Effect of ultrasonic and alkaline pretreatment on sludge degradation and electricity generation by microbial fuel cell

J. Q. Jiang, Q. L. Zhao, K. Wang, L. L. Wei, G. D. Zhang and J. N. Zhang

ABSTRACT

Both ultrasonic and alkaline pretreatment of excess sewage sludge were investigated to enhance organic degradation and electricity generation from sludge by the subsequent microbial fuel cell (MFC). The ultrasonic pretreatment showed that the degree of sludge disintegration was directly related to the energy input, ultrasonic density and duration. Alkaline pretreatment demonstrated that more soluble organic matters were released from the sludge with more NaOH dose and longer reaction time, and the degree of sludge disintegration within 30 min accounted for 45–76% of that for 24 h. When ultrasonic and alkaline pretreatment were combined, the released chemical oxygen demand (COD) was higher than those with ultrasonic or alkaline pretreatment alone. Ultrasonic and alkaline (pH = 11) pretreatment could enhance electricity generation from sludge by the subsequent MFC, resulting in more degradation of total COD (TCOD) and volatile solids (VS). Slight change in power output from the MFC was observed due to the higher soluble chemical oxygen demand (SCOD) in the pretreated sludge. By using the combined ultrasonic and alkaline pretreatment of sludge, the removal efficiencies of TCOD and VS were increased from 27.1% to 61.0% and 35.2% to 62.9% in comparison with raw sludge, respectively, and the power output in MFC was slightly increased from 10.3 W/m³ to 12.5 W/m³.

Key words | alkaline pretreatment, microbial fuel cell (MFC), sludge, ultrasonic pretreatment

INTRODUCTION

Treatment and disposal of excess sewage sludge represent about 25–60% of the total operating cost in most wastewater treatment plants (Zhang et al. 2009). Conventionally, anaerobic digestion has found wide application for sludge treatment because of its advantages such as less energy consumption (no aeration) and nutrient requirement, and potential energy recovery from the produced biogas. However, the main disadvantages for anaerobic digestion include high heating requirement under mesophilic or thermophilic operation, longer hydraulic retention time than 20 days, complicated operation, and sensitivity to shock loads and toxic materials.

To overcome the above-mentioned drawbacks of anaerobic digestion, microbial fuel cells (MFCs) might be another alternative process for sludge degradation and simultaneous electricity generation. A MFC is such a device that generates electricity by harnessing the oxidizing potential of anaerobic bacteria, which consists of an anode and a cathode separated by a membrane. At the anode, microorganisms oxidize various substrates including glucose (Chaudhuri & Lovely 2003), manure sludge (Scott & Murano 2007), and organic wastewater (Logan 2005; Min et al. 2005), and use the anode electrode as electron acceptor (Bond & Lovley 2005). The electrons that the
anode accepts flow through an external circuit to the cathode, where an oxidant (electron acceptor) such as oxygen or ferricyanide is reduced. Generally, MFCs have some inherent advantages such as mild reaction conditions (ambient temperature, normal pressure, and neutral pH), high energy conversion efficiency, no secondary pollution, no requirement of off-gas cleaning equipment, no need of energy input, and direct recovery of electrical energy.

Comprising abundant organic matters, sewage sludge could be a good potential substrate for electricity generation with MFC. Dentel et al. (2004) have reported that a maximum electrical current of about 60 μA and a potential of several hundreds of millivolts could be obtained by using a reactor with graphite foil electrodes in an aerated aerobic and anaerobic sludge zone. Our previous works (Jiang et al. 2009) also demonstrated that a maximum power density of 8.5 W/m³, the corresponding open circuit voltage (OCV) of 0.725 V and TCOD removal efficiency of 46.4% had been obtained by using a dual-chamber MFC reactor with sewage sludge as fuel (operation for 250 h). Unfortunately, raw sewage sludge presents mostly in the insoluble and large particulate form, whereas the microbe within MFC can only make use of soluble and easily-biodegradable organic matters such as proteins (Heilmann & Logan 2006), carbohydrates (Niessen et al. 2004), and other small organic molecules (Liu et al. 2005) as their substrates, which means that raw sludge needs to be hydrolyzed. For the conventional anaerobic digestion process, hydrolysis has been identified as the rate-limiting step (Shimizu et al. 1993; Lishman & Murphy 1994), however, some methods can be adopted to accelerate sludge hydrolysis, including thermal (Valo et al. 2004), alkaline (Mace et al. 2001), ultrasonic (Tiehm et al. 2001), and mechanical (Baier & Schmidheiny 1997) disintegration. Among these methods, alkaline and ultrasonic pretreatments are simple, convenient, and highly efficient (Kim et al. 2003; Zhang et al. 2007). Although many researchers have investigated sludge pretreatment for anaerobic digestion, no reports have been found about the effect of sludge pretreatment on sludge degradation and electricity generation in MFCs. This study aims at investigation of the effect of ultrasonic and alkaline pretreatment on sludge degradation and electricity generation by MFC.

