Volatile fatty acids production from food waste: Effects of pH, temperature, and organic loading rate

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HIGHLIGHTS

- The concentration and yield of VFAs were highest at pH 6.0.
- A more efficient and economical temperature for VFAs production is 35 °C.
- An OLR of 11 g/L d is suitable for VFAs production.
- Ammonia nitrogen was released during the anaerobic acidification.

ARTICLE INFO

Article history:
Received 8 April 2013
Received in revised form 6 June 2013
Accepted 10 June 2013
Available online 17 June 2013

Keywords:
VFAs
pH
Temperature
Organic loading rate
Food waste

ABSTRACT

The effects of pH, temperature, and organic loading rate (OLR) on the acidogenesis of food waste have been determined. The present study investigated their effects on soluble chemical oxygen demand (SCOD), volatile fatty acids (VFAs), volatile solids (VS), and ammonia nitrogen (NH₄⁻N). Both the concentration and yield of VFAs were highest at pH 6.0, acetate and butyrate accounted for 77% of total VFAs. The concentrations of VFAs, SCOD, and NH₄⁻N increased as OLR increased, whereas the yield of VFAs decreased from 0.504 at 5 g/L d to 0.306 at 16 g/L d. Acetate and butyrate accounted for 60% of total VFAs. The percentage of acetate and valerate increased as OLR increased, whereas a high OLR produced a lower percentage of propionate and butyrate.

1. Introduction

Biological nutrient removal (BNR) is widely used in modern municipal and industrial wastewater treatment plants (WWTP) in China. A significant factor in the success of the BNR process is the availability of a suitable carbon source. One such carbon source is methanol, which has been used for many years. However, methanol can be expensive and may contribute up to 70% of the total operating and maintenance costs of a municipal wastewater treatment facility (Elefsiniotis and Wareham, 2007). Hence, it is necessary and important to develop alternative carbon sources such as volatile fatty acids (VFAs) (Llabres et al., 1999; Kampas et al., 2007).

VFAs can be produced by anaerobic digestion of food waste (Kim et al., 2006). Recently, the demands for reduction and utilization of municipal solid waste (MSW) have rapidly increased in China. In 2006, the total amount of MSW collected and transported was 148 million tons, about 60% of which was food waste (Zhang et al., 2010). The most common disposal method for MSW, including food waste, is moving it to a sanitary landfill. However, there are some problems associated with this, including the leachate produced from landfills (Shu et al., 2006), the emission of greenhouse gases (Abichou et al., 2006), and limited landfill space.

Food waste has a high content of moisture and organic matter, and thus is an ideal substrate for anaerobic digestion. The process of anaerobic digestion consists of four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (De la Rubia et al., 2009). VFAs are produced in the first three steps. Acidogenesis of food waste can also produce valuable products such as H₂, which is a clean fuel (Kim et al., 2011; Lee et al., 2010; Li et al., 2008).

VFAs, which mainly contain acetate, propionate, iso-butyrate, n-butyrate, iso-valerate, and n-valerate, can be used as a carbon source in BNR processes (Llabres et al., 1999; Barber and Stuckey, 2000; Elefsiniotis et al., 2004). Thus, there is a vital need to obtain a higher concentration of VFAs during anaerobic digestion. There are some literature related to VFAs production from food waste. Elbeshbishy and Naikha (2011) studied the effect of ultrasonication on the solubilization, biogas (hydrogen and methane) production,
and anaerobic biodegradability of food waste in single and two-stage systems. Komemoto et al. (2009) evaluated the effect of temperature on solubilization and acidogenesis of food waste and found that high solubilization rates and biogas production were observed under mesophilic conditions. Leaching bed reactor were used to evaluate the effect of inoculum to substrate ration (Xu et al., 2012), pH and bulking agent (Xu et al., 2011) on the hydrolysis and acidification of food waste. Some literature also reported VFAs production from food waste and other substrates such as sludge (Chen and Wu, 2010) and organic fraction of municipal solid wastes (OFMSW) (Sans et al., 1995; Dogan et al., 2008). The influences of operational parameters, such as hydraulic retention time (HRT), on anaerobic fermentation were investigated in the above-mentioned researches, however, it was also found that pH, temperature, and OLR are important factors for the production of VFAs from food waste.

