

EVALUATION OF THE PERFORMANCE OF METAL-CARBON ELECTRODES ON POWER PRODUCTION FROM SYNTHETIC WASTEWATER IN A MICROBIAL FUEL CELL

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ABSTRACT

Microbial fuel cell (MFC) is an emerging bioprocess for sustainable energy production from wastewater. In this study, we investigated the long-term operation of two dual-chamber MFCs made with low-cost metal-carbon electrodes: cartridges of stainless-steel woven filled with activated carbon (MFC 1) and graphite (MFC 2). Reactors were operated in fed-batch mode with synthetic medium, and an HRT progression from 4 to 2d, for 160 days. Power and polarization curve analysis showed that activated carbon outperformed graphite, with a maximum power and current density of 1.62 W/m³ and 12.58 A/m³ on MFC 1 and 1.12 W/m³ and 8.32 A/m³ on MFC 2. Regarding synthetic wastewater treatment, both materials presented similar COD and Nitrogen removal efficiencies. Moreover, both reactors reached a 95% COD removal with HRT of 2d. These results suggest that activated carbon provided an increased surface area for the growth and attachment of electroactive microorganisms and, therefore, a better option to improve the recovery of electricity from wastewater treatment.

Keywords: Microbial Fuel Cells. Low-cost electrodes. Activated carbon. Graphite. Long-term operation.

1 INTRODUCTION

The ever-increasing demand for clean energy and reliable wastewater treatment are complex and intertwined challenges ongoing on a global scale¹. In this scenario, wastewater emerges as a potential source for energy generation and recovery of value-added products. Conventionally, wastewater treatment aims to ensure environmental protection and mitigate health risks through physical, chemical, and biological processes. However, the water and wastewater sectors are going through a paradigm shift to transform conventional wastewater treatment plants (WWTP) into a platform for resource recovery². Therefore, developing technologies to harness wastewater potential is essential.

In this context, microbial fuel cell (MFC) stands out as a promising technology for energy recovery from organic waste oxidation. Thus, MFC combines pollutant removal with clean energy production to achieve a neutral or positive energy balance process. Furthermore, the low cell yields of exoelectrogenic bacteria and the harvesting of electrons to produce current, reduce the sludge production in these systems, reducing process environmental impact and the costs of sludge disposal³.

To advance toward the real-world application of MFCs, some practices in current laboratory-scale MFCs should be reviewed. It is still common to find studies employing compounds with good electrochemical properties e.g., ferricyanide as catholyte or platinum as electrode material^{3,4}. However, despite their electrochemical advantages, these compounds often pose practical challenges due to their toxicity or high costs, which are prohibitive for real-world applications. Moreover, obstacles that may affect the long-term performance of MFCs are not yet well known, as most studies focus on short operations, lasting just a few days or weeks. In this sense, this study aims to evaluate the long-term performance of two MFCs made with affordable electrode materials (stainless steel with activated carbon or graphite) and characterize the power production and the pollutants removal.

2 MATERIAL & METHODS

We conducted the experiments using two double-chamber MFCs made of acrylic. Each chamber had a working volume of 150 mL, and they were separated by a cationic exchange membrane ($\varnothing = 5$ cm, CMI-7000S, Membranes International). Anode and cathode electrodes were composed of two cartridges of stainless-steel woven (2.5 x 5.0 cm², 200 mesh, Telas Rocha Ltd, Brazil) filled with 2.0 g of either coconut shell activated carbon (Smart Carbon, Brazil) or granular graphite (mean size of 300 μ m, Nacional de Grafite Ltd, Brazil). MFC1 operated with activated carbon electrodes, while MFC2 operated with graphite electrodes. The carbon-metal electrodes were attached to a stainless-steel rod for electrical connection, and a 560 Ω resistor closed the electric circuit.

