Journal of Bioscience and Bioengineering
VOL. 118 No. 6, 672–678, 2014

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Electricity generating capacity and performance deterioration of a microbial fuel cell fed with beer brewery wastewater

Emre Oğuz Köroğlu,[1,*] Bestamin Özkaya,[1,3] Cenk Denktaş,[2] and Mehmet Çakmakci[1]

Department of Environmental Engineering, Yildiz Technical University, Istanbul, Turkey,[1] *Department of Physics, Yildiz Technical University, Istanbul, Turkey,*[2] *and Department of Chemistry and Bioengineering, Tampere University of Technology, Tampere, Finland*[3]

Received 7 November 2013; accepted 6 May 2014
Available online 21 June 2014

This study focused on using beer brewery wastewater (BBW) to evaluate membrane concentrate disposal and production of electricity in microbial fuel cells. In the membrane treatment of BBW, the membrane permeate concentration was 570 ± 30 mg/L corresponding to a chemical oxygen demand (COD) removal efficiency of 75 ± 5%, and the flux values changed between 160 and 40 L/m^2-h for all membrane runs. For electricity production from membrane concentrate, the highest current density in the microbial fuel cell (MFC) was observed to be 1950 mA/m^2 according to electrode surface area with 36% COD removal efficiency and 2.48% CE with 60% BBW membrane concentrate. The morphologies of the cation exchange membrane and the MFC deterioration were studied using a scanning electron microscope (SEM), attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy, differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). A decrease in the thermal stability of the sulfonate (−SO_3H) groups was demonstrated and morphological changes were detected in the SEM analysis.

[**Key words:** Microbial fuel cell; Membrane concentrate; Wastewater treatment; Membrane morphology; Thermal stability]

The increasing global energy requirement is making it mandatory for us to find resources for cost-efficient, low-energy wastewater treatment (1). Because current predictions show a stable and uncontrollable increase in population, such water pollution problems will grow in conjunction with the increasing population (1) and global industrial growth will increase the demand for energy (2). New treatment technologies such as microbial fuel cells (MFC) with the ability to concurrently treat wastewater and generate electricity in the same system will be a critical technology in the future. MFC is a promising wastewater treatment technology that allows us to harvest the chemical energy stored in wastewater directly in the form of electricity via the catalytic reactions of micro-organisms (3). The MFC technology is a different approach to wastewater treatment, because the treatment process can become a method of capturing energy in the form of electricity. Hence, there is significant energy saving associated with the use of MFC for wastewater treatment as well as electricity generation (4). This novel technology is important for industrial wastewater management in terms of electricity generation during treatment. Wastewater is one of the most significant waste products of the beer brewing industry. Even though substantial technological improvements have been made in the past, it has been estimated that approximately 3–10 L of waste effluent is generated per liter of beer produced in breweries. The characteristics of beer brewery wastewater depend on the production and the specific water usage, but beer brewery wastewater generally has a high biochemical and chemical oxygen demand from all the organic components (e.g., sugars, soluble starch, ethanol, volatile fatty acids) (5). The nitrogen and phosphorus levels are dependent on the raw material and the amount of yeast present in the effluent (5,6; Driessen, W. and Vereijken, T., unpublished data).

Different processes used in beer brewery wastewater treatment are up-flow sludge blanket reactor, aerobic reactor, membrane bioreactor, nanofiltration, and reverse osmosis (7–12). Although membrane processes have a good removal efficiency, these systems have major disadvantages as well as positive aspects. One of the most significant disadvantages is that a concentrate is produced as a result of treatment. Usually, the concentrate has negligible effects when it is sent back to the source. However, to preserve existing surface water, new technologies are required to treat specific components of concentrate before discharge. Thus, an innovative system microbial fuel cell is attractive for concentrate treatment as well as electricity production. An integrated system should be developed to use electricity from MFCs for membrane systems that require high amounts of energy.

In this study, electricity generation from the membrane concentrate of beer brewery wastewater in a dual-chambered MFC was investigated for simultaneous treatment of the membrane concentrate stream and generation of electricity in the MFC. In this study cation exchange membrane (CMI7000) were used instead of high cost proton exchange membranes (PEM) such as Nafion. These

* Corresponding author at: 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 53 58.
E-mail addresses: eoguzkoroglu@hotmail.com, emreoguzkoroglu@gmail.com (E.O. Köroğlu).

