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Simultaneous production of bioelectricity and treatment of membrane concentrate in multitube microbial fuel cell

Emre Oguz Koroglu,* Afsin Y. Cetinkaya, Bestami Ozkaya, and Ahmet Demir

Yildiz Technical University, Department of Environmental Engineering, 34220, Esenler, Istanbul, Turkey

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The performance of upflow multitube microbial fuel cell (UM^2FC) from membrane concentrate of domestic wastewater (50% concentrate or a volume to concentration ratio of 2) has been investigated in a laboratory test. The test found that the UM^2FC with the tin-coated copper mesh and coil spring under different hydraulic retention times (HRTs) produced maximum electricity of 916 ± 200 mW/m^3 (61 mW/m^2) at an HRT of 0.75 day with a 78% soluble chemical oxygen demand (sCOD) removal efficiency and 3% and 20% Coulombic efficiencies (CEs). The whole-cell resistance as calculated from the Nyquist plot and equivalent circuit were approximately 134 and 255 Ω for HRTs of 0.5 and 0.75 days, respectively. Considering HRT, the current increase with longer HRT could be due to longer contact time between organic material and biofilm, which results in a higher electrical efficiency. The results showed that UM^2FC could represent an effective system for simultaneous membrane concentrate treatment and electricity production after further improvements on MFC and operating conditions.

[**Key words:** Tubular microbial fuel cell; Multielectrode connection; Electrochemical impedance spectroscopy; Surface morphology; Membrane concentrate]

Microbial fuel cells (MFCs) are microbiological systems that can be used in wastewater treatment for energy recovery and biomass reduction. The studies conducted in the last decade have focused on effective MFC design and economical electrode and separator materials. Optimizing the other operating conditions is also another important approach to improve the performance of MFCs. The MFC design, electrode performance, external operating conditions, resistance, and rate of substrate degradation principally increase the power output from MFCs (1,2). Much effort is being devoted to more effective and applicable MFC design and materials. Tubular MFC designs have attracted much attention recently to make the MFCs feasible to scale up and improve electrical performance. For example, tubular MFCs with spiral spacers were developed by creating a helical flow to increase electricity generation and investigated in both laboratory and on-site tests (3). The energy production in the tubular MFCs ranged from 0.071 to 0.073 kWh/kg chemical oxygen demand (COD), and it was proved to be an effective approach to improve energy production. In this study, an upflow multitube microbial fuel cell (UM^2FC) was tested for its ability to simultaneously treat concentrate streams of domestic wastewater and produce electricity (4). The pipe-in-pipe electrode assemblies and compact design represented a new treatment technology for membrane concentrate treatment as well as electricity generation. A tubular configuration makes it possible to achieve distribution close to optimal spatial distribution of anode, cathode, and separator in an MFC. A granular carbon anode MFC with an external cathode surrounding the vertical upflow containment tube was considered by Rabaey et al. (5). Maximum and average power densities of 90 and 52 W/m^3 were obtained with acetate at an organic loading rate (OLR) of 1.1 kg COD/m^3/day. A similar configuration of tubular reactor was investigated with an open-air biocathode generating 65 W/m^3 of power density at an OLR of 1.5 kg COD/m^3/day (6).

A recent development of tubular MFCs has aimed to optimize operating conditions to increase the production of electricity and understand electrochemical behavior of cells and physical properties such as surface morphology and elemental analysis. Li et al. (7) tested the feasibility of bioelectricity production from animal carcass wastewater under different hydraulic retention times (HRTs). After a start-up period of approximately 55 days, when HRT was set at 3 days, MFC showed best bioelectricity performance with the maximum power density of 2.19 W/m^3 and minimum internal resistance of 30.3 Ω. Increasing HRT from 3 to 6 days increased COD and nitrate removal efficiency, but reduced the rate of production of ammonia. Kim et al. (8) investigated the energy recovery using longitudinal tubular MFC reactors with influent sucrose OLRs between 0.04 and 0.42 g COD/l/day. The maximum energy production was 1.75 Wh/g COD at an OLR of 0.24 g/l/day and Coulombic efficiency (CE) ranged from 9% to 92%. Therefore, the tubular MFC design is promising for wastewater treatment and electricity generation.

