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The effect of pH on anaerobic fermentation of primary sludge at room temperature

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ABSTRACT

The effect of pH in the range of 3.0–11.0 on anaerobic fermentation of primary sludge (PS) was investigated at room temperature. The experimental results showed that the concentrations of soluble chemical oxygen demands (SCOD), soluble protein and carbohydrate and short-chain fatty acids (SCFAs) under alkaline conditions were significantly higher than those under other pHs. At fermentation time of 5 days, the average SCFAs concentration increased from 968 to 3511 mg COD/L with the increase of pH from 3.0 to 10.0. However, further increasing pH to 11.0 resulted in the decrease of SCFAs. At pH 10.0, acetic, propionic and iso-valeric acids were the three main products, and the volatile suspended solids (VSS) reduction reached 38%. It was also observed that at any pH value investigated, there were obvious ammonia and phosphorus releases during fermentation. According to this study it is obvious that alkaline pH benefited the soluble organic carbon production from PS.

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1. Introduction

As we all known, the chemical oxygen demands (COD) concentration of wastewater, especially soluble chemical oxygen demands (SCOD) plays an important role on biological nutrients removal (BNR). However, the influent water contains insufficient carbon source in some wastewater treatment plant, particularly in urban wastewater treatment plant. Accordingly, it becomes necessary to add extra carbon source to such wastewater to achieve satisfying BNR performance. Recently, production of SCOD, especially short-chain fatty acids (SCFAs) by fermentation of sludge generated in municipal wastewater treatment plants (MWTP) has attracted much attention, because it can not only take advantage of organic wastes for reclamation but also improve the SCOD concentration of influent.

Primary sludge (PS) and waste activated sludge (WAS) are the two different wastes generated in MWTP. Most of the studies on PS fermentation especially for SCOD and SCFAs production were conducted under uncontrolled pH (i.e. natural). During the fermentation of sludge, the protein and carbohydrate, the key organic compounds of sludge, are hydrolyzed, which results in the decrease of sludge volatile suspended solids (VSS) and increase of SCOD. Maharaj and Elefsiniotis [1] achieved the highest values of the SCFAs, SCOD concentrations and specific production rates in the uncontrolled pH experiment. Banister and Pretorius [2] investigated the ways of optimizing the performance of primary sludge acidogenic fermentation system without any pH adjusted; results showed that retention time, seeding, solids concentration and mixing were the important variables governing SCFAs production, and most of potential SCFAs yield was reached within the fermentation time. Furthermore, it had been revealed by Elefsiniotis et al. [3] that naturally-produced SCFAs provided an excellent carbon source for denitrification and SCFAs were preferred over other soluble organic carbon forms, and among SCFAs, acetic acid were preferred by denitrifiers over other SCFA species. The next most favored SCFA types were butyric acid and propionic acid. In addition, in fermentation experiences conducted without pH control, Cokgor et al. [4] had also found that PS fermentation could generate SCOD with a corresponding SCFAs generation in the uncontrolled condition of pH.

The studies on PS fermentation under pH adjustment with an aim at the SCFAs generation, however, are still largely focused on acidic, neutral or near neutral pH. Elefsiniotis and Oldham [5] has indicated that although acid production is not affected by a decrease in pH from 5.1–4.5, the production is significantly lower (25–30%) at pH of about 6.0. It has also been revealed that the specific rates of SCFAs production and COD solubilization, in either a completely mixed reactor (CMR) or an upflow anaerobic sludge blanket (UASB) unit, were not affected by the variation in pH between 4.3 and 5.2, but at higher pH values (5.9–6.2) a significant decline in both parameters was observed [6]. Gomec and Speece [7] investigated the effect of pH on anaerobic solubilization of domestic PS; results showed that the destruction of VSS was better and its reductions

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was found to be 32% in the pH-controlled reactors of PS. When PS was used as substrate, the same reactors removed VSS with a corresponding production of SCFAs and SCOD and their productions stopped earlier as compared with pH-uncontrolled reactor. In addition, Yu et al. [8] indicated that VSS decreased with a corresponding SCFAs increase with a pH changing from 4.0 to 6.5. When pH ranged in 5.5-6.5, Wu and Wang [9] observed identically SCFAs production. Also, it was observed that pH adjustment and control in the range of 5.5-6.0 had a negative effect on fermentation efficiency, mainly observed as lower SCFAs generation and delay in acidification and longer fermentation times. A similar negative effect was also observed when the pH was increased to 7.5, which only improved hydrolysis but not acidification. Identically, pH control in the 6.5-7.0 range, close to the initial pH of the primary sludge essentially yielded the same results and did not prove meaningful. Nutrient releases were also observed with increase of SCOD and SCFAs [4].