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http://dx.doi.org/10.1016/j.jbiosc.2014.05.006

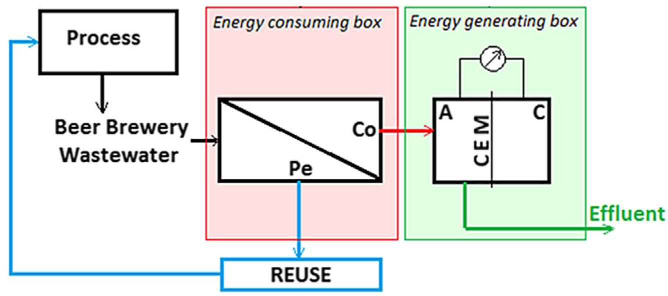

FIG. 1. Schematic view of combined membrane and MFC system (first box: cross-flow membrane system; second box: microbial fuel cell; Pe: permeate; Co: concentrate; A: anode; C: cathode).

PEMs such as Nafion are currently the most commercially membranes for MFCs, with chemical stability, conductivity and mechanical properties. While PEMs have satisfactory properties for fuel cells, they limit commercial use due to high costs (13). To improve electricity production and columbic efficiency (CE), the development of low-cost materials is essential for scaling up MFCs and creating low-cost treatment systems. The CEM membrane used here represent a significance decrease in cost compared to PEMs. The cost of the CEM membrane was $111/m2, which is much less than the price of Nafion ($1400/m2) (14).

MATERIALS AND METHODS

Analytical methods In this study, beer brewery wastewater was sampled from the beer production industry in İstanbul, Turkey. All parameters were estimated using the standard APHA–AWWA–WEF methods (15). Wastewater was stored at +4°C under anaerobic conditions. The beer industry wastewater had a chemical oxygen demand (COD) of 2200 ± 140 mg/L, five-day biochemical oxygen demand (BOD_5) of 1520 ± 120 mg/L, suspended solids (SS) of 590 ± 27 mg/L, pH of 8.12 ± 0.5, and conductivity of 3.85 ± 0.5 mS/cm.

Membrane concentrate production The experiment was performed in a laboratory-scale flat-sheet membrane system. The main purpose of this system was to treat beer brewery wastewater and to produce a concentrate for the MFC system. The effective area of the flat-sheet membrane cell was 155 cm^2, and the concentrate was re-circulated into the feed tank. The temperature in the feed tank was maintained at 23 ± 2°C by an online heat exchanger system. The amount of permeate was recorded online by a digital balance connected to the computer. Before the flat sheet membrane cell, 5-μm cartridge filters were used in the pretreatment step. Then, the wastewater was filtered with UP150 manufactured by Microdyn-Nadir. The properties of UP150 were as follows: pore size (molecular weight cut off, MWCO): 0.04 μm (approximately 150 kD), membrane material: polyethersulfon (PES), water flux [L/(m^2h)]: >200 at 0.7 bar and 20°C, stirring rate: 700 rpm, pH range: 0–14, and maximum temperature: 95°C.

The membrane study was conducted at a constant transmembrane pressure (TMP) of 3 bar. Beer brewery filtration was performed until the desired concentrate ratios of 50, 60, and 70% were obtained. The raw brewery wastewater had a COD concentration of 2200 ± 140 mg/L. The average COD values were measured as 2900 ± 80, 3200 ± 110, and 4000 ± 75 mg/L for 50, 60, and 70% concentrate, respectively. The COD concentrations in effluents (permeate) were measured as 570 ± 30 mg/L for a removal efficiency of 75%, and the flux value range of 40–160 L/m^2-h for all the membranes used. The sustainable combined membrane and MFC system is schematically illustrated in Fig. 1.

MFC construction A dual-chamber plexiglass MFC with a total net volume of 275 mL was constructed. The anode and the cathode were separated by a cation exchange membrane (CEM) from Ultrex Company (Ultrex CMI7000, Membranes

TABLE 1. CMI7000 cation exchange membrane technical specifications.

