Bioelectricity generation in microbial fuel cell by a membrane electrode assemble: Startup assessment

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Abstract

For the last two decades, microbial fuel cell (MFC) has been studied to treat wastewater and simultaneously produce electricity. This innovative bioelectrochemical technology offers the possibility of generating electric current from wide a range of complex organic wastewater. From this perspective, the MFC requires knowledge of structural and material modification in electrodes aimed to enhance the overall performance. Therefore, membrane electrode assembly (MEA) was developed through a combination of electrodes and proton exchange membrane. The MEA provides maximized power generation and extended cell lifetime on the MFC system. In this study, the MFC-MEA was analyzed during the acclimation stage in scale-up aimed at chemical oxygen demand (COD) removal and energy generation from a growth medium rich in acetate. Electrochemical analysis and water quality measurements were assessed. We show that the selection and biofilm acclimatization procedure is a simplified process, starting from anaerobic sludge. The results showed the efficiencies of COD removal and maximum power density were 74.60% and 47.49 mWm^{-2}, respectively. Thus, this study indicates a successful startup and a promising reactor configuration for MFC technology.

Keywords: Acclimation; air cathode microbial fuel cell; COD removal; renewable energy; energy recovery

I. INTRODUCTION

In recent years, microbial fuel cell (MFC) technology has received increased attention. This technology consists of an bioelectrochemical reactor, which generates electricity directly from an organic fuel using electroactive microorganisms [1]. Wastewater can be used as the electron donor, solving two worldwide issues: energy supply and wastewater treatment [2], [3].
Unfortunately, the production of high power generation is still a challenge for practical applications [4]. Significant work has been done to overcome this issue, such as improvement in materials and structure [5]. A promising alternative to improve the MFC energy production is the employment of membrane electrode assembly (MEA) as an electrode [6], [7]. The MEA structure consists of the proton exchange membrane sandwiched between the anode (GDE – gas diffusion electrode) and cathode (GDL – gas diffusion layer). The benefits from this setup consist in electrode-membrane contact improvement and internal resistance reduction [8]. Moreover, the use of MEA dismisses the use of aeration and dissolved oxygen (DO) diffusion, improving energy production.
Despite the broad interest in many engineering aspects of the MFC, the electroactive bacteria play the most crucial aspect. Therefore, providing conditions that promote the development of electroactive bacteria contributes to the performance of the MFC system [9]. The bacteria present at the anode, builds a biofilm on the electrode surface, which is named electroactive biofilm [10]. The biofilm acts as a biocatalyst to oxidize the carbon source, produce electrons and protons, and generate electrical power from their metabolism [11]. Many of these abilities and potentials are expressed during the initial biofilm formation period and affect MFC performance thereafter. The startup time of MFC is directly related to the biofilm formation on the anode [12].
From this perspective, the aim of this work has been focused on the acclimation of a scaled-up MEA-MFC. In this research, an MEA was introduced as a high-performance air-cathode in MFC with the gowl to increase bioenergy generation and reduce the chemical oxygen demand (COD) using a growth medium rich in acetate

II. METHODOLOGY

A. MFC construction

The set-up used in this work consisted of a scaled-up single-chamber MFC. The MFC was fabricated using acryl sheets, with an anodic work volume of 2 L. The electrode consists of MEA, with a nominal area of 144 cm² (Figure 1). Air cathode was composed of an MEA. Each MEA was made up of a Nafion™ (212) membrane, which operated as the chamber separator. The membrane was sandwiched between a carbon felt anode (GDL) and a carbon cloth cathode (GDE) coated with a catalyst loading of 0.4 mg Pt cm^{-2} (Novo- cell, Americana, Brazil). The MEA also contain carbon nanoparticle (Vulcan XC 72R), which provides excellent electron conductivity, and polytetrafluoroethylene (PTFE) layer, to prevent the oxygen diffusion into the anode and water leak in the air-cathode. Stainless steel (SS) plates were used as electron collectors. A single copper wire connected the electrodes externally.

