The effects of electrode spacing on the performance of microbial fuel cells under different substrate concentrations

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ABSTRACT

In this study, the electricity generation and organic removal in microbial fuel cells (MFCs) were examined for electrode spacing (ES) covering 5.8, 10.2, 15.1, and 19.5 cm, and for each ES the MFCs were discharged with a series of influent substrates (CODin). Results indicate that organic removal was related to CODin but not to ES. Best chemical oxygen demand (COD) removals of 64–71% could be achieved at CODin around 100 mg COD/L (0.11–0.14 kg COD/m3-day). Best power output 3.32 mW/m2 occurred at ES 5.8 cm and nominal CODin 300 mg COD/L. For every ES, the relationship of electricity generation to local substrate near anode (CODad) could be adequately modeled by Monod-type kinetics. The estimated kinetic constants involve maximum current production, \( I_{\text{max}} \), 15.3–19.6 mA/m2; maximum attainable power output, \( P_{\text{p,\ max}} \), 4.0–2.5 mW/m2; half-saturation constant of current, \( K_{\text{si}} \), 22–30 mg COD/L; and half-saturation constant of power, \( K_{\text{sp}} \), 24–90 mg COD/L. This study reveals that the control over ES for improving electricity generation is dependent on the level of CODad, which profoundly affects the optimal design of electrode placement.

Key words | aqueous substrate, effluent concentration, electrode spacing, power density

INTRODUCTION

Microbial fuel cells (MFCs) are novel devices that directly convert chemical energy in organic substrate into electricity. This emerging technology has much potential in the treatment of organic wastewater for pollution abetment and electricity captured. To improve the efficiency of MFCs, it is essential to identify individual factors governing MFC operation and clarify their interaction effects among them. Much attention has been paid to evaluating the effect of substrate concentration. Reports have shown that the magnitude of electricity generation could be expressed as a function of: wastewater strength in a Monod-type relationship (Min & Logan 2004); chemical oxygen demand (COD) load (Rabaey et al. 2005; Campo et al. 2012); and substrate removed (Jadhav & Ghongrekar 2009). Electricity generation expressed as a function of influent substrate could be adequately modeled by Monod-type kinetics. The estimated kinetic constants involve maximum current production, \( I_{\text{max}} \), 15.3–19.6 mA/m2; maximum attainable power output, \( P_{\text{p,\ max}} \), 4.0–2.5 mW/m2; half-saturation constant of current, \( K_{\text{si}} \), 22–30 mg COD/L; and half-saturation constant of power, \( K_{\text{sp}} \), 24–90 mg COD/L. This study reveals that the control over ES for improving electricity generation is dependent on the level of CODad, which profoundly affects the optimal design of electrode placement.

Reports that support the improvement in electricity production by reducing ES can be widely found in the literature, such as: potential increased as ES reduced from 30 to 10 cm (Jang et al. 2004) and power output increased from 21.52 to 58.5 mW/m2 as the ES decreased from 6 to 2 cm (Pandit et al. 2012). On the contrary, Ghongrekar & Shinde (2007) pointed out that the effect of distance between electrodes on current production was of little significance. Srikanth & Mohan (2012) also demonstrated an optimum spacing of 3 cm existing between electrodes. Moreover, a sound body of literature indicates that ES could be associated with other factors in controlling electricity production, whereas these factors include: external resistance (Ghongrekar & Shinde 2007); advective flow through anode to cathode (Cheng et al. 2006); iron strength in medium (Liu et al. 2005); and fluid dynamics (Raman & Lan 2012). Up to now, no study has ever examined the effect of substrate concentration on electrode spacing.

In this study, we focus on examining electricity generation in response to the interactions between electrode placement causing ohmic losses (Rozendal et al. 2008).
placement and substrate concentration. Specifically, this study (1) analyses the performance of MFCs under different conditions in electrode spacing (ES) and influent substrate concentration (COD_{in}), (2) examines the adequacy of modeling electricity generation against local substrate near anode (COD_{ad}) by Monod-type kinetics, and (3) evaluates the practicability of controls over ES under different effluent substrates (COD_{eff}) in engineering practice. Our results provide new insights into the design and operation of efficient MFCs for waste treatment.

