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

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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_{ext}), organic load and cathode area (S_a) on MFC performance under reaeration rate (K_2) of 0.5-1.5 d^{-1}in cathode chamber. Two MFCs, consisting of MFC-A (with R_{ext}10 Ω) and MFC-B (R_{ext}1000 Ω), were operated in parallel and continuously fed with influent chemical oxygen demand (COD_{in}) 324–561 mg/L to anode chamber; and in each MFC the S_a covering 184, 553, 992 and 1290 cm^2 was tested. Results indicated that in MFC-A the current production increased with aqueous COD in anode chamber, in which the relationship between current and aqueous COD can be modeled with Monod kinetics. The estimated kinetic constants of maximum current I_{max} is 3 mA, and half-saturation constant of current K_s is 310 mg/L. The lowest dissolved oxygen (DO) of 1.9 mg/L occurred at highest COD_{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_{in}. The S_a had insignificant influence on electricity generation in both MFCs. This study demonstrated the importance of electrical load, organic load, and their interactions among them in designing reaeration-assisted MFC for organic waste treatment.

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 rivers was to calculate the maximal organic loads related to reaeration coefficient, K_2. The K_2 is dependent on stream characteristics including the flow velocity, water depth, and channel slope, varied substantially between 0.1 d^{-1} and 50 d^{-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 mechanical aeration is usually used for supplying dissolved oxygen in cathode chamber, which is energy intensive. However, if a MFC is built on river bank or costal 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_2/m^3 transferred is equivalent to the production of 1 kWh/m^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_{ext}), and cathode area [8-13]. In this study, under a basic reaeration rate of still water surface, two MFCs with different R_{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_{in}) and cathode area (S_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.

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

$$dDO/dt = K_2 (DO^* - DO) - OR, \quad (1)$$

Where K_2 is the oxygen reaeration coefficient (d^{-1}), DO* 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

$$OR = K_2 (DO^* - DO). \quad (2)$$

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_2 (DO*- DO). That is, based on oxygen half-reaction, one mole of O_2 transferred will produce 4 eq e^-:

$$O_2 + 4H^+ + 4\,e^- = 2\,H_2O \quad (3)$$

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.

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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_{ext} of 10 Ω and MFC-B with1000 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 cm^2, consisting of one plain graphite plate of 184 cm^2 and graphite granules of 606 cm^2. In the cathodic a specific number of chamber plain graphite plates were placed for each test run, including 1 (surface area, S_a, 184 cm^2), 3 (S_a, 553 cm^2), 5 (S_a, 992cm^2), and 7 (S_a,1290 cm^2). The schematic diagram of experimental set-up 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 $NaH_2PO_4 \cdot H_2O$, 48 mg/L of NH_4Cl, 7.6 mM of KH_2PO_4, and 42.4 mM of Na_2HPO_4. In the experiment, the influent concentrations of 324-561 mg COD/L was continually discharged into the anode chamber at a flow rate of 0.6 L/d. The hydraulic retention times was 1 day based on the volume of anode chamber, equivalent to organic loading rate of 0.3-0.6 kg COD/m^3 cathode chamber-d. The electrolyte in the cathode chamber consisted of 50 mM of H_3PO_4 and 100 mM of NaCl.

Analysis

The reaeration coefficient (K_2) was determined using absorption measurement, where DO probe (YSI) was installed 15 cm from the bottom of cathode chamber [15]. Influent and effluent COD were monitored periodically 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: $I=V/R_{ext}$ and $P=IV$, respectively, where I is current (A), V is the voltage (V), R_{ext} is the electrical load (Ω), and P is power (W). We placed an Ag/AgCl reference electrode 0.5-1 cm from the cathode to measure the cathode potential. The polarization test was conducted by placing a series of resistors ranging from 1 to 3000 kΩ as the external resistance. Internal resistance was calculated using $R_{int} = (OCV- E_{cell})/I_L$, where OCV is open-circuit voltage, E_{cell} is the cell voltage, and I_L is the current. Coulombic efficiency (CE%) was derived as follows: CE(%) = the measured coulombs/theoretical coulombs of COD removals.