MATERIALS AND METHODS

Excess sewage sludge characterization

The sludge sample was obtained from the secondary sedimentation tank in Harbin Municipal Wastewater Treatment Plant (China) and stored at 4°C before use. The sludge had a water content of 99%, pH of 6.96, total solids (TS) of 9,433 mg/L, volatile solids (VS) of 7,763 mg/L, TCOD of 12,303 mg/L and SCOD of 218 mg/L, respectively.

Sludge disintegration by ultrasonic and alkaline pretreatment

The major effect of ultrasonication on sludge disintegration had been well known for disrupting sludge flocs and lysing biological cells (Gonze et al. 2003). Ultrasoundization might lead to the solubilization of sludge and release of organic matters measured as COD, proteins, nucleic acids, polysaccharides, reduction of floc size, biodegradability improvement (Zhang et al. 2007). In this study, the sludge ultrasonication was performed in an ultrasonic cell disintegrator (KS-250, Ningbo Kesheng Co., Ltd, China) as depicted in Figure 1. The disintegrator, which was equipped with a probe and sound-proof box, was operated at a frequency of 20 kHz and 0–250 W. During ultrasonic pretreatment of sludge, the probe was centrally placed 1 cm into the 100 ml sludge sample. Ultrasonic power was calculated by multiplying ultrasonic power density (W/ml) by sample volume (ml). The sludge pH was not adjusted.

Figure 1 | Scheme of ultrasonic disintegration of sludge.
At extremely high pH values, the cell lost its viability and could not maintain an appropriate turgor pressure. The disruption of sludge cells led to the leakage of intracellular material out of the cell. In this study, alkaline sludge disintegration was performed in a completely-mixed batch reactor of 200 ml, which was placed in a water bath to maintain the reaction temperature of 20 ± 2°C. The pH of the alkalized sludge was adjusted by 1 M NaOH, ranging from 8 to 13.

Besides, the combined ultrasonic and alkaline pretreatment of sludge were conducted, i.e. ultrasonication followed by alkalinization, and alkalinization followed by ultrasonication.

MFC for sludge degradation and electricity generation

The MFC used in this study comprised two Plexiglas chambers and a proton exchange membrane (PEM) (Nafion 112) located between the anode and cathode. The anodic chamber was a semicircular cylinder (Φ10 × 9 cm) and the cathode chamber was a cube (10 × 2.5 × 9 cm). The two chambers were positioned and held together by bolts with the membrane in the middle providing a large surface area. Both the anode and cathode electrodes consisted of a graphite fiber brush and titanium wire that collected electrons for the external circuit. The effective volume of the anodic chamber was 320 ml and that of the cathodic chamber was 190 ml. The anodic compartment of the MFC was inoculated with sludge and repeatedly filled with sludge until bacteria in the sludge colonized on the electrode and generated electricity. The catholyte consisted of 50 mM K₃Fe(CN)₆ aqueous solution in a 100 mM KH₂PO₄ buffer adjusted to pH 7 with 1 M NaOH (Aelterman et al. 2006).

Analytical procedures

Sludge analysis

The sludge samples were used directly for the measurement of water content, TS, VS, pH, TCOD and SCOD according to the Standard Methods (APHA 1998). The pH was measured by a pH meter (pHs-3c, Shanghai Weiyi Co., Ltd, China). The soluble fraction within sludge was evaluated after centrifugation at 4,000 × g for 20 min and filtration through a 1.2 μm membrane.

The degree of sludge disintegration (DDCOD) was calculated as the ratio of the SCOD increment after alkaline or ultrasonic pretreatment to the maximum possible SCOD increment (Frolund et al. 1996):

\[
DD_{\text{COD}} = \frac{(\text{SCOD} - \text{SCOD}_0)}{(\text{SCOD}_{\text{NaOH}} - \text{SCOD}_0)} \times 100\% \tag{1}
\]

where, SCOD and SCOD₀ values are for the treated and raw sludge samples, respectively. A reference (100%) was defined as the SCOD NaOH obtained by chemical sludge disintegration in 1 mol L⁻¹ sodium hydroxide for 24 h at 20°C.