B. Inoculation and operation conditions

The inoculum source was sludge taken from an anaerobic tank installed at a municipal wastewater treatment plant (Florianopolis, Brazil). The sludge had a volatile suspended solids concentration of 20 g L^{-1}. MFC was inoculated with a mixture of anaerobic sludge (50 mL) and a growth medium. The medium contained 1 g L^{-1}

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sodium acetate, vitamins (5 ml L^{-1}), and minerals (12.5 ml L^{-1}), in 50mM phosphate buffer solution (PBS) (4.576 g Na_2HPO_4, 2.452 g $NaH_2PO_4 \cdot H_2O$, 0.31 g NH_4Cl, 0.13 g KCl) [13]. The acclimation was conducted by feeding the reactors with sludge and growth medium, each 24 h, until voltage generation. Thereafter, only sodium acetate (1 g L^{-1}) and PBS were fed to the reactor. In fed-batch operation, reactors were refilled each time when the voltage decreased to less than 50 mV, forming one complete cycle of operation. The experiment was conducted with an external resistance (R_{ext}) of 1000 Ω, in a constant temperature room of 30 ºC.

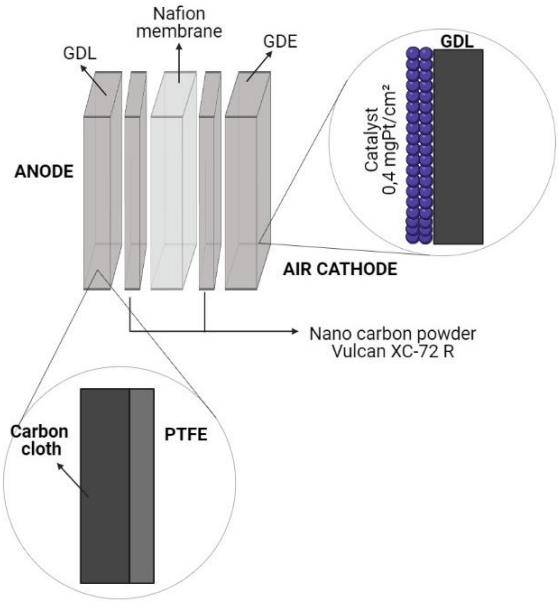

Figure 1. MEA electrode structure.

C. Calculations and measurements

The voltages across the resistor were measured every 3 min using a digital multimeter (ET-2615A, Minipa). Current, I [mA], was calculated according to Ohmic law, $I = E/R_{ext}$, where E is the voltage [mV] and R_{ext} is the external resistance [Ω]. Power, P [mW], was calculated according to P = I.E. Current density [mA cm^{-2}] and power density [mW m^{-2}] were determined by normalizing by area of the electrode. Polarization curves were generated by varying the external resistance, setting the MFC to open circuit for at least 30 min, or until a stable voltage was observed, and lowering the external resistance from 1000, 500, 200, 100, 50, 20, 10 Ω at 10 min intervals. Moreover, the MFC performance was evaluated in terms of COD. For this purpose, the MFC influent and effluent were collected at the start and end of each cycle. COD was measured by spectrophotometry (Hach DR5000) according to the adapted methodology from standard methods for the examination of water and wastewater, using the procedure of the analytic described in Hach 8000 (Hach Co., Loveland, CO). COD removal efficiency [%], was calculated based on the initial and final COD. pH and conductivity were obtained using a multiparametric probe (AKSO, AK88). Coulombic efficiency (CE), defined as the fractional recovery of electrons from the substrate, was calculated according to Eq 1:

$$CE = \frac{M \int_{t_0}^{t_1} I dt}{nvFv\Delta COD} \quad (1)$$

Where M is the molecular weight of oxygen (32 g mol^{-1}), I is the average current (mA), t is the hydraulic retention time (s), F is Faraday's constant (96,485 C mol^{-1}), n is the number of electrons exchanged per mole of oxygen (4 mol e^- mol^{-1}), v is the MFC volume (L), and ΔCOD is the change in COD over time t (g L^{-1}) [24].

III. RESULTS AND DISCUSSION

A. Voltage generation

Startup time was defined here as the time needed to produce repeatable current output over multiple cycles. Moreover, is related to biofilm development. According to voltage generation (measured over a 1000 Ω resistor), a latency phase was observed during the two first days, followed by an exponential increase up to day 3 to 5. After that, the voltage reached a plateau of around 650 mV. The MFC produced a maximum voltage of 795 mV. The start-up time took 15 days. This data can be seen in Fig. 2.