In recent years, more attentions have been paid to the effect of pH on sludge fermentation especially on SCFAs generation. Most of the studies are, nevertheless, mainly focused on the effect of pH on WAS fermentation. Gomec and Speece [7] also investigated the effect of pH on WAS anaerobic solubilization and observed the solubilization was occurring and acetic acid was the main SCFA produced. The production of SCFAs from activated sludge fermentation had also been evaluated at different pH values ranging from 4.0 to 11.0; the result showed that the production of SCFAs at pH 10.0 was 256 mg COD/gVSS, which was over 3 or 4 times that at pH 5.0 and uncontrolled [10].

With the reduction of VSS, apart from the production of SCOD and SCFAs by hydrolysis and acidification of sludge, nitrogen and phosphorus releases are also observed during fermentation of PS. Usually, the nitrogen release comes from the hydrolysis of sludge protein, and the phosphorus release generates from the degradation of intracellular polyphosphate by polyphosphate accumulating organisms (PAOs). The organic nitrogen and phosphorus releases had ever been observed by Moser-Engeler et al. [11]. Compared with the above result, Banister and Pretorius [2] found relatively high levels of ammonia and phosphate in the fermentation liquor of PS. Cokgor et al. [4] achieved lower NH_4^+ -N concentration in pH controlled experiments as compared to uncontrolled sets, especially at pH levels of 5.5 and 6.0. Soluble P release, however, was practically the same for experiments with pH controlled and uncontrolled runs. The reverse results were reported that lower N and P release at pH in the range of 9.0–11.0 [12,13].

PS and WAS have different biodegradation characteristics. WAS is a settling material produced at the secondary sedimentation tank of the wastewater treatment plant after biological treatment. It contains small amounts of nonhydrolyzable particulate materials and biomass by bacteria due to biological metabolism. In contrast, PS consists of a high portion of organic matter such as feces, vegetables, fruits, textiles and paper, a significant organic carbon fraction for the subsequent nutrient removal processes [14-16]. Meanwhile, PS has different biodegradation characteristics in comparison with WAS. Some researchers had drawn a conclusion that the VSS in PS were more biodegradable than in secondary sludge (87% versus 43%) and biodegradable fraction in the VSS contained more viable biomass in PS than in secondary sludge [14]. In the light of research results of Yuan et al. [10] in the WAS fermentation, we think if pH is adjusted to the alkaline range during PS fermentation, the conclusions different from the previously reported on PS fermentation can be attained, which can be due to different properties of PS from that of WAS. Therefore, this text studied in detail the effluences of pH 3.0-11.0 on the hydrolysis of PS and its substitutional products. Moreover, the releases of nitrogen and phosphorus as well as VSS variations in the process of PS fermentation were investigated.

2. Material and methods

2.1. PS source

The PS used in this study was obtained from the primary sedimentation tank of a MWTP in Shanghai, China. The sludge was concentrated by settling at 4 °C for 24 h and adjusted to the required concentration, and its main characteristics are shown in Table 1. As shown in Table 1, proteins and carbohydrates are the two predominant types of organic compounds in primary sludge and they account for about 69% of the VSS.

