**ABSTRACT**

Anaerobic digestion of wastewater sludge is the preferred method for sludge treatment as it produces energy in the form of biogas as well as a stabilised product that may be land applied. Different pre-treatments have been proposed to solubilise organic matter and increase biogas production. Sludge electrooxidation with boron-doped diamond electrodes was used as pre-treatment for waste activated sludge (WAS) and its effect on physicochemical properties and biomethane potential (BMP) was evaluated. WAS with 2 and 3% total solids (TS) achieved 2.1 and 2.8% solubilisation, respectively, with higher solids requiring more energy. After pre-treatment, biodegradable chemical oxygen demand values were close to the maximum theoretical BMP, which makes sludge suitable for energy production. Anaerobic digestion reduced volatile solids (VS) by more than 30% in pre-treated sludge with a food to microorganism ratio of 0.15 g VS fed g⁻¹ VS biomass. Volatile fatty acids were lower than those for sludge without pre-treatment. Best pre-treatment conditions were 3% TS and 28.6 mA cm⁻².

**Key words** | advanced oxidation, biomethane potential, boron-doped diamond electrodes, electrooxidation, organic matter solubilisation, pre-treatment

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**INTRODUCTION**

Anaerobic digestion is the preferred treatment process for sludge stabilisation (Tyagi & Lo 2011); however, it is hydrolysis limited and it only degrades about 20 to 50% of the organic matter present in sludge (Tyagi et al. 2014). To overcome this limitation, sludge pre-treatment has been proposed to increase solubilisation of organic matter, which in turn improves biogas production and reduces treatment times (Carrère et al. 2010). This pre-treatment may be physical, chemical, mechanical, biological, or thermal (Dogan & Sanin, 2009; Carrère et al. 2010), and while many of these methods have important benefits, research is still needed to evaluate their full-scale potential (Tyagi & Lo 2011).

Usually, facilities combine primary sludge and waste activated sludge (WAS) before anaerobic digestion. However, WAS separation and an adequate pre-treatment improve hydrolysis, which releases intracellular and extracellular constituents to the aqueous phase, increasing its biomethane potential (BMP) (Zhang et al. 2010; Shehu et al. 2012).

Recently, studies have evaluated the electrooxidation (EO) of sludge for conditioning (Yuan et al. 2011), degradation of emerging pollutants (Barrios et al. 2015), or as a pre-treatment for aerobic (Song et al. 2010) or anaerobic digestion (Xu et al. 2014). These studies report that EO may be feasible and cost effective for conditioning, degrades emerging pollutants, enhances aerobic and anaerobic digestion, and, in the latter, compared to other pre-treatment methods, results in the largest cumulative biogas production. In this respect, EO, considered an advanced oxidation process, is a technology widely used for degrading organic compounds in a variety of effluents by generating different free radicals (Rivera-Utrilla et al. 2015), such as the hydroxyl radical (OH⁻) which is one of the most powerful molecules for oxidation (Chen 2004; Barrera-Díaz et al. 2014). In particular, the use of boron-doped diamond (BDD) electrodes has been widely reported as one of the most stable materials for electrochemical applications (Souza et al. 2016). Nonetheless, this type of electrode has not been evaluated as a pre-treatment of sludge for anaerobic digestion. As a result, this work reports on the use of EO with boron-doped diamond electrodes as a pre-treatment for anaerobic digestion with the purpose of increasing biogas production.

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METHODS

Collection of sludge samples

WAS was obtained from a wastewater treatment plant in Mexico City. The plant treats 2 m³ s⁻¹ and includes the following processes: degritting, screening, flow equalisation, primary sedimentation, activated sludge, clarification, and disinfection. Sludge samples (100 L) were obtained directly from the sludge-wasting pipe after letting the sludge flow for about 1 minute. Samples were collected in plastic containers (10 L) and cooled down to 4 °C, then transported to the laboratory.

Sludge solids concentration

To evaluate the process with different solids conditions, sludge was concentrated by sedimentation (24 h) and supernatant decantation, followed by centrifugation at 1,400 × g for 20 minutes. Total solids (TS) were adjusted to fixed values (2 and 3%) with supernatant collected.

Electrochemical reactor

The EO assays were carried out in a single compartment electrochemical cell (DiaClean®, WaterDiam Sarl, Switzerland). Diamond-based material (p-Si–BDD) was used as anode and cathode. Both electrodes were circular (100 mm diameter) with a surface area of 70 cm².