MATERIALS AND METHODS

Microbial fuel cell

Two MFCs were constructed of acrylic, each having a volume of 2.163 L (15.7 cm in length × 13 cm in width × 10.6 cm in depth) in the anodic chamber, and of 1.462 L (9 cm × 13 cm × 12.5 cm) in the cathodic chamber. The anodic and cathodic chambers were separated by a 7 cm × 7 cm Nafion membrane (NRE212; DuPond, USA), with a copper wire loaded with an external resistance of 500 Ω connecting the anode and cathode. Both the anode and cathode were plain graphite, each having an area (double side) of 184 cm². Locations of sampling ports, including SP1, SP2, and the effluent port, are shown in Figure 1(a). The MFC reactor with ESs 5.8 and 10.2 cm had anode location in Slot b, while that with ESs 15.1 and 19.5 cm in Slot a. The location for the cathode was either in Slot c or d (Figure 1(b)) in accordance with the ES required. Such electrode placements resulted in the electrode spacing covering 5.8, 10.2, 15.1, and 19.5 cm.

MFC operation

Before the two MFCs started to operate, the anodes were inoculated with electricogens in supernatant from the primary settling tank at the Beisa wastewater treatment plant, Taiwan. During the period of bacteria seeding, 150 mg COD/L supernatant was pumped continuously into the anodic chamber at a flow rate of 3.6 L/day for about 1 week. The influent was then replaced with acetate solution, into which nitrogen gas was injected for 2 min to expel oxygen. The nutrient composition in the acetate solution was (per litre): NaHCO₃ 2.5 g, CaCl₂·2H₂O 0.1 g, KCl 0.1 g, NH₄Cl 1.5 g, NaH₂PO₄ 0.6 g, NaCl 0.1 g, MgCl₂·6H₂O 0.1 g, MgSO₄·7H₂O 0.1 g, MnCl₂·4H₂O 0.005 g, and NaMoO₄·2H₂O 0.001 g. Distilled water was used as the catholyte in the cathodic chamber. In each run, each MFC reactor was continuously discharged with a specified concentration of acetate solutions for a period during which at least 7 days of steady-state operation were maintained. The flow rate was 2.15–3 L/day, corresponding to hydraulic retention times of 0.72–1 days. The prepared acetate solution was stored at 4 °C in a refrigerator before use. The MFCs were operated at room temperature of 25 °C on average, and the dissolved oxygen in the cathode was maintained at 4.15–5.63 mg/L without artificial aeration throughout all runs.

Analysis

Measurements of COD in the influent and in samples from sampling points were conducted using the Hach technique (Hach Company, USA). Voltage was measured using a CHY model-48R digital multimeter (CHY Firemate Co. Ltd, Taiwan). Current and power were calculated according to the following equations: \( I = \frac{V}{R} \), and \( P = \frac{IV}{A} \), respectively, where \( I \) is current (A), \( V \) is voltage (V), \( R \) is external
In each run, when electricity generation was maintained at a steady state for about 1 week, a polarization curve experiment was conducted to determine maximum power density ($P_p$) and open circuit voltage (OCV). This was done by placing a series of resistors over 1–3,000 kΩ as the external resistance. Coulombic efficiency (CE%) was derived as follows: CE(%)\[=\frac{\text{measured coulombs (} C_p\text{)}}{\text{theoretical coulombs (} C_T\text{)} of COD removals, where } C_p \text{ was calculated using computed current and } C_T \text{ was the COD removed based on the difference between the influent and effluent COD.}

### RESULTS AND DISCUSSION

#### MFC performance analysis

The variations of aqueous substrates, including COD in SP1, COD in SP2, and CODeff, are shown in Figure 2, using the test run of ES 5.8 cm and nominal CODin of 300 mg COD/L as an illustrative example. During a week of steady-state operation (COD variation within ±10% for each sampling point), averaged COD consistently decreased from CODin 305 mg/L at the influent port to CODeff 212 mg COD/L at the effluent port. This result shows that aqueous COD decreased gradually along the flow path, implying that the reactor was characterized by a plug-flow pattern. Other runs exhibited a similar flow pattern.

