Impact of electrode configurations on retention time and domestic wastewater treatment efficiency using microbial fuel cells

Kyoung-Yeol Kim, Wulin Yang, Bruce E. Logan*

Department of Civil and Environmental Engineering, The Pennsylvania State University, 231Q Sackett Building, University Park, PA 16802, USA

ARTICLE INFO

Article history:
Received 20 March 2015
Received in revised form 5 May 2015
Accepted 7 May 2015
Available online 14 May 2015

Keywords:
Microbial fuel cell
Continuous flow mode
Brush anode electrode
Flow pattern
Hydraulic retention time

ABSTRACT

Efficient treatment of domestic wastewater under continuous flow conditions using microbial fuel cells (MFCs) requires hydraulic retention times (HRTs) that are similar to or less than those of conventional processes such as activated sludge. Two MFCs in series were compared at theoretical HRTs of 8.8, 4.4 and 2.2 h using two different brush-electrode MFC configurations: a full brush evenly spaced between two cathodes (S2C); and trimmed brush anodes near a single cathode (N1C). The MFCs with two cathodes produced more power than the MFCs with a single cathode, with 1.72 mW for the S2C, compared to 1.12 mW for the N1C at a set HRT = 4.4 h. The single cathode MFCs with less cathode area removed slightly more COD (54.2 ± 2.3%, N1C) than the two-cathode MFCs (48.3 ± 1.0%, S2C). However, the higher COD removal was due to the longer HRTs measured for the MFCs with the N1C configuration (10.7, 5.3 and 3.1 h) than with the S2C configuration (7.2, 3.7 and 2.2 h), despite the same theoretical HRT. The longer HRTs of the N1C MFCs also resulted in slightly higher coulombic efficiencies (≥37%) than those of the S2C MFCs (32.9%). While the S2C MFC configuration would be more advantageous based on electrical power production, the N1C MFC might be more useful on the basis of capital costs relative to COD removal efficiency due to the use of less cathode surface area per volume of reactor.

1. Introduction

Microbial fuel cells (MFCs) have been studied as an energy-neutral process which can produce electrical energy from organic compounds while accomplishing wastewater treatment (Li et al., 2014; Rabaey and Verstraete, 2005; Zhang et al., 2013). However, recent studies have shown that both high power densities and low effluent concentrations of chemical oxygen demand (COD) cannot be simultaneously achieved in MFCs under continuous flow conditions (Akman et al., 2013; Nam et al., 2010; Zhuang et al., 2012). When the COD concentration is reduced to a range of ~100 mg/L, there is minimal current generation relative to higher COD concentrations (Ren et al., 2014a; Zhang et al., 2015). Thus, a secondary treatment process such as an anaerobic fluidized bed membrane bioreactor (AFMBR) is needed to reduce the COD to levels suitable for discharge (Ren et al., 2014b). The goal of MFC treatment is therefore not COD removal to a level suitable for discharge, but COD reduction to levels that maintain good power production. The low COD levels needed for discharge can be achieved using AFMBRs or other types of processes such as biofilters or solids contact systems (Chernicharo, 2006; Kim et al., 2011; Ren et al., 2014b).

The materials used in larger-scale MFCs for wastewater treatment need to be inexpensive, effective for treatment of actual wastewaters that contain particulate organic matter, and produce stable power over time. Flat anodes made of carbon cloth or mesh can allow close electrode spacing and high power densities with acetate solutions (Liu et al., 2005), but they have been found to result in unstable power production when used in MFCs treating domestic wastewater (Hays et al., 2011) and small electrode spacing could result in reactor clogging. Graphite fiber brush anodes can be used in MFCs to achieve good rates of COD removal, they have high surface areas and porosities for growth of exoelectrogenic microorganisms, and they produce stable power over time using actual domestic wastewaters (Ahn and Logan, 2013; Logan et al., 2007). MFCs have been designed and tested with multiple brush anodes configured primarily in two ways: with space between the anodes and the cathodes in the presence and absence of a separator; or with brushes placed directly on top of the separator with little space between the electrodes (Ahn et al., 2014; Zhang et al., 2014a). The two configurations have different advantages relative to power...
production, but separators are needed for both configurations to reduce cathode biofouling (Ren et al., 2014b). Cathode materials and performance are also important factors in MFC designs. Activated carbon cathodes have been shown to produce power densities similar to, or even larger than, cathodes made with a Pt catalyst (Cheng and Wu, 2013; Zhang et al., 2009, 2014b). The performance of activated carbon is maintained much better over time compared to Pt, and power production can be nearly restored to levels comparable to new cathodes using an acid treatment. Cathode performance typically limits power generation in MFCs at higher COD concentrations. Doubling the cathode surface area, for example, increased maximum power densities from domestic wastewater by 62% in fed-batch tests (Cheng and Logan, 2011).