Sludge was stirred in a glass reactor with an overhead agitator (stainless steel paddle area: 49 cm²) to avoid solids settling. The stirrer speed was low (100 rpm) in order to prevent floc breakage but enough to keep the sludge homogeneous and avoid phase separation (liquid–solid). The amount of sludge treated was 1 L. The system worked in recirculation mode, with a peristaltic pump (JP Selecta Percom N-M328) continuously feeding the DiaClean reactor (2.8 L min⁻¹). Power was supplied by a Delta Elektronika ES030-10 (maximum current = 2 A). The temperature of the system was kept constant (25 °C) with a water bath/heat exchanger. All tests were carried out in discontinuous mode (semi-batch). EO conditions tested were 14.3, 21.4, and 28.6 mA cm⁻² for 30 minutes.

BMP assays

Anaerobic digestion batch assays were performed in an OxiTop® Control OC 110 (WTW, Germany), with a working volume of 80 mL, in 250 mL serological bottles with gas sampling ports. OxiTop is a respirometric measuring system for evaluating anaerobic degradation tests under controlled conditions with different samples at a time. Biogas production was automatically measured by the system at 160-minute intervals. Anaerobic sludge from a mesophilic laboratory reactor adapted to secondary sludge (WAS) was used as inoculum. The amounts of secondary sludge and inoculum were determined based on the food to microorganism (F/M) ratio and the solids concentration. Eight assays were performed with two WAS concentrations (2 and 3%) and two F/M ratios (0.10 and 0.15 g VSedu g⁻¹ VSBiomass), both with untreated (UT) sludge and pre-treated with EO. The operating conditions of the batch assays were mesophilic temperature (36 ± 2 °C), pH adjusted to 7, and shaking at 150 rpm for 21 days. The controls used were: substrate without inoculum and a bottle to correct pressure measurements of the system as temperature compensation is required.

Chemical analysis

TS, volatile solids (VS), fixed solids, pH, total alkalinity, and soluble chemical oxygen demand (COD) (1:20 dilution of sludge supernatant after centrifugation at 1,400 g for 20 minutes and then filtered through 0.45 μm cartridge filters) were determined according to Standard Methods (APHA 2014). Alkalinity ratio was determined by dividing the partial alkalinity by the total alkalinity. The concentration of volatile fatty acids (VFA) was evaluated by gas chromatography (SRI 8610-10 with flame ionisation detector and column Alltech EC-1000). The biogas volume was determined by the OxiTop itself while biogas composition was analysed by gas chromatography (Fisher chromatograph with thermal conductivity detector and column Porapak Q).

RESULTS AND DISCUSSION

EO pre-treatment

Substrate solubilisation, as a result of sludge pre-treatment, increases the degradation rate of organic matter during anaerobic digestion (Carlsson Lagerkvist & Morgan-Sagastume 2012). As mentioned before, this is achieved with different sludge pre-treatment methods, including EO, which should be applied at conditions that promote solubilisation of organic matter but limit its oxidation to favour anaerobic digestion of readily available organics and
increase biogas yield. Previous studies (Barrios et al. 2015) reported a slight soluble COD reduction under similar operating conditions (pH: 7.0; time: 30 min; current density: 20 mA cm$^{-2}$); however, sludge used for those tests was of industrial origin and with lower TS content (1.54%). As a result, the process achieved partial oxidation of soluble organics (<10% of soluble COD). For that reason, this study evaluated a range of current densities that included lower values to avoid this effect. Table 1 presents the effect of EO on physicochemical characteristics of sludge.

According to these results, EO increased the amount of soluble COD due to cell breakage and release of intracellular material. As mentioned before, the solubilisation of organic matter into low molecular weight compounds improves hydrolysis and biodegradability during anaerobic digestion (Xu et al. 2014). Nonetheless, in all cases, some oxidation of soluble organics was observed (indicated by a reduction in total COD). This is consistent with prior EO studies for conditioning (Yuan et al. 2011), which report that this process solubilises intracellular substances but it may oxidise some of them.

However, when 28.6 mA cm$^{-2}$ was applied to sludge with 3% TS, the efficiency of the process diminished (observed in a lower COD$_{total}$ reduction). As reported by Song et al. (2010), the efficiency of EO decreases with increasing sludge solids content since the process is mass transfer limited. In addition, higher current densities may result in oxygen evolution which in turn decreases oxidation (Chen 2004; Tissot et al. 2012). This behaviour is positive since there is more organic material available for digestion and biogas production.

Figure 1 shows the COD$_{total}$ profiles for sludge pre-treated with EO at different current densities. For sludge with 2% TS, a linear behaviour was obtained ($R^2 = 0.99$) as the oxidation of organic matter is proportional to current density. During this process, COD reduction is attributable to direct oxidation through hydroxyl radicals (OH$^\cdot$). In contrast, when sludge with 3% TS was treated, an initial COD$_{total}$ reduction was observed, followed by a slight increase. In this case, the larger amount of solids reduces the contact of particles with the electrode surface, where hydroxyl radicals generate, and for the highest current density tested, these radicals react with certain compounds, such as carbonates, chlorides, and sulphates, producing less powerful oxidising species, which reduces organic matter oxidation (Barrios et al. 2016).

