Effect of combined pretreatment of waste activated sludge for anaerobic digestion process

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Abstract

Alkaline and low-temperature thermal pretreatment has been used to the subsequent anaerobic digestion of waste activated sludge (WAS) respectively. Different combinations of these two methods were investigated and biochemical methane potential (BMP) test was used to assess the anaerobic digestibility of pretreated WAS. In this study, an optimal reaction condition was obtained by combined pretreatment and BMP test. The combination was after alkalized for 24h, adding 0.05 g NaOH/g TS with 9 hours at 70°C. Under this condition the removal of SS was achieved 21% and soluble chemical oxygen demand (SCOD) was more than 200 times of control group. The ratio of soluble carbohydrate/total carbohydrate can reach 72.8%. For BMP test, it’s nearly 6 times higher biogas production was obtained than the control and the average value of methane content of biogas production is 64%. Thus, combined (alkaline + low-temperature thermal) pretreatment was efficiency for solubilization and biogas production.

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Keywords: Anaerobic digestion; Pretreatment; Alkaline; Low-temperature thermal pretreatment; BMP

1. Introduction

The considerable increase in the amount of sewage sludge production in wastewater treatment plant (WWTP) becomes a serious and pressing problem to the rapidly and healthy development of the city [1]. Before disposing the sewage sludge, it has to be stabilized sufficiently to reduce its organic content, odor problem and pathogen contamination. Neyens reported on that sludge handling and disposal already accounts for up to 50% of total treatment costs of wastewater purification in 2004[2].

Anaerobic digestion is common method for sludge stabilization to achieve sludge reduction, harmlessness and resource reuse. Compared with other processes, its advantages are less energy required, a better stabilized product and useable gas [3]. Anaerobic digestion has three basically steps: hydrolysis,
acidogenesis and methanogenesis [4]. However, it has limitation in terms of long retention times and low overall degradation efficiency of the organic matter. All those limitations are associated with the first step: hydrolysis. Because in the sewage sludge, most organic matters are in cells, the cell envelope of microorganisms is a semi-rigid structure which to protect the cell from osmotic lysis.

Thus, many pretreatment methods have been suggested in literature for overcoming the limitation enhancing the digestion rate. With a pretreatment process, not only hydrolysis is accelerated by the increase of dissolved components but improvement of biodegradability, sludge dewatering and reduction of pathogens and foaming can also be achieved as well[5]. Pretreatment methods have been shown to have a positive effect on anaerobic digestion include physical (thermal, mechanical, ultrasonic, microwave), chemical (alkaline, ozone oxidation), and biological hydrolysis (enzymatic) or combination of any two of those methods (alkaline +thermal, alkaline + microwave, alkaline+ ultrasonic).

Alkaline pretreatment is a commonly subject of investigation; it has advantages of simple device, convenient operation and high efficiency [6]. Sodium hydroxide at relatively low dosage level is effective in disintegrating municipal waste activated sludge (WAS) at ambient temperature [2]. Thermal hydrolysis includes high temperature thermal pretreatment (>100°C) and low temperature thermal pretreatment (<100°C). Most papers reported on high temperature thermal pretreatment. It was shown that the higher temperature, the more efficient the treatment is. However, when the temperatures higher than 180°C, it will lead to the production of recalcitrant soluble organics or toxic/inhibitory intermediates, hence reducing the biodegradability [7]. It has two significant drawbacks that we can not neglect is its high energy requirement and high quality equipments need. This largely reduces the overall profitability of the process. Low-temperature thermal pretreatment can overcome those disadvantages, and it has been pointed out as an effective treatment for improving biodegradability and increasing biogas production. Some authors have concluded that the solids solubilization at temperatures around 70°C is enhanced because of biological activity of some thermophilic bacteria populations with optimum activity temperatures in the high values of the thermophilic range [8].

In most reports, alkaline treatment and thermal pretreatment were studied independently as pretreatment of anaerobic digestion. Since low-temperature thermal pretreatment and alkaline treatment are based on different mechanisms of sludge dissolution, the combination of these two methods means the advantages of both methods can be attained and better treatment efficiency can be achieved. In this work, the purpose is to find the more suitable combination of these two methods for increasing the WAS anaerobic digestibility of WWTP.