In order for large-scale wastewater treatment using MFCs to be feasible using these low-cost brush anodes and activated carbon cathodes, the hydraulic retention times (HRTs) in the reactors has to be reduced to be more similar to that used for conventional activated sludge processes. However, there have been relatively few studies focused on achieving wastewater treatment with HRTs in the range of ~10 h or less using domestic wastewater (Min and Logan, 2004; Puig et al., 2011). Short HRTs can be accomplished by improving current densities, and therefore achieving higher power to COD ratios. Two different graphite fiber brush anode reactor configurations were examined here for wastewater treatment at HRTs of less than 10 h: anodes (trimmed flat on one side) placed directly on top of a separator covering a single cathode so that they are very near, in order to reduce solution ohmic resistance (N1C), resulting in no flow between the electrodes; and anodes (full brush) positioned in the middle of the chamber with space for flow between the brush and the two cathodes each covered by a separator (S2C). The two types MFCs were operated under continuous flow conditions at three different theoretical HRTs (8.8, 4.4, and 2.2 h) using two MFCs in series to minimize the change in COD in a single reactor. Power generation and COD removal were monitored over time, with maximum power densities evaluated using polarization data. The different anode configurations can affect flow patterns in these reactors, and thus the actual HRTs were measured using a salt tracer.

2. Materials and methods

2.1. MFC construction

Anodes were graphite fiber brushes (Mill-Rose, Mentor, OH) with a titanium core (25 mm diameter by 35 mm length) heat treated at 450 °C for 30 min before use. Cathodes (40 cm², projected surface area) were made by a phase inversion technique using a poly(vinylidenefluoride, PVDF) binder and a mixture of activated carbon (AC, 8.8 mg/cm²) and carbon black (CB, Vulcan XC-72, Cabot Corporation, USA) as previously described (Yang et al., 2014).

Four single-chamber, air-cathode MFCs were constructed using three graphite fiber brush anodes per reactor. Two of these reactors had the anodes placed directly next to a single cathode (N1C) similar to previous designs (Ahn et al., 2014) (Fig. 1). The other two MFCs had the anodes placed in the middle of the anode chamber with a space between the edge of the anodes and two cathodes on either side of the brushes (S2C). The spaced electrode reactor design is different from previous spaced electrode designs as two cathodes each containing separators were used per anode array, compared to MFCs tested with a single cathode without a separator (Zhang et al., 2014a). Brushes used in the N1C reactor (100 mL empty bed volume) were trimmed along their length to form a half cylinder, with the flat side placed on the separator that was positioned against the air-cathode (0.5 cm distance from the cathode). Full brushes were used in the S2C reactors (140 mL empty bed volume) with an edge-cathode distance of 0.8 cm (Fig. 1). Four single-chamber, air-cathode MFCs were constructed using three graphite fiber brush anodes per reactor. Two of these reactors had the anodes placed directly next to a single cathode (N1C) similar to previous designs (Ahn et al., 2014) (Fig. 1). The other two MFCs had the anodes placed in the middle of the anode chamber with a space between the edge of the anodes and two cathodes on either side of the brushes (S2C). The spaced electrode reactor design is different from previous spaced electrode designs as two cathodes each containing separators were used per anode array, compared to MFCs tested with a single cathode without a separator (Zhang et al., 2014a). Brushes used in the N1C reactor (100 mL empty bed volume) were trimmed along their length to form a half cylinder, with the flat side placed on the separator that was positioned against the air-cathode (0.5 cm distance from the cathode). Full brushes were used in the S2C reactors (140 mL empty bed volume) with an edge-cathode distance of 0.8 cm (Fig. 1). Theoretical HRT was calculated from the set flow rate (Q, mL/h) and reactor volume (V, mL) as HRT = V/Q. Flow rates were chosen to obtain the same theoretical HRTs for the two reactors of: 8.8 h (31.8 mL/h, S2C: 22.8 mL/h, N1C); 4.4 h (63.6 mL/h, S2C: 45.6 mL/h, N1C); 2.2 h (127.2 mL/h, S2C: 91.2 mL/h, N1C). A salt tracer test was conducted to measure the actual residence time of solutes in the two pairs of MFCs during continuous mode operation. A NaCl solution (1M) was injected into the flow line of the upstream flow line of the MFC for 36 min (8.8 h HRT), 18 min (4.4 h HRT), or 9 min (2.2 h HRT), with the effluent conductivity monitored using a meter (SB90M5S, VWR International, USA). Measured HRTs were defined as the time to the peak of the tracer input as previously described (Min et al., 2004; Zhang et al., 2006). The HRT measured using this approach includes the entrance and exit volumes (not working area) of the reactors. Thus, the measured HRTs were adjusted by multiplying a ratio of working volume to total reactor volume. A dispersion number (d) was calculated from the normalized variance of the salt tracer curve. A Pelet number (Pe) was calculated as Pe = 1/d, where Pe = uL/E is a ratio of mass transfer by advection to that of dispersion, where u is the average cross-sectional velocity, L is the distance of flow, and E is the dispersion coefficient.
interval of one HRT), and \(C_{th}\) was the theoretical amount of coulombs available based on the COD removed in the MFC over the same amount of time, calculated as \(C_{th} = \frac{Fb (COD_{in} - COD_{out}) Q \Delta t}{M}\), where \(F\) is Faraday’s constant, \(b = 4\) is the number of electrons exchanged per mole of oxygen, \(COD_{in}\) and \(COD_{out}\) are the influent and effluent COD, \(\Delta t\) is the time interval (HRT), and \(M = 32\) is the molecular weight of oxygen (Logan et al., 2006). Total COD was measured following standard methods (method 5220, HACH company, Loveland, CO).