To evaluate hydrolysis of sludge, soluble COD/total COD ratio may be used as an indicator (Eskicioglu et al. 2006). In particular, the degree of solubilisation (DS) has been used to report the effect of pre-treatments on soluble organics (Xu et al. 2014) and it is defined as (Appels et al. 2010):

$$\text{Degree of solubilisation} = \frac{\text{soluble COD}_{\text{treated sludge}} - \text{soluble COD}_{\text{untreated sludge}}}{\text{total COD}_{\text{untreated sludge}}} \times 100$$

Based on this equation, Figure 2 presents the DS for sludge treated with EO. It is clear that higher solids content sludge requires greater current densities to achieve equivalent DS. In contrast, sludge with lower solids content shows oxidation of soluble organic matter and thus the DS decreases with higher current densities, being even negative when

### Table 1 | Effect of EO on physicochemical characteristics of sludge

<table>
<thead>
<tr>
<th>Parameter</th>
<th>2% TS</th>
<th>3% TS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density (mA cm$^{-2}$)</td>
<td>0 (raw)</td>
<td>14.3</td>
</tr>
<tr>
<td>pH</td>
<td>6.08 ± 0.01</td>
<td>6.38 ± 0.04</td>
</tr>
<tr>
<td>TS (%)</td>
<td>2.02 ± 0.00</td>
<td>1.87 ± 0.13</td>
</tr>
<tr>
<td>COD$_{total}$ (g L$^{-1}$)</td>
<td>24.50 ± 0.71</td>
<td>23.18 ± 1.94</td>
</tr>
<tr>
<td>COD$_{soluble}$ (g L$^{-1}$)</td>
<td>1.53 ± 0.99</td>
<td>2.04 ± 1.26</td>
</tr>
<tr>
<td>Current density (mA cm$^{-2}$)</td>
<td>0 (raw)</td>
<td>14.3</td>
</tr>
<tr>
<td>pH</td>
<td>6.23 ± 0.03</td>
<td>6.25 ± 0.04</td>
</tr>
<tr>
<td>TS (%)</td>
<td>2.90 ± 0.09</td>
<td>2.87 ± 0.11</td>
</tr>
<tr>
<td>COD$_{total}$ (g L$^{-1}$)</td>
<td>45.10 ± 0.07</td>
<td>38.45 ± 0.07</td>
</tr>
<tr>
<td>COD$_{soluble}$ (g L$^{-1}$)</td>
<td>1.39 ± 0.19</td>
<td>1.96 ± 0.34</td>
</tr>
</tbody>
</table>
28.6 mA cm⁻² was applied. Apparently, the DS of sludge with 3% TS might increase with higher current densities; however, increasing current and treatment times may have a deleterious effect on dewaterability, as reported by Yuan et al. (2011), which may offset some benefits of an increased biogas production with a higher polymer demand for sludge conditioning. As a result, higher DS values were obtained with 14.3 and 28.6 mA cm⁻² for 2 and 3% TS, respectively. These conditions were further tested for anaerobic digestion trials.

BMP potential assays

The results showed that the total biogas production from two F/M ratios evaluated was higher for assays with EO pre-treatment than for the assays without pre-treatment (Figure 3). Methane production from sludge samples without pre-treatment appears to have been limited throughout the period of the experiment. Zhang et al. (2010) reported that secondary sludge contains inhibitors of methanogenesis such as propionic acid, which make
it less digestible. Therefore, these results are consistent with the lower accumulated methane from secondary sludge without pre-treatment (55–70 N-L g\(^{-1}\) VS) and the average methane content in biogas (46%). WAS without pre-treatment is less competitive for the production of methane and energy compared with EO sludge. EO pre-treatment showed that biodegradable COD was close to the maximum theoretical BMP (115 N-L CH\(_4\) kg\(^{-1}\) VS), irrespective of the F/M ratio. Hence, these results suggest that secondary sludge after EO may be used in energy production.