The pH and temperature affect the growth of microorganisms and the hydrolysis of particulate organic matter to soluble substances (Kim et al., 2003; Mahmoud et al., 2004), while the hydrolysis is rate-limiting step of anaerobic digestion of food waste. It tends to produce higher concentration VFAs at a high OLR, but the operation of the reactor at too high OLR is unstable (Lim et al., 2008). The pH, temperature, and OLR could affect the fermentation process, however, there are few researches on the effects of these factors on VFAs production from food waste.

Hence, this study aimed to investigate the effects of pH, temperature, and OLR on the production of VFAs from food waste to obtain maximum concentration of VFAs. In addition, we assessed the effects on soluble chemical oxygen demand (SCOD), volatile solid (VS), and ammonia nitrogen.

2. Methods

2.1. Substrates and inoculum

Simulated food waste was used in this study, composed of 35% rice, 45% cabbage, 16% pork, and 4% tofu by weight. The four components were mixed and crushed using a food waste disposer, and then stored in a refrigerator at 4 °C. The characteristics of the food waste are presented in Table 1. Mesophilic anaerobic digested sludge from the Gaobeidian wastewater treatment plant in Beijing, China, was used as the inoculum, after natural sedimentation for 3 days. The TS, VS/TS, and C/N of the inoculum were 5.62%, 44.69%, and 8.5%, respectively.

Table 1

<table>
<thead>
<tr>
<th>Characteristics of food waste used in this study.</th>
<th>Food waste</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS (%)</td>
<td>20.53 ± 2.04</td>
</tr>
<tr>
<td>VS (%)</td>
<td>19.95 ± 2.21</td>
</tr>
<tr>
<td>VS/TS (%)</td>
<td>97.17 ± 1.11</td>
</tr>
<tr>
<td>SCOD (g/L)</td>
<td>125.65 ± 3.70</td>
</tr>
<tr>
<td>NH4–N (mg/L)</td>
<td>76.86 ± 30.33</td>
</tr>
<tr>
<td>VFAs (mg/L)</td>
<td>829.53 ± 103.16</td>
</tr>
<tr>
<td>pH</td>
<td>4.59 ± 0.17</td>
</tr>
<tr>
<td>C/N</td>
<td>13.45 ± 0.18</td>
</tr>
</tbody>
</table>

Average ± standard deviation of three samples.

2.2. Experimental set-up

2.2.1. Effects of pH and temperature

Four identical reactors with a working volume of 4.5 L were used and operated in batch mode. About 800 ml inoculum and 3 L diluted food waste (500 ml tap water added to 1 L food waste) were put into each reactor. The reactor was mechanically mixed at a constant speed of 250 rpm by an agitator. The temperature was controlled using a water circulator and water jacket system. The pH of the four reactors was automatically controlled by a pH controller via the addition of hydrochloric acid (HCl) or sodium hydroxide (NaOH).

The effect of temperature was investigated by operating the reactor at 35, 45, and 55 °C at pH 6.0. The effect of pH was investigated by operating the reactor at pH 5.0, 6.0, 7.0, and uncontrolled at 35 °C. At the start of the experiment, nitrogen gas was flushed through the system to create anaerobic conditions. The reactors were run for 8 days when the SCOD and VFA content of the effluent were stable.

2.2.2. Effect of OLR

Three identical reactors with a mixer were used and operated in a semi-continuous mode (once-a-day feeding and draw-off). Experiments were conducted at a constant temperature (35 °C), pH (6.0), and HRT (5 days). The effect of OLR was investigated by operating the reactor at OLRs of 5, 11, and 16 g TS/L d.

