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Microbial Fuel Cell for Nitrate Reduction

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Abstract

Microbial electrochemical systems present a breakthrough for environmental technology, perhaps even a promising solution to the magnifying problem of waste management. Our current research focuses on simultaneous energy production and organic matter removal from wastewaters by Microbial Fuel Cells (MFCs). An MFC system was inoculated with microbial cultures obtained from the silt of a river basin that regularly accepts heavy loads of nitrates from the local agriculture; the organic load was collected from the Facai Wastewater Treatment Plant in Romania.

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Keywords: Power generation; microbial cultures; wastewater treatment; organic matter removal

1. Introduction

Wastewater biomass from agricultural, municipal, and industrial sources is rich in carbohydrates that store chemical energy; thus, it can be used as a substrate for the direct energy conversion of sugars to electrical power with the help of microorganisms. An alternative strategy for waste treatment can be traced to a new technology under development: Microbial Fuel Cells (MFCs), specialized fuel cells capable of generating electric energy from organic matter through microbial metabolism [1-3]. Direct conversion of microbial metabolic products into

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electricity offers the potential to recover energy from wastewaters, marine sediments, and biomass; with promising applications in wastewater treatment, biosensors, and even medical devices [4-6].

MFCs consist of an anode, where organic matter is oxidized by microorganisms, and a cathode that hosts the electron acceptor (oxidant); various oxidants have been employed as electron acceptors, the most sustainable being oxygen due to its capacity to give a high reduction potential and its accessibility through the atmosphere [3,7]. The latest approach in MFC research targets nitrate reduction, with nitrates obtainable from different water sources: ground waters [8,9], wastewaters [10,11], or synthetic wastewaters [12].

We have assembled an MFC experimental prototype that employed naturally occurring microorganisms from a Romanian river which regularly accepts heavy loads of organic fertilizers from local agricultural activities, and we have loaded it with wastewaters collected from the Facai Wastewater Treatment Facility in Oltenia, Romania. The system was characterized according to its capacity for simultaneous organic matter and nitrate removal, as well as current and power production.

2. Materials and Methods

2.1. Materials

The following materials were used in the assembly of the MFC:

Anolyte solution: the anolyte total volume of 300mL was comprised of 150mL wastewater and 150mL of sediment bearing microorganism cultures. Wastewater samples were collected from the Facai Wastewater Treatment Plant in Oltenia. The sediment used for MFC inoculation was collected from a depth of 10cm below the Burtea River silt basin; it housed a naturally occurring mixture of microorganisms: bacteria, microalgae, and protozoa. All anolyte ingredients were used as received.

Electrodes: both anode and cathode electrodes were fabricated from carbon felt (AM&T VDG) with a surface area of 56.54cm2, and activated as follows: a.) soaked in HCl (1M) for one hour, washed with distilled water (DW), then soaked for a full day in HCl (1M) and washed again with DW; b.) soaked for a day in NaOH (1M), washed with DW, then soaked for another day in HCl (1M) and rewashed with DW; and c.) soaked for a day in NaOH (1M), washed several times with DW until the pH was close to neutral, and kept in DW until use.

The mono-chamber MFC system was assembled from acrylic, having a single chamber of 6cm height by 9cm diameter (available volume of 382mL), containing the anode and the cathode at opposite sides of the chamber (activated carbon felt electrodes of 56.54cm2 surface area each), and the 300mL of anolyte. A cylindrical Plexiglas of 3cm height was used as a spacer between the electrodes, each one connected with titanium wire to a data acquisition unit (Picotech ADC 10/11) that monitored the electrical potential in real time.

2.2. Analytical techniques

The following techniques were used in our analysis:

Polarization and power density profiles: obtained using a variable resistor box to set the external loads ranging from 20MΩ to 5Ω in a periodical decreasing order. Current density was calculated according to:

$$I = E/R \cdot A \tag{1}$$

where E is the cell voltage [V], R is the external resistance [Ω], and A is the projected surface area of the anode (56.54cm2).

Power density was calculated according to:

$$P = \left(I \cdot E\right)/A \tag{2}$$

Cyclic voltammetry: conducted using a Voltalab 401 system to examine the electrochemical behavior of the MFCs, to determine the double layer capacity (CDL) of the bioelectrodes, and to observe the microbial redox activity. The setup consisted of three electrodes, with the opposite electrode acting as auxiliary electrode, and the reference electrode placed close to the working electrode. We considered 25 cycles as being sufficient for an equilibrated response; the potential range was between -500mV and 500mV with a 50mV·s-1 scan rate.