2.2. Batch fermentation experiments

In order to investigate the effect of pH on anaerobic fermentation of PS, 10 identical reactors, each with working volume of 3 L, internal diameter of 120 mm, and height of 350 mm, were maintained at room temperature. A 30 L portion of PS was divided equally into 10 reactors. All the reactors were mixed with a mechanical stirrer operated at a rate of 70 rpm (revolutions per minute) to sustain homogenous mixing during fermentation. From reactors 1-9, the pH was adjusted and maintained at 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0 and 11.0, respectively. Meanwhile, the pH in reactor 10 was not adjusted and was set as the blank test. The pH was adjusted using 2 M NaOH or 2 M HCl stock solution. Samples were periodically taken from the reactors to monitor SCFAs, SCOD, total suspended solids (TSS), VSS, soluble protein, carbohydrate, ammonia nitrogen (NH_4^+-N) and ortho-phosphate $(PO_4^{3-}-P)$. This experiment was conducted in triplicate, and one way analysis of variance (ANOVA) at the 0.05 level was used to analyze the data.

2.3. Analytical methods

The analyses of COD, SCOD, BOD₅, TSS, VSS, NH₄⁺-N, and PO₄^{3–}–P were conducted in accordance with standard methods [17]. After sludge samples from reactors were centrifuged and then filtered through a Whatmann GF/C glass microfiber (0.45 µm pore size), the filtrate was collected in a 1.5 mL gas chromatography (GC) vial, and 3% H₃PO₄ was added to adjust the pH to approximately 3.0. SCFAs compositions were analyzed by means of gas chromatography (Agilent 6890N GC) with flame ionization detector and DB-WAXETR column (30 m \times 1.0 μ m \times 0.53 mm). Nitrogen was the carrier gas and the flux was 25 mL/min. The injection port and the detector were maintained at 220 and 250 °C, respectively. The oven of GC was programmed to begin at 110 °C and to remain there for 2 mins, then to increase at a rate of 10 °C /min to 220 °C, and to hold at 220 °C for an additional 2 mins. The sample injection volume was 1.0 µL. The filtrate was also used for analyzing soluble protein and carbohydrate. Soluble protein was determined by the

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Characteristics of the primary sludge.^a.

Parameter	Mean	SD ^b
pН	6.0	0.2
TSS	19 300	165
VSS	11 641	32
SCFAs (as COD)	52	1
SCOD	1 759	88
TCOD	20 631	631
BOD ₅	106	4
PO4 ³⁻ -P	12	1
NH4 ⁺ -N	53	4
Total carbohydrate (as COD)	312	12
Total protein (as COD)	7 718	144

^a All values are expressed in mg/L except pH. The data are the averages in triplicate tests.

^b SD: standard deviation.

Lowry-Folin method with bovine serum albumin (BSA) as standard [18]. Carbohydrate was measured by the phenol-sulfuric method with glucose as standard [19].

SCFAs concentrations were converted to COD by using appropriate conversion factors as 1.07 for acetic acid, 1.51 for propionic acid, 1.82 for butyric and iso-butyric acids, and 2.04 for valeric and isovaleric acids. Protein and carbohydrate, however, were converted to COD with the conversion factors of 1.5 and 1.07, respectively [20].

3. Results and discussion

3.1. Effect of pH on SCOD production

Sludge hydrolysis can be expressed by the changes of SCOD concentrations [21,22]. The effect of pH on the observed SCOD concentrations at different fermentation times is shown in Fig. 1. It was obvious that concentrations of SCOD at different pHs had a similar trend with change in time except at pH 11.0. The average SCOD increased from the initial 1759 mg/L to their respective maximum on the 5th day (pH 10.0 (5755 mg/L)>pH 9.0 (5690)>pH 8.0 (4450)>pH 6.0 (4083)>pH 7.0 (4003)>pH 5.0 (3914)>pH 4.0 (3775)>pH 3.0 (3577)>blank test (2771)) in all reactors except pH 11.0 (F = 980, $F_{crit} = 2$, $P = 4 \times 10^{-22} < 0.05$), which indicated that more and more particulate organics in PS became soluble substrates. The SCOD concentration on the 5th day was about 3.3 times higher than the initial at pH 10.0. After the 5th day, the SCOD concentration in all reactors decreased with fermentation time. At pH 11.0, however, the average concentration of SCOD was up to its maximal value (6931 mg/L) on the 14th day, which was very different from that at other pHs.