Nevertheless, the disposal and treatment of membrane concentrates besides wastewater is a serious problem that constrains the application of membrane technology (9). MFCs could represent

* Corresponding author. Yildiz Technical University, Faculty of Civil Engineering, Department of Environmental Engineering, Davutpasa Campus, 34220 Esenler, Istanbul, Turkey. Tel.: +90 212 383 54 02; fax: +90 212 383 51 02.
E-mail address: emreoguzkoroglu@gmail.com (E.O. Koroglu).

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an effective system for membrane concentrate treatment and electricity production simultaneously. The feasibility of membrane concentrate treatment and electricity production has not been considerably tested in the MFCs. Koroglu et al. (4) studied the generation of electricity from membrane concentrate using a UM^{2}FC. In this study, different electrode materials were installed in a tubular MFC differently from Koroglu et al. (4) with the same substrate and inoculum. The objectives of this study were to (i) investigate the performance of UM^{2}FC for electricity generation and wastewater treatment from membrane concentrate; (ii) investigate the effect of HRT; (iii) evaluate the electrochemical behavior of UM^{2}FC and identify the distribution of the internal resistance; and (iv) investigate the surface morphology, dispersion, and functional groups by scanning electronic microscopy (SEM) and attenuated total reflection–Fourier transform infrared (ATR–FTIR) spectroscopy.

MATERIALS AND METHODS

Reactor configuration and operation In this study, a patented (by Turkish Patent Institute with number of TR-201106609B) tubular UM^{2}FC was used with a tin-coated mesh (LessEMF, USA) as anode–cathode electrode, stainless steel coil spring (0.5-mm wire diameter, 5-mm outer diameter, and 1.1×10^{-3}-Ω cm^{-1} electrical resistivity) to obtain a mechanical support between mesh electrodes, cylindrical glass reactor, and a tubular Nafion (Perma Pure) membrane. The volume of the anode chamber was 100 ml and the total surface area of the electrodes was 15 cm^2. The electrodes were constructed by entwining the membrane over spring and rolling up tin-coated copper meshes around the springs (Fig. 1). Five electrode configurations were connected in parallel by a titanium wire with 100-Ω external resistance and their electrical responses were monitored together. Before setting up the electrode, membranes were pretreated in accordance with Koroglu et al. (4) described previously by sequential immersion in a 30% volume fraction H_2O_2 solution, 49.04 g L^{-1} H_2SO_4 solution, and deionized water at 85°C for 1 h.

During the initial start-up period, the UM^{2}FC was inoculated with a sediment sample (2:10 v:v) obtained from Golden Horn in İstanbul, Turkey, and the anodic liquid was collected from the ISKI Domestic Wastewater Pretreatment Plant in Yenikapi (41° 00′ 09.28″ N 28° 56′ 56.87″ E). The UM^{2}FC was operated for approximately 48 h until the desired current generation and biofilm formation were observed. The cathode chambers were recirculated continuously with oxygen-saturated distilled water. The experimental setup was the same as that of Koroglu et al. (4). The reactor was operated in batch mode at room temperature (20 ± 2°C) with raw domestic wastewater and anodic liquid was recirculated via a circulating pump to produce gentle shear on the surface of the anode to obtain an active biofilm. After 48 h of enrichment and adaptation period, the UM^{2}FC switched to continuous mode with concentrated wastewater with an HRT of 0.75–0.5 day. The molecular weight (MW) distribution analysis and membrane concentrate production using membrane filtration were done as described in Koroglu et al. (4) using a stirred filtration apparatus (Amicon-8400, Merck Millipore) under 200-kPa absolute pressure for MW distribution analysis and a laboratory scale cross-flow mode filtration apparatus with a flat sheet membrane system for membrane concentrate production of domestic wastewater. The 50% retained ratio or a volume concentration ratio (VCR) of 2 was used in this study, and the former represents the percentage ratio of filtered wastewater volume to initial feed volume or VCR was used to express the degree of concentration of a target compound, as shown by the following equation:

$$VCR = CF = \frac{V_0}{V_r} = 1 + \frac{V_p}{V_r} \quad (1)$$

where V_0 is the initial feed tank volume, V_p is the volume of the permeate, and V_r is the volume retained (10).