Nitrate content: measured every 24 hours using a nitrate ion selective electrode (Vernier ISE Nitrate NO3-BTA).

Organic matter removal (ΔCOD): calculated by measuring the water samples initial and final COD values on the first and final steps of operation. The COD measurements were conducted using an AquaFast AQ4000 Colorimeter (Thermo Scientific Orion) at a wavelength of 610nm, equipped with a COD125 thermo-reactor, and using an Orion CODHP0 (0 to 15mg·L-1) kit.

Coulombic efficiency (ηc): determined from the total amount of electrons recovered as current from the initial organic matter, calculated by integrating the measured electric current relative to the theoretical electric current based on the consumed COD:

$$\eta_c = \frac{1}{F}\frac{M_O}{n_e V_{an}\Delta COD}\int_0^t Idt \tag{3}$$

where M_O is the molecular weight of oxygen (M_O=32), F is Faraday's constant (96485.3365C·mol^{-1}), n_e is the total number of electrons exchanged per mole of oxygen (n_e=4), V_{an} is the volume of the anode, and ΔCOD is the organic matter removed from the water samples [4].

3. Results and Discussion

3.1. Cyclic voltammetry

Cyclic voltammetry (CV) measurements were conducted after polarization and power densities measurements. CV profiles showed a stable oxidation peak at the anode (with no returning reduction peak), determined by the microbial capacity to oxidize the organic matter, at a potential of -128mV over a current density of 117μA·cm-2. The CV for the cathode displayed a milder electrochemical response with no oxidation or reduction peaks (Figure 1). This implies that microorganisms forming the biofilm at the anode had a pronounced electrochemical activity compared to the ones in the cathode. The anoxic microbiota presented a direct electron transfer mechanism, generating their metabolic energy by oxidizing the substrate and using the anodic electrode as the final electron acceptor - cathodic electrochemical activity was diminished, as neither catalysts nor aerobic species were used to augment the oxygen reduction reaction.

Double layer capacities (CDL) of the bioelectrodes were calculated from the voltammograms by measuring the electrodes open circuit potential (OCP) and the anodic and cathodic currents, Ia and Ic, corresponding to the OCP and introducing them to the formula:

$$\frac{I_a - I_c}{2} = C_{DL}\frac{dE}{dt} \tag{4}$$

C_{DL}'s determined for both electrodes were: 1.2μF·cm^{-2} for the anode at an OCP of -267mV, and 0.87μF·cm^{-2} for the cathode at an OCP of 412mV. This indicates that the anodic microorganisms were electrochemically active, in contrast to the cathodic ones.

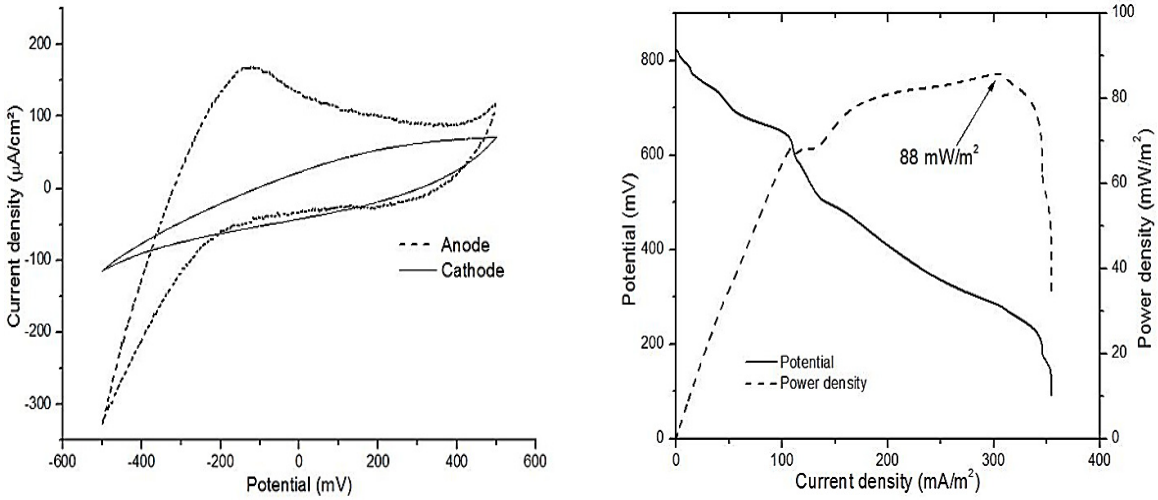

Fig. 1 - (*left*) Cyclic voltammetry profile showing a stable oxidation peak at the MFC anode, and a mild electrochemical response at the cathode; and (*right*) Polarization and power density profile.

