH	6.70
▪TS (g/L)	24.5
▪VS (g/L)	13.2
▪Soluble Total Carbon (STC) (mg/L)	275.65
▪Soluble Total Organic Carbon (STOC) (mg/L)	195.58
▪Soluble Total Inorganic Carbon (STIC) (mg/L)	80.08
▪Soluble Total Nitrogen (STNb) (mg/L)	120.02
▪Soluble Chemical Oxygen Demand (SCOD) (mg/L)	120
▪Soluble protein / (mg/L)	74.78
▪Soluble carbohydrate / (mg/L)	24.79
▪Moisture content (%)	97.72
▪VFAs (mg/L)	0.58

2.2. Start-up

Each reactor with a volume of 400mL was fed with 100mL WAS at intervals of 24h. During feed events, approximately 100 mL of feed was pumped through the system. The systems were operated for over one and a half month when approached a steady-state. During this period, the temperature of each system was maintained at 60℃ and the pH was uncontroled.

2.3. Experiments of WAS thermophilic anaerobic digestion at different pH

Based on the steady-state of the systems, the effect of pHs on WAS thermophilic anaerobic digestion was experimentally analyzed in a series of identical reactors with a volume of 400mL for each. Each inoculated with anaerobic sludge was fed with concentrated WAS daily in a draw and fill manner at HRT 4d and adding ratio of 25%. 6 batch reactors were used and maintained at 60±2℃, respectively. The 6 reactors were operated at pH 3.0, 5.0, 7.0, 9.0, 11.0, and pH uncontrolled, respectively, by adding 1M sodium hydroxide (NaOH) or 1M hydrochloric (HCl). All reactors were continually mixed using magnetic stirrer bars.

2.4. Experiments of WAS thermophilic anaerobic digestion at different temperature

3 batch reactors with a volume of 400mL for each were maintained at optimum pH obtained in experiments of WAS thermophilic anaerobic digestion at different pH, and were operated at 50℃, 60℃,

and 70℃, respectively,with feeding WAS daily in a draw and fill manner at HRT 4d and adding ratio of 25%.

2.5. Experiments of WAS thermophilic anaerobic digestion at different adding ratio

4 batch reactors were used. Each reactor had a volume of 400mL and maintained at optimum pH and optimum temperature obtained in above experiments, and were operated at adding ratio of 12.5%, 25%, 50%, and 75%, respectively, with feeding WAS daily in a draw and fill manner at HRT 8d, HRT 4d, HRT 2d and HRT 1d

3. Analysis

Analyses were performed for pH, TS, VS, STC, STOC, STIC, STNb, VFAs, SCOD, Soluble protein and Soluble carbohydrate. pH was determined by glass electrode method. Determinations of the TS, VS and SCOD were carried out according to Standard Methods (APHA, 1998). Soluble protein was measured according to the Lowry's method (LOWRY et al., 1951). Soluble carbohydrate were measured by the phenol sulfuric acid method (DuBois et al., 1956). STC, STOC, STIC and STNb were determined with a TOC analytic apparatus. For measurement of STC, STOC, STIC, STNb, SCOD, VFAs, Soluble protein and Soluble carbohydrate, the liquid samples were centrifuged at 5000g for 5min and filtered through 0.45μm PFS membrane prior to analysis.

4. Results and discussion

4.1. Overall performance of WAS thermophilic anaerobic digestion system during start-up operation

It can be seen from the Figure 1 and Figure 2 that WAS thermophilic anaerobic digestion system reached a stable state after operated for about 45 days, as was demonstrated by the fact that the Total Solids (TS), Volatile Solids (VS) and VFAs contents kept stabilization. During the start-up phases, the VFAs content increased from 0.58mg/L to 44mg/L, and the system achieved about 17.6% TS destruction and 33.3% VS destruction compared to the raw WAS, showing that the WAS solubilization improved significantly after thermophilic anaerobic digestion. Under such an environment, the content and activity of hydrolytic enzyme were enhanced substantially, leading to some insoluble organics converted into soluble matter and then transfered into liquid phase environment, characterized by the reduction of TS and VS. However, in this circumstances where acid-forming bacteria was at a disadvantage so as not to be helpful for VFAs accumulation, this is because part of soluble substrate was utilized by other microorganisms. On the other hand, part of VFAs was consumed by other microbes. Therefore, parameter optimization of passive control system needs to be done to promote the growth of acid-forming bacteria to improve VFAs production.

