The Electricity Generation in Microbial Fuel Cells Using Reaeration Mechanism for Cathodic Oxygen Reduction

Chi-Yuan Lee* and Yu-Hsuan Lin

Water Resources and Environmental Engineering Program, Department of Harbor and River Engineering, National Taiwan Ocean University, Keelung 20224, Taiwan

Abstract

Electricity generation in microbial fuel cell (MFC) using reaeration mechanism to facilitate cathodic oxygen reduction is sustainable and economical. This study examined the effects of operational parameters of electrical load (R\text{ext}), organic load and cathode area (S\text{a}) on MFC performance under reaeration rate (K\text{2}) of 0.5-1.5 d\textsuperscript{-1} in cathode chamber. Two MFCs, consisting of MFC-A (with R\text{ext} \text{10 Ω}) and MFC-B (R\text{ext} \text{1000 Ω}), were operated in parallel and continuously fed with influent chemical oxygen demand (COD\text{in}) 324–561 mg/L to anode chamber; and in each MFC the S\text{a} covering 184, 553, 992 and 1290 cm\textsuperscript{2} was tested. Results indicated that in MFC-A the current production increased with aequous COD in anode chamber, in which the relationship between current and aequous COD can be modeled with Monod kinetics. The estimated kinetic constants of maximum current I\text{max} is 3 mA, and half-saturation constant of current K\text{S} is 310 mg/L. The lowest dissolved oxygen (DO) of 1.9 mg/L occurred at highest COD\text{in} of 561 mg/L. In MFC-B, constant current of 0.4 mA and DO at 3.2-3.7 mg/L were maintained for all COD\text{in}.

Current generation in reaeration-assisted MFC

The current generation in reaeration-assisted MFC related to oxygen supply rate in cathode chamber can be analyzed using the mass balance of DO in cathode chamber, which is expressed as

\[ \text{dDO/dt} = K_2 (DO^* - DO) - OR, \]  

where

\[ K_2 = \frac{\text{DO}}{\text{W R x V}} \]  

is the oxygen reaeration coefficient (d\textsuperscript{-1}), DO\textsuperscript{*} is the saturated DO (e.g., 8.2 mg/L at 25°C), and OR is the cathodic reduction rate (oxygen consumption rate) during electricity generation. Suppose that the changes in DO are in a steady state in cathode chamber, dDO/dt = 0, yielding

\[ OR = K_2 (DO^* - DO). \]

The above equation indicates that in cathode chamber at steady state, oxygen consumption rate for producing current, OR, equals the oxygen transfer rate from reaeration mechanism, K\text{2} (DO\textsuperscript{*} - DO). That is, based on oxygen half-reaction, one mole of O\textsubscript{2} transferred will produce 4 eq e\textsuperscript{-}:

\[ O_2 + 4H^+ + 4 e^- = 2 H_2O \]

Equation (1-3) is a theoretical basis that can be used to predict the relationship of current production to oxygen transfer rate in reaeration-assisted MFC.

Keywords: Current generation; Dissolved oxygen; Electrical load; Reaeration rate

Introduction

Reaeration is a natural process in which oxygen is transferred from the atmosphere to water body when dissolved oxygen (DO) is under saturated. The use of reaeration process in rivers for partially treating and disposing of waste has been practiced for several decades. A key issue of avoiding DO drop to critical condition during discharging waste to waters was to calculate the maximal organic loads related to reaeration coefficient, K\text{2}. The K\text{2} is dependent on stream characteristics including the flow velocity, water depth, and channel slope, varied substantially between 0.1 d\textsuperscript{-1} and 50 d\textsuperscript{-1} [1-3].

A microbial fuel cell is a promising system that directly converts chemical energy in organic substrate into electricity, with advantages in recovering electrical energy during wastewater treatment. The most challenge in commercializing MFCs is to develop sustainable processes that are cost effective. In a typical two-chambered MFC system mechanism is usually used for supplying dissolved oxygen in cathode chamber, which is energy intensive. However, if a MFC is built on river bank or coastal area, the water flow can be diverted into cathode chamber, thus, reaeration mechanism [4] can be applied for supplying oxygen to facilitate cathodic reaction. The novel reaeration-assisted MFC had latent benefit of aeration energy savings, where about 1 kg O\textsubscript{2}/m\textsuperscript{3} transferred is equivalent to the production of 1 kWh/m\textsuperscript{3} [5]. In addition, the proposed MFC only abstracts the oxygen in river, but avoiding the direct contact of pollutants with water, thus the water quality can be better protected. Though numerous studies on the relationship of MFC performance to dissolved oxygen by mechanical aeration were conducted previously [6,7], no investigation has ever been done on revealing the performance of MFC related to reaeration rate. Except for reaeration rate, in practical application of MFC to wastewater treatment the electricity generation can be affected by many factors, such as organic loads, electrical loads (external resistance, R\text{ext}), and cathode area (S\text{a}). In this study, under a basic reaeration rate of still water surface, two MFCs with different R\text{ext} were employed and operated in parallel for the purpose of examining MFC performance in response to the changes in influent chemical oxygen demand (COD\text{in}) and cathode area (S\text{a}). The specific purpose of this study is three-fold: first to compare the effects of these operational parameters on the electricity generations; second to examine the importance of electrical load in the design of reaeration-assisted MFC; and third to verify the prediction of current generation based on oxygen supply rate.
Materials and Methods