Table 2 summarises the response variables for all assays. VFA levels indicate that the substrates were not completely consumed for biogas production. As a result, the alkalinity ratio decreased due to the accumulation of organic acids, mainly propionic, as reported by Speece et al. (2006). In addition, methanogenic specific activities (MSA) were lower than expected for both assays, due to the WAS hydrolysis producing more VFA than the inoculum can consume. Consequently, the VS destruction was relatively low in all tests, but in most cases this value was higher in samples pre-treated. Moreover, EO reduced the time needed for digestion of sludge, potentially reducing the solids retention time and thus the volume of reactors. Overall, the best condition tested, in terms of process operation, was with EO pre-treatment of sludge with 3% TS and with an F/M ratio of 0.15 g VS\(_{\text{fed}}\) g\(^{-1}\) VS\(_{\text{biomass}}\).

![Figure 3](image.png)

**Figure 3** | Normalised BMP from WAS at two different F/M ratios and two TS concentrations (2 and 3%) for UT and EO pre-treated sludge.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>F/M = 0.10 g VS(<em>{\text{fed}}) g(^{-1}) VS(</em>{\text{biomass}})</th>
<th>F/M = 0.15 g VS(<em>{\text{fed}}) g(^{-1}) VS(</em>{\text{biomass}})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2% TS</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VS removal efficiency (%)</td>
<td>14.7 ± 2.1</td>
<td>12.5 ± 3.8</td>
</tr>
<tr>
<td>Alkalinity ratio</td>
<td>0.73 ± 0.3</td>
<td>0.41 ± 0.4</td>
</tr>
<tr>
<td>VFA(_{\text{total}}) (g COD L(^{-1}))</td>
<td>1.48 ± 1.4</td>
<td>1.09 ± 1.2</td>
</tr>
<tr>
<td>MSA (g COD-CH(_4) g(^{-1}) VSS d(^{-1}))</td>
<td>0.03 ± 0.01</td>
<td>0.14 ± 0.04</td>
</tr>
<tr>
<td><strong>3% TS</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VS removal efficiency (%)</td>
<td>7.5 ± 2.5</td>
<td>15.6 ± 2.3</td>
</tr>
<tr>
<td>Alkalinity ratio</td>
<td>0.53 ± 0.2</td>
<td>0.53 ± 0.5</td>
</tr>
<tr>
<td>VFA(_{\text{total}}) (g COD L(^{-1}))</td>
<td>2.76 ± 1.0</td>
<td>1.21 ± 0.5</td>
</tr>
<tr>
<td>MSA (g COD-CH(_4) g(^{-1}) VSS d(^{-1}))</td>
<td>0.09 ± 0.02</td>
<td>0.16 ± 0.03</td>
</tr>
</tbody>
</table>

Table 2 | Results of BMP assays
**ENERGY BALANCE**

An energy balance (Table 3) was performed based on the methane production of UT sludge and EO-treated sludge. Energy input was equivalent to the electrical energy required for pre-treatment in the electrochemical cell. At the same time, energy output was calculated based on the methane produced after 21 days in the Oxitop reactor assuming 55% heat and 30% power recovery (Pilli et al. 2016). Based on these results, the largest net energy is obtained with UT sludge (3.17 and 4.92 Wh L\(^{-1}\) for 2 and 3% TS, respectively). When sludge was pre-treated with EO, the net energy was less than 50% of that without any treatment for sludge with 2% TS or even negative for sludge with 3% TS. It should be mentioned that VS removal is higher after EO, which in turn would reduce the amount of solids that need further management (by between 13 and 24%). A global energy balance that considers other costs, such as transportation and land application or disposal, should determine whether the overall energy balance becomes positive. Moreover, the use of renewable energies may increase the feasibility of the pre-treatment proposed by reducing primary energy consumption (Alvarez-Guerra et al. 2017).

**CONCLUSIONS**

EO with BDD electrodes as pre-treatment of WAS increased soluble COD but reduced total COD as a result of partial organic matter oxidation. According to the results, higher solids in sludge limit direct oxidation at the surface of the electrode, promoting mediated oxidation through less reactive species. Even though the DS was less than 3%, biogas production increased by 76 and 80% after anaerobic digestion due to organic matter solubilisation into low molecular weight compounds that enhance hydrolysis. In addition, it appears to modify sludge structure, as there is not a correlation between solubilisation and methane production. Biomethane tests showed results close to the maximum theoretical BMP (115 N-L CH\(_4\) kg\(^{-1}\) VS). The energy balance of the process indicates that the increase in biogas production does not justify the EO as pre-treatment under tested conditions. At this experimental stage, statistical analysis resulted in a confidence interval higher than 55% and thus it is not conclusive of significant differences between treatments (\(p > 0.05\)). Further studies are needed to optimise the EO step in terms of current density, treatment time, and flow within the EO cell prior to anaerobic digestion. In addition, the use of renewable energies (e.g. solar) may supply the electricity needed for the pre-treatment, making the proposed process a viable alternative for sludge management.

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