ENHANCEMENT OF ANAEROBIC DIGESTION OF DEWATERED-SEWAGE SLUDGE THROUGH ANAEROBIC PRE-TREATMENT.

NGES IVO ACHU AND JING LIU
Department of Biotechnology, Center for Chemistry and Chemical Engineering, Lund University, P.O. box 124, SE-22100 Lund, Sweden.
E-mail: Nges.Ivo_Achu@biotek.lu.se; Jing.Liu@biotek.lu.se

Abstract The effect of anaerobic pre-treatment was carried out on dewatered-sewage sludge in order to improve its degradation through anaerobic digestion. Pre-treatment was conducted in laboratory scale at 25 °C, 50 °C and 70 °C for an incubation time of two days. As a reference, sludge samples were also autoclaved at 121°C for 2 hour to determine the thermal effect on sludge digestion. Dewatered-sludge characteristics such as viscosity, pH and soluble chemical oxygen demand (SCOD) were affected by the pre-treatment. In fact, pre-treatment led to a great improvement in SCOD. The normalised methane yields (NmICH₄/gVS added) achieved in batch reactors at 37 °C were in the order of 298 and 276 for pre-treated and untreated sludge, respectively. This however indicated an 8% increase in methane yield for pre-treated sludge in comparison with untreated sludge. Methane content in biogas increased from an average of 65% to 69% for pre-treated and untreated substrates, respectively. Volatile solids (VS) reduction increased from 40% to 51%. Overall digestion time was not affected by pre-treatment but 90% of biogas was produced within the first 12 days of incubation for 50 °C the pre-treated samples while it was much longer for the rest (14-17 days). It was observed that thermophilic anaerobic digestion was a better option in terms of shorter digestion time and higher VS-reduction, but mesophilic anaerobic digestion showed higher methane yields.

Keywords anaerobic digestion; mesophilic; methane yield; pre-treatment; thermophilic; VS-reduction

INTRODUCTION
Anaerobic digestion is a technology that can extract energy from regionally abound biomass such as municipal waste/wastewater. The process is a multi-step process comprising hydrolysis, acidogenesis, acetogenesis and methanogenesis. Hydrolysis is known to be the rate-limiting step especially in the degradation of complex substrates containing particulates such as sewage sludge from wastewater treatment plants (Chiu et al., 1997). The efficiency of anaerobic degradation may be improved by incorporating a pre-treatment step that will enhance the hydrolysis of particulate organic matter. Pavlosthisis and Gossett (1986) stated that the rigid structure of the microbial walls, which prevents the inner cell products from leaking out hampered digestion of sewage sludge. Sludge solubilisation is therefore a logical approach to improve digestion of sewage sludge. Several methods have been investigated to hydrolyse or solubilise sludge. These include mechanical pre-treatment which is good in solubilising microbial cells but complicated and expensive. Chemical and thermal treatments (Chiu et al., 1997) which are based on strong acidic or basic conditions in combination with high temperatures and pressure. This method is efficient in enhancing sludge digestion (Li and Noike, 1992), however, the aggressive reaction conditions often impose special material requirements. Thermal pre-treatment is reported to be efficient in sludge hydrolysis but it consumes a substantial amount of energy and in some cases, there is formation of toxic, refractory compounds during pre-treatment which is a major drawback (Delgenes et al., 2000). Also, deactivation of enzymes may occur. The formation of hardly degradable materials, i.e. the possibility of the formation of dioxins at temperatures of 200°C has also been reported (Huag et al., 1978). As an alternative approach, biological pre-treatment has the potential to be more cost efficient, this is because endogenous enzymes secreted by bacteria present in the sludge can carry out hydrolysis. The purpose of this study was to investigate the effects of anaerobic pre-treatment on anaerobic degradation of dewatered-sewage sludge.
EXPERIMENTAL

Sample/Inoculums. Dewatered-sewage sludge was collected from Källby WWTP in Lund, Sweden. This sludge was obtained by collecting primary and secondary treatment sludge and letting collected sludge to go through dewatering process by adding high molecular flocculants based on polyacrylamide. The dewatered-sludge total solid has (TS) ranged from 8% to 9% and VS was about 75% of TS. Thermophilic seed sludge from Källby had TS of 5.61%, VS 56% of TS. The mesophilic seed sludge was collected from the anaerobic digester (Ellinge WWTP in Eslöv, Sweden). TS was in the order of 4.31% and VS was 47% of TS. Characteristics of dewatered-sludge and inoculum are listed in Tables 1 and 2.