The development of an electroactive biofilm is responsible for MFC performance. In a typical startup of MFCs, the biofilm formation can be divided into three stages, such as reversible attachment, irreversible attachment, and biofilm generation [12], [14]. In stage 1, bacteria adapt to the new environment, flow around in the anode chamber, contact, and isolate with the anode reversibly. In this stage, typically no voltage can be generated, as can be seen on the first day. Stage 2 is characterized by the irreversible attachment of electroactive bacteria, and the increase in MFC voltage (Day 2-5). Subsequently, the microcolonies quickly grow to achieve stable voltage output. Following on, in stage 3, microcolonies turn to biofilm, generating continuous and stable power output (Day 6-15). These steps could be identified in Fig. 2.

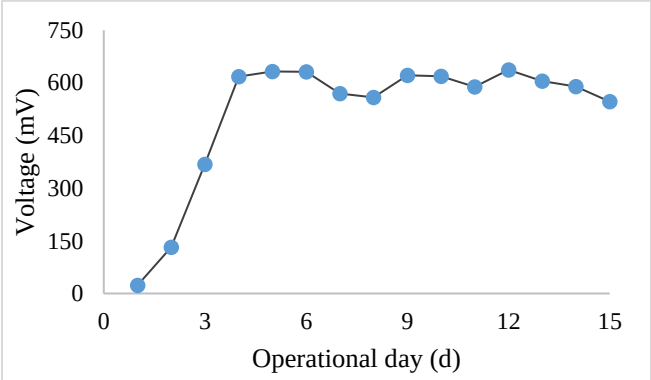

Figure 2 – Voltage measured across 1000 Ω resistor.

Similar results were found by Min et al. [15]. The authors pointed out that the MEA-MFC produced electric power after about a 50 h lag and stable operation with an average voltage was 519 ± 2 mV between 104 and 168 h after the start-up. In addition, the authors explain that a mixed culture obtained from domestic wastewater as inoculum, can easily within a short period immobilize on the anode electrode even though the anode was very close to the aerobic cathode chamber [15]. Moreover, in anaerobic sludge, the anaerobic environment is more selective and houses only species prone to reduce a terminal electron acceptor different from oxygen, which facilitates the adaptation [16]. MFCs inoculated with the mixed culture consistently produced more power than MFCs inoculated with the pure culture [17]. Vicari et al. [16]. compare the performance of different inoculum sources, anaerobic and anaerobic sludge. The authors noted that the MFC inoculated with the anaerobic sludge gave the best power density of 4.59 W m^{-2}, corresponding to 1.38 W m^{-3}.

In addition to the inoculum source, other factors such as external resistance [18], the electrode material [19], and appropriate methodology for inoculation [8], may have contributed positively to

the acclimatization period. Such benefits will reflect on the long-term performance.

In this present study, after MFC achieved 0.625 mV (Day 4), the sludge addition was suspended. Then, MFC was fed only with PBS, acetate, vitamin, and mineral solution. This procedure was repeated after the voltage drops to 50 mV, approximately. The voltage always increased immediately after the solution was replaced with a fresh medium, maintained a constant value for a period, and gradually decreased as the organic matter (e.g. COD) was consumed. This cycle took approximately 5 days (hydraulic retention time – HRT).

B. Power density and polarization test

In the start-up phase, the scaled-up MEA-MFC achieved a maximum current density of 60.11 mAm^{-2} and power density of 47.79 mWm^{-2}. This value is obtained at an open-circuit voltage (OCV) of 680 mV. The theoretical OCV value for an MFC fed with acetate is 805 mV [20]. This discrepancy could be attributed to high activation overpotentials, ohmic losses and concentration polarization, typical MFC disadvantages [21]. However, the current generation confirms the activity of electroactive bacteria. Nevertheless, analysis of inoculum and biofilm bacteria would be interesting to assess which electroactive species was present in MEA-MFC.

Table 1 shows the maximum power production obtained on different days during the acclimation stage. It is important to note the increase in value during the period. This performance could be attributed to the adaptation and growth of electroactive microorganisms and biofilm development.