The COD removal efficiencies appeared to be related to CODin but not to ES. For example, when ES was 5.8 cm, COD removal efficiencies achieved 68, 52, and 71% with nominal CODin 25, 50, and 100 mg COD/L, respectively. When the nominal CODin increased to 300 mg/L, COD removal efficiency was abruptly decreased to 31%. Similar experimental results were obtained for ESs of 10.2, 15.1, and 19.5 cm (Table 1). These results strongly indicated that if the best COD removal is to be achieved, the CODin should be kept at around 100 mg COD/L (volumetric loading rates 0.11–0.14 kg COD/m$^3$-day) regardless of ES. Such loading rates are rather low as compared to those of conventional anaerobic processes, 1–2 kg COD/m$^3$-day. The activity of anaerobic microorganisms in the MFC reactor was estimated to be about one-tenth of that in a conventional anaerobic reactor.

The averaged cell voltage ($V_{age}$) for all test runs is shown in Table 1. Figure 3(a) displays the changes of current density in response to ES and CODin, in which the current density was calculated based on $V_{age}$, along with given process parameters of external resistance load 500 Ω and anode project area 184 cm$^2$. We found that the current density increased with increasing CODin for every ES. For examples, when the nominal CODin increased from 25 to 300 mg COD/L, the current density increased from 0.4 to 15.9 mA/m$^2$ at ES 10.2 cm, and it increased from 1.6 to 15.0 mA/m$^2$ at ES 15.1 cm. A similar relationship of the maximum power densities, $P_p$, to CODin prevailed in all ESs (Figure 3(b)), where the value of $P_p$ was measured from the polarization curve experiment, as shown in Figure 4 for a typical example of $P_p = 2.12$ mW/m$^2$. Not surprisingly,
the highest values of $P_p$ all occurred at a nominal COD\textsubscript{in} of 300 mg COD/L regardless of ES. Finally, Figure 3(c) shows that the highest Coulombic Efficiency for all ESs occurred at a COD\textsubscript{in} of about 50 mg COD/L, an interesting finding which needs further investigation. The above results indicated that for a particular MFC reactor under different waste strength, the organic removal and electricity generation were dependent on COD\textsubscript{in}.

However, as the electricity generation was compared for different MFC operations, each having distinctive ES but all operated at the same level of COD\textsubscript{in}, the effect of ES reduction on improving electricity generation became uncertain. As COD\textsubscript{in} was high, electricity generation could be improved by reducing ES. For example, under nominal COD\textsubscript{in} of 300 mg COD/L, the current density improved stepwise from 14.3 to 18.3 mA/m² (Figure 3(a)) and maximum power density from 2.05 to 3.32 mW/m² (Figure 3(b)) when ES was reduced from 19.5 to 5.8 cm. However, while COD\textsubscript{in} was at appreciably low levels, improvement of electricity generation could not be accomplished by reducing ES. For example, for a nominal COD\textsubscript{in} of 25 mg COD/L, MFC at ES 19.5 cm (anode near sampling port, SP1) produced current density 1.5 mA/m², while at ES 5.8 cm (anode near effluent port) only 0.07 mA/m². This unexpected result might be attributable to the anode biofilm being exposed to different aqueous COD. To verify this postulation, we used the local COD around the anode (COD\textsubscript{ad}) in the analysis. Practically, the value of COD\textsubscript{ad} for ES of 5.8 equals the measured COD\textsubscript{eff}, while that for ES 19.5 cm equals the COD in SP1. As shown in Table 1, at ES 5.8 cm the COD\textsubscript{ad} was only 8 mg COD/L, but at ES 19.5 cm COD\textsubscript{ad} increased to 25 mg COD/L. The low COD\textsubscript{ad} for ES 5.8 cm would limit the flux of substrate into anode biofilm, making the MFCs produce less current. The above analysis demonstrates that for a plug-flow reactor the location of the anode affects the COD\textsubscript{ad}, and the level of COD\textsubscript{ad} has a direct effect on current production. Furthermore, when COD\textsubscript{in} is low, the COD\textsubscript{ad} will interact with ES in determining electricity generation.