Analytical methods. TS, VS and pH were determined (standard methods APHA, 1995) to evaluate the physico-chemical changes in sludge after pre-treatment and batch test. Biogas composition was determined using a gas chromatograph (Varian 3350 Walnut Creek, CA, USA). The compounds detected were methane, carbon dioxide, oxygen, and nitrogen. Total gas volume was measured using a graduated 100-ml gas-tight syringe with a sample lock (Fortuna, Germany). Methane yield was calculated as the net amount of methane produced per unit VS added to the digester and normalised the volume at 0 °C. Sample weight was determined with the aid of a 3-digit precision scale balance. VFAs were analysed with HPLC, Varian Star 9000 (Varian, Walnut, USA), with a BioRad column, Cat. 125-0115 (Hercules, USA) as previously described by Parawira (2004). The alkalinity was evaluated as partial alkalinity (PA) by titration to a 5.75 end-point and total alkalinity (TA) by titration to a 4.3 end-point with the aid of TIM800 Titration Manager (Radiometer, Copenhagen, Denmark). The soluble chemical oxygen demand (SCOD) was determined by oxidation of the organic compounds with K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7}. The Cr\textsuperscript{3} produced thus was analysed calorimetrically (Tiehm A et al., 2001).

Anaerobic pre-treatment. The basic experimental set-up for pre-treatment was a 500 ml Erlenmeyer flask into which 300 ml of dewatered-sludge was introduced, flushed with nitrogen for 3 minutes in order to create anaerobic conditions. The flasks were immediately corked with butyl rubber septa. The flasks (triplicates) were incubated at room temperature (25±2 °C), 50 °C and 70 °C in shaking water baths (GFL 1086; Gesellschaft fur Labortechnik GmbH, Burgwedel, Germany) at a frequency of 70 rpm, for 12 hours, 1 day a 2 days and three days. For a second trial, pre-treatment was done only at 50°C and the treatment time varied from 12 hours to three days. Samples were also autoclaved at 121 °C for 20 minutes to study (only) the thermal effect on sludge digestion.

Methane potential test. Pre-treated dewatered-sludge and untreated (control) dewatered-sludge were used as substrates for the methane potential test to assess sludge biodegradability at both mesophilic and thermophilic conditions. The inoculum to substrate ratio (ISR) was set at 1:1 gVS. The basic experimental unit consisted of a 500 ml Erlenmeyer flasks incubated at 37°C in shaking water baths (GFL 1086; Gesellschaft fur Labortechnik GmbH, Burgwedel, Germany) at a frequency of 70 rpm. The active volume was 300ml, anaerobic conditions were established by flushing the headspace of flasks with nitrogen for 3 minutes, and the flasks were immediately sealed with butyl rubber septa. An outlet in the stopper was used for biogas collection in a gas-tight aluminium foil bag. All tests were conducted in triplicates. During the experiment, gas composition and total gas volume were monitored on a daily basis. Volatile fatty acids (VFAs), pH, TS, VS and alkalinity were determined at the end of each batch experiment. Thermophilic and mesophilic anaerobic assays were conducted using thermophilic inoculum to evaluate the effect of operational temperature on degradation of dewatered-sludge. Controls containing only the inoculum were used to measure the indigenous methane production from the inoculum and this was subtracted from the
total gas production. The experiments were run for about a month and terminated when methane production was less than 5ml/day. Methane yields were normalised by correcting the temperature at 0 ºC and compensating for water in the gas phase.