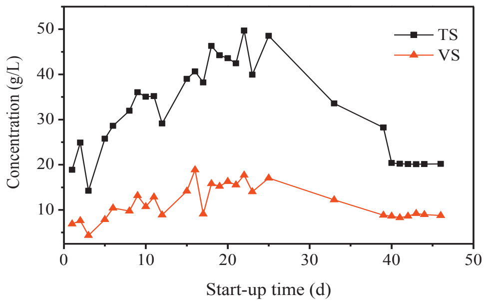

Fig. 1. The variation of TS and VS contents during the start-up of thermophilic anaerobic digestion system;

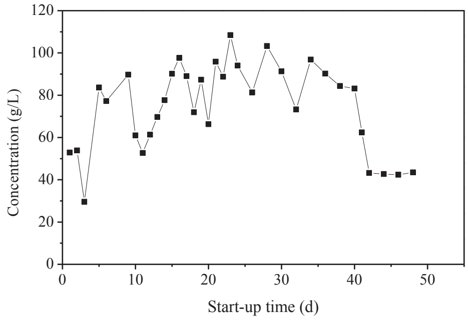

Fig. 2. The variation of VFAs content during the start- up of thermophilic anaerobic digestion system

4.2. The effect of pH on WAS acidification under thermophilic conditons

The Figure 3 and Figure 4 indicated that the WAS acidification at pH 9.0 was the greatest of any pHs (VFAs content was about 148mg/L), followed by the pH uncontrolled (105mg/L) and the neutral pH (87mg/L). Compared to the conditions of pH uncontrolled (pH was fluctuated between 6.5 and 7.5), the VFAs accumulation was enhanced obviously at pH 9.0, but was retarded at acidic (pH 3.0 and pH 5.0), neutral (pH 7.0) or strong alkaline pHs (pH 11.0).

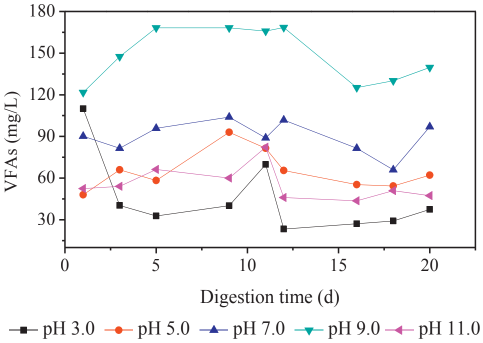

Fig. 3. The relation curves of VFAs and Time at different pHs;

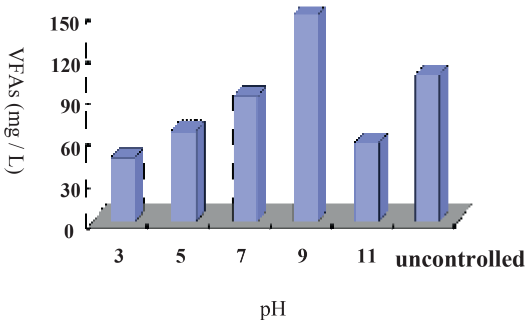

Fig. 4. Mean production of VFAs at different pHs

The reason can be seen from Figure 5. Soluble substrates, such as SCOD, Soluble protein and Soluble carborhydrate were maximum dissolved out from the WAS under pH 11.0, while the VFAs production was not the best. This was because acid-forming bacteria cannot live very well in the highly alkaline environment, in which the activity of microbe reduced resulting in the decrease on the use of soluble substrate.