Table 1. HRT, COD removal, coulombic efficiency, and power production from MEA-MFC

Operational day	HRT (d)	COD removal (%)	CE (%)	Max power density (mWm^{-2})
1	1	19.34	2.47	0.76
3	1	31.36	5.92	11.71
9	5	74.31	20.82	29.25
13	5	74.60	23.91	47.49

A polarization test was conducted on the last day of the start-up period, to characterize the overall performance of MFC and illustrate the potential losses. The maximum power density (P_{max}), i.e. the top of the parabola (Fig. 3), was 179.05 mWm^{-2} at a current density of 60.85 mAm^{-2} (R_{ext} = 500 Ω). Based on polarization data, decreasing the external load has increased the electrical current and decreased the cell voltage, which is typical fuel cell behavior [22]. According to Logan et al.[20], the polarization curve can be divided into three zones, which represent a kind of loss, such as activation, Ohmic, and mass transport. These three zones are observed, suggesting that the system is meeting the steady-state and showing a good performance [23].

At high current density, the polarization curve shows an overshoot phenomenon (Figure 3). Its presence could indicate that microbial biofilm has not matured to a sufficient level. However, Winfield et al. [24] explain that time favors this process. Then, more few days provide the establishment of a healthy biofilm and the disappearance of the overshoot. The assessment of electrode potentials could contribute to understanding this phenomenon in the MEA-MFC.

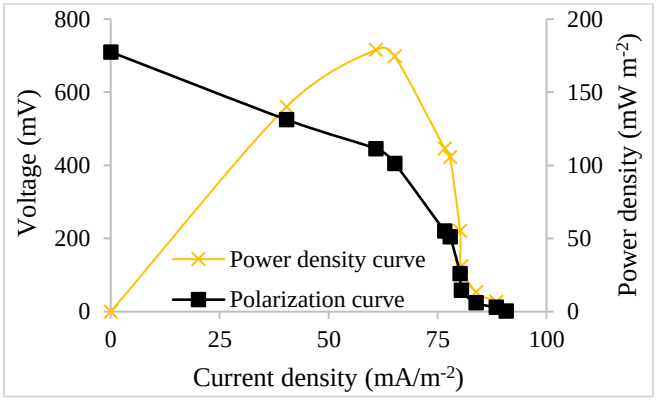

Figure 3. Polarization and power density curve.

C. COD removal

In evaluating an MFC as a bioelectrochemical device able to produce an electric current from the oxidation of organic matter, the COD concentration in the outlet of the MFC (effluent) is worth to be evaluated as one important parameter [16]. The acetate-fed medium has a COD concentration equal to 745 mg L^{-1}, pH 7, and 6.9 mS cm^{-1}. The depletion of COD remains in the current generation. However, in the biofilm, coexist the electroactive and no-electroactive microorganisms. Both groups are responsible for COD degradation.

It is important to note that over the days, the COD removal increased. In the first moment, the COD removal was not satisfactory, but expected, due to the adaptation period. After that, the operation condition changed, and the HRT became 5 days. The COD removal efficiency increased with the increase in time, which means, how much longer the influent spend inside the reactor, more available time for biodegradation [25].

This performance could be attributed to several factors. The composition of inoculum also severely influences the performance of COD removal efficiency, as the carbon source (glucose, acetate, sucrose) [26]. In addition, the external resistor also contributes to MFC performance. For a COD initial concentration of 840 mg L^{-1}, Zhang et al. [27] found rates equal to 0.030 h^{-1} with 100 Ω and 0.065 h^{-1} for 1000 Ω, then in lower resistance, COD removal rate increased.

The relation between COD removal and power production is expressed by CE (Table 1). The CE increased with COD removal, indicating microbial electroactive activity. Other studies reported similar values for the start-up phase [16], [17], [19].

Furthermore, despite the low percentage of COD removal in the first days, it can be inferred in Table 1 that a very efficient and robust bacterial community has grown in the anode as it is capable of converting 23,91% of the energy content of the medium into electricity.

IV. CONCLUSION

In this study, an air-cathode MEA-MFC equipped with the membrane electrode assembly (MEA) of 2 L was used for in situ power generation. Stable power generation could be obtained in 15 days. The inoculum source provides a rapid growth in voltage, resulting in a short inoculation period. After this acclimatization period. The scaled-up MEA-MFC can be applied for energy recovery from wastewater

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VI. REFERENCES

[1] J. Yu, Y. Park, E. Widyaningsih, S. Kim, Y. Kim, and T. Lee, "Microbial fuel cells: Devices for real wastewater treatment, rather than electricity production," *Sci. Total Environ.*, vol. 775, p. 145904, Jun. 2021, doi: 10.1016/j.scitotenv.2021.145904.