3. Results and discussion

3.1. Power generation as a function of theoretical HRT

When the MFCs were started up at the longest HRT of 8.8 h (200 \(\Omega\) external resistance), there was inconsistent power produced for the similar reactor configurations (Fig. 2). For example, the S2C upstream MFC produced the most power, but the downstream S2C produced the least power. When operation was switched to shorter HRTs of 4.4 and 2.2 h, there was more consistent power production, with the S2C MFCs consistently producing more power (1.36 mW at 4.4 h, and 1.30 mW at 2.2 h) than the N1C MFCs (1.01 mW at 4.4 h, and 1.22 mW at 2.2 h). The upstream MFCs generally produced greater power than the downstream MFCs, likely due to the higher COD concentrations in the upstream MFCs. After these tests at the two shortest HRTs, the reactors were switched back to the longer 8.8 h HRT, and a fresh wastewater sample was used. This time at this longer HRT, the MFCs produced more consistent power densities based on reactor configuration, with power by the two-cathode MFCs (1.14 mW, S2C) larger than that produced by the single-cathode MFCs (0.85 mW, N1C).

Power and polarization curves (Fig. 3) also demonstrated that higher power could be produced by the S2C MFCs than the single cathode N1C MFCs at all HRTs. For example, at the shortest HRT of 2.2 h, the maximum power of the two S2C MFCs was 1.67 mW, compared to 1.20 mW for the N1C MFCs. In most cases, similar power densities were produced by both the upstream and downstream MFCs. At the shortest theoretical HRT, however, the maximum power produced by the downstream MFCs was 0.89 ± 0.03 mW compared to 0.78 ± 0.04 mW for the upstream reactor (Fig. 3c). For the N1C reactors, the downstream reactor produced 0.65 ± 0.03 mW, compared to 0.55 ± 0.02 mW for the upstream MFC. Together, these averaged 209 mW/m² for the S2C and 300 mW/m² for the N1C. There were smaller differences between the upstream and downstream MFCs at the longer HRTs, with average power produced of 1.72 mW (S2C) and 1.12 mW (N1C) at a 4.4 h HRT, and 1.61 mW (S2C) and 1.06 mW (N1C) at an 8.8 h HRT.