2.3. Analytical methods

TS and VS were measured according to standard methods (APHA, 1999). Elemental compositions were determined using a CE-440 Element Analyzer. SCOD, VFAs, ethanol, and ammonia nitrogen were measured after centrifugation (15,000 rpm for 15 min) and filtration (0.45 μm). VFAs (acetate, propionate, butyrate, isobutyrate, valerate, and isovalerate) and ethanol were measured using a gas chromatograph (Shimadzu, GC-2010 plus) equipped with a capillary column (stabilwax-DA, 30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID). The temperature of the injector and detector were 220 and 250 °C, respectively. The column temperature was increased from 60 to 150 °C at a rate of 7 °C/min, kept at 150 °C for 5 min, and then increased to 230 °C at a rate of 20 °C/min, and kept at 230 °C for an additional 10 min. The pH of the samples was adjusted to below 2.0 using 25% H3PO4. The concentration of ammonia nitrogen was determined by Nessler reagent spectrophotometry. SCOD was measured by the titration method after digestion with a digestion instrument.

3. Results and discussion

3.1. Effect of pH

Four reactors were operated for 8 days at 35 °C. The pH of the uncontrolled reactor dropped quickly to 3.0 due to the production and accumulation of VFAs and similar trend was reported previously (Kim et al., 2003; Dogan et al., 2008). The pH of other three reactors were controlled at 5.0, 6.0 and 7.0, respectively, and were stable throughout the experiment indicating that the online pH control was accurate. In the first step of anaerobic digestion, insoluble organic polymers such as carbohydrates, proteins, and fats are broken into simple sugars, fatty acids, and amino acids. The solubilization of the solid organic fraction of food waste can cause increase in soluble COD in the reactor. In this study, SCOD increased gradually with time to a stable value under all pH conditions (Fig. 1(a)). The maximum SCOD concentrations were observed at pH 6.0 and 7.0, which was in agreement with the reports of Kim et al. (2003) and Lim et al. (2008).

VFAs were produced in the acidogenesis and acetogenesis steps. Fig. 1(b) shows the variation in VFAs concentration in the reactor at different pH conditions. Under all pH conditions, the concentration increased rapidly at first and then was relatively stable and changed little. The maximum VFAs concentrations at pH uncontrolled, 5.0, 6.0, and 7.0 were 3.94, 17.08, 39.46 and 37.09 g/L, respectively,
indicating that the greatest VFAs production was occurred at pH 6.0, which was similar to Lim et al. (2008). The hydrolytic enzymes activities were optimum at pH 6.0 and hence lead to a highest concentration of VFAs (Parawira et al., 2005). The VFAs concentration was very low when the pH was uncontrolled. This is because VFAs are undissociated at this very low pH and inhibit microbial growth by passing through the cell membrane of microbes (Warnecke and Gill, 2005). The VFAs yield at pH 6.0 was 0.316 g/gVSfed, which was 2.3-fold higher than pH 5.0 and 9.8-fold higher than uncontrolled.

The ratio of VFA to SCOD is very important, as it shows how much soluble substance is converted into VFAs. As shown in Fig. 1(c), this ratio increased with time before reaching a stable value and showed a similar trend as the VFAs concentration curve. At the end of digestion, VFAs accounted for 6.6%, 28.9%, 72.8%, and
70.5% of SCOD at pH uncontrolled, 5.0, 6.0, and 7.0, respectively. The low ratio of VFA/SCOD at pH uncontrolled and 5.0 also showed that the fermentation was in some extent inhibited under these conditions. It is important to maximize VFAs production for use as a carbon source in biological nutrient removal processes, but other metabolites such as ethanol can also be used as carbon sources. The concentration of ethanol was relatively stable during anaerobic digestion, measuring 5.63, 2.13, 1.36, and 4.62 g/L when the pH was uncontrolled and controlled at 5.0, 6.0, and 7.0, respectively, and accounting for 15.1%, 5.6%, 3.5%, and 11.8% of SCOD.