RESULTS AND DISCUSSIONS
Both biological anaerobic pre-treatment and thermal treatment led to changes of the physico-chemical characteristics of sludge. For instance, pH decreased up to 1 pH unit (Tables 1&2). The decrease in pH can be explained by the formation of acidic compounds. In fact, it seems that organic compound such as lipids and proteins were degraded in order to form volatile fatty acids during the pre-treatment, which decreased the pH (Bougrier C 2003). These soluble monomers were transferred into the liquid phase thereby increasing the SCOD from 1.9 g/l to a value of 20.62 g/l by the anaerobic pre-treatment and to 24.49 g/l after autoclaving (thermal effect). Li and Noike (1992) reported that the optimal pre-treatment temperature and contact time for improving anaerobic digestion of sludge were 170 °C and 60 minutes but autoclaving which was done for a reference to biological treatment was carried out for 20 minutes at 121 °C. SCOD improvement was considered as a result of break down of sludge cells and the content released into the digestion broth.

Table 1. Dewatered-sludge characteristics before and after pre-treatment

<table>
<thead>
<tr>
<th>Variables</th>
<th>Inoculum</th>
<th>Untreated</th>
<th>70°C P.T</th>
<th>50°C P.T</th>
<th>25°C P.T</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS (%w/w)</td>
<td>5.61</td>
<td>9.03</td>
<td>8.89</td>
<td>9.01</td>
<td>9.01</td>
</tr>
<tr>
<td>VS (%w/w)</td>
<td>3.1</td>
<td>6.03</td>
<td>5.81</td>
<td>5.85</td>
<td>6.03</td>
</tr>
<tr>
<td>CO₂(ml)</td>
<td>0</td>
<td>0</td>
<td>7.1</td>
<td>6.2</td>
<td>9.3</td>
</tr>
<tr>
<td>CH₄(ml)</td>
<td>0</td>
<td>0</td>
<td>2.4</td>
<td>1.5</td>
<td>3</td>
</tr>
<tr>
<td>pH</td>
<td>8.3</td>
<td>6.8</td>
<td>6.6</td>
<td>6.4</td>
<td>5.8</td>
</tr>
</tbody>
</table>

The solubilisation of insoluble biomass and increase of soluble biomass in pre-treated sludge could be due to both biological and thermal effects during anaerobic incubation at various temperatures. Pre-treatment at room temperature has mainly biological effect whereas both biological and thermal effects were involved for 50 °C and 70 °C anaerobic pre-treatment. Jacob, (1991a) reported that anaerobes that hydrolyse sludge (through the intermediate of secreted hydrolytic enzymes) were quite active within the temperature range from 60 °C up to 75 °C. Similarly, Li Y et al., (1992) reported that improvement in hydrolysis could be observed at temperatures above 60 °C. This enhanced enzymatic action could be the reason for the increased sludge solubilisation at higher incubation temperatures than at the room temperature. The viscosity of the thick sludge was reduced especially with thermal pre-treatment (visual observation). This can be likened to the ‘potato effect’ reported by Hans P. (1985) describing the action of thermal hydrolysis of dewatered-sludge as being similar to cooking a potato, resulting in volatile solids being easily digested. Slight decreases in TS, and VS were realised, and this could be explained by the conversion of some carbonaceous solids to carbon dioxide and methane during pre-treatment (Table 1&2).
Methane potential tests were conducted in order to determine the effect of anaerobic pre-treatment for subsequent biogas (methane) production. Methane production for treated samples was higher than for the untreated sludge (Figure 1B), but there were no significant differences in methane yields (Figure 2). However, 90% of methane was produced within the first two weeks of fermentation for 50 °C pre-treated substrates (figure 1A). Peak methane production also occurred within the first week of digestion. Higher normalised methane yields (NmlCH₄/gVS added) in order of 293 and 298 were observed for 50 °C and autoclaved sample respectively indicating a 7% and 8% increment for 50 °C and autoclave pre-treatments respectively (Table 3 and figure 2). The rest were a little higher or the same as the untreated samples.

This implies that pre-treatment enhanced the early steps of anaerobic digestion (hydrolysis and acidogenesis) but had little effect on the down stream steps (acetogenesis and methanogenesis). The VS-reduction increased from 40% to 51% but had no correlation with degradation speed or methane production, a higher VS-reduction did not immediately lead to higher methane production (Figure 1). This indicated that organic compounds were not all converted to biogas but some other compounds.
Methane content oscillated between 62 and 69% (Table 3), this could be due to increase in specific activity of methanogens (Parawira 2004). Similar phenomenon has also been observed in thermal sludge disintegration (Hiraoka et al., 1984). It took about 30 days in all experiments to reduce daily methane production to less than 5 ml methane per flask. This indicated that pre-treatment had no effect on the total degradation rate but could enhance the early degradation steps (i.e. hydrolysis and acidification).