MFC construction

Two MFC systems consisting of MFC-A and MFC-B were employed in this study, where MFC-A was loaded with $R_{\text{ext}}$ of 10 Ω and MFC-B with 1000 Ω. The MFC was constructed of acrylic with a volume of 0.6 L in an anode chamber (14 cm in length × 10 cm in width × 8.5 cm in depth) and of 1.7 L in a cathode chamber (14 cm × 12.6 cm × 9.5 cm, respectively). The anodic and cathodic chambers were separated using a 7 cm × 7 cm Nafion membrane (NRE212, DuPont, USA), and a copper wire loaded with an external resistance (electrical load) was used to connect the anode and cathode. The total graphite surface area in the anodic chamber was 790 cm², consisting of one plain graphite plate of 184 cm² and graphite granules of 606 cm². In the cathodic a specific number of chamber plain graphite plates were placed for each test run, including 1 (surface area, $S_a$ 184 cm²), 3 ($S_a$ 553 cm²), 5 ($S_a$ 992 cm²), and 7 ($S_a$ 1290 cm²). The schematic diagram of experimental setup is shown in Figure 1.

MFC operation

Before the MFC was operated, the anode was seeded with bacteria in soil, extracted 30 cm from the surface in a public park in Keelung, Taiwan. The soil samples were pretreated by performing heat-shock at 104°C in an oven for 2 h. The samples were then sieved through a #20 mesh, and stored in bottles in a refrigerator (4°C) until use [14]. During bacteria seeding, the anode was inoculated with electricigens in the soil samples with the addition of 5 g to the anode chamber. Artificial organic waste was prepared by dissolving sodium acetate and inorganic nutrient into tap water pretreated by conducting dechlorination. The nutrient and buffer components for the fuel consisted of 13 mg/L of NaH₂PO₄, 48 mg/L of NH₄Cl, 7.6 mM of KH₂PO₄, and 42.4 mM of Na₂HPO₄. In the experiment, the influent concentrations of 324–561 mg COD/L, equivalent to organic loadings of 0.3-0.6 kg COD/m³ cathode chamberized. These loading rates, within the levels of conventional activated sludge process and anaerobic contact process, were selected to insure that the electron flow from anode to cathode was not a limiting factor in cathodic oxygen reduction. It was observed that in MFC-A the aqueous COD in anode chamber (CODₐ) was maintained to 516 mg/L. Since aqueous COD in the anode chamber determines a limiting factor in cathodic oxygen reduction. It was observed that in MFC-A the aqueous COD in anode chamber (CODₐ) was maintained to 516 mg/L. Since aqueous COD in the anode chamber determines

Determination of $K_2$

All of the test runs for evaluating MFC performance were conducted under the reaeration conditions of still water surface and at room temperature (24-26°C). The electrolyte in the cathode chamber at a still water surface represents a basic condition, enabling us to evaluate the critical generation of electricity. Figure 2 shows the oxygen deficit as a function of lapse time in a typical reaeration coefficient test at 25°C. Based on this oxygen deficit curve, the reaeration coefficient ($K_2$) was determined using linear regression ($R²=0.98$) to be 0.8 d⁻¹ (0.034 h⁻¹). All of the tested $K_2$ values in this study were in the range of 0.5-1.5 d⁻¹, which is similar to other report [16].