Electrochemical analysis

Electrical voltage drop by the MFC was recorded using a multimeter voltage collection instrument (12-bit A/D-conversion chips US) connected to a personal computer via a universal serial bus (USB) (Intel, USA) interface and calibrated with a digital multimeter (Agilent HP 34970; Agilent, USA) before each test. The circuit consisted of a 10–99999 Ω resistor. Except for those mentioned, the measurement of cathode working potential was performed by a reference electrode (Ag/AgCl, +195 mV vs. standard hydrogen electrode (SHE)) connected to a multimeter (Agilent HP 34970). Voltage was converted to volume power density \( P_v \) (W/m³) via the equation \( P_v = U/I/V_a \), where \( U \) is voltage (V), \( I \) is current (A), and \( V_a \) is the net liquid volume in the anodic chamber (m³). The maximum power density and polarization curve were determined by adding fresh substrate to the MFC to reach a constant power, and then by adjusting the external resistance to 10–9999 Ω for recording the corresponding voltage drop.

RESULTS AND DISCUSSION

Sludge disintegration by ultrasonic pretreatment

The effect of ultrasonic density (from 0.2 W/mL to 1.5 W/mL) on sludge disintegration was studied in order to find out the optimum sonication conditions, and the parameter of \( DDC_{\text{COD}} \) was used to evaluate the efficiency of
sludge disintegration. During ultrasonic sludge disintegration, temperature was not controlled. Experimental result indicated that DDCOD increased almost linearly with ultrasonic density and time (Figure 2). The same DDCOD could be obtained under the conditions of lower ultrasonic density with longer time and higher ultrasonic density with shorter time. During the test, the initial SCOD in raw sludge was about 218 mg/L and the SCOD in the sludge supernatant was increased significantly after ultrasonication, which suggested that insoluble sludge flocs were destructed and transformed into colloidal and soluble organics. It could be noted that DDCOD was 20.7% at 0.6 W/mL ultrasonic density (15 min), and DDCOD was 57.0% at 1.5 W/mL (15 min). In the subsequent tests, ultrasonic density was set at 0.6 W/mL and 1.5 W/mL (15 min), respectively, for the purpose of comparison.

**Sludge disintegration by alkaline pretreatment**

The effect of alkaline NaOH dose on sludge disintegration is reflected by DDCOD increase (Figure 3). The supernatant SCOD was increased remarkably with pH (from 8 to 13). At sludge pH of 11, the DDCOD was increased from 21.1% (0–0.5 h) to 31.0% (0.5–24 h), which meant that SCOD increase experienced an initial rapid stage (0–0.5 h) and the subsequent slow stage. The similar result can also be found in literature (Cai et al. 2004). During the tests, the DDCOD values for 0.5 h accounted for 45–76% of those for 24 h. To maintain the final supernatant pH below 8, it was suggested that the initial pH was controlled below 11 when alkaline pretreatment of sludge was used.

**Sludge disintegration by the combined ultrasonic and alkaline pretreatment**

The effect of the combined ultrasonic and alkaline pretreatment on sludge disintegration is shown in Figure 4. SCOD was increased in the order of NaOH pretreatment < Ultrasonic pretreatment < NaOH followed by Ultrasonic pretreatment < Ultrasonication followed by NaOH pretreatment. These results were in agreement with the report by Wang et al. (2005). Ultrasonic pretreatment can disintegrate sludge flocs, but the fragments can re-flocculate and form compact flocs. However, when alkaline pretreatment was added after ultrasonic pretreatment, alkali could further promote sludge hydrolysis and flocs solubilization.
Effect of sludge pretreatment on electricity generation in MFC

After sludge was pretreated by ultrasonication, alkalinization or their combination, the pretreated sludge was introduced into the subsequent dual-chamber MFC with 100 mM K₃Fe(CN)₆ aqueous solution in cathode chamber for further degradation and simultaneous electricity generation. Each test lasted for 5 days. Both TCOD and VS removals were used to evaluate sludge degradation, and maximum power density was obtained to evaluate electricity generation from sludge, respectively.