[2] H. Liu, R. Ramnarayanan, and B. E. Logan, "Production of Electricity during Wastewater Treatment Using a Single Chamber Microbial Fuel Cell," *Environ. Sci. Technol.*, vol. 38, no. 7, pp. 2281–2285, 2004, doi: 10.1021/es034923g.

[3] J. Vilas Boas, V. B. Oliveira, L. R. C. Marcon, M. Simões, and A. M. F. R. Pinto, "Optimization of a single chamber microbial fuel cell using Lactobacillus pentosus: Influence of design and operating parameters," *Sci. Total Environ.*, vol. 648, pp. 263–270, Jan. 2019, doi: 10.1016/j.scitotenv.2018.08.061.

[4] B. Fu, T. Xu, X. Guo, P. Liang, X. Huang, and X. Zhang, "Optimization and simulation of a carbon-based flow-through composite anode configuration to enhance power generation and improve effluent quality simultaneously for microbial fuel cells," *J. Clean. Prod.*, vol. 229, pp. 542–551, 2019, doi: 10.1016/j.jclepro.2019.04.308.

[5] H. Ni, K. Wang, S. Lv, X. Wang, L. Zhuo, and J. Zhang, "Effects of Concentration Variations on the Performance and Microbial Community in Microbial Fuel Cell Using Swine Wastewater," *Energies*, vol. 13, no. 9, p. 2231, May 2020, doi: 10.3390/en13092231.

[6] J. R. Kim, G. C. Premier, F. R. Hawkes, R. M. Dinsdale, and A. J. Guwy, "Development of a tubular microbial fuel cell (MFC) employing a membrane electrode assembly cathode," *J. Power Sources*, vol. 187, no. 2, pp. 393–399, Feb. 2009, doi: 10.1016/J.JPOWSOUR.2008.11.020.

[7] Y. Hubenova, G. Borisov, E. Slavcheva, and M. Mitov, "Gram-positive bacteria covered bioanode in a membrane-electrode assembly for use in bioelectrochemical systems," *Bioelectrochemistry*, vol. 144, p. 108011, Apr. 2022, doi: 10.1016/J.BIOELECHEM.2021.108011.

[8] G. K. S. Prakash, F. A. Viva, O. Bretschger, B. Yang, M. El-Naggar, and K. Nealson, "Inoculation procedures and characterization of membrane electrode assemblies for microbial fuel cells," *J. Power Sources*, vol. 195, no. 1, pp. 111–117, Jan. 2010, doi: 10.1016/J.JPOWSOUR.2009.06.081.

[9] K. L. Dinh *et al.*, "Lactate and acetate applied in dual-chamber microbial fuel cells with domestic wastewater," *Int. J. Energy Res.*, vol. 45, no. 7, pp. 10655–10666, Jun. 2021, doi: 10.1002/er.6550.

[10] M. J. Angelaalincy, R. Navanietha Krishnaraj, G. Shakambari, B. Ashokkumar, S. Kathiresan, and P. Varalakshmi, "Biofilm Engineering Approaches for Improving the Performance of Microbial Fuel Cells and Bioelectrochemical Systems," *Front. Energy Res.*, vol. 6, p. 63, Jul. 2018, doi: 10.3389/fenrg.2018.00063.

[11] B. E. Logan, R. Rossi, A. Ragab, and P. E. Saikaly, "Electroactive microorganisms in bioelectrochemical systems," *Nat. Rev. Microbiol.*, vol. 17, no. 5, pp. 307–319, 2019, doi: 10.1038/s41579-019-0173-x.

[12] P. Zhang *et al.*, "Accelerating the startup of microbial fuel cells by facile microbial acclimation," *Bioresour. Technol. Reports*, vol. 8, p. 100347, Dec. 2019, doi: 10.1016/J.BITEB.2019.100347.

[13] F. L. Lobo, X. Wang, and Z. J. Ren, "Energy harvesting influences electrochemical performance of microbial fuel cells," *J. Power Sources*, vol. 356, pp. 356–364, Jul. 2017, doi: 10.1016/J.JPOWSOUR.2017.03.067.

[14] M. Mukherjee, N. Zaiden, A. Teng, Y. Hu, and B. Cao, "Shewanella biofilm development and engineering for environmental and bioenergy applications," *Curr. Opin. Chem. Biol.*, vol. 59, pp. 84–92, Dec. 2020, doi: 10.1016/J.CBPA.2020.05.004.