Obviously, the SCOD at alkaline pH (pH 9.0, 10.0 and 11.0) was significantly higher than that at near neutral pH (pH 6.0, 7.0 and 8.0) or acidic pH (pH 3.0, 4.0 and 5.0), and the blank test (without pH adjustment) showed the lowest SCOD concentration, which stated clearly that controlling the fermentation pH was more beneficial for hydrolysis of PS and the alkaline pH was more efficient than acidic and neutral pHs. At any fermentation time, the same observations could be made (Fig. 1). Apparently, the PS hydrolysis rate was accelerated under alkaline conditions, which has also been observed by other researchers [23,24].

3.2. Effects of different pHs on the concentrations of soluble protein and carbohydrate

During PS fermentation, the sludge protein and carbohydrate were firstly converted to soluble protein and carbohydrate (compositions of SCOD), respectively. Fig. 2 shows the effect of pH on the



Fig. 1. Effect of pH on the observed SCOD concentrations at different fermentation times (@t=0, SCOD = 1 759 mg/L). Error bars represent standard deviations of triplicate tests.



Fig. 2. Effect of pH on the observed concentrations of soluble protein. Error bars represent standard deviations of triplicate tests.



Fig. 3. Effect of pH on the observed concentrations of soluble carbohydrate. Error bars represent standard deviations of triplicate tests.

observed concentrations of soluble protein. Fig. 3 shows the effect of pH on the observed concentrations of soluble carbohydrate. As seen in Fig. 2 and Fig. 3, the concentrations of these two substrates under alkaline conditions were greater than other conditions. Obviously, pH had almost the same effect on soluble protein and carbohydrate concentrations as on SCOD concentration. It was observed that concentrations of soluble protein (Y_{protein}) and carbohydrate ($Y_{\text{carbohydrate}}$) under alkaline pH (8.0–11.0) increased linearly with pH on the 5th day (F = 1454, $F_{\text{crit}} = 4$, $P = 3 \times 10^{-11} < 0.05$ and F = 1370, $F_{\text{crit}} = 4$, $P = 4 \times 10^{-11} < 0.05$), respectively for soluble protein and carbohydrate (Eq. (1), Eq. (2)).

$$Y_{\text{protein}} = 486.8 \, pH + 284.7, \quad R^2 = 0.99 \tag{1}$$

$$Y_{\text{carbohydrate}} = 85.7 \, pH - 17.1, \quad R^2 = 0.99$$
 (2)

At pH 10.0, their average values were respectively 1747 mg COD/L and 226 mg COD/L. The concentrations of soluble protein and carbohydrate, on the contrary, fluctuated slightly with the increase of fermentation time. This might be explained that the observed concentrations of soluble protein and carbohydrate were the result of a net balance between competing rates of release and degradation. When the degradation rate exceeded the release, the concentrations were observed to decline.

It could be concluded from the above that alkaline conditions were similarly helpful to solubilization of protein and carbohydrate which were the main constituents of sludge [25,26]. This might be attributable to the reason that the alkaline pH resulted in the dissociation of acidic groups in extracellular polymeric substances (EPS) of sludge which mainly consisted of protein and carbohydrate and repulsions between the negatively charged EPS, and solubility of protein and carbohydrate in water therefore increased [27].

3.3. Effect of pH on total SCFAs concentration

The effect of pH on SCFAs concentration at different fermentation times is shown in Fig. 4. It could be seen that the average SCFAs concentrations at pH 3.0–10.0 increased from the initial 52 mg COD/L to their respective maximum on the 5th day (pH 10.0 (3511 mg COD/L) > pH 9.0 (3390) > pH 8.0 (3361) > pH 7.0 (3135) > pH 5.0 (2536) > pH 6.0 (2401) > pH 4.0 (1693) > pH 3.0 (968)) (*F* = 1507, *F*_{crit} = 3, *P* = 2 × 10⁻²¹ < 0.05), and then decreased gradually. For pH 11.0 and the blank test, however, the maximum SCFAs (with the average of 3643 mg COD/L and 2216 mg COD/L) occurred on the 14th day and 9th day, respectively.

