Enhancement of waste activated sludge anaerobic digestion by a novel chemical free acid/alkaline pretreatment using electrolysis

W. Charles, B. Ng, R. Cord-Ruwisch, L. Cheng, G. Ho and A. Kayaalp

ABSTRACT

Anaerobic digestion of waste activated sludge (WAS) is relatively poor due to hydrolysis limitations. Acid and alkaline pretreatments are effective in enhancing hydrolysis leading to higher methane yields. However, chemical costs often prohibit full-scale application. In this study, 12 V two-chamber electrolysis using an anion exchange membrane alters sludge pH without chemical dosing. pH dropped from 6.9 to 2.5 in the anode chamber and increased to 10.1 in the cathode chamber within 15 h. The volatile suspended solids solubilisation of WAS was 31.1% in the anode chamber and 34.0% in the cathode chamber. As a result, dissolved chemical oxygen demand increased from 164 to 1,787 mg/L and 1,256 mg/L in the anode and cathode chambers, respectively. Remixing of sludge from the two chambers brought the pH back to 6.5, hence no chemical neutralisation was required prior to anaerobic digestion. Methane yield during anaerobic digestion at 20 d retention time was 31% higher than that of untreated sludge. An energy balance assessment indicated that the non-optimised process could approximately recover the energy (electricity) expended in the electrolysis process. With suitable optimisation of treatment time and voltages, significant energy savings would be expected in addition to the benefit of decreased sludge volume.

Key words | anaerobic digestion, electrolysis, pretreatment, waste activated sludge

INTRODUCTION

Waste activated sludge (WAS) is the excess biomass from secondary wastewater treatment systems. Most of the organic content of WAS comprises microbial cells. These cells are hard to degrade as their cell wall and membrane are composed of complex organic materials such as peptido-glycan, teichoic acids, and complex polysaccharides that are not readily biodegradable as they serve as a protective cover to resist osmotic lysis (Weemaes & Verstraete 1998).

WAS contains a mixed community of microbial groups, including facultative bacteria which can survive in an anaerobic digester. The tendency of WAS bacteria to survive slows down their hydrolysis in anaerobic digestion hence requiring longer hydraulic retention times (Appels et al. 2008).

In order to increase the efficiency of anaerobic digestion of WAS, the rate of hydrolysis needs to be increased. Applying pretreatment prior to anaerobic digestion is one option to increase WAS degradability. A number of different pretreatment processes have been proposed including biological pretreatment, thermal hydrolysis, mechanical treatment, and chemical treatment. Acid and alkaline pretreatments have previously proven to be effective in enhancing the hydrolysis of WAS in anaerobic digestion (Lin et al. 1997; Chen et al. 2007). However, acid/alkaline pretreatments are usually achieved by adding costly chemicals, not only for the pretreatment itself but also for the neutralisation after the pretreatment (Appels et al. 2008). Further, chemical neutralisation leads to increased salt concentrations.

In order to avoid chemical pretreatment and the associated cost, this study proposes a novel approach using electrolysis as a means to change pH without chemical dosing. This method is an adaptation of water electrolysis, where water molecules are split into hydrogen and hydroxide ions with the application of adequate voltage, forming a pH gradient across the anode and cathode electrodes (Teschke 1982; Salem 2011). By separating cathode and anode chambers with a selective ion exchange membrane,
it is possible to maintain high pH in the cathode chamber and low pH in the anode chamber. Based on this principle, we investigated the effectiveness of two-chamber electrolysis, as a pretreatment of WAS prior to anaerobic digestion.

**METHODS**

**Sludge samples**

Samples of WAS were collected from return sludge of Woodman Point wastewater treatment plant (WWTP), Western Australia. This plant uses a sequencing batch reactor process after a primary sedimentation step. The sludge characteristics are displayed in Table 1. Anaerobic sludge used as inoculum for batch anaerobic digestion was collected from the same WWTP. To avoid interference of biogas production from the background substrate, the anaerobic sludge inoculum was exhausted by incubating at 37°C without feed until the background methane production rate was less than 0.01 L/L/d before use.