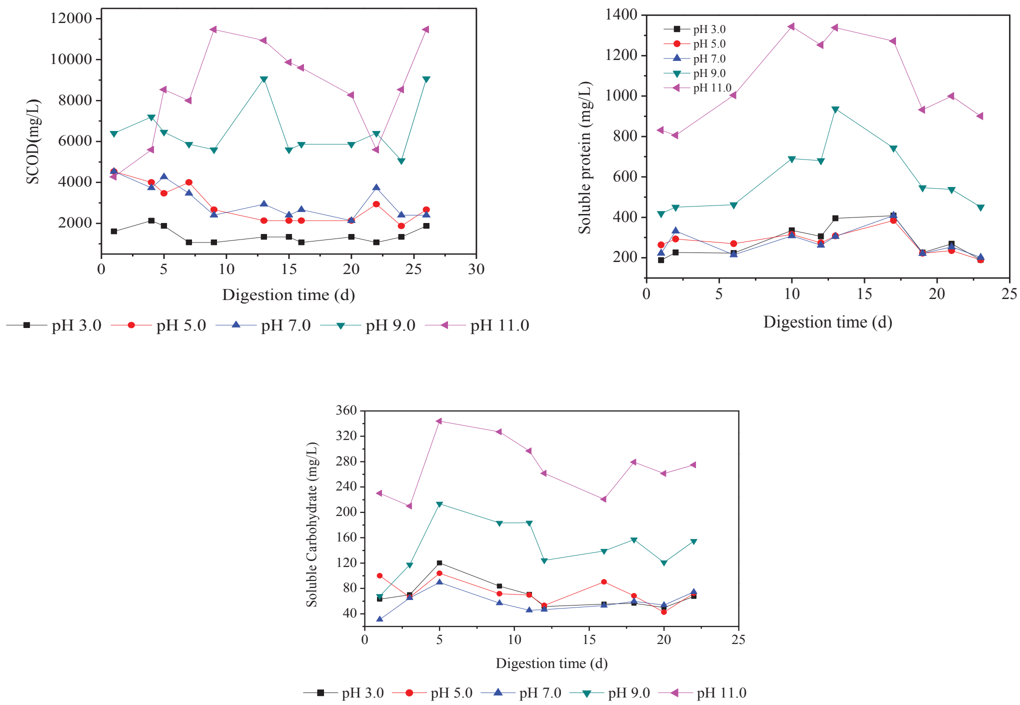

Fig. 5. The relation curves of soluble organics and Time at different pHs

Moreover, it also can be seen that the VFAs accumulation and the soluble substrate release were all restrained under acid pHs in which the activity of microorganism was also inhibited. The conclusion indicated that too high or too low pH values were detrimental to the VFAs accumulation.

4.3. The effect of temperature on WAS acidification under thermophilic conditons

As seen in Figure. 6, with other conditions remaining unchanged (pH 9.0, adding ratio of 25%, HRT 4d), the VFAs accumulation increased first, then decreased with the rising of temperature from 50℃ to 70℃. And we can find that the soluble substrate released greatest during thermophilic anaerobic digestion as operated at 60℃, providing more feeds to the acid-forming bacteria to improve VFAs accumulation obviously.

The conclusion indicated that 60℃ was the best choice for VFAs accumulation. Low (50℃) or excessive (70℃) temperature would influence the final quality of the VFAs products. On one hand, lower or higher temperatures were bound to the relesae of slouble substrate. On the other hand, activity of acid-forming bacteria was markedly inhibited under low or excessive temperatures.

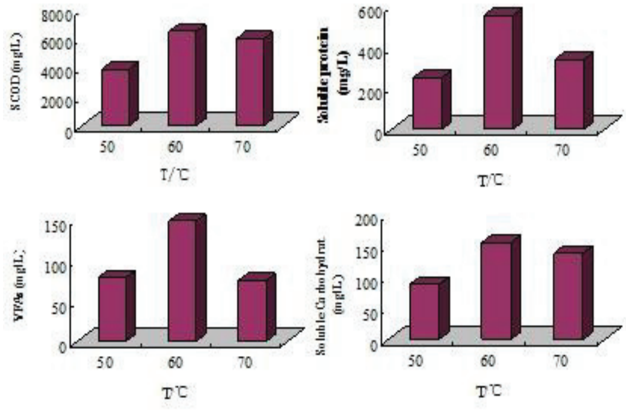

Fig. 6. The effect of temperature on WAS acidification and solubilisation

4.4. The effect of adding ratio on WAS acidification under thermophilic conditons

Based on the pH 9.0 and T 60℃, the influence of adding ratio of WAS on acidification during thermophilic anaerobic digestion was investigated. For the adding ratios of 12.5%, 25% and 50%, the release of Soluble protein and Soluble carbohydrate appeared two peaks at 12h and 48h, while appeared one peak at 48h for the adding ratio of 75%. It was likely to conclude that the fraction of quickly hydrolysed of WAS led to the first peak at 12h and the fraction of slowly hydrolysed led to the second peak at 48h for adding ratios of 12.5%, 25% and 50% (Mottet et al., 2009), while for the adding ratio of 75%, the content of the quickly hydrolysed fraction was more than other adding ratios, requiring more time to hydrolyse, so as to appear only one peak within 60 hours.

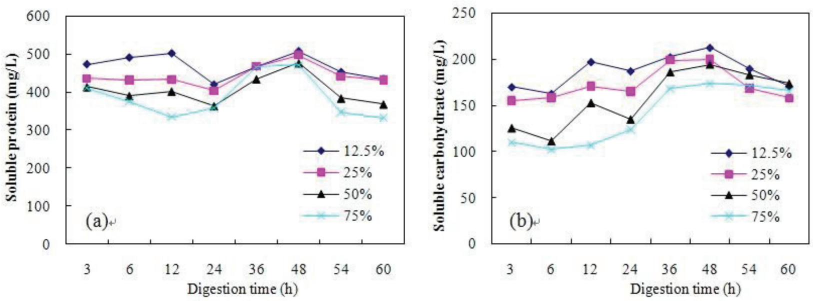

Fig. 7. The relation curves of soluble organics and Time at different adding ratios

Another phenomenon was that the content of Soluble protein declined rapidly from 12h to 24h, and reached minimum within 24 hours for the adding ratios of 12.5%, 25% and 50%, and for the adding ratio of 75%, the first minimum appeared at 12h, however, the Soluble carbohydrate content were little changed. While, table 2 indicated that VFAs accumulation of adding ratios of 12.5%, 25%, 50% and 75% achieved maximum at 24h, 24h, 24h and 12h, respectively. It concluded that the accumulation of VFAs was highly dependent on Soluble protein and less influenced by Soluble carbohydrate.