It was obvious that the SCFAs concentrations at alkaline pHs (pH 8.0, 9.0, 10.0 and 11.0) were significantly higher than that at near neutral pHs (pH 6.0 and 7.0) or acidic pHs (pH 3.0, 4.0 and 5.0) or in the blank test, similar to the results observed with SCOD. In addition, although the highest SCFAs production as mean value in the pH range 3.0-11.0 was 3643 mg COD/L appearing at pH 11.0, it took a much longer time to produce the same mount of SCFAs as that produced at pH 10.0. One can calculate the SCFAs production rate at pH 10.0 (60 mg COD/g VSS·d) and pH 11.0 (22 mg COD/g VSS d) in terms of investigated VSS concentration, which indicated that the production of SCFAs at pH 10.0 was more efficient than at pH 11.0. Thus, pH 10.0 and fermentation time 5 days were regarded as the optimal conditions for SCFAs production from PS. Besides, it can be seen from Fig. 4 that the concentration of SCFAs at pH 3.0 was extremely low, which might be due to the inhibition of strong acidity on the activity of acidogenic bacteria. In the blank test, however, SCFAs production was close to that at neutral pH, which might attribute to the pH in the blank test varying from 5.95 to 7.07 during the fermentation time.

At pH 10.0, the average of specific SCFAs production was 302 mg COD/g VSS, which was much higher than others reported in the literature. Banerjee et al. [28] showed that acidogenesis was feasible and the net SCFAs production ranged from 66 to 137 mg COD/gVSS as pH value varied from 5.1 to 6.2 when industrial wastewater and PS were fermented together. Chen et al. [12] investigated the effect of pH from 4.0 to 11.0 on the hydrolysis and acidification of WAS, and experimental results showed that alkaline conditions were helpful to the production of SCFAs, the concentration of SCFAs on the 8th day of fermentation at pH 4.0, 7.0 and 10.0 was 33, 78 and 250 mg COD/g VSS, respectively.



Fig. 4. Effect of pH on total SCFAs production at different fermentation times (@t = 0, total SCFAs = 52 mg COD/L). Error bars represent standard deviations of triplicate tests.

Table 2

Effect of pH on the percentage of individual SCFA accounting for total SCFAs at 5-day fermentation time.

pН	HAc (%)	HPr (%)	i-HBu (%)	HBu (%)	i-HVa (%)	HVa (%)
Blank test	39	31	3	16	6	5
3.0	38	38	1	17	2	4
4.0	46	32	1	16	2	3
5.0	44	32	2	13	5	4
6.0	34	35	4	14	8	5
7.0	34	36	5	11	10	4
8.0	38	35	5	11	8	3
9.0	42	31	5	9	9	4
10.0	45	25	4	13	10	3
11.0	48	26	4	13	6	3

Note: HAc = acetic, HPr = propionic, i-HBu = iso-butyric, HBu = n-butyric, i-HVa = iso-valeric, HVa = valeric. The data reported are the average of triplicate tests.

3.4. Effects of pH on the constituents of SCFAs

Six SCFAs, i.e., acetic, propionic, iso-butyric, n-butyric, isovaleric, and *n*-valeric acids were all detectable in pH controlled (pH 3.0-11.0) and in blank tests. Table 2 summarizes the effect of pH on the percentage of individual SCFA accounting for total SCFAs at 5-day fermentation time; Table 3 shows the percentage of individual SCFA accounting for total SCFAs with time at pH 10.0. As seen in Table 2, acetic acid had the highest percentage (34–48%) at pH 3.0-11.0 and in the blank test. Also, the concentration of acetic acid maintained the following order: alkaline > acidic > blank test > neutral pH. The percentage of propionic acid ranged between 25% and 38% in either pH controlled or in the blank test on the 5th day. In most cases, the order of individual SCFAs concentration was acetic > propionic > n-butyric > iso-valeric > (n-valeric, n-butyric). Additionally, acetic, propionic and *n*-butyric acid were the three main products at any pH investigated in 5-day fermentation time. At pH 5.0, 7.0 and 10.0, the averages of these three SCFAs accounted for 89%, 80% and 83% of total SCFAs, respectively.