The VFAs contained acetate, propionate, iso-butyrte, n-butyrate, iso-valerate, and n-valerate. It was very important to analyze the production of each organic acid, because the distribution of fermentation products may affect the application of the hydrolyzate, as individual VFAs have different efficiencies in biological nutrient removal processes. The denitrification rate of acetate was two times higher than that of propionate. The most effective acid is acetate, followed by butyrate, valerate, and finally propionate (Elefsiniotis and Wareham, 2007). Table 2 shows the percentage of individual VFAs at the end of fermentation. The VFAs composition was significantly affected by pH. When the pH was uncontrolled and 5.0, acetate was the main product, followed by butyrate, propionate, and valerate. When the pH was controlled at 6.0 and 7.0, butyrate was the main product, followed by acetate, propionate, and valerate.

The variation in NH₄⁺—N concentration in the hydrolyzate under different pH conditions was shown in Fig. 1(d). The ammonia concentration was relatively stable, and was maintained at between 600 and 700 mg/L when the pH was uncontrolled and controlled at 5.0, respectively, whereas it increased rapidly to a value of about 2140 mg/L at the end of the experiment at pH 6.0 and 7.0, indicating that a higher pH (6.0 and 7.0) leads to a higher release of ammonia, which was also observed by Xu et al. (2011). The NH₄⁺—N yields considering the VS fed in the reactor were 5.15, 5.41, 17.24, and 17.15 mg/gVS at pH uncontrolled, 5.0, 6.0, and 7.0, respectively. In anaerobic fermentation, ammonia was produced by the biological degradation of nitrogenous compounds, mostly in the form of protein, which was hydrolyzed into amino acids and further degraded into ammonia (Dong et al., 2009). Under neutral conditions, proteins are more easily hydrolyzed and hence lead to a higher concentration of NH₄⁺—N. As mentioned above, a significant amount of NH₄⁺—N was released during the fermentation of food waste at pH 6.0 and 7.0. Thus, NH₄⁺—N should be removed before the hydrolyzate is used as a carbon source in the biological nutrient removal processes.

Fig. 1(e) shows the decrease in VS due to anaerobic acidification. VS levels were lowest at pH 6.0 and 7.0, representing reductions of 64.7% and 64.3%, respectively.

Taken together, these data show that VFAs concentration, SCOD concentration, and the VFA/SCOD ratio were highest, and VS levels were lowest, when the pH was controlled at 6.0. Hence, a pH of 6.0 is most suitable for VFAs production from food waste.

Table 2: Effect of pH on VFAs production from food waste.

<table>
<thead>
<tr>
<th>pH</th>
<th>Uncontrolled</th>
<th>5.0</th>
<th>6.0</th>
<th>7.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>VFAs (g/L)</td>
<td>3.94</td>
<td>17.08</td>
<td>39.46</td>
<td>37.09</td>
</tr>
<tr>
<td>Acetate (%)</td>
<td>66.97</td>
<td>60.40</td>
<td>23.75</td>
<td>34.06</td>
</tr>
<tr>
<td>Propionate (%)</td>
<td>3.67</td>
<td>8.32</td>
<td>13.46</td>
<td>19.69</td>
</tr>
<tr>
<td>Butyrate (%)</td>
<td>29.36</td>
<td>31.13</td>
<td>53.27</td>
<td>42.66</td>
</tr>
<tr>
<td>Valerate (%)</td>
<td>66.97</td>
<td>60.40</td>
<td>23.75</td>
<td>34.06</td>
</tr>
<tr>
<td>Ethanol (g/L)</td>
<td>5.63</td>
<td>2.13</td>
<td>1.36</td>
<td>4.62</td>
</tr>
<tr>
<td>VFAs (g/g VSfed)</td>
<td>0.032</td>
<td>0.137</td>
<td>0.316</td>
<td>0.297</td>
</tr>
<tr>
<td>VFAs (g/g VSremoved)</td>
<td>0.076</td>
<td>0.254</td>
<td>0.471</td>
<td>0.446</td>
</tr>
</tbody>
</table>

3.2. Effect of temperature

Table 3 shows the results of acidogenesis at each temperature. SCOD concentration increased as temperature increased, however, the VFAs concentration of 14.90 g/L at 55 °C was significantly lower than that of 41.34 and 47.89 g/L at 35 and 45 °C, indicating a higher solubilization and a lower acidogenesis of food waste at a higher temperature. Similar observations were reported by Komemoto et al. (2009) and Kim et al. (2003). The ratio of VFA/SCOD was 75.6% and 82.6% at 35 °C and 45 °C, whereas it was only 26.4% at 55 °C.