**Kinetic modeling**

To unravel the interactions between the COD\textsubscript{ad} and ES in electricity generation, we performed a kinetic study for each ES. To do this, the modeling of the relationship of current production to COD\textsubscript{ad} was conducted using Monod-type kinetics, which is expressed as

$$I = \frac{I_{\text{max}}S}{K_s + S}$$  \hspace{1cm} (1)
where $I$ is average current density under steady-state operation for $S$, COD near the anode (COD$_{ad}$); kinetic constant $I_{\text{max}}$ is maximum current density, and constant $K_{si}$ is the estimated COD$_{ad}$ when current density equals half of $I_{\text{max}}$. The modeling equation for power density is

$$ P_p = \frac{P_{p,\text{max}} S}{K_s + S} $$

(2)

where $P_p$ is the maximum power output obtained from a polarization curve experiment at pseudo-steady state; kinetic constant $P_{p,\text{max}}$ is the maximum attainable power density when $S$ (COD$_{ad}$) is infinite, and constant $K_{sp}$ is the estimated COD$_{ad}$ at half of $P_{p,\text{max}}$. To solve these kinetic constants, a relative least square method was applied.

Figure 5(a) presents the modeling results of current densities, where the prediction lines and measurements were in good agreement. The estimated coefficient constants for each ES are listed Table 2. While ES was decreased from 15.1 to 5.8 cm, $I_{\text{max}}$ increased from 15.3 to 19.6 mA/m$^2$. But, as ES was reduced from 19.5 to 15.1 cm the $I_{\text{max}}$ remained at 15.3 mA/m$^2$. This result was similar to the finding by Ghangrekar & Shinde (2007), who indicated that for electrode spacings of 20–28 cm, the ES had little effect on current. The estimated $K_{si}$ values are in a very narrow range of 22–31 mg COD/L, only slightly increasing with increasing ES. Figure 5(b) shows the modeling results of maximum attainable power density against COD$_{ad}$. Again the prediction and measurement were in good agreement, and the estimated coefficients of $P_{p,\text{max}}$ and $K_{sp}$ are listed in Table 2. It appeared that the value of $P_{p,\text{max}}$ also increased with decreasing ES for ES within 15.1 cm. The $K_{sp}$ values, 24–90 mg COD/L, increased with increasing ES. These results implied that in designing efficient and controllable MFCs the ES should be kept within 15.1 cm, and if the ES is limited in this range the $P_{p,\text{max}}$ is very sensitive to the reduction of electrode spacing. For example, the reduction of ES from 15.1 to 5.8 cm would result in a $P_{p,\text{max}}$ increased of 60%.

### Implications in waste treatment practice

The above modeling results, especially power density (Figure 5(b)), have significant implications for MFCs when applied in waste treatment practice. Two distinctively operating zones of COD$_{\text{eff}}$ deserve special discussion. First, MFCs are used in the pretreatment of highly concentrated organic wastewater or sludge digestion. For example, in the pretreatment of food processing wastewater containing COD above 1,000 mg/L, where the COD$_{\text{eff}}$ might fall to a level of 500 mg COD/L, which is sufficiently higher than constant $K_{sp}$, the power output would approach $P_{p,\text{max}}$. Under such conditions, the fluctuation in aqueous COD has little influence on power output, thus, the location of anode placement becomes unimportant. To enhance