Performance comparisons

The two MFCs were discharged with influent concentration of 324-561 mg COD/L, equivalent to organic loadings of 0.3-0.6 kg COD/m³ cathode chamberized. These loading rates, within the levels of conventional activated sludge process and anaerobic contact process, were selected to insure that the electron flow from anode to cathode was not a limiting factor in cathodic oxygen reduction. It was observed that in MFC-A the aqueous COD in anode chamber (CODₐ) was maintained to 232-355 mg/L, whereas in MFC-B it was at 247-447 mg/L. The two MFCs had similar COD removal efficiencies, 23-44% v.s. 17-41%, implied that the electrical loads was indifferent to organic removal. To improve COD removal, it can be done by decreasing organic load but not changing electrical load. The voltage generations in the two MFCs were different, as compared in Figure 3. MFC-A, with low electrical load ($R_{\text{ext}}$) of 10 Ω, produced a low cell voltage ($V_{\text{avg}}$), 10 mV to 20 mV, while MFC-B ($R_{\text{ext}}$ 1000 Ω) produced $V_{\text{avg}}$ of 300-400 mV. Furthermore, MFC-A had averaged current ($I_{\text{avg}}$) of 0.9-2.0 mA (or 530-1180 mA/m³), while in MFC-B it greatly increased to 0.14-0.16 mW (80-90 mW/m³) (Table 1). These results clearly indicated that electrical load had significant impact on the electricity generations.

Effects of organic load

The effect of organic load for each MFC was tested by changing the influent COD. In MFC-A, the current generation was 1.0 mA at CODₐ 324 mg/L, and the current became doubled when COD in increased to 516 mg/L. Since aqueous COD in the anode chamber determines the substrate flux diffused to anode biofilm, it is practical to use CODₐ instead of CODₐ as a key parameter in analyzing the relationship.
with high electrical load the electron transfer from anode to cathode (electron flow not a limiting factor), will produce 0.88 electron flow of meq e-/d [(0.22 mM O2/d)(4 meq e-/mM O2)], or equivalent to theoretical current at 0.99 mA [(0.88 meq e/d)(96500 c/eq e)(d/86400 sec)]. This current represents theoretical production in reaeration-assisted MFC operated at K2 0.5 d-1. In case the reaeration rate increased to 1.5 d-1, the maximum oxygen supply rate is 0.66 mM O2/d and equivalent electron flow of 2.64 meq e/d (3.0 mA). Obviously, the current at K2 of 1.5 d-1 increased 3 times than that at the reaeration rate of 0.5 d-1. The predicted current 3.0 mA coincides with Ieqv which confirms the maximum current generation in reaeration-assisted MFC at still water surface would be 3.0 mA. Table 2 further lists the Ieqv values computed from oxygen supply in response to K2 and DO. Again, the Ieqv appeared to increase with K2 value at a specific DO level. For example, at DO 2.8 mg/L (similar to Test run A1), the Ieqv values were 0.6, 1.2, and 1.8 mA when K2 was 0.5, 1.0, and 1.5 d-1, respectively. In comparison of the Ieqv values with the measured currents Iavg (Table 1), it was apparent that the Ieqv for MFC-A was within the range of the Iavg, implying that the current production correlated well with oxygen transfer rate. Nevertheless, in MFC-B the Ieqv was slightly higher than the Iavg indicating that a few oxygen generated from reaeration mechanism was lost, which might be diffused from cathode to anode because DO in cathode chamber was at relatively high level.

Discussion

In conventional practice of discharging waste to river that has a specific reaeration rate, the applied organic load solely control DO level. However, in this study, we have demonstrated that in reaeration-assisted MFC the DO not only was affected by organic loading but also by electrical load. Compared to MFC-A having low electrical load, the MFC-B with high electrical load could maintain the DO above 3.2 mg/L because high electrical load restricts the electron flow from anode to cathode. In addition, the electrical load also affected electricity of substrate concentration to current generation [17]. Figure 4 shows that current generation strongly depends on substrate concentration in terms of COD, and a Monod kinetics modeling could be well established. The estimated kinetic constants of maximum current Imax is 3 mA, and half-saturation constant of current Ks is 310 mg/L. This result clearly showed that under low electrical load, applied COD was a limiting factor in controlling current generation. Furthermore, it was observed that the DO decreased from 2.8 mg/L to 1.9 mg/L (cathode potential varied from -11 to -216 mV) when COD increased from 324 to 516 mg/L. The DO level appeared to be negatively correlated with current generation. In conventional practice of discharging waste to river that has a specific reaeration rate, the applied organic load solely control DO level. However, in this study, we have demonstrated that in reaeration-assisted MFC the DO not only was affected by organic loading but also by electrical load. Compared to MFC-A having low electrical load, the MFC-B with high electrical load could maintain the DO above 3.2 mg/L because high electrical load restricts the electron flow from anode to cathode. In addition, the electrical load also affected electricity to cathode was limited by the electrical resistance, resulting in insignificant variations of current production. Thus, the DO could be maintained at a relatively high level, 3.2–3.7 mg/L (cathode potential varied from +64 to +170 mV), a condition can be assured completely aerobic.