As shown in Table 3, although acetic acid was the dominant SCFA with the mean percentage of more than 45% in most fermentation time, the percentage of propionic acid increased gradually and even exceeded that of acetic acid at the end of fermentation time (34% and 27%, respectively). With the further increase of fermentation time, as seen in Table 3, the percentages of propionic and iso-valeric acid increased gradually whereas the percentage of *n*-butyric acid decreased rapidly. Thus, in most cases, acetic, propionic and isovaleric acids were the three main products at pH 10.0, and their average total amount accounted for 83% of total SCFAs. This was consistent with the findings of prior studies on WAS by Chen et al. [12]. Wang et al. [29] also revealed that the top three SCFAs were acetic, propionic and iso-valeric acids and the decomposition rates of the SCFAs (C2-C6) with a straight chain (normal form) were greater than those of their respective isomers with a branched chain (iso form).

According to the above study, it is obvious that alkaline condition had more advantage over improvement of yields of acetic acid

Table 3

Variations of percentage of individual SCFA accounting for total SCFAs with time at pH 10.0.

Time (d)	2	5	9	14	20
HAc (%)	44	45	49	45	27
HPr (%)	23	25	26	29	34
i-HBu (%)	6	4	7	7	15
HBu (%)	9	13	3	0	0
i-HVa (%)	15	10	12	13	18
HVa (%)	3	3	3	6	6

Note: HAc = acetic, HPr = propionic, i-HBu = iso-butyric, HBu = n-butyric, i-HVa = iso-valeric, HVa = valeric. The data reported are the average of triplicate tests.



Fig. 5. Effect of pH on VSS reduction at different fermentation time (@t = 0, VSS = 11 641 mg/L). The data reported are the average of triplicate tests.

than acidic or neutral condition. In the operation, the propionic percentage was significantly improved to more than 23%, which were much more than those in WAS fermentation (less than 20% as shown by Yuan et al. [10]). Thus, when PS fermentation liquid was used as the carbon source of enhanced biological phosphorus removal (EBPR), its performance would be better than pure acetic acid. It had also been found that propionic acid-enriched wastewater was much more efficient for EBPR and had a higher phosphorus removal rate in the long-term cultured experiment [30,31].

3.5. Effect of pH on VSS reduction

When PS was fermented with the production of SCOD, the corresponding VSS reduction was observed, which has also been reported by other researchers [4,32]. As seen from Fig. 5, there was different VSS reduction at different pHs in spite of the same initial VSS. Generally, a higher rate in the initial period of fermentation compared to the later fermentation time was observed. Besides, it was easy to see that there was no significant VSS reduction at pH 3.0, which is consistent with few SCFAs produced. The highest VSS reduction was at pH 10.0 with an average of 49% on the 20th day. When the fermentation time was 5 days and pH 10.0, there was a 38% VSS reduction.

3.6. Effects of pH on soluble NH_4^+ –N and PO_4^{3-} –P concentrations

It has been reported that both nitrogen and phosphorus were released during sludge fermentation [11,13], but very few discussed the influence of pH on their releases. The effects of pH on the observed nitrogen and phosphorus concentrations are shown in Figs. 6 and 7, respectively.



Fig. 6. Effect of pH on the observed NH_4^+-N concentration. The data reported are the average of triplicate tests.



Fig. 7. Effect of pH on the observed soluble $PO_4^{3-}-P$ concentration. The data reported are the average of triplicate tests.

As shown in Fig. 6, the concentrations of NH₄⁺-N in pH controlled (pH 3.0-11.0) and in blank tests were all kept increased during fermentation. A sequencing of even NH_4^+ – N concentration at near neutral pH (pH 6.0 and 7.0) > acidic pH (pH 5.0) > alkaline pH (pH 8.0, 9.0, 10.0 and 11.0) > blank test > strong acidic pH (pH 3.0 and 4.0) was observed after 9 days of fermentation (P < 0.05). The data in Fig. 7 showed a different order with regard to the even concentration of phosphorus, acidic pH (pH 3.0, 4.0, 5.0) > near neutral pH (pH 6.0 and 7.0) > blank test > alkaline pH (pH 8.0, 9.0, 10.0 and 11.0) after 9 days of fermentation (P < 0.05). Seen as both Figs. 6 and 7, the NH_4^+ -N releases were greater than PO_4^{3-} -P in most cases. The same result was observed in the literature [2,12]. Also, the effects of pH on the concentrations of released nitrogen and phosphorus were different with those of SCOD and SCFAs. The concentrations of NH4+-N and PO₄³⁻ – P under alkaline pHs were lower than those under other pHs, which might be due to their precipitation in the formation of struvite at alkaline pHs, which need further investigation.