3.2 Polarization and power density curves

Once the MFC reached a stable voltage output of 806mV, we initiated measurements of current and voltage. Current and power densities were calculated by normalizing the values over the anode surface area. From the polarization curve (Figure 1) we observed that from the OCV at zero current to decreasing high-load resistances, the voltage presents a steep decrease from 806mV to 653mV (activation losses). It also revealed a step in which the voltage is dropping linearly with the current from 653mV to 240mV (108mA·m^{-2} to 336mA·m^{-2} respectively) that corresponds to the ohmic losses pertaining to microbial metabolism. The last part of the polarization curve shows an abrupt voltage fall (from 240mV to almost 93mV) at high current densities (from 336mA·m^{-2} to 354mA·m^{-2} respectively), which corresponds to mass losses [12,13]. From the power density curve, we determined the maximum power density of 88mW·m^{-2}, the internal resistance of the system at 50Ω, the optimum current density of 310mA·m^{-2}, and the maximum current density (short circuit current) of 353mA·m^{-2}.

3.3 Coulombic efficiency, nitrate and organic load removal efficiencies

Nitrate removal efficiency: NO_3^- content was measured every 24 hours using a nitrate-selective electrode for the full 14 days of MFC operation: the nitrate content decreased from an initial value of 83mg/L to 3.3mg·L^{-1}, giving a 96% nitrate removal efficiency (Figure 2). This indicates that the Burdea microbial culture contains denitrifying bacterial species, which combine the oxidation of organic matter with the reduction of nitrate [15].

Organic load removal efficiency: for the organic load removal, we conducted COD measurements during the first and the final step of MFC operation. The analysis determined the system's initial value of organic load at 7.8g·L^{-1} - after 14 days the organic load decreased to 20mg·L^{-1}, resulting in an organic load removal efficiency of 97%, a promising factor for water treatment.

Coulombic efficiency: calculated by integrating the total collected current over time at an external resistance of 150Ω (Eq. 3). The system attained a coulombic efficiency score of 43%, implying that the majority of microorganisms present in the sample were not exoelectrogenic, and that 57% of the substrate was consumed for biomass growth [7].

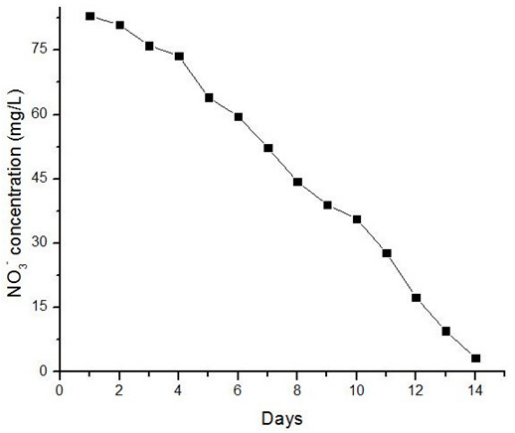

Fig. 2 - Nitrate concentration over two weeks of MFC operation, demonstrating high nitrate removal efficiency.

4. Conclusions

Our research demonstrated electric energy production through the biodegradation of the organic fraction present in wastewaters, by using an Microbial Fuel Cell (MFC) inoculated with naturally-grown microbiota collected from Burdea riven - a river that regularly accepts heavy loads of nitrate originating from the local agricultural economy.

Using an inexpensive, simplified mono-chamber MFC, we managed to generate up to 88mW·m-2 of power with an optimum current density of 310mA·m-2, to reduce the organic load present in wastewaters using a natural microbial ecosystem with an efficiency of 97%, and to reduce the nitrate concentration with an efficiency of 96%. Power production was accompanied by organic matter removal (biodegradation), demonstrating the waste processing potential of MFC technology. This experiment has also provided more support to current trends in MFC technology that advocate the use of mixed-species microbial communities -especially systems that have grown and evolved in vivo- over specialized monocultures.

Our future research will focus on scalability issues to fully explore the potential of MFCs to function as mobile waste-processing units.

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