Table 2. Digestion time of maximum VFAs content at the condition of different adding ratios

▪Adding ratio/%	digestion time/h	HRT/d
▪12.5	24	8
▪25	24	4
▪50	24	2
▪75	12	1

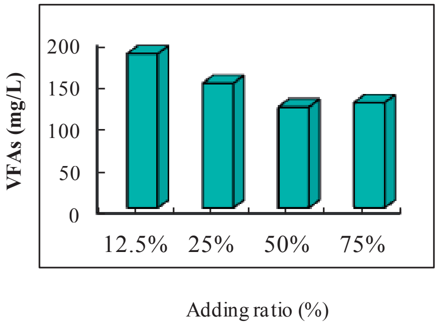

Fig. 8. Comparison of maximum VFAs content at different adding ratios

In conclusion, the accumulation of VFAs was attained peak value at dosing 12.5% and HRT 8d (about 184mg/L) during thermophilic anaerobic digestion compared to other adding ratios of WAS (Figure 8).

4.5. Overall performance of WAS thermophilic anaerobic digestion under optimal acidification conditions

Increased TS and VS destruction were showed in Table 3 during thermophilic anaerobic digestion process from Start-up phases to Acidification phases operated under optimal acidification conditions of WAS thermophilic anaerobic digestion, which was good for the improvement of sludge dewaterability, so as to bring lower costs of disposal.

From the statistics given in the Table 3, over the period from Start-up phases to Acidification phases, the STOC content increased and the STIC content decreased, while the STC content basically remained level, indicating that the convertion from STIC to STOC. And compared to Raw WAS, the soluble organics was greatly released after thermophilic anaerobic digestion under optimal acidification conditions. Besides, STOC/STNb were tending to increase during the whole process, which may be helpful to the growth of the acid-forming bacteria to accumulate more VFAs.

A corresponding higher VFAs production can be found throughout the process, which can be used to additional carbon resource for denitrification. In addition, there was a considerable component of soluble organics which could not be attributed to VFAs.

Table 3. Comparison of sludge characteristics at different stages

▪properties	Raw WAS	Start-up phases	Acidification phases
▪TS (g/L)	24.5	20.2	16.69
▪VS (g/L)	13.2	8.8	6.6
▪STC (mg/L)	275.65	2836.1	2799.4
▪STOC (mg/L)	195.58	1134.6	1907.8
▪STIC (mg/L)	80.08	1701.5	891.5
▪STNb (mg/L)	120.02	532.7	704.5
▪STOC/STNb	1.63	2.13	2.71
▪Soluble protein (mg/L)	74.78	692.88	591.91
▪Soluble Carbohydrate (mg/L)	24.79	183.57	154.75
▪VFAs (mg/L)	0.58	44.1	183.52

5. Conclusion

During the start-up process, the TS, VS and VFAs contents reached a stable state after operated for about 45 days. The TS and VS contents achieved about 17.6% destruction and 33.3% destruction, while achieving 14.4% higher TS destruction and 16.6% higher VS destruction respectively under optimal acidification conditions during thermophilic anaerobic digestion.

In order to maximize the accumulation of VFAs for providing more carbon, the optimal operating conditions for WAS thermophilic anaerobic digestion observed in this study. Firstly, compared to the conditions of pH uncontrolled, the VFAs accumulation was enhanced obviously at pH 9.0, but was retarded at acidic, neutral or strong alkaline pHs. The hydrolysate was greater at alkaline pHs than that at acidic pHs or neutral pH. Secondly, the influence of temperature during thermophilic anaerobic digestion process was little analysised by researchers, while, the conclusion of this study indicated that 60℃ was the best one, and low (50℃) or excessive (70℃) temperatures would influence the final quality of the VFAs products. At last, each adding ratio had its own optimal HRT to producing maximum VFAs, however, the excess adding ratio of WAS cannot improve VFAs products. The results showed that adding ratio of 12.5% and its optimal HRT 8d were the best choice for VFAs accumulation.

Furthermore, the maximal VFAs accumulation at above situation was mainly due to the reasons that sufficient soluble substrates for acidogenic bacteria and less VFAs consumed by other bacterias. And the accumulation of VFAs was highly dependent on soluble protein and less influenced by soluble carbohydrate. Also, in WAS thermophilic anaerobic digestion system, the solubilization was substantially improved under optimal VFAs accumulation conditions.

Acknowledgements

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