Activated sludge from a secondary clarifier of a municipal wastewater treatment plant (WWTP) in Florianópolis, SC, served as inoculum for the MFCs. Before inoculation, the sludge was sieved to remove solids and washed twice with NaCl 0.5 g·L⁻¹, reaching a final concentration of 2.213 g·VSS·L⁻¹. MFCs were started up with a mixture of 55 mL of inoculum and 85 mL of synthetic medium (composition in g·L⁻¹: 1.68 NaC₂H₃O₂; 0.24 (NH₄)₂SO₄; 5.88 KH₂PO₄; 1.19 K₂HPO₄; 2.00 NaHCO₃; 0.1 CaCl₂·2H₂O; 0.1 KCl; 0.1

NaCl; 0.1 MgCl₂·6H₂O; 0.1 MgSO₄·7H₂O; 0.05 yeast extract; 0.005 MnCl₂·4H₂O; and 0.001 Na₂MoO₄·2H₂O) at the anode and deionized water at the cathode. For the start-up, MFCs were operated in batch mode and changed to fed-batch mode with HRT progression from 4 to 2d. MFC cathodes were continuously aerated with an airstone connected to an air pump. On the 73rd operating day, we replaced the catholyte and cleaned the electrodes with a brush to remove the biofilm that had grown on its surface. We repeated this procedure on day 149. The MFCs were operated for 160 days at room temperature (23 ± 1 °C).

We monitored MFCs by measuring ammonia⁵, nitrate⁶, nitrite⁷, chemical oxygen demand (COD)⁷, pH, conductivity, and electric parameters. i.e., voltage, current density, and power density. Chemical analyses were made weekly by taking samples from the anode and cathode at the end of the operational cycle. On the 155th day, we made the kinetic assays for all the chemical parameters monitored in the MFCs. The kinetic assay lasted one operational cycle (2 days) taking periodic samples of the anodic chambers.

Electrical parameters were taken by connecting an Arduino to the electrical circuit to read, process the values using Ohm's first law, and send them to a computer, where data were treated by Python script. Polarization and power curves were carried out on day 143. We fed the MFCs and operated them under open circuit voltage for approximately one hour; then we closed the circuit by varying the external resistors. Each resistor was maintained until a pseudo-steady-state condition was established for each load⁸.

3 RESULTS & DISCUSSION

MFCs operation lasted 160 days. Until the 8th operating day, MFC 2 presented a slightly better current and power density than MFC 1, afterwards they switched electrochemical performance. On the 27th day, the current and power densities in MFC 1 were, respectively, 95% and 284% higher than MFC 2. However, between the 58th and 73rd days, we observed a sharp decrease in the electrical parameters of MFC 1 a few hours after the feeding. We associated this with biofilm growth on the cathode electrode surface, which could hinder power production by increasing cathode potential⁹. Therefore, on the 73rd day, we executed a mechanical cleaning of the cathode electrodes of both MFCs and replaced the electrolyte with distilled water. This strategy recovered the power production on MFC 1, which continued growing until day 100, when the reactor reached a plateau in current and power densities of 3.91 ± 0.6 A/m³ and 1.28 ± 0.04 W/m³. During the operation, we also observed intertwined periods of increased and decreased current that matched the feeding cycle and were caused by substrate consumption.

In agreement with these data, results from polarization and power curves showed that MFC 1 outperformed MFC 2, as depicted in Figure 1(a). MFC 1 generated a maximum power density of 1.621 W/m³ and a maximum current density of 12.58 A/m³ which were 44.16% and 51.07% higher than MFC 2, respectively.

Regarding pollutant removal monitoring, COD removal at the anodes of MFC 1 and MFC 2 were similar during MFC operation (Figure 1(b)). After the start-up period, COD removal in both reactors was below 20%, but it gradually increased until stabilizing close to 95% after the 121st day. The highest COD removal in MFC 1 and MFC 2 were 96.66% on day 160 and 97.38% on day 141, respectively. The anode pH on both reactors was also similar, varying around 6.9. Nitrogen removal efficiency at MFC's anode varied frequently during the experiments, the last 39 days were considered a relatively stable period for nitrogen removal with averages of 32.16 ± 8.34% for MFC 1 and 32.61 ± 9.25% for MFC 2.