Technical specification	CMI7000
Polymer structure	Gel polystyrene/divinylbenzene
Functional X-change group/Solvated ion	SO_3^{2-}/Na^+
Permselectivity (%), 0.1 mol KCl/kg/0.5 mol KCl/kg	94
Total exchange capacity (meq/g)	1.6 ± 0.1
Chemical stability range (pH)	1–10

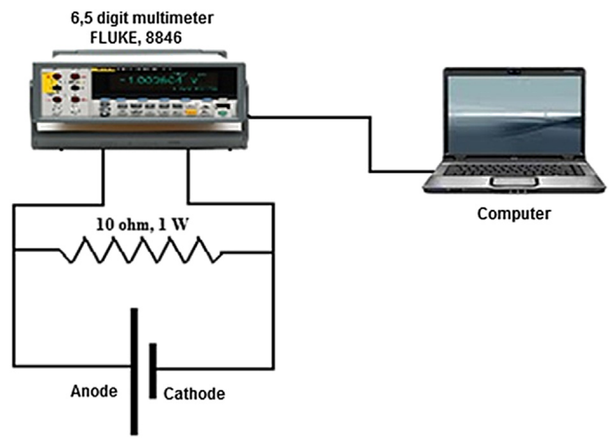

FIG. 2. The schematically view of circuit for online measurement system.

International Inc., USA), CEM specifications are given in Table 1. The electrodes were made of Ti–TiO_2 (Akat Engineering Company, Turkey) and were 5 cm high, 2 cm long, and 1.5 mm thick. The active surface area of electrodes was 7 cm^2. The electrodes and the cation exchange membrane were tightly coupled together, and the external resistance was set to 10 Ω to transfer electrons from the anode to the cathode via copper wires. The measurements were recorded using an online digital multimeter (Fluke-8846) with 6.5 digits. The current was calculated via the voltage over the 10-Ω, 1-w metal film resistor connected between the anode and the cathode ends. The schematically view of circuit for on-line measurement system is shown in Fig. 2. As is known external resistance in MFC affects current generation, bacterial diversity as well as intermediate metabolism. Lower external

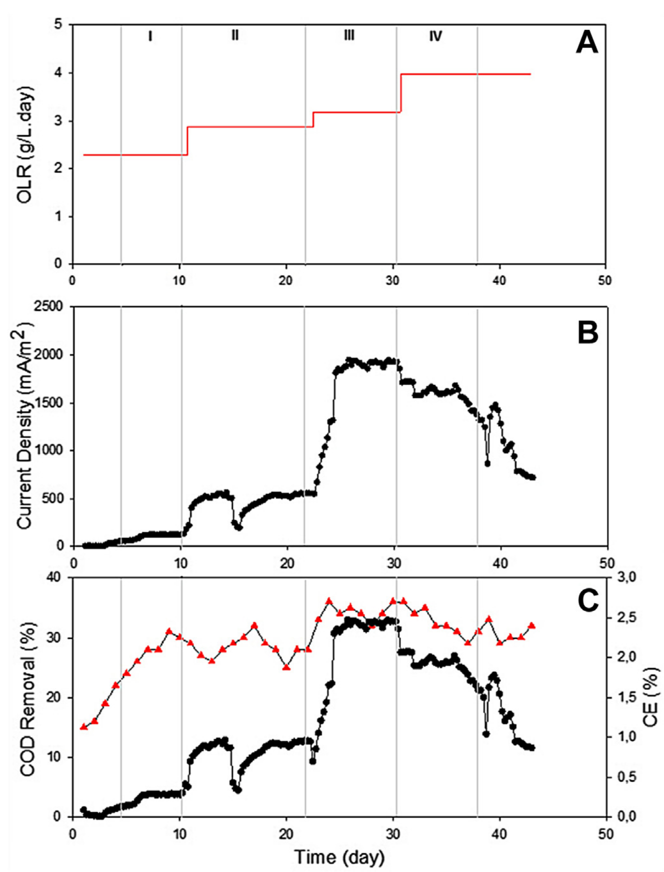

FIG. 3. Time courses of operational parameters OLR (A), current density (B), COD removal and CE (C) in the MFC experiment: I: Raw BBW; II: 50% concentrated BBW; III: 60% concentrated BBW; IV: 70% concentrated BBW; triangles: COD removal; circles: CE.