[15] B. Min, F. W. Poulsen, A. Thygesen, and I. Angelidaki, "Electric power generation by a submersible microbial fuel cell equipped with a membrane electrode assembly," *Bioresour. Technol.*, vol. 118, pp. 412–417, Aug. 2012, doi: 10.1016/J.BIORTECH.2012.04.097.

[16] F. Vicari *et al.*, "Influence of the initial sludge characteristics and acclimation on the long-term performance of double-compartment acetate-fed microbial fuel cells," *J. Electroanal. Chem.*, vol. 825, pp. 1–7, Sep. 2018, doi: 10.1016/J.JELECHEM.2018.08.003.

[17] V. J. Watson and B. E. Logan, "Power Production in MFCs Inoculated With Shewanella oneidensis MR-1 or Mixed Cultures," *Biotechnol. Bioeng*, vol. 105, pp. 489–498, 2010, doi: 10.1002/bit.22556.

[18] G. Pasternak, J. Greenman, and I. Ieropoulos, "Dynamic evolution of anodic biofilm when maturing under different external resistive loads in microbial fuel cells. Electrochemical perspective," *J. Power Sources*, vol. 400, pp. 392–401, Oct. 2018, doi: 10.1016/J.JPOWSOUR.2018.08.031.

[19] S. Hays, F. Zhang, and B. E. Logan, "Performance of two different types of anodes in membrane electrode assembly microbial fuel cells for power generation from domestic wastewater," *J. Power Sources*, vol. 196, no. 20, pp. 8293–8300, Oct. 2011, doi: 10.1016/J.JPOWSOUR.2011.06.027.

[20] B. E. Logan *et al.*, "Microbial fuel cells: Methodology and technology," *Environ. Sci. Technol.*, vol. 40, no. 17, pp. 5181–5192, 2006, doi: 10.1021/es0605016.

[21] A. ElMekawy, H. M. Hegab, X. Dominguez-Benetton, and D. Pant, "Internal resistance of microfluidic microbial fuel cell: Challenges and potential opportunities," *Bioresour. Technol.*, vol. 142, pp. 672–682, Aug. 2013, doi: 10.1016/J.BIORTECH.2013.05.061.

[22] S. B. Pasupuleti, S. Srikanth, S. Venkata Mohan, and D. Pant, "Continuous mode operation of microbial fuel cell (MFC) stack with dual gas diffusion cathode design for the treatment of dark fermentation effluent," *Int. J. Hydrogen Energy*, vol. 40, no. 36, pp. 12424–12435, Sep. 2015, doi: 10.1016/J.IJHYDENE.2015.07.049.

[23] M. A. Rodrigo, P. Cañizares, H. García, J. J. Linares, and J. Lobato, "Study of the acclimation stage and of the effect of the biodegradability on the performance of a microbial fuel cell," *Bioresour. Technol.*, vol. 100, no. 20, pp. 4704–4710, Oct. 2009, doi: 10.1016/J.BIORTECH.2009.04.073.

[24] J. Winfield, I. Ieropoulos, J. Greenman, and J. Dennis, "The overshoot phenomenon as a function of internal resistance in microbial fuel cells," *Bioelectrochemistry*, vol. 81, no. 1, pp. 22–27, 2011, doi: 10.1016/j.bioelechem.2011.01.001.

[25] Y. Sharma and B. Li, "Optimizing energy harvest in wastewater treatment by combining anaerobic hydrogen producing biofermentor (HPB) and microbial fuel cell (MFC)," *Int. J. Hydrogen Energy*, vol. 35, no. 8, pp. 3789–3797, Apr. 2010, doi: 10.1016/J.IJHYDENE.2010.01.042.

[26] Z. Ullah and S. Zeshan, "Effect of substrate type and concentration on the performance of a double chamber microbial fuel cell," *Water Sci. Technol.*, vol. 81, no. 7, pp. 1336–1344, Apr. 2020, doi: 10.2166/wst.2019.387.

[27] X. Zhang, W. He, L. Ren, J. Stager, P. J. Evans, and B. E. Logan, "COD removal characteristics in air-cathode microbial fuel cells," *Bioresour. Technol.*, vol. 176, pp. 23–31, 2015, doi: 10.1016/j.biortech.2014.11.001.