Effects of cathode area

The limitation of cathodic reaction was tested with increasing cathode surface. It was found that in MFC-A the current was 0.9 mA at 184 cm2 and slightly increased to 1.0 mA when S a was greatly increased to 1290 cm2. This result indicated that Sa had negligible effect on current generation. Similarly, it showed that cathode surface area was not a limiting factor in current generation for MFC-B, where the current was maintained at 0.4 mA regardless of Sa increasing from 184 cm2 to 1290 cm2. The above results demonstrated that under the reaction rate of 0.5-1.5, plain graphite with 184 cm2 was sufficient for cathodic reduction. Though the plain graphite had been criticized for being poor in catalyzing oxygen reduction, it is demonstrated herein that this material is suitable to facilitate cathodic reaeration when low reaeration coefficient of 0.5-1.5 d-1 was employed as passive oxygen supply.

Correlation of current generation with oxygen transfer

The extreme currents can be generated through reaeration mechanism is computed using Equations 1-3. Supposed that the reaeration rate is 0.5 d-1, the maximum oxygen can be supplied in cathode chamber is 5.0(8.2-0)(1.7) = 7.0 mg O2/d = 0.22 mM O2/d, assuming that saturated DO is 8.2 mg/L and actual DO in cathode chamber is completely depleted. Such oxygen supply, if fully consumed in reaction by electrons transported from anode to cathode (electron flow not a limiting factor), will produce 0.88 electron flow of meq e-/d [(0.22 mM O2/d)(4 meq e-/mM O2)], or equivalent to theoretical current (Ieqv) of 0.99 mA [(0.88 meq e/d)(96500 c/eq e)(d/86400 sec)]. This current represents theoretical production in reaeration-assisted MFC operated at K2 0.5 d-1. In case the reaeration rate increased to 1.5 d-1, the maximum oxygen supply rate is 0.66 mM O2/d and equivalent electron flow of 2.64 meq e/d (3.0 mA). Obviously, the current at K2 of 1.5 d-1 increased 3 times than that at the reaeration rate of 0.5 d-1. The predicted current 3.0 mA coincides with Ieqv which confirms the maximum current generation in reaeration-assisted MFC at still water surface would be 3.0 mA.
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Test run | Duration | $S_a$ | COD$_{in}$ | COD$_{ef}$ | COD$_{rv}$ | DO | $V_{avg}$ | $I_{avg}$ | $P_{avg}$ | $R_{ext}$ | CE | $V_e$
---|---|---|---|---|---|---|---|---|---|---|---|---
MFC-A
A1 | 0-33 | 184 | 415 | 232 | 44 | 2.8 | 9 | 0.9 | 0.01 | 475 | 6 | -216
A2 | 34-42 | 553 | 516 | 355 | 31 | 1.9 | 21 | 2.0 | 0.04 | 305 | 16 | -11
A3 | 43-52 | 992 | 478 | 299 | 37 | 2.5 | 18 | 1.8 | 0.03 | 270 | 12 | -158
A4 | 53-68 | 1290 | 324 | 249 | 23 | 2.5 | 10 | 1.0 | 0.01 | 352 | 17 | -145
MFC-B
B1 | 0-33 | 184 | 415 | 247 | 41 | 3.2 | 354 | 0.4 | 0.14 | 358 | 3 | +136
B2 | 34-42 | 553 | 358 | 278 | 22 | 3.3 | 395 | 0.4 | 0.16 | 385 | 5 | +64
B3 | 43-52 | 992 | 561 | 438 | 22 | 3.7 | 351 | 0.4 | 0.14 | 407 | 3 | +96
B4 | 53-68 | 1290 | 537 | 447 | 17 | 3.6 | 397 | 0.4 | 0.16 | 351 | 5 | +170

Table 1: Summarized performance of microbial fuel cells under different experimental conditions. Note: The abbreviation for item is shown below. Duration: test period in days, $S_a$: cathode surface area ($cm^2$), COD$_{in}$: influent substrate (mg COD/L), COD$_{ef}$: effluent substrate (mg COD/L), COD$_{rv}$: COD removal efficiency (%), DO: dissolved oxygen in cathode chamber (mg/L), $V_{avg}$: averaged cell voltage (mV), $I_{avg}$: averaged current generation (mA), $P_{avg}$: averaged power output (mW), $R_{ext}$: internal resistance (Ω), CE: Coulombic efficiency (%), $V_c$: cathode potential vs NHE (mV), and $R_{ext}$: electrical load (Ω).