Results and Discussion

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 elapse 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 (R^2=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/m^3 cathode chambered. 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 (COD_{eff}) was maintained at 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_{ext}) of 10 Ω, produced a low cell voltage (V_{avg}), 10 mV to 20 mV, while MFC-B (R_{ext} 1000 Ω) produced V_{avg} of 300-400 mV. Furthermore, MFC-A had averaged current (I_{avg}) 0.9-2.0 mA (or 530-1180 mA/m^3 based on cathode chamber volume of 1.7 L) and Coulombic efficiency (CE) 6-17%, much higher than those in MFC-B, which had only 0.4 mA (240 mA/m^3) and CE of 3-5%. The power output in MFC-A was only 0.01-0.04 mW (6-20 mW/m^3), while in MFC-B it greatly increased to 0.14-0.16 mW (80-90 mW/m^3) (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 COD_{in} 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 COD_{eff} instead of COD_{in} as a key parameter in analyzing the relationship

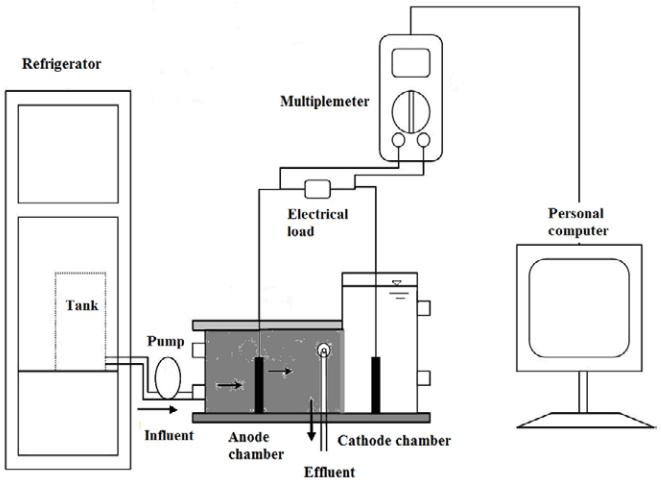

Figure 1: The schematic diagram of experimental reaeration assisted MFC system used in this study.

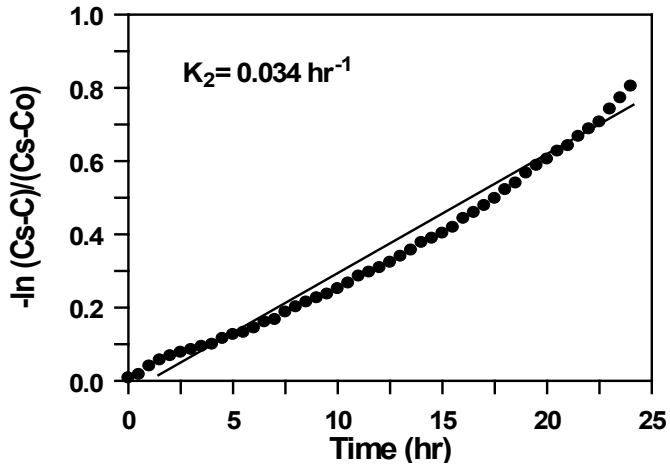

Figure 2: Determination of reaeration coefficient under a still water surface condition in the cathodic chamber. The linear regression line with R^2 = 0.98.

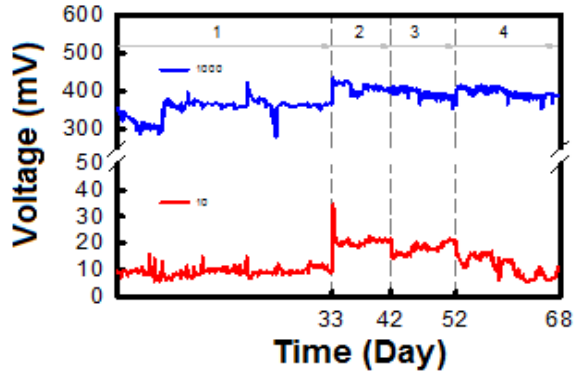

Figure 3: Variations in cell voltage during the course of continuous operation of two MFCs, MFC-A loaded with 10 Ω and MFC-B with 1000 Ω. Arabic number indicates the test run.