Methane content and methane production were loosely related (Figure 1B). 50 °C pre-treated samples had the highest methane production and methane content. Thermophilic anaerobic digestion was much faster than mesophilic anaerobic digestion (Figure 3). It took two weeks for 90% of biogas to be generated under thermophilic conditions while it was almost a month for mesophilic digestion. This could be due to higher specific growth rate of thermophilic microbes compared to their mesophilic analogues (Mladenovska and Ahring, 2000). De la Rubia et al. (2002) indicated that hydrolysis is faster under thermophilic condition than under mesophilic conditions, while it is the opposite as far as the methanogenesis is concerned. The percentage of methane in biogas and methane yield was higher from mesophilic digested sample than from thermophilic digested samples (Figure 2 and Table 3). This could also be due to the solubility of CO₂ decreased by rising the operational temperature. There was 11% improvement in methane yield for mesophilic digestion as opposed to a 4% increment for thermophilic digestion of pre-treated sludge. Sludge pre-treatment carried out at 50 °C resulted in a higher methane yield. This is the reason why a separate test was only conducted at 50 °C with varied time (Figure 2C).

![Fig. 1 Total methane production, methane content and VS-reduction during anaerobic pre-treatment of dewatered-sewage sludge.](image)

![Fig. 2 (A) Normalised methane yields (NmLCH₄/gVS added) after thermophilic; (B) mesophilic anaerobic digestion of pre-treated sludge; (C) Methane yield for 50°C pre-treated sample (C)](image)
Methane production under mesophilic condition with thermophilic inoculum increased dramatically in the second week (Figure 3). It seems the micro-organisms took approximately two weeks to get acclimatised to the mesophilic condition. The relatively fast adaptation of the system to mesophilic conditions indicates the presence mesophilic micro-organisms in the thermophilic inoculum. In fact, the digester (Källby WWTP, Sweden) where the inoculum was collected operates in mesophilic (40 °C) condition in winter and thermophilic condition in summer (50-55 °C). Total volatile fatty acids were in the range of 200-450 mg/l (Table 4) and the dominating VFAs were acetic and propionic acids at the end of the experiment. The initial pH ranged from 5.8 and 6.8 while the final pH values range from, 7.9 and 8.2. Total and partial alkalinity values were within operational range (Table 3). This indicated that the pH was conducive for biogas production.

**Table 4** Methane yield, methane content, VS- reduction, and pH after thermophilic and mesophilic anaerobic digestion of pre-treated dewatered-sewage sludge

<table>
<thead>
<tr>
<th>Variable</th>
<th>Thermophilic fermentation</th>
<th>Mesophilic fermentation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70°C, 50°C, 25°C, Control</td>
<td>70°C, 50°C, 25°C, Control</td>
</tr>
<tr>
<td>pH</td>
<td>8.2, 8.2, 8.1, 8.2</td>
<td>7.9, 7.9, 8, 8</td>
</tr>
<tr>
<td>VS-reduction (%)</td>
<td>41, 42, 39, 38</td>
<td>42, 42, 39, 39</td>
</tr>
<tr>
<td>Methane content (%)</td>
<td>68, 68, 66, 63</td>
<td>69, 68, 67, 64</td>
</tr>
<tr>
<td>Methane yield (mlCH4/gVSadded)</td>
<td>264, 258, 252, 247</td>
<td>268, 284, 271, 254</td>
</tr>
</tbody>
</table>

**CONCLUSION**

Biological anaerobic pre-treatment had an improvement in methane production as well as methane yield but the increase was not every significant (8%). VS-reduction was improved from about 40% to 51% and the content of methane in biogas also increased from 62 to 69% through sludge pre-treatment. Degradation time was not affected by pre-treatment and 90% sludge was degraded within the first 12 days for 50°C pre-treated sludge. A major conclusion drawn from this study is that most of the degradable matter in dewatered-sludge was degraded in the first 14 days. It is therefore
interesting to digest the dewatered-sludge at short solid retention time (SRT) under the condition of keeping methanogens and thereby avoiding cell being washed out.

REFERENCES