The reaeration-assisted microbial fuel cell (MFC) that operated under reaeration rate of 0.5-1.5 d$^{-1}$ are feasible for electricity generation. It was observed that MFC-B produced higher power output than MFC-A. This result might be attributed to the MFC-B having close proximity of electrical load to internal resistance [8]. Thus, selection an optimal electrical load in accordance with internal resistance is important in designing reaeration assisted MFC. Another important issue needed to be addressed is the impact of reaeration rate on MFC performance. Subsequent study is suggested to get deeper understanding into the effects of increasing reaeration rate on improving the performance of reaeration assisted-MFC.

Conclusions

1. The reaeration-assisted microbial fuel cell (MFC) that operated under reaeration rate of 0.5-1.5 d$^{-1}$ are feasible for electricity generation.

2. Under organic loading 0.3-0.6 kg COD/m$^3$ anode compartment and the MFC-B with electrical load (R$_{ext}$) 1000 Ω had better performance than MFC-A with R$_{ext}$ 10 Ω. The MFC-B produced 80-90 mW/m$^3$ cathode compartment and had DO 3.2-3.7 mg/L while MFC-A produced power 6-20 mW/m$^3$ cathode compartment and had DO 1.9-2.8 mg/L.

3. The current production can be estimated by oxygen transfer rate, based on reaeration coefficient and dissolved concentration in cathode chamber.

4. The organic load, electrical load, and their interactions among them were crucial in the designing reaeration-assisted MFC. The optimal organic and electrical loads should be cautiously determined to maintain appropriate DO and improve electricity generation.

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References

1. Wilcock RJ (1988) Study of river reaeration at different flow rates. J Environ Eng 114: 91-105.
2. Cleveland KD (1989) Predicting reaeration rates in Texas streams. J Environ Eng 115: 620-632.
3. Melching CS, Flores HE (1999) Reaeration equations derived from U. S. geological survey data base. J Environ Eng 125: 407-414.
4. O’Connor DJ, Dobbins WE (1956) Mechanism of reaeration in natural streams. J Sanitary Eng 82: 641-666.
5. Rittmann BE, McCarty PL (2001) Environmental Biotechnology: Principles and Applications. McGraw-Hill Book Co., New York.

6. He Z, Shao H, Angenent T (2007) Increased power production from a sediment microbial fuel cell with a rotating cathode. Biosensors and Bioelectronics 22: 3252-3255.

7. Oh S, Min B, Logan BE (2004) Cathode performance as a factor in electricity generation in microbial fuel cells. Environ Sci Technol 38: 4900-4904.

8. Logan BE, Hameiers B, Rozendal R, Schröder U, Keller J et al. (2006) Microbial Fuel Cells: Methodology and Technology. Environ Sci Technol 40: 5181-5192.

9. Aelterman P, Versichele M, Marzorati M, Boon N (2008) Loading rate and external resistance control the electricity generation of microbial fuel cells with different three-dimensional anodes. Bioresource Technol 99: 8895-8902.

10. Katuri KP, Scott K, Head IM, Piccioreanu C (2011) Microbial fuel cells meet with external resistance. Bioresource Technol 102: 2758-2766.

11. Lyon DY, Buret F, Vogel TM, Monier JM (2010) Is resistance futile? Changing external resistance does not improve microbial fuel cell performance. Bioelectrochemistry 78: 2-7.

12. Jadhav GS, Ghangrekar MM (2009) Performance of microbial fuel cell subjected to variation in pH, temperature, external load and substrate concentration. Bioresource Technol 100: 717-723.

13. Rabaey K, Verstraete W (2005) Microbial fuel cells: novel biotechnology for energy generation. TRENDS in Biotechnology 23: 291-298.

14. Niessen J, Harnisch F, Rosenbaum M, Schröder U, Schulz F (2006) Heat treated soil as convenient and versatile source of bacterial communities for microbial electricity generation. Electrochemistry Communications 8: 869-873.

15. Boyle WC (1984) Measurement of oxygen transfer in clean water (ASCE standard 2-91). American Society of Civil Engineers, New York, NY.

16. Kakuno S, Saitoh M, Nakata Y, Oda K (1995) The air-water oxygen transfer coefficients with waves determined by using a modified method, B. Jähne and E. Monahan (eds.), Air-Water Gas Transfer, by AEON Verlag and studio 577-587.

17. Lee CY, Huang YN (2013) The effects of electrode spacing on the performance of microbial fuel cells under different substrate concentrations. Water Sci and Technol 68: 2028-2034.