**Electrolysis pretreatment**

Electrolysis pretreatment was carried out in two adjoining PVC chambers, separated by an anion exchange membrane (Membranes International Inc. AM7001S, Gel polystyrene cross linked with divinylbenzene; 0.45 mm thickness; electrical resistance \(< 40 \Omega \text{ cm}^2\)). In each chamber, 500 mL of WAS was added. To increase the contact area between electrode and sludge sample, five graphite electrodes (\(\phi 7 \text{ cm} \times 10 \text{ cm}\)) connected to graphite fabric (20 cm \(\times\) 6 cm) were used in each chamber. The voltage supplied was 12 V, and a 5 \(\Omega\) resistor was connected sequentially with the electrolysis cell to measure the current (A) of the system from the voltage drop over the resistor of the system. Copper wires were used for electrical circuits. The current and pH in the chambers were logged using LabVIEW 7.1 software interfaced with a National Instrument data acquisition card (DAQ).

The experiment was operated at 25°C until pH was stable. Samples of sludge were then taken from each chamber for volatile suspended solids (VSS) and dissolved chemical oxygen demand (COD) measurement. After the completion of electrolysis, sludge samples from both chambers were mixed, pH measured, and then the mixed sludge was tested for its methane production potential in batch anaerobic digestion compared to untreated sludge.

**Batch anaerobic digestion**

All batch anaerobic digestion experiments were performed in 100 mL serum bottles with 20% (v/v) of WAS addition to previously exhausted anaerobic digester sludge at 37°C in triplicate. Details of experimental set up and methane analysis have been fully described in Charles et al. (2009).

**Analysis**

Raw WAS and electrolysed WAS were analysed for VSS, total and dissolved COD according to American Public Health Association (2005). VSS solubilisation represents the transfer of the particulate fraction of the sludge to the soluble fraction of the sludge. VSS solubilisation is calculated using the difference between VSS of WAS before and after electrolysis compared to the initial VSS (Equation (1)).

\[
\text{VSS solubilisation (\%)} = \frac{\text{initial VSS} - \text{VSS after electrolysis}}{\text{initial VSS}} \times 100
\]  

**RESULTS AND DISCUSSION**

**Effect of electrolysis on pH changes in cathode and anode chambers**

During electrolysis, the generation of oxygen and hydrogen at the anode and cathode respectively indicated that the splitting of water molecules occurred in both chambers, with a pH difference forming across the two chambers. The pH of WAS gradually changed in both cathode and anode chambers and reached 10.1 and 2.5 in the cathode

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**Table 1 | Characteristics of WAS used in this study**

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids (TS g/L)</td>
<td>10.7</td>
</tr>
<tr>
<td>Volatile solids (VS g/L)</td>
<td>8.9</td>
</tr>
<tr>
<td>Total chemical oxygen demand (COD) (g/L)</td>
<td>17.2</td>
</tr>
<tr>
<td>Dissolved COD (g/L)</td>
<td>0.16</td>
</tr>
<tr>
<td>Carbohydrate (%VS)</td>
<td>60.9</td>
</tr>
<tr>
<td>Protein (%VS)</td>
<td>32.7</td>
</tr>
<tr>
<td>Fat (%VS)</td>
<td>6.4</td>
</tr>
</tbody>
</table>
and anode chambers respectively, after running for 15 h (Figure 1).

The WAS pH levels achieved by electrolysis in this study are within the pH range that has previously been found to be effective in enhancing hydrolysis of WAS (Lin et al. 1997; Devlin et al. 2011). After recombining the sludge from the two chambers pH was 6.5, only slightly lower than the original sludge pH of 6.9. The pretreated pH was only 0.2 lower than the pH range (6.7-7.2) required for optimum operation of an anaerobic digester (Gerardi 2005). As a result, no chemical dosing was necessary for pH neutralisation prior to anaerobic digestion.