4. Conclusion

Based on the experimental results outlined in the previous sections, the conclusions of this study could be summarized as follows:

Compared with the studies on PS fermentation under conditions of acidic or near neutral pHs reported in the literature, it was observed in this paper that an alkaline pH greatly improved the hydrolysis of PS, and produced more SCOD, especially soluble protein and carbohydrate. The first and second maximal SCOD, occurring at pH 11.0 on the 14th day and at pH 10.0 on the 5th day, were up to more than 4 and 3 times than the initial, respectively.

Also, it was found in this study that due to more soluble hydrolysis products provided for acidification, the accumulation of SCFAs under alkaline pH was significantly greater than that at acidic or near neutral pHs. At pH 10.0 and fermentation time of 5 days, the average concentration of total SCFAs was 3511 mg COD/L with acetic acid percentage of around 45% and propionic acid percentage of 25%. The corresponding VSS decrease was of 38% under the same condition. In most fermentation time, acetic, propionic and isovaleric acids accounted for the majority (with an average of 83%) of SCFAs at any pH value investigated. Meanwhile, releases of soluble ammonia and phosphorus were observed.

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References

- I. Maharaj, P. Elefsiniotis, The role of HRT and low temperature on the acidphase anaerobic digestion of municipal and industrial wastewaters, Bioresour. Technol. 76 (2001) 191–197.
- [2] S.S. Banister, W.A. Pretorius, Optimisation of primary sludge acidogenic fermentation for biological nutrient removal, Water SA. 24 (1998) 35–41.
- [3] P. Elefsiniotis, D.G. Wareham, M.O. Smith, Use of volatile fatty acids from an acid-phase digester for denitrification, J. Biotechnol. 114 (2004) 289–297.
- [4] E.U. Cokgor, S. Oktay, D.O. Tas, G.E. Zengin, D. Orhon, Influence of pH and temperature on soluble substrate generation with primary sludge fermentation, Bioresour. Technol. 100 (2009) 380–386.
- [5] P. Elefsiniotis, W.K. Oldham, Acid-phase anaerobic digestion of primary sludge and its role in the biological phosphorus removal process, Water Pollut. Res. J. Can. 28 (1993) 513–528.
- [6] P. Elefsiniotis, W.K. Oldham, Influence of pH on the acid-phase anaerobic digestion of primary sludge, J. Chem. Technol. Biotechnol. 60 (1994) 89–96.
- [7] C.Y. Gomec, R.E. Speece, The role of pH in the organic material solubilization of domestic sludge in anaerobic digestion, Water Sci. Technol. 48 (2003) 143– 150.
- [8] H.Q. Yu, X.J. Zheng, Z.H. Hu, G.W. Gu, High-rate anaerobic hydrolysis and acidogenesis of sewage sludge in a modified upflow reactor, Water Sci. Technol. 48 (2003) 69–75.
- [9] Y.P. Wu, X.D. Wang, Study on primary sludge hydrolysis as biological nitrogen and phosphorus removal, J. Xi'an Univ. Arch. Technol. 37 (2005) 508, 501-503.
- [10] H.Y. Yuan, Y.G. Chen, H.X. Zhang, S. Jiang, Q. Zhou, G.W. Gu, Improved bioproduction of Short-chain Fatty Acids(SCFAs) from excess sludge under alkaline conditions, Environ. Sci. Technol. 40 (2006) 2025–2029.
- [11] R. Moser-Engeler, K.M. Udert, D. Wild, H. Siegrist, Products from primary sludge fermentation and their suitability for nutrient removal, Water Sci. Technol. 38 (1998) 265–273.
- [12] Y.G. Chen, S. Jiang, H.Y. Yuan, Q. Zhou, G. Gu, Hydrolysis and acidification of waste activated sludge at different pHs, Water Res. 41 (2007) 683–689.
- [13] Y.H. Ahn, R.E. Speece, Elutriated acid fermentation of municipal primary sludge, Water Res. 40 (2006) 2210–2220.
- [14] Z.C. Arnai, J.C. Gutierrez, J. Lebrato, Biomass stabilization in the anaerobic digestion of wastewater sludges, Bioresour. Technol. 97 (2006) 1179–1184.