Table 3: Effects of temperature on VFAs production from food waste.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>SCOD (g/L)</th>
<th>VFAs (g/L)</th>
<th>Acetate (%)</th>
<th>Propionate (%)</th>
<th>Butyrate (%)</th>
<th>Valerate (%)</th>
<th>Ethanol (g/L)</th>
<th>NH₄⁺—N (mg/L)</th>
<th>VFA/SCOD (%)</th>
<th>VS reduction (%)</th>
<th>VFA/SCOD (%)</th>
<th>VFs (g/g VSfed)</th>
<th>VFs (g/g VSremoved)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 °C</td>
<td>84.20</td>
<td>41.34</td>
<td>36.47</td>
<td>31.74</td>
<td>21.89</td>
<td>9.89</td>
<td>2.85</td>
<td>1753</td>
<td>75.6</td>
<td>59.36</td>
<td>59.36</td>
<td>0.379</td>
<td>0.619</td>
</tr>
<tr>
<td>45 °C</td>
<td>86.92</td>
<td>47.89</td>
<td>33.36</td>
<td>38.04</td>
<td>25.57</td>
<td>3.02</td>
<td>0.99</td>
<td>2208</td>
<td>82.6</td>
<td>59.08</td>
<td>59.08</td>
<td>0.440</td>
<td>0.690</td>
</tr>
<tr>
<td>55 °C</td>
<td>95.74</td>
<td>14.90</td>
<td>15.35</td>
<td>3.52</td>
<td>81.12</td>
<td>0.00</td>
<td>1.08</td>
<td>815</td>
<td>26.4</td>
<td>32.53</td>
<td>32.53</td>
<td>0.137</td>
<td>0.443</td>
</tr>
</tbody>
</table>

Fig. 2. Results of acidogenesis of food waste at an OLR of 5 g TS/L d: (a) VFA concentration, (b) the percentage of individual VFA.
Acetate and propionate were the most prevalent VFA generated at 35°C and 45°C, accounting for about 70% of total VFAs. Butyrate was the main product at 55°C, accounting for 81% of all products, followed by acetate and propionate; valerate was not detected. The percentage of acetate and valerate decreased as temperature increased, whereas the percentage of butyrate increased. The VFAs distribution was different from that reported by Komemoto et al. (2009) who found that butyrate concentration of 5600–6000 mg/L was highest at 35, 45 and 55°C and acetate concentration was low (1000–2000 mg/L). Perhaps the absence of inoculation in their research lead to the difference.

Ammonia nitrogen was released during anaerobic digestion, and its concentration was highest at 45°C, about 2208 mg/L. The reduction in VS at 35°C was similar to that at 45°C, and was much greater than that at 55°C.

Taken together, these data show that VFAs concentration and VFA/SCOD were highest, and VS levels were lowest, at 45°C, but the differences compared to 35°C were slight. Considering that more energy is consumed to control the temperature at 45°C, a more efficient and economical temperature for VFA production is 35°C.

### 3.3. Effect of OLR

The effect of OLR on VFAs production was conducted at a constant temperature (35°C), pH (6.0), and HRT (5 days). The OLR of reactors were controlled at 5, 11, and 16 g TS/L d by adjusting the TS contents of the feed.

Figs. 2–4 show the variation in VFA concentration and composition at ORs of 5, 11, and 16 g TS/L d, respectively. At an OLR of 5 g TS/L d, the concentrations of VFAs and SCOD increased in the first 7 days and then remained stable until the end of the experiment; at an OLR of 11 g TS/L d, the steady-state was reached at day 14. However, at an OLR 16 g TS/L d, the VFAs concentration increased until day 12, at which point it declined sharply for 5 days. Lim et al. (2008) proved that operation of a reactor at a high loading rate was unstable because the fermentation broth was very viscous. Hence, in further tests, the OLR was reduced from 16 to 10 g TS/L d on day 14 until the end of the experiment to avoid failure of the reactor. After adjustment, the concentration of VFAs no longer increased.