of substrate concentration to current generation [17]. Figure 4 shows that current generation strongly depends on substrate concentration in terms of COD_{eff}, and a Monod kinetics modeling could be well established. The estimated kinetic constants of maximum current I_{max} is 3 mA, and half-saturation constant of current K_s 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_{in} increased from 324 to 516 mg/L. The DO level appeared to be negatively correlated with current generation, where the R^2 for current against DO regression was 0.64 (Figure 5). The low DO yielding high current production in reaeration assisted-MFC could be attributed to the fact that low DO gives high oxygen transfer rate (Equations 1-3). Notably, the lowest DO of 1.9 mg/L occurred at COD_{in} 516 mg/L, implying that subjected to the highest organic load, the cathode chamber was exposed to the highest risk of anaerobic condition. A quite different outcome occurred in MFC-B, where current generation was maintained at the level of 0.4 mA, regardless of variations in COD_{in}, implying that under high electrical load the influent COD lose its influence on electricity generation. With high electrical load in MFC-B the electron transfer from anode 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 S_a 184 cm^2 and slightly increased to 1.0 mA when S_a was greatly increased to 1290 cm^2. This result indicated that S_a 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 S_a increasing from 184 cm^2 to 1290 cm^2. The above results demonstrated that under the reaction rate of 0.5-1.5, plain graphite with S_a 184 cm^2 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 0.5(8.2-0)(1.7) = 7.0 mg O_2/d = 0.22 mM O_2/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 O_2/d)(4 meq e-/mM O_2)], or equivalent to theoretical current (I_{eqv}) 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 K_2 0.5 d^{-1}. In case the reaeration rate increased to 1.5 d^{-1}, the maximum oxygen supply rate is 0.66 mM O_2/d and equivalent electron flow of 2.64 meq e$^-$/d (3.0 mA). Obviously, the current at K_2 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 I_{max}, which confirms the maximum current generation in reaeration-assisted MFC at still water surface would be 3.0 mA. Table 2 further lists the I_{eqv} values computed from oxygen supply in response to K_2 and DO. Again, the I_{eqv} appeared to increase with K_2 value at a specific DO level. For example, at DO 2.8 mg/L (similar to Test run A1), the I_{eqv} values were 0.6, 1.2, and 1.8 mA when K_2 was 0.5, 1.0, and 1.5 d^{-1}, respectively. In comparison of the I_{eqv} values with the measured currents I_{avg} (Table 1), it was apparent that the I_{eqv} for MFC-A was within the range of the I_{avg}, implying that the current production correlated well with oxygen transfer rate. Nevertheless, in MFC-B the I_{eqv} was slightly higher than the I_{avg} 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

Test run	Duration	S_a	COD_{in}	COD_{eff}	COD_{rv}	DO	V_{avg}	I_{avg}	P_{avg}	R_{int}	CE	V_c
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	388	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, Sa: cathode surface area (cm^2), COD_{in}: influent substrate (mg COD/L), COD_{eff}: 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_{int}: internal resistance (Ω), CE: Coulombic efficiency (%),V_c: cathode potential vs NHE (mV), and R_{ext}: electrical load (Ω).

Test Run	MFC-A I_{eqv} (mA)			MFC-B I_{eqv} (mA)		
	K_2 (d^{-1})			K_2 (d^{-1})		
	0.5	1.0	1.5	0.5	1.0	1.5
1	0.6	1.2	1.8	0.6	1.2	1.8
2	0.7	1.4	2.1	0.6	1.2	1.8
3	0.7	1.4	2.1	0.5	1.0	1.5
4	0.7	1.4	2.1	0.5	1.0	1.5

Table 2: Prediction of current generation from reaeration coefficients. Note: The value of I_{eqv} is calculated according to Equations (2) and (3).The dissolved oxygen in cathode chamber (DO) is shown in Table 1; saturated DO is assumed to be 8.2 mg/L; the K_2 estimated is based on the experimental results conducted at still water surface, ranging over 0.5-1.5 d^{-1}; and the volume of cathode is 1.7 L.

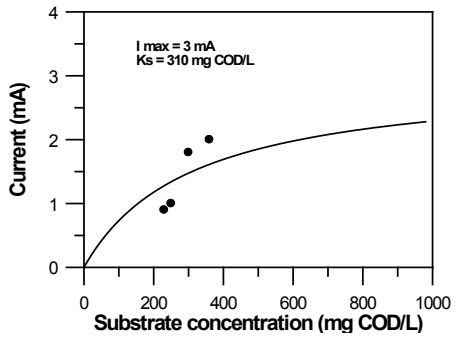

Figure 4: Electricity generations in current are expressed as functions of aqueous COD using Monod kinetics.

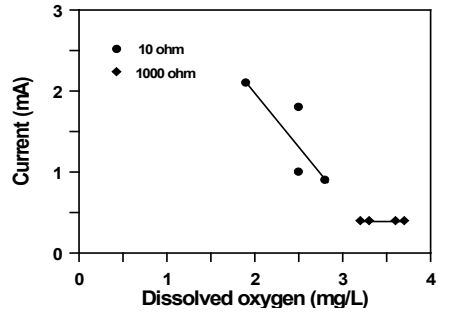

Figure 5: Electricity generations in current are expressed as functions of DO. The circle is the measurement for MFC-A, and the diamond is the measurement for MFC-B. The linear regression line for current in MFC-A with $R^2 = 0.64$, and that in MFC-B with $R^2 = 1$.

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 cells (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-d, 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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