<table>
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<tr>
<th>Electrode spacing (cm)</th>
<th>$I_{\text{max}}$ (mA/m$^2$)</th>
<th>$K_{si}$ (mg/L)</th>
<th>$P_{p,\text{max}}$ (mW/m$^2$)</th>
<th>$K_{sp}$ (mg/L)</th>
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<tbody>
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<td>5.8</td>
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<td>22</td>
<td>4.0</td>
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<tr>
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<td>22</td>
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<td>67</td>
</tr>
<tr>
<td>19.5</td>
<td>15.3</td>
<td>31</td>
<td>2.5</td>
<td>90</td>
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![Figure 5](https://example.com/figure5.png) Current density (a) and maximum power density (b), as a function of substrate concentration near anode (COD$_{ad}$) are fitted by Monod-type kinetics. The solids symbols, circle (ES 5.8 cm), square (ES 10.2 cm), diamond (ES 15.1 cm), and triangle (ES 19.5 cm) represent measurements and the lines represent prediction. Estimated coefficients are listed in Table 2.
power generation, one may simply reduce ES. Nevertheless, it should be noted that when highly concentrated organic waste is discharged into the anodic chamber, it might incur massive organic acid production, leading to a drop of pH. Once acid production prevails in the anodic chamber, the electricity generation would be inhibited. The important issue, prevention of pH drop and even improvement of electricity generation by adjusting the acidic environment, is not within the scope of the present work, but can be found elsewhere (Torres et al. 2008).

Second, MFCs are applied in the treatment of municipal sewage to produce effluent to meet discharge permission, where the COD_{ad} might be close to, or lower than, the constant K_{sp}. In such operation, the power density is very sensitive to the small change of aqueous COD. For simplified analysis of power output in relation to effluent regulation, the anodic chamber is assumed completely mixing, so that COD_{ad} is basically the same as COD_{eff}. At present the effluent standard in Taiwan is 30 mg COD/L. To meet this permission the MFCs would produce 1.8–2 mW/m² at ESs 5.8–10.2 cm and 0.7 mW/m² at 15.1 cm. A small decrease of COD_{eff} to 20 mg COD/L would bring significant reductions in power, down to 1.3 mW/m² for ESs 5.8–10.2 cm and to 0.6 mW/m² for ES 15.1 cm. The above analysis implies that MFCs having closely designed ES would suffer greater reductions in power production than those with more loosely designed ES when COD_{eff} is decreased. Furthermore, as COD_{eff} keeps decreasing, the merits of using small ES to increase power output will gradually diminish. Therefore, to achieve both goals of producing low COD_{eff} and high electrical energy, environmental engineers will face a big challenge in the design of efficient MFCs, which requires optimal placement of electrodes in accordance with discharge requirements and reactor configuration.

**CONCLUSIONS**

The effects of electrode spacing on the performance of MFCs in relation to substrate concentration have been clarified in this study. On the COD removal, the ES had an insignificant effect. But the influent substrate concentration (COD_{in}) is important in COD removal. Best COD removal efficiencies of 69–71% were achieved at COD_{in} around 100 mg COD/L. In governing electricity generation, it was the local substrate near the anode (COD_{ad}) that interacted with ES. For every ES, the relationship of electricity generation to COD_{ad} has been successfully modeled by Monod-type kinetics. The modeling results demonstrate the significant implications of COD_{ad}, ES, and their interactions in MFC design and operation. When COD_{ad} is sufficiently higher than half-saturation constant K_{sp}, only reduction of ES can improve the electricity production. However, when COD_{ad} is within the regions of K_{sp}, the advantage of reducing ES is dependent on the level of COD_{ad}.

**ACKNOWLEDGEMENTS**

The authors would like to thank the National Science Council of the Republic of China, Taiwan, for financially supporting this research under Contract No. NSC No. NSC 96-2221-E-019-008.

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First received 23 May 2013; accepted in revised form 26 June 2013. Available online 19 October 2013