2. Materials and methods

2.1. Sludge sampling and characterization

The sample waste activated sludge was obtained from the second sedimentation in the 4th WWTP in Xi’an, China, which is used by A2/O process. In order to increase the total solid of sample, the raw sludge was treated by concentration and then stored at 4°C in the laboratory prior to the pretreatment and test. The characteristics of raw sludge from WWTP and the concentrated substrate as control sludge used in the experiments are shown in Table 1.

2.2 Combined alkaline + low-temperature thermal Pretreatment

Some authors have concluded that the solids solubilization at temperatures around 70°C is enhanced, so the thermal treatment to start with 70°C at first. The first pretreatment step is alaklized in different dose of NaOH for 24h (A24h), and then thermal treated at 70°C for 2h (A24h+T2h) and 9h (A24h+T9h). After
the concentration, the substrate was divided into six portions, No.1 to No.6. Those six portions were solubilized by adding sodium hydroxide (NaOH) at different dose (0, 0.05, 0.10, 0.15, 0.20, 0.25 g NaOH /g TS), respectively, put them at ambient temperature for 24h, then put the alkalized sludge into thermostatic water bath at 70°C for 2h and 9h.

Table 1. Characteristics of raw and control sludge.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>pH</th>
<th>TS</th>
<th>SS</th>
<th>VS</th>
<th>VSS</th>
<th>COD Total</th>
<th>Carbohydrate Total</th>
<th>Carbohydrate Soluble</th>
<th>Protein Total</th>
<th>Protein Soluble</th>
<th>VFA Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>6.53</td>
<td>20300</td>
<td>19750</td>
<td>11930</td>
<td>11490</td>
<td>18450</td>
<td>117</td>
<td>2769</td>
<td>54.0</td>
<td>45.7</td>
<td>79.6</td>
</tr>
<tr>
<td>Control</td>
<td>6.9</td>
<td>28990</td>
<td>29870</td>
<td>18010</td>
<td>19910</td>
<td>26697</td>
<td>293.2</td>
<td>4447</td>
<td>113</td>
<td>126</td>
<td>113.5</td>
</tr>
</tbody>
</table>

The unit of those parameters is mg/L except pH.

2.3 Biochemical methane potential (BMP) test

BMP test was carried out to assess the efficiency of anaerobic digestibility and to evaluate the biogas production [9, 10]. The anaerobic degradability of the control (untreated) and alkaline + low-temperature thermal pretreated samples were determined by shaking batch thermophilic (35 ± 1°C) BMP tests in 120 mL serum bottles sealed with butyl rubber stoppers (50mL pretreated sludge+50mL inoculum), including blanks, duplicates and controls, everyday to take down the biogas production until there has no biogas produced. The pretreatment conditions (NaOH dose, thermal holding time) were determined on former experiment of the combined pretreatment in this paper, the thermal temperature varied on 50, 60, 70, 80, 90°C for test the efficiency of anaerobic digestibility and find out an optimal temperature for the combined pretreatment.

2.4 Analytical methods

The following parameters of pretreated substrate and anaerobic digestion effluent (BMP) were analyzed: pH, TS, VS, SS, VSS, total chemical oxygen demand (TCOD), soluble chemical oxygen demand (SCOD), volatile fatty acid (VFA), furthermore, pretreated substrate still measured total carbohydrate, soluble carbohydrate, total protein, soluble protein, ammonia nitrogen (NH₄⁺-N). The pH, TS, VS, SS, VSS, COD, NH₄⁺-N were determined following procedures outlined in Standard Methods [11]. Carbohydrates were measured by the Phenol-H₂SO₄ method, and proteins were measured by the Lowry method. Gas composition was detected by a gas chromatograph with TCD (3420A, BEIFEN Corp. China). VFA was determined by gas chromatography with FID (3420A, BEIFEN Corp. China). Samples used for the measurement of SCOD, soluble proteins, soluble carbohydrates, VFA, P and NH₄⁺-N were prepared by centrifugation at 10,000 r/min for 10 minutes and filtration through 0.45 μm membrane filters.

3. Results and discussion

3.1. Effect of pretreatment sequence on WAS disintegration

Combined alkaline + low-temperature thermal pretreatment of sludge was performed to improve the treatment efficiency. The pretreatment conditions were varies in different dose of NaOH and different temperature. The expected effect of the pretreatment of sludge was an increase in soluble materials, with interest focused on SCOD solubilization, soluble carbohydrate and protein release, VFA and biogas
production, thus enhancing hydrolysis in order to improve the anaerobic digestibility of sludge. Table 2 shows the concentration of the components of the alkaline+70°C thermal treated sludge.