There are several possible reasons for the slightly higher maximum power densities in the downstream MFCs. Polarization data represent the capability of the MFCs for power production based on short-term tests, but with longer acclimation the power densities may have been more similar. For example, in Fig. 2 it was shown that under steady flow conditions, and at the same external resistance, the upstream reactor produced higher voltages than the downstream reactors. Power overshoot, where the power density curve doubles back to lower current densities oftentimes before a higher power density that is possible with further reactor acclimation, could also be a factor as overshoot was observed in several tests (Fig. 3). Differences in the composition and quality of the wastewater in the upstream and downstream reactors could also be important. Domestic wastewater contains both soluble and particulate COD, and it thus there may be more fermentation and particle hydrolysis occurring in the upstream reactor, with more labile and biodegradable organics in the downstream reactor.

The higher power production of the S2C MFCs with two cathodes is consistent with previous results showing that increasing

Fig. 1. (A) Full brush anodes spaced evenly between two cathodes (S2C) and trimmed brush anodes near a single cathode (N1C), not drawn to scale. (B) Experimental set-up used in this study. Pairs of S2Cs and N1Cs were arranged in a series, and domestic wastewater was continuously provided through the inlet channel to each of the paired reactors.

Fig. 2. Power generation (external resistor of 200 \(\Omega\) for each MFC) produced by S2Cs and N1Cs (U = upstream, D = downstream) during continuous operation under different theoretical HRTs (8.8, 4.4 and 2.2 h).
cathode area can result in higher power densities (Cheng and Logan, 2011). The S2C reactors had 43% more surface area (57 m²/m³) than the N1C reactors (40 m²/m³), and produced 39–53% more power on average at the three different flow rates based on polarization data. In contrast, only a difference of 16% was observed previously when the three anodes were placed closer to a single cathode (Ahn et al., 2014). Thus, the closer placement of the anode to the cathode in the N1C reactors, which would reduce ohmic resistance, was less important for higher power production than the use of more cathode surface area.

3.2. COD removals as a function of HRTs

COD removals with the two-cathode S2C MFCs decreased in proportion to HRTs, with removals of 64.8 ± 1.7% at an HRT of 8.8 h, decreasing to 48.3 ± 1.0% at 4.4 h, and 32.8 ± 1.9% at 2.2 h (Fig. 4). It was expected that the S2C MFC would have greater COD removal than the N1C MFC due to higher current densities (Zhang et al., 2015) and greater cathode surface area per volume of reactor (which would allow more leakage of oxygen into the reactor) at the same set HRT. However, the COD removals with the single-cathode N1C MFC were higher than those of the S2C MFCs, with removals of 69.0 ± 0.4% at 8.8 h, 54.2 ± 2.3% at 4.4 h, and 40.7 ± 2.7% at 2.2 h. This is 6.4–24.4% greater COD removal for the single cathode MFCs than the two-cathode MFCs at each of these set HRTs.

3.3. Effect of reactor configuration on HRTs in continuous flow mode MFCs

The unexpected results showing better COD removals for single cathode MFCs compared to the two-cathode suggested that configuration of the MFCs may have produced HRTs different than the theoretical ones (calculated from reactor empty bed volume and flow rate). Therefore, salt tracer tests were conducted to measure the actual residence time of solutes through the two types (S2C and N1C) of reactors. The results showed that the actual HRTs of S2C reactors were less than or equal to the theoretical HRTs, with actual:theoretical HRTs of 7.4:8.8 h, 3.8:4.4 h, and 2.2:2.2 h (Table 1). A slight reduction in HRT due to short circuiting in these MFCs was likely a result of the reactor volume occupied by the brushes as there may not have been advective flow through the brushes. However, the HRTs of the two N1C reactors were longer than those measured for the S2C reactors by 39% (7.4:10.3 h for...
S2C:N1C, 37% (3.8:5.2 h), and 32% (2.2:2.9 h). Thus, the greater removal by the N1C reactors was likely due to the much longer HRTs produced using this configuration compared to that obtained with the S2C configuration.

A comparison of the COD removals on the basis of the measured HRTs shows that there was generally good agreement with the observed COD removals and measured HRTs despite differences in the two reactor configurations (Fig. 5). The COD removals for both types of reactors show good agreement with measured HRTs based on a non-linear regression. However, there was little agreement between the two configurations in terms of COD removal on the basis of the theoretical HRTs, with slightly better COD removals indicated to occur for the N1C MFC than the S2C MFC. These results suggest that the COD removal was more a function of the HRTs, and thus how the HRT was altered by the use of the two different brush configurations, rather other factors such as cathode surface area. The main impact of the reactor geometry was on power production, with more power generated when using two cathodes than one cathode with closely-spaced electrodes.