The effect of sludge pretreatment by ultrasonication on TCOD and VS removals as well as power output in MFC are summarized in Figure 5. It could be noted both TCOD and VS were remarkably removed after ultrasonic pretreatment. In comparison with the case of untreated sludge, TCOD and VS removal efficiencies were increase by 50.3% and 42.7% at ultrasonic density of 1.5 W/mL, respectively. This might be ascribed that ultrasonic pretreatment of sludge led to the release of soluble organic matters containing more protein and polysaccharide, and these matters could be easily degraded in MFC (Rabaey et al. 2003, 2005; Heilmann & Logan 2006). These results demonstrated that the ultrasonic pretreatment of sludge was efficient in accelerating organic matter disintegration and enhancing organic degradation in the subsequent MFC treatment. There was essentially no obvious change of the maximum power density when the ultrasonically pretreated sludge was introduced in MFC (Figure 5). The maximum power density was only increased by 13.4% when the sludge was pretreated at 1.5 W/mL ultrasonic density, simply because that the SCOD in the pretreated sludge was high enough (e.g. initial SCOD = 2,084 mg/L at 0.6 W/mL ultrasonic density) and the substrate concentration was not the limiting factor for electricity generation in MFC.

During alkaline pretreatment, raw sludge was adjusted to pH 11 and reaction lasted for 24 h. Then the treated sludge was buffered to neutral pH with phosphate buffer solution before it was fed into MFC. The effect of ultrasonication, alkalinization and their combination on sludge TCOD and VS removal efficiencies and power density of MFC are summarized in Table 1. It could be noted that TCOD removal after MFC operation for 2 days had been increased remarkably as compared with that of the untreated (16.5%), while both TCOD and VS removal efficiencies after MFC operation for 5 days were further increased to a relatively similar level. The power density was

![Figure 5: Effect of ultrasonic pretreatment on sludge organic degradation and electricity generation from MFC (Ultrasonic time: 15 min).](https://iwaponline.com/wst/article-pdf/61/11/2915/445937/2915.pdf)

**Table 1** | Effect of alkaline, ultrasonic and the combined pretreatment on electricity generation from sludge by MFC

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>TCOD removal (%)</th>
<th>VS removal (%)</th>
<th>Power density (W/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinization (pH = 11, 24 h)</td>
<td>21.9</td>
<td>51.5</td>
<td>11.9</td>
</tr>
<tr>
<td>Ultrasonication (0.6 W/mL, 15 min)</td>
<td>29.7</td>
<td>53.6</td>
<td>11.9</td>
</tr>
<tr>
<td>Alkalinization (pH = 11, 24 h) + Ultrasonication (0.6 W/mL, 15 min)</td>
<td>42.2</td>
<td>53.6</td>
<td>12.1</td>
</tr>
<tr>
<td>Ultrasonication (0.6 W/mL, 15 min) + Alkalinization (pH = 11, 24 h)</td>
<td>45.4</td>
<td>54.3</td>
<td>12.1</td>
</tr>
<tr>
<td>Ultrasonication (1.5 W/mL, 15 min)</td>
<td>33.0</td>
<td>54.5</td>
<td>11.9</td>
</tr>
<tr>
<td>Alkalinization (pH = 11, 24 h) + Ultrasonication (1.5 W/mL, 15 min)</td>
<td>44.8</td>
<td>60.1</td>
<td>12.3</td>
</tr>
<tr>
<td>Ultrasonication (1.5 W/mL, 15 min) + Alkalinization (pH = 11, 24 h)</td>
<td>48.3</td>
<td>61.0</td>
<td>12.5</td>
</tr>
</tbody>
</table>
increased only slightly for the same reason mentioned before. These results indicated that both alkaline and ultrasonic pretreatment and their combination could enhance organic matter removal as well as electricity generation by MFC, among which the combination of ultrasonic and alkaline pretreatment showed the best performance.

**CONCLUSIONS**

Based on the study of effect of ultrasonic and alkaline pretreatment on sludge degradation and electricity generation by MFC, conclusions could be drawn as follows.

Ultrasonic pretreatment of sludge at different ultrasonic density (from 0.2 to 1.5 W/mL) and ultrasonication time (from 2 to 25 min) led to efficient sludge disintegration, and correspondingly sludge SCOD was increased. The same DDCOD could be obtained under the conditions of lower ultrasonic density with longer time and higher ultrasonic density with shorter time. Alkaline pretreatment of sludge resulted in remarkable increase of SCOD with more NaOH dose, and the DDCOD values for 0.5 h accounted for 45–76% of those for 24 h. The combined ultrasonic and alkaline pretreatment on sludge disintegration demonstrated that SCOD was increased in the order of NaOH pretreatment < Ultrasonic pretreatment < NaOH followed by Ultrasonic pretreatment < Ultrasonication followed by NaOH pretreatment.

The sludge pretreatment of ultrasonication, alkalization and their combination could enhance organic matter removals measured as TCOD and VS removal efficiencies during electricity generation by MFC, among which the combination of ultrasonication and alkalization showed the best performance. The improvement of sludge pretreatment on power output during MFC treatment was not significant.

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**REFERENCES**