Table 2. The parameters of the organic components of the alkaline+70°C thermal treated sludge.

<table>
<thead>
<tr>
<th>Dose (g NaOH/g TS)</th>
<th>SS (mg/L)</th>
<th>COD SCOD (mg/L)</th>
<th>SCOD/TCOD (%)</th>
<th>Carbohydrate Soluble carbohydrate (mg/L)</th>
<th>S/T (%)</th>
<th>Protein Soluble protein (mg/L)</th>
<th>S/T (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>30850</td>
<td>288.9</td>
<td>1.4</td>
<td>117.9</td>
<td>5.2</td>
<td>150.5</td>
<td>2.8</td>
</tr>
<tr>
<td>0.05</td>
<td>34480</td>
<td>574.8</td>
<td>2.2</td>
<td>184.3</td>
<td>3.6</td>
<td>234.7</td>
<td>2.7</td>
</tr>
<tr>
<td>0.10</td>
<td>34620</td>
<td>844.2</td>
<td>3.4</td>
<td>184.3</td>
<td>4.1</td>
<td>415.1</td>
<td>4.7</td>
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<tr>
<td>0.15</td>
<td>32220</td>
<td>5873</td>
<td>40.6</td>
<td>2475</td>
<td>41.9</td>
<td>8043</td>
<td>63.8</td>
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<tr>
<td>0.20</td>
<td>32060</td>
<td>7078</td>
<td>61.0</td>
<td>2570</td>
<td>47.4</td>
<td>8194</td>
<td>60.2</td>
</tr>
<tr>
<td>0.25</td>
<td>34880</td>
<td>6626</td>
<td>81.5</td>
<td>2356</td>
<td>47.6</td>
<td>8706</td>
<td>60.2</td>
</tr>
<tr>
<td>Alkalized 24 h</td>
<td>0.05</td>
<td>27040</td>
<td>4870</td>
<td>593.8</td>
<td>10.6</td>
<td>1877</td>
<td>21.1</td>
</tr>
<tr>
<td>0.10</td>
<td>28900</td>
<td>5221</td>
<td>21.5</td>
<td>639.9</td>
<td>13.0</td>
<td>2135</td>
<td>22.9</td>
</tr>
<tr>
<td>0.15</td>
<td>32920</td>
<td>29053</td>
<td>78.1</td>
<td>2179</td>
<td>51.3</td>
<td>9281</td>
<td>61.0</td>
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<tr>
<td>0.20</td>
<td>32160</td>
<td>24321</td>
<td>75.0</td>
<td>2273</td>
<td>50.8</td>
<td>9962</td>
<td>62.0</td>
</tr>
<tr>
<td>0.25</td>
<td>33320</td>
<td>31934</td>
<td>82.9</td>
<td>2620</td>
<td>65.8</td>
<td>10244</td>
<td>64.7</td>
</tr>
<tr>
<td>Alkalized 24h+thermal treated 2h</td>
<td>0.05</td>
<td>24260</td>
<td>65190</td>
<td>68.2</td>
<td>17917</td>
<td>72.8</td>
<td>3403</td>
</tr>
<tr>
<td>0.10</td>
<td>27840</td>
<td>36641</td>
<td>59.6</td>
<td>4812</td>
<td>63.9</td>
<td>3442</td>
<td>34.6</td>
</tr>
<tr>
<td>0.15</td>
<td>31640</td>
<td>7729</td>
<td>29.5</td>
<td>2123</td>
<td>58.5</td>
<td>10364</td>
<td>69.9</td>
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<tr>
<td>0.20</td>
<td>31720</td>
<td>10872</td>
<td>44.3</td>
<td>2371</td>
<td>59.7</td>
<td>11494</td>
<td>70.4</td>
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<tr>
<td>0.25</td>
<td>32640</td>
<td>9615</td>
<td>27.1</td>
<td>2371</td>
<td>58.8</td>
<td>10912</td>
<td>69.2</td>
</tr>
</tbody>
</table>

SS reduction is an indication of sludge stability, and it is used for assessing the effectiveness of a process in stabilizing sludge which might be regarded as a threshold for the pre-digestion step [11]. Table 2 shows the SS reduction during pretreatments. The model of adding 0.05 g NaOH /g TS (A24h+T9h) achieves 21% reduction of SS, it is similar to the result of R. Uma Rani (2012) [9].