The low dispersion numbers and high Peclet numbers indicate that flow through the reactors was consistent with plug flow reactors with dispersion. For both reactor configurations there was little dispersion, with the dispersion increasing slightly with flow rate (Table 1). Given the high Peclet numbers at the longest theoretical HRT, the reactors could be modeled as a series of completely mixed, constant flow reactors (CSTRs). For example, the S2C MFCs (Pe = 36) could be modeled as 19 CSTRs in series, with a rate constant of $-0.0066 \text{ h}^{-1}$ (Logan, 1999).

### 3.4. CE as a function of the HRTs

The highest CE obtained was 36 ± 2% at theoretical HRT of 8.8 h for the two N1C MFCs in series (Fig. 6). The CEs ranged from 18 ± 2 to 36 ± 2% for the N1C MFCs, compared to 18 ± 5 to 29 ± 3% for the S2C MFCs. While the CEs were generally higher for N1C MFCs for each pairwise comparison of the two reactor configurations on the basis of theoretical HRT, as noted above the measured HRTs were longer for the N1C MFCs than the S2C MFCs. The downstream MFCs consistently had higher CEs than the upstream MFCs (Fig. 6) although there was a much greater percentage of COD removal in the upstream than downstream MFCs (Fig. 4). This indicated that more of the COD removed in the upstream MFC was not used for electricity generation, and was lost to alternate electron acceptors, such as in dissolved oxygen. The CEs are known to be much lower in MFCs with domestic wastewater than with defined media such as acetate in a phosphate buffer solution.

### 4. Conclusions

Brush anode and activated carbon cathodes can be used as effective and inexpensive electrode materials in MFCs. The use of closely spaced electrodes and high cathode specific surface areas have been shown to improve power generation in MFCs, but little attention has been paid to treatment performance in these systems. Higher power production was achieved using reactors with greater cathode specific surface area than reactors with a configuration based on close electrode spacing. However, there was little difference in COD removals in these two reactor designs on the basis of measured HRTs. The MFC with the closely spaced electrodes had longer measured HRTs, and thus slightly greater COD removals than

<table>
<thead>
<tr>
<th>Configuration</th>
<th>HRT (h)</th>
<th>Q (L/m² h)</th>
<th>Dispersion number (d)</th>
<th>Pe</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2C</td>
<td>Theoretical</td>
<td>Measured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.8 (9.9)</td>
<td>7.4 (8.4)</td>
<td>18.2</td>
<td>0.028</td>
<td>36</td>
</tr>
<tr>
<td>4.4 (4.9)</td>
<td>3.8 (4.3)</td>
<td>36.3</td>
<td>0.035</td>
<td>28</td>
</tr>
<tr>
<td>2.2 (2.5)</td>
<td>2.2 (2.5)</td>
<td>72.7</td>
<td>0.077</td>
<td>13</td>
</tr>
<tr>
<td>N1C</td>
<td>Theoretical</td>
<td>Measured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.8 (10.5)</td>
<td>10.3 (12.4)</td>
<td>18.2</td>
<td>0.020</td>
<td>49</td>
</tr>
<tr>
<td>4.4 (5.3)</td>
<td>5.2 (6.2)</td>
<td>36.5</td>
<td>0.015</td>
<td>68</td>
</tr>
<tr>
<td>2.2 (2.6)</td>
<td>2.9 (3.5)</td>
<td>73.0</td>
<td>0.043</td>
<td>23</td>
</tr>
</tbody>
</table>

* HRTs shown are corrected to include only the working reactor volume. Values in parentheses include the whole reactor volume (includes the entrance and exit volumes).
MFCs with spaced electrodes despite the same set HRT. This different results in terms of power and COD removal suggest that there is a tradeoff in MFC design. The use of more cathode surface area per volume of reactor will increase power production, but that design would have a higher capital cost due to the use of more cathodes. It might be that the use of less cathode area per reactor would be more cost effective than the recovery of more electrical power. Thus, the benefits of power production will need to be considered relative capital costs and advantages of the different reactor designs.

Acknowledgments

This research was supported by the grant from the Strategic Environmental Research and Development Program (SERDP).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2015.05.021.

References