### Table 4

Effects of OLR on VFAs production from food waste.

<table>
<thead>
<tr>
<th>OLR (g TS/L d)</th>
<th>5</th>
<th>11</th>
<th>16 (11th day)</th>
<th>16 (30th day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCOD (g/L)</td>
<td>22.37</td>
<td>34.22</td>
<td>56.62</td>
<td>45.27</td>
</tr>
<tr>
<td>VFAs (g/L)</td>
<td>13.27</td>
<td>21.44</td>
<td>24.93</td>
<td>12.98</td>
</tr>
<tr>
<td>Acetate (%)</td>
<td>27.46</td>
<td>34.07</td>
<td>36.55</td>
<td>59.66</td>
</tr>
<tr>
<td>Propionate (%)</td>
<td>23.57</td>
<td>17.70</td>
<td>14.70</td>
<td>6.52</td>
</tr>
<tr>
<td>Butyrate (%)</td>
<td>33.26</td>
<td>31.00</td>
<td>28.62</td>
<td>28.87</td>
</tr>
<tr>
<td>Valerate (%)</td>
<td>15.71</td>
<td>17.23</td>
<td>20.12</td>
<td>4.95</td>
</tr>
<tr>
<td>Ethanol (g/L)</td>
<td>0.67</td>
<td>0.87</td>
<td>1.79</td>
<td>2.56</td>
</tr>
<tr>
<td>NH₄⁻-N (mg/L)</td>
<td>468.6</td>
<td>750.8</td>
<td>841.67</td>
<td>423.5</td>
</tr>
<tr>
<td>VFA/SCOD (%)</td>
<td>93.4</td>
<td>96.8</td>
<td>68.9</td>
<td>40.8</td>
</tr>
<tr>
<td>VFAs (g/g VSfed)</td>
<td>0.504</td>
<td>0.411</td>
<td>0.306</td>
<td>0.261</td>
</tr>
</tbody>
</table>
longer decreased and remained stable. Table 4 shows the difference between the first stage (days 0–14) and second stage (days 15–30). The concentrations of VFAs, SCOD, and NH$_4^+$—N were lower in the second stage due to a lower OLR and death of some fermentation microorganisms in the first stage. The percentage of propionate and valerate decreased, and the percentage of acetate increased in the second stage.

The concentration of VFAs, SCOD, and NH$_4^+$—N increased as OLR increased, whereas VFAs yield decreased. This is in accordance with the observation of Lim et al. (2008) who investigated the effect of OLR at HRT of 8 days, but the yields of VFAs at OLRs of 5 and 11 g TS/L d in this research were significantly higher than their experiments. Acetate and butyrate accounted for 60% of the total VFAs. The percentage of acetate and valerate increased as OLR increased, whereas a high OLR produced a lower percentage of propionate and butyrate. Similar observation was reported by Lim et al. (2008). At OLRs of 5 and 11 g TS/L d, VFAs accounted for 93.4% and 96.8% of SCOD, respectively, indicating that most soluble substances were converted into organic acids. Although a higher concentration of VFAs can be achieved at an OLR of 16 g TS/L d, the high OLR will lead to the rapid decrease of VFAs concentration and the failure of the reactor. Therefore, an OLR of 11 g/L d is suitable for VFAs production.

4. Conclusions

When the pH was controlled at 6.0, VFAs reached a concentration of 39.46 g/L and a yield of 0.316 g/g VS$_{fed}$, the highest among all pH conditions. VFAs concentration, VS reduction, and VFA/SCOD were highest at 45 °C, but the differences from the values at 35 °C were slight. The concentrations of VFAs, SCOD, and NH$_4^+$—N increased as OLR increased, whereas the VFAs yield decreased; acetate and butyrate accounted for 60% of the total VFAs at all OLRs, whereas the percentage of individual acid changed as OLR changed.

Acknowledgements

This work was financially supported by the Major Science and Technology Program for Water Pollution Control and Treatment (2012ZX07301-001).

References


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