Thermal pre-treatment of primary and secondary sludge at 70 °C prior to anaerobic digestion

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Abstract In general, mesophilic anaerobic digestion of sewage sludge is more widely used compared to thermophilic digestion, mainly because of the lower energy requirements and higher stability of the process. However, the thermophilic anaerobic digestion process is usually characterised by accelerated biochemical reactions and higher growth rate of microorganisms resulting in an increased methanogenic potential at lower hydraulic retention times. Furthermore, thermal pre-treatment is suitable for the improvement of stabilization and could be realized at relatively low cost especially at low temperatures. The present study investigates the effect of the pre-treatment at 70 °C on thermophilic (55 °C) anaerobic digestion of primary and secondary sludge in continuously operated digesters. Thermal pre-treatment of primary and secondary sludge at 70 °C enhanced the removal of organic matter and the methane production during the subsequent anaerobic digestion step at 55 °C. It also greatly contributed to the destruction of pathogens present in primary sludge. Finally it results in enhanced microbial activities of the subsequent anaerobic step suggesting that the same efficiencies in organic matter removal and methane recovery could be obtained at lower HRTs.

Keywords Activity; pre-treatment; primary sludge; secondary sludge; thermophilic digestion

Introduction
Anaerobic digestion is an appropriate technique for the treatment of sludge before final disposal and it is employed worldwide as the oldest and most important process for sludge stabilisation (Metcalf and Eddy, 1991). The microbiology of anaerobic digestion is complicated involving several bacterial groups. However, four major steps can be distinguished: the hydrolysis, the acidogenesis, the acetogenesis and methanogenesis (Pavlostathis and Giraldo-Gomez, 1991). The methanogenesis is, in most of the cases, the rate-limiting step of the overall process; however, the hydrolysis is the rate-limiting step during the anaerobic digestion of wastewater rich in organic solids, such as primary and/or secondary sludge (Valentini et al., 1997; Li and Noike, 1992). It has been proved that the thermal pretreatment of sludge at elevated temperature (100–275 °C) significantly increases the disintegration and solubilisation of sludge solids and thus improves the sludge stabilization (Müller, 2001). However, high temperature pre-treatment has high-energy requirements and is difficult to operate. Therefore, pre-treatment at temperatures below 100 °C becomes more attractive. To date, there are several studies showing the effectiveness of lower temperature pre-treatment (60–100 °C) on anaerobic digestion of sludge (Wang et al., 1997). Most of these studies focus on the investigation of the temperature selection and pre-treatment duration. Recently, the effect of a pre-treatment at 70 °C on the outcome of mesophilic and thermophilic anaerobic digestion of primary and secondary sludge has been examined (Gavala et al., 2003).

In general, mesophilic anaerobic digestion of sewage sludge is more widely used compared to thermophilic digestion, mainly because of the lower energy requirements and higher stability of the process. However, the thermophilic anaerobic digestion process is usually characterised by accelerated biochemical reactions, higher growth rate of
microorganisms and accelerated interspecies hydrogen transfer resulting in an increased methanogenic potential at lower hydraulic retention times (Zábranská et al., 2000). The scope of the present study is to investigate the effect of the pre-treatment at 70 °C on thermophilic (55 °C) anaerobic digestion of primary and secondary sludge in continuously operated digesters. Also the activities of the different microbial groups are extracted in order to adequately characterize the sludge digestion combined with a thermal pre-treatment step.

Methods

Analytical methods

Determinations of solids and chemical oxygen demand (COD) were carried out according to Standard Methods (APHA, 1989). For the quantification of volatile fatty acids, acidified samples with 17% H₃PO₄ were analysed on a gas chromatograph (Hewlett Packard 5890 series II) with a flame ionisation detector and a capillary column (Hewlett Packard FFAP 30 m, inner diameter 0.53 mm, film 1 μm). Biogas composition in methane was quantified with a gas chromatograph (Shimadzu GC-8A) equipped with a flame ionisation detector and a packed column (Porapak Q, 80/100-mesh). The medium (BA medium) used in batch tests was prepared from the following stock solutions (chemicals in g l⁻¹ of distilled water): (A) NH₄Cl, 100; NaCl, 10; MgCl₂·6H₂O, 10; CaCl₂·2H₂O, 5; (B) K₂HPO₄·3H₂O, 200; (C) resazurin, 0.5; (D) trace metals and selenite solution: FeCl₂·4H₂O, 2; H₃BO₃, 0.05; ZnCl₂, 0.05; CuCl₂·2H₂O, 0.038; MnCl₂·4H₂O, 0.05; (NH₄)₆Mo₇O₂₄·4H₂O, 0.05; AlCl₃, 0.05; CoCl₂·6H₂O, 0.05; NiCl₂·6H₂O, 0.092; ethylene-di-amine-tetra-acetate, 0.5; Na₂SeO₃·5H₂O, 0.1; HCl 37%, 1 ml; (E) vitamin solution according to Wolin et al. (1963). The following volumes of stock solutions were added to 916 ml of distilled water: A, 10 ml; B, 2 ml; C, 1 ml; D, 1 ml; E, 10 ml. 50 ml of a 52 g l⁻¹ NaHCO₃ solution were added as well. The medium was gassed with 80% N₂ – 20% CO₂, dispensed and autoclaved. Before inoculation the medium was reduced with a 25 g l⁻¹ Na₂S·9H₂O solution to a ratio of 0.1 ml/10 ml of medium. The pathogen reducing effect (PRE) was determined by using faecal streptococci (FS) as indicator organism according to the “Nordic Committee on Food Analysis” (1992). The concept of the method is to carry out a quantitative evaluation of FS expressed by the average FS number per millilitre of sludge. By comparing the numbers of FS colonies in specially treated sludge samples before and after treatment the PRE value is obtained in log₁₀ reduction units:

\[
\text{PRE} = \log_{10} N_i - \log_{10} N_e
\]

where \( N_i \) = number of FS in the influent sample and \( N_e \) = number of FS in the effluent sample.

Experimental details

Continuous experiments. Two continuous processes were operated in order to investigate the usefulness and efficiency of a thermal pre-treatment step at 70 °C prior to the anaerobic digestion of primary and secondary sludge (Figure 1). Process A was a two-step process, where sludge was first treated at 70 °C in digester P at a Hydraulic Retention Time (HRT) of 2 d and then digested at 55 °C in digester A at a HRT of 13 d. Process B served as control and was a one-step process, where sludge was digested at 55 °C in digester B at a HRT of 15 days. All digesters were CSTR-type and their performance was monitored by measuring the pH, the concentration of VFAs, solids and COD, the pathogen reducing effect and the biogas production and composition. Once a steady state was reached measurement of the reactors characteristics took place and the
performance of processes A and B was compared regarding organic matter removal and methane recovery.

**Batch experiments.** Batch tests for the determination of the substrate consumption activities were performed in order to investigate the effect of the pre-treatment step on the different process steps (acetogenesis and methanogenesis) of the thermophilic anaerobic digestion of primary and secondary sludge. Batch tests were carried out in triplicates at 55 °C in 58 ml serum vials sealed with butyl rubber stoppers and aluminium crimps. The serum bottles contained 15 ml of BA medium and acetate or propionate or butyrate as sodium salts at a final concentration of 20, 10 and 5 mM respectively. The bottles were inoculated with 5 ml of anaerobic mixed liquor from the thermophilic digester A or B. When hydrogen was used as the substrate, the serum bottles were pressurised to 2 atm with a gas mixture (20/80) of CO₂/H₂. Triplicate controls were also prepared containing only 15 ml of BA medium and 5 ml of anaerobic mixed liquor (no substrate added). VFA concentration and methane production were followed throughout the experiments. The activities of acetogenic bacteria to degrade intermediate VFA (e.g. butyrate, propionate) to acetate and the activities of methanogenic archaea to convert acetate to methane (by aceticlastic methanogens) and H₂/CO₂ to methane (by hydrogen-utilizing methanogens) were determined. In case of experiments with hydrogen as substrate, the calculations for the determination of the activities were based on the methane production. Specific methanogenic activity (SMA) and maximum specific substrate consumption rate (MSSCR) were used to describe the above-mentioned microbial activities. SMA was defined as the substrate-dependent methane production rate per unit mass of biomass. In the plot of methane produced versus time, the initial slope divided by the VSS mass gives the SMA. In the plot of VFA concentration versus time, the initial slope divided by the VSS concentration gives the MSSCR.

**Results and discussion**

Digester P was an acidogenic reactor and no significant methane production was detected in it. Total VFA concentration was about 1,500 mg/l and the pH value was 6.4. Methanogenic digesters A and B were very stable, with pH values at 7.2 and very low VFA concentration (<100 mg/l). The characteristics of the primary and secondary sludge used for the experiments are shown in Table 1. The performance characteristics of processes A and B under steady state and during the treatment of primary or secondary sludge are presented in Table 2. The respective steady-state characteristics of the individual digesters (P, A and B) can be seen in Table 3. Process A was found to be more efficient regarding VSS removal and methane recovery than Process B. The VSS removal in process A was 28% and 617% higher than the removal in process B for primary sludge and secondary
sludge respectively. When primary sludge was fed to process A, the 33% out of the total 55% removal of solids (measured as VSS) took place in digester P while the remaining 22% took place in digester A. When In case of secondary sludge fed to process A, the 33% out of the total 43% removal of solids took place in digester P while only the rest 10% took place in reactor A. The above support the initial hypothesis that a pre-treatment at 70°C enhances the solubilisation of solids thus resulting in increased digestibility of the sludge. As it was expected secondary sludge resulted in lower methane production than primary sludge. However, the methane produced with process A is 11% higher when primary sludge was treated and 37.5% higher when secondary sludge was treated.