VSS and COD solubilisation of WAS during electrolysis

VSS destruction/solubilisation after pretreatment is generally used as a predictive parameter of sludge reduction and methane production enhancement during subsequent anaerobic digestion (Salsabil et al. 2010). In this study, the electrolysis pretreatment significantly improved the solubilisation of VSS in WAS (Table 2). The anode chamber solubilised 34% of VSS, slightly higher than that in the cathode chamber, 31.1%. The VSS solubilisation obtained in this study is comparable to those obtained by thermo-chemical pretreatment (Valo et al. 2004; Liu et al. 2008). However, the results are significantly higher than that obtained by Song et al. (2010) using single chamber electrolysis (no pH gradient) of around 9%. The solubilisation of about 31% VSS from WAS suggests that by simply employing a selective membrane between electrodes during electrolysis to enhance the electrolytic pH gradient, WAS hydrolysis is significantly enhanced. As a result of VSS solubilisation during electrolysis, the dissolved COD of the sludge in both chambers gradually increased (Figure 2) from 164 to 1,787 mg/L and 1,256 mg/L in the anode and cathode chambers respectively. This average increase of dissolved oxygen demand of 1,358 mg/L would account for an additional 0.52 L of methane produced per litre of WAS, if the COD was completely converted to methane gas. Considering the VS level of 8.9 g/L of the WAS tested, the additional dissolved COD released would produce about 58.4 mL additional methane per gram of VS.

Effect of electrolytic WAS treatment on methane yield

Biodegradability batch anaerobic digestion tests of electrolysed WAS confirmed results obtained from WAS solubilisation. Electrolytic pretreatment enhanced the methane production of WAS from 242 ± 20 mL/gVS in untreated sludge to 318 ± 15 mL/gVS in electrolysed sludge. This increase of about 76 mL/gVS is more than expected from additional dissolved COD released and suggests that the WAS electrolysis made further organics available for methanogenesis, possibly by partial hydrolysis. The improved methane production indicates that the impact of the rate-limiting hydrolysis step could be reduced by electrolysis pretreatment. To discriminate whether the improvement of methane production was a result of combined pH changes/electrochemical effects or merely of a single pH change effect (either anodic acidification or cathodic alkalisation), a separate experiment was set up. After electrolysis pre-treatment, the pHs of WAS from the

![Figure 1](https://iwaponline.com/wst/article-pdf/67/12/2827/440494/2827.pdf)  
**Figure 1** | Current flow and anodic/cathodic pH during electrolysis with 12 V of WAS.

![Table 2](https://iwaponline.com/wst/article-pdf/67/12/2827/440494/2827.pdf)  
**Table 2** | Characteristics of WAS before and after electrolysis

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>VSS (g/L)</th>
<th>VS solubilisation (%)</th>
<th>Dissolved COD (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated WAS</td>
<td>6.9</td>
<td>8.9</td>
<td></td>
<td>164</td>
</tr>
<tr>
<td>Cathode</td>
<td>10.1</td>
<td>6.1</td>
<td>31.1</td>
<td>1,256</td>
</tr>
<tr>
<td>Anode</td>
<td>2.5</td>
<td>5.8</td>
<td>34.0</td>
<td>1,787</td>
</tr>
</tbody>
</table>

![Figure 2](https://iwaponline.com/wst/article-pdf/67/12/2827/440494/2827.pdf)  
**Figure 2** | Changes of dissolved COD concentration on WAS in the cathode and anode chambers during electrolysis.
anode and cathode chambers were neutralised separately to the original pH of 6.9. The methane production potential of these sludge samples was then compared with that of conventional acid (HCl) and alkaline (NaOH) pretreatment using the same retention time (15 h) as electrolysis pretreatment before neutralising to pH 6.9.

Results in Figure 3 show that the method of acidification or alkalisation – either chemical or electrochemical – had only little effect on the final methane production from WAS, although the methane production rate profiles were slightly different. The methane production rate of anode sludge was lower during the beginning when compared with the cathode sludge and the control (non-treated) and then accelerated during day 13–18 (Figure 3). This could be explained by the fact that the anodic sludge was not only acidic but also visibly oxidised (change of sludge colour from black to grey) and even supersaturated with oxygen that was released in the anode. The presence of oxygen is known to cause a delay in anaerobic digestion.

Based on total methane production, the treatments in both the anode and cathode chambers were equally effective in improving methane production. This implies that the enhancement of methane production in WAS from 2-chamber electrolysis is due to the effect of pH change rather than electrolytic effect on the sludge biomass. This finding appears to disagree with the finding of Song et al. (2010) that electrolysis itself (in a single chamber without pH change) could disrupt cell membranes in WAS and therefore enhance biodegradation in subsequent aerobic digestion.