SCOD calculations were considered the main parameter for evaluation of sludge particulate material, and it enables an evaluation of the maximum level of sludge solubilization. The COD solubilization of A and A+T pretreatment at 70°C were presented in Table 2. The SCOD of alkalized for 24h is increased with increasing dose of NaOH, but the low dose of NaOH (0.05, 0.15 g NaOH/g TS) do not work well, which is similar to the solubilization of carbohydrate and protein. But the SCOD tendency of A24h+T9h is different, the SCOD value decrease as the NaOH dose exceed 0.05 g NaOH /g TS. Because increasing the dose of NaOH and the long thermal time lead the recalcitrant soluble organics or toxic/inhibitory intermediates produced. Increased SCOD is determined as the substance that can be readily used to produce methane during anaerobic digestion [12]. The SCOD of A24h+T9h reaches the max value 65190 mg/L at 0.05 g NaOH /g TS, it is nearly 16 times of the sludge treated A24h+T2h (4870 mg/L) and more than 200 times of control sludge (289 mg/L).

Soluble carbohydrate and protein can also indicate the efficiency of solubilization about the pretreatment. Compare with others, adding 0.05 g NaOH /g TS (A24h+T9h) can get the max concentration of soluble carbohydrate (17917 mg/L) and the ratio of soluble carbohydrate/total carbohydrate can reach 72.8%. Thus, 0.05 g NaOH /g TS (A24h+T9h) is significant benefit for carbohydrates release. Cell lysis releases protein content into the medium is the first stage of flocc disintegration. Proteins are the principal constituents of organisms, and they contain carbon, which are a
common organic substance as well as hydrogen, oxygen and nitrogen [13]. After the treatment, the max value can reach 11495 mg/L, it is more than 90 times of the control sludge (125.5 mg/L). That is to say, the NaOH dose adding is a major factor which influenced the protein release.

From all above, we know that the alkaline treatment can resale more soluble organic materials when combined with thermal pretreatment. Furthermore, from Table 2 we found that thermal pretreatment is more effective for low dose NaOH than high dose NaOH.

3.2. BMP test

For assessing the efficiency of A+T pretreatment anaerobic digestibility and evaluating the biogas production, BMP test was used. The sample sludge were treated by adding 0.05 g NaOH /g TS (A24h+T9h) at various temperature (50°C, 60°C, 70°C, 80°C, 90°C), the NaOH dose and thermal treatment holding time were obtained from the combined pretreatment (A+T) in this work. Biogas production and the reduction of TCOD, VSS can illustrate the efficiency of anaerobic biological degradation. SCOD, VFA, soluble carbohydrate and protein can be readily used to produce methane during anaerobic digestion [14].

Fig.1 shows the cumulative biogas production of BMP test. The daily biogas productions increase quickly at fist 3 days, then decrease rapidly in 4 days, after 10 days the daily biogas production tend to flat keep in a low amount. Ray had pointed that pretreatment with sodium hydroxide increased gas production by between 29% and 112% over the control sludge[15].The accumulated biogas production at the end of 30 days of the digestion period is nearly 45 mL for control sample, and at 70°C (A24h+T9h) it is around 329 mL, nearly 630% higher biogas production is obtained than the control sludge, it is much more efficiency than untreated sludge. The average value of methane content of biogas production is 64 %. Fig.2 shows the data about VSS of BMP test. VSS contents 95% organic matters in WAS. The reduction of VSS can indicate the organic matters removal. Similarly, it gets the max value of VSS reduction (27.1%) at 70°C(A24h+T9h), this is similar to the result of Rani [9].

4. Conclusions

The results of this study indicated that the alkaline + low-temperature thermal pretreatment has the potential to damage excess sludge structure and cell membranes and to release extracellular and possibly intracellular compounds with high solubility. It also increased the bioavailability of waste activated...
sludge components under thermophilic BMP tests. Under the conditions of 70°C, adding 0.05 g NaOH/g TS with 9 hours thermal holding time, SS reduction achieved 21%, SCOD value was nearly 16 times of the sludge treated A24h+T2h and more than 200 times of control group. For BMP test, it’s nearly 83% higher biogas production was obtained than the raw sludge and got 27.1% VSS reduction. So the solubilization and anaerobic digestibility for the treatment of alkaline + low-temperature is satisfactory.

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