Regarding pathogen reducing effect (PRE) it was calculated that process B resulted in a PRE of 2.63. On the other hand process A resulted in almost complete destruction of faecal streptococci (PRE = 567) indicating that the pre-treatment at 70°C had a decisive effect on pathogens destruction.

Representative results from the batch tests for the determination of MSSCR and SMA are shown in Figure 2. The MSSCR and SMA have been calculated for both digesters A and B fed with primary or secondary sludge and are presented in Table 4. Digester A was characterized by a higher activity compared to digester B regarding VFAs consumption and methane production from hydrogen when the processes A and B were fed with primary sludge. This was due to the higher VFAs concentration in the influent of digester A, which was thermally pre-treated and thus partly hydrolyzed primary sludge from digester P. On the other hand, acetate, propionate and butyrate consumption activities in

### Table 1 Characteristics of the influent sludge

<table>
<thead>
<tr>
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<th>Primary sludge</th>
<th>Secondary sludge</th>
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<tbody>
<tr>
<td>TSS (g/l)</td>
<td>14.48 ± 0.03</td>
<td>9.09 ± 0.87</td>
</tr>
<tr>
<td>VSS (g/l)</td>
<td>9.05 ± 0.16</td>
<td>5.42 ± 0.54</td>
</tr>
<tr>
<td>Dissolved COD (g/l)</td>
<td>2.411 ± 0.036</td>
<td>0.890 ± 0.004</td>
</tr>
<tr>
<td>Total COD (g/l)</td>
<td>17.106 ± 0.768</td>
<td>9.964 ± 0.850</td>
</tr>
<tr>
<td>FS/ml</td>
<td>Not measured</td>
<td>4.7 × 10^5</td>
</tr>
</tbody>
</table>

### Table 2 Performance characteristics of process A (two steps: P and A digesters) and process B (one step: B digester) under steady state

<table>
<thead>
<tr>
<th></th>
<th>Process A</th>
<th>Process B</th>
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<tbody>
<tr>
<td></td>
<td>Primary sludge</td>
<td>Secondary sludge</td>
</tr>
<tr>
<td>% CH₄ in CH₄</td>
<td>69</td>
<td>49</td>
</tr>
<tr>
<td>Methane production, ml l⁻¹ d⁻¹</td>
<td>162</td>
<td>55</td>
</tr>
<tr>
<td>Efficiency in VSS removal, %</td>
<td>55</td>
<td>43</td>
</tr>
<tr>
<td>Pathogen reducing effect</td>
<td>5.67</td>
<td>2.63</td>
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</tbody>
</table>

### Table 3 Steady-state characteristics of digesters P, A and B under steady state

<table>
<thead>
<tr>
<th></th>
<th>Digester P</th>
<th>Digester A</th>
<th>Digester B</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Primary sludge</td>
<td>Secondary sludge</td>
<td>Primary sludge</td>
</tr>
<tr>
<td>VSS, g/l</td>
<td>6.02</td>
<td>3.65</td>
<td>4.03</td>
</tr>
<tr>
<td>dis. COD, g/l</td>
<td>3.160</td>
<td>1.230</td>
<td>0.436</td>
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</table>
digester A were not significantly different from those in digester B when the processes A and B were fed with secondary sludge. However, the hydrogenotrophic methanogenic activity of digester A was 40% higher compared to that of digester B. The latter, in combination with the considerably higher methane production of digester A, indicates that a significant amount of the organic matter was converted to methane through hydrogen metabolism when process A was fed with secondary sludge. The enhanced microbial activities in digester A suggest that the same efficiencies in organic matter removal and methane recovery could be obtained at lower HRT thus resulting in reduced digester volume for a full-scale plant.

Conclusions

The present study examines the effect of a hyper-thermophilic (70°C) pre-treatment step on the thermophilic (55°C) anaerobic digestion of primary and secondary sludge. It has been shown that the process with the pre-treatment step (process A) resulted in higher organic matter removal efficiency than the one-step thermophilic process (process B). This suggests that the pre-treatment at 70°C enhances the solubilisation of sludge solids thus increasing the digestibility of sludge. Also process A completely destroyed the faecal streptococci, which had been chosen as an indicator pathogen in the primary sludge, compared to the process B that resulted in a lower pathogen reducing effect.
Acknowledgements

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References