- [15] E.U. Cokgor, G.E. Zengin, D.O. Tas, S. Oktay, C.W. Randall, D. Orhon, Respirometric assessment of primary sludge fermentation products, J. Environ. Eng. ASCE. 132 (2006) 68–74.
- [16] S. Puig, M. Coma, H. Moncluĭ s, M.C.M. van Loosdrecht, J. Colprima, M.D. Balaguer, Selection between alcohols and volatile fatty acids as external carbon sources for EBPR, Water Res. 42 (2008) 557–566.
- [17] American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), Standard methods for the examination of water and wastewater, 20th ed., Washington, DC: American Public Health Association, 1998.
- [18] O.H. Lowry, N.J. Rosebrough, A.L. Farr, R.J. Randall, Protein measurement with the Folin phenol reagent, J. Biol. Chem. 193 (1951) 165–175.
- [19] D. Herbert, P.J. Philipps, R.E. Strange, Methods Enzymol. 5B (1971) 265–277.
- [20] G.C.P. Leslie, S.T. Dsigger, H.C. Lim, Biological wastewater treatment, 2nd ed., Marcel dekker, Inc., New York, 1999, p. 63.
- [21] K. Andreasen, G. Petersen, H. Thomsen, R. Strube, Reduction of nutrient emission by sludge hydrolysis, Water Sci. Technol. 35 (1997) 79–85.
- [22] G.J. Hatziconstantinou, P. Yannakopoulos, A. Andreadakis, Primary sludge hydrolysis for biological nutrient removal, Water Sci. Technol. 34 (1996) 417–423.
- [23] E. Neyens, J. Baeyens, C. Creemers, Alkaline thermal sludge hydrolysis, J. Hazard. Mater. 97 (2003) 295–314.
- [24] A.G. Vlyssides, P.K. Karlis, Thermal-alkaline solubilization of waste activated sludge as a pre-treatment stage for anaerobic digestion, Bioresour. Technol. 91 (2004) 201–206.
- [25] N. Mahmoud, G. Zeeman, H. Gijzen, G. Lettinga, Anaerobic stabilisation and conversion of biopolymers in primary sludge-effect of temperature and sludge retention time, Water Res. 38 (2004) 983–991.
- [26] S. Tanaka, T. Kobayashi, K. Kamiyama, M.N. Bildan, Effects of thermochemical pretreatment on the anaerobic digestion of waste activated sludge, Water Sci. Technol. 35 (1997) 209–215.
- [27] H. Liu, H.H.P. Fang, Extraction of extracellular polymeric substances (EPS) of sludges, J. Biotechnol. 95 (2002) 249–256.
- [28] A. Banerjee, P. Elefsiniotis, D. Tuhtar, The effect of addition of potato-processing wastewater on the acidogenesis of primary sludge under varied hydraulic retention time and temperature, J. Biotechnol. 72 (1999) 203–212.
- [29] Q.H. Wang, M. Kuninobu, H.I. Ogawa, Y. Kato, Degradation of volatile fatty acids in highly efficient anaerobic digestion, Biomass Bioenergy 16 (1999) 407–416.
- [30] Y.G. Chen, Y.S. Chen, Q. Xu, Q. Zhou, G.W. Gu, Comparison beteen acclimated and unacclimated biomass affecting anaerobic-aerobic transformations in the biological removal of phosphorus, Process Biochem. 40 (2005) 723–732.
- [31] Y.G. Chen, Y. Liu, Q. Zhou, G.W. Gu, Enhanced phosphorus biological removal from wastewater-effect of microorganism acclimatization with different ratios of short-chain fatty acids mixture, Biochem. Eng. J. 27 (2005) 24–32.
- [32] A.G. Ibrahim, F.H. Mohamed, A.E.G. Mohamed, Nitrogen transformations during aerobic/anoxic sludge digestion, Bioresour. Technol. 85 (2002) 147–154.