The kinetic study of pollutant removal in the MFCs also reached a COD removal efficiency at the anode of 95% on MFC 1 and MFC 2. On both reactors, the maximum COD removal rate occurred in the first 3 operating hours: 39.49 mgCOD/L.h for MFC 1 and 33.69 mgCOD/L.h for MFC 2. In contrast, ammonia conversion efficiency at the anode of MFC 1 and MFC 2 was 22.51 ± 7.24% and 17.62 ± 7.17%, respectively. As expected, ammonia was not highly consumed, and acetate was the main electron donor substrate for electricity production.

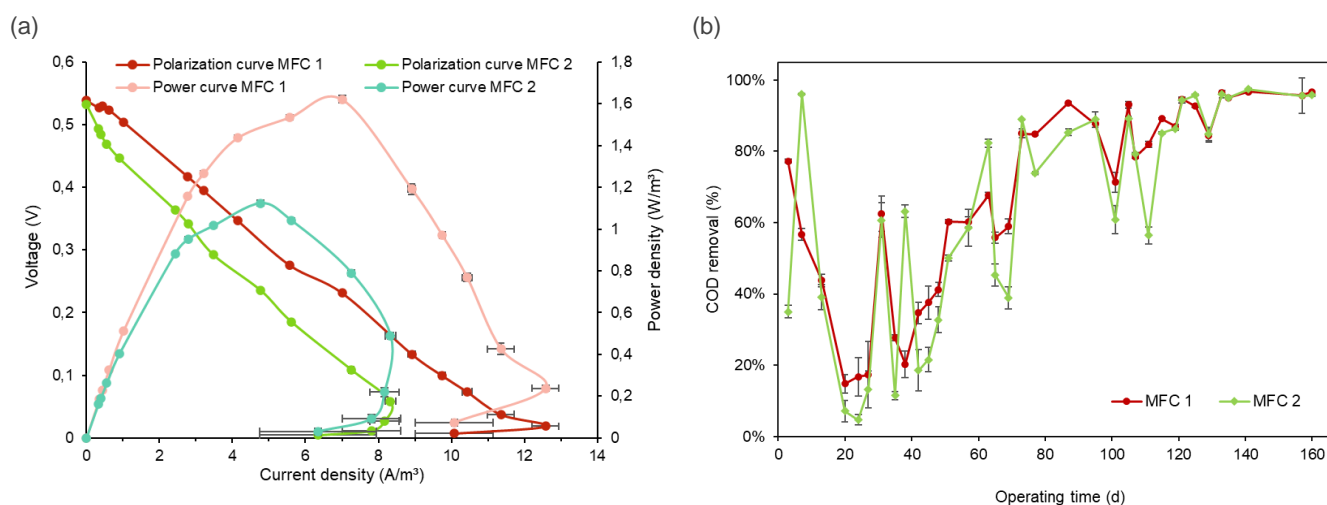


Figure 1 (a) Polarization and power curves; (b) COD removal of MFC 1 (activated carbon electrodes) and MFC 2 (graphite electrodes).

4 CONCLUSION

In this study, we explored the long-term power generation and pollutant removal in MFCs with different and affordable electrodes. MFC 1 outperformed MFC 2 in current and power generation, as evidenced by its higher maximum current and power density values in the polarization and power curves. This indicates that the activated carbon electrode provided an increased surface area for the growth and attachment of electroactive microorganisms and electron transfer in contrast with graphite. Although long-term operation showed that power production in activated carbon electrodes deteriorated faster than graphite, it was easily recovered by a simple mechanical cleaning procedure. Therefore, activated carbon proved to be a better material than graphite for long-term power generation in MFCs. On the other hand, pollutant removal profiles did not indicate a significant difference between reactors regarding COD and N. Thus, the choice of electrode material did not affect wastewater treatment efficiency. In summary, this study contributes to the scientific knowledge of MFCs demonstrating the feasibility of a long-term operation with low-cost electrode materials as an alternative for simultaneous electricity production and wastewater treatment.

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