The characteristics of the domestic wastewater and membrane concentrate were: pH 6.9 ± 0.8, conductivity 900 ± 300 mS m^{-1}, soluble chemical oxygen demand (sCOD) 480 ± 70 g m^{-3}, and total suspended solid (TSS) 240 ± 28 g m^{-3} for raw wastewater and pH 7.2 ± 0.0, conductivity 950 ± 210 mS m^{-1}, sCOD 685 ± 31 g m^{-3}, and TSS 348 ± 24 g m^{-3} for 50% concentrate stream.

Measurement and analysis The electrochemical impedance spectroscopy (EIS) analysis represents the limiting factors as internal resistance in MFCs and in this study, internal resistance of UM^{2}FC cell was segmented in various specific resistances such as Ohmic resistance (R_Ω), anodic charge transfer resistance (R_a), cathodic charge transfer resistance (R_c), and constant phase element (CPE) as a component of equivalent electrical circuit. The impedance data of the UM^{2}FC were analyzed by fitting them to an equivalent electrical circuit model. The magnitude of the impedance can be expressed in terms of the real and imaginary components, as given in Eq. 3:

$$|Z| = \sqrt{Z_r^2 + Z_j^2} \quad (2)$$

Electrochemical measurements were monitored by a computer-based potentiostat system (Ludre L02/V01, Ludre Software, Istanbul, Turkey) every 5 min (4). EIS data were recorded on a Ludre potentiostat in a frequency range of 100 kHz to 1 MHz and amplitude of 10 mV. The impedance spectra were recorded when the maximum power was observed, because the power reaches its maximum values as a result of the maximum biochemical conversion rate. The internal resistances were calculated by fitting and simulating the experimental data with equivalent circuits using the ZsimpWin 3.22 software (11).

The concentrations of sCOD and TSS were measured using the standard methods (method 5220 D and 2540 D). All samples for SCOD measurements were filtered through 0.45-mm syringe filters (polyvinylidene difluoride (PVDF), 25 mm, Restek). Measurement of pH and conductivity was made using a probe (WTW Multi 3420, Germany) after sampling. CE was calculated as given by Logan (12):

$$CE = \frac{M_s \cdot I}{F \cdot b_{es} \cdot q \cdot \Delta C} \quad (3)$$

where M_s is the MW of the substrate added, I is the circuit current, F is the Faraday's constant, b_{es} is the number of electrons exchanged per mole of oxygen, q is the flow rate, and ΔC is the difference between the influent and effluent CODs.

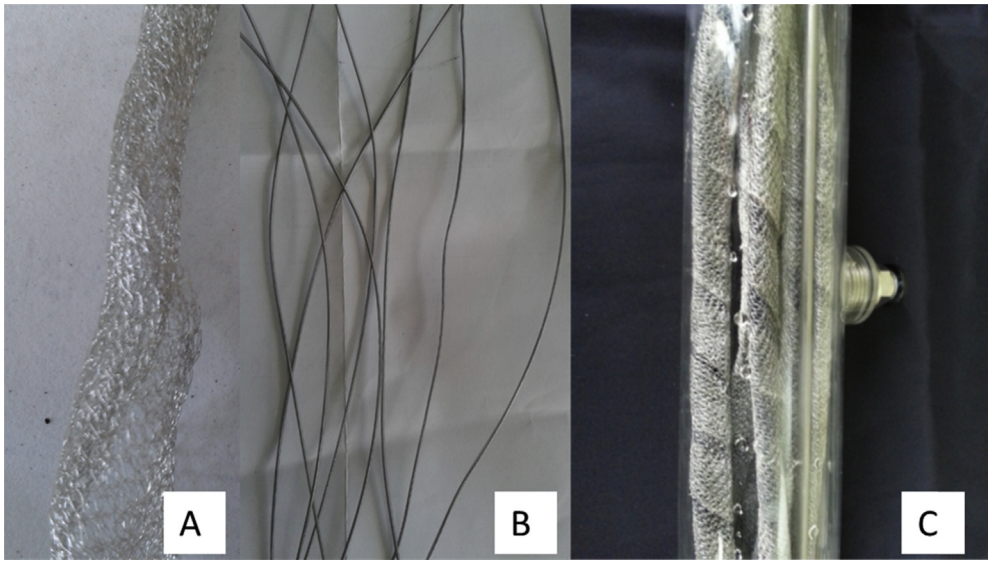

FIG. 1. Configuration of UM^{2}FC: (A) tin-coated copper mesh; (B) stainless steel coil springs; and (C) the assembled UM^{2}FC for the test.

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