Energy analysis

While methane production was significantly improved through electrolysis pretreatment, there was also energy expended as electricity during electrolysis. For industrial application of a suitable pretreatment the energy invested in this pretreatment should be regained as extra methane formed.

The energy consumption of the described electrolysis process can be calculated by the following equation (Equation (2)):

$$W_{\text{electrolysis}} = \int_{0}^{T} U \times I \times dt$$

where, $U$ is the supplied voltage, $I$ is the current, $T$ is the operation time.

The energy consumption of the electrolysis system over a treatment time of 15 h was 0.73 kWh/kgVS, suggesting that even without any optimisation the energy expended as

![Figure 3](https://iwaponline.com/wst/article-pdf/67/12/2827/440494/2827.pdf)

**Table 3** | Energy analysis of mesophilic anaerobic digestion with electrolysis pretreatment compared to other pretreatment methods (modified from Carrere et al. (2010))

<table>
<thead>
<tr>
<th>Pretreatment method</th>
<th>Treatment condition</th>
<th>Electrical energy consumed (kWh kg⁻¹ VS)</th>
<th>Thermal energy consumed (kWh kg⁻¹ VS)</th>
<th>Total (kWh kg⁻¹ VS)</th>
<th>Max biogas (kWh kg⁻¹ TS fed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No pretreatment</td>
<td></td>
<td>0.04</td>
<td>0.5</td>
<td>0.54</td>
<td>1.9</td>
</tr>
<tr>
<td>Thermal hydrolysis</td>
<td>170°C 15–30 min</td>
<td>0.04</td>
<td>2.0</td>
<td>2.04</td>
<td>2.9</td>
</tr>
<tr>
<td>Sonication</td>
<td>100 W, 16 s, 30 kW m⁻³</td>
<td>0.37</td>
<td>0.5</td>
<td>1.24</td>
<td>2.4</td>
</tr>
<tr>
<td>Ball milling</td>
<td></td>
<td>1.04</td>
<td>0.5</td>
<td>1.54</td>
<td>2.4</td>
</tr>
<tr>
<td>High pressure</td>
<td>200 bar</td>
<td>0.33</td>
<td>1.0</td>
<td>1.33</td>
<td>2.6</td>
</tr>
<tr>
<td>Electrolysis (present study)</td>
<td>12 V, 15 h</td>
<td>0.73 + 0.04 (electrolysis + anaerobic digestion)</td>
<td>0.5</td>
<td>1.23</td>
<td>2.9</td>
</tr>
</tbody>
</table>

*The analysis assumes a hydraulic retention time of 20 d for mesophilic anaerobic digestion. Energy consumption is electrical and thermal. Electrical requirements are mainly feed and mixing and are approx. 0.1–0.2 kWh/m³/d, 0.12 kWh/m³/d has been used in this analysis.
time is 15 and 30 h respectively. and 6.2% of the anaerobic digester when the electrolysis of WAS for the downstream anaerobic digestion. For example, (2), the total energy consumption is half the 12 V electrolysis pretreatment. However, longer electrolysis time requires (2), the total energy consumption is half the 12 V electrolysis pretreatment. However, longer electrolysis time requires bigger volume of electrolysis cells to produce the treated WAS for the downstream anaerobic digestion. For example, if the WAS retention time in the anaerobic digester is 20 d, the operating volume of the electrolysis cell should be 3.1 and 6.2% of the anaerobic digester when the electrolysis time is 15 and 30 h respectively.

CONCLUSION

Electrolysis of WAS in an electrolytic cell in which the anode and cathode are separated by an ion exchange membrane enhanced sludge hydrolysis and hence improved biodegradability of WAS during subsequent anaerobic digestion. In this proof-of-concept study, electrolysis of WAS was tested using a power supply of 12 V. To optimise the process, further investigations using different voltages, reaction duration, types of electrodes and concentrations of WAS, are required.

ACKNOWLEDGEMENTS

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REFERENCES