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Article

# Electricity production by a microbial fuel cell fueled by brewery wastewater and the factors in its membrane deterioration

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ABSTRACT

Electricity production from brewery wastewater using dual-chamber microbial fuel cells (MFCs) with a tin-coated copper mesh in the anode was investigated by changing the hydraulic retention time (HRT). The MFCs were fed with wastewater samples from the inlet (inflow, MFC-1) and outlet (outflow, MFC-2) of an anaerobic digester of a brewery wastewater treatment plant. Both chemical oxygen demand removal and current density were improved by decreasing HRT. The best MFC performance was with an HRT of 0.5 d. The maximum power densities of 8.001 and 1.843 $\mu W/cm^2$ were obtained from reactors MFC-1 and MFC-2, respectively. Microbial diversity at different conditions was studied using PCR-DGGE profiling of 16*S* rRNA fragments of the microorganisms from the biofilm on the anode electrode. The MFC reactor had mainly *Geobacter*, *Shewanella*, and *Clostridium* species, and some bacteria were easily washed out at lower HRTs. The fouling characteristics of the MFC Nafion membrane and the resulting degradation of MFC performance were examined. The ion exchange capacity, conductivity, and diffusivity of the membrane decreased significantly after fouling. The morphology of the Nafion membrane and MFC degradation were studied using scanning electron microscopy and attenuated total reflection-Fourier transform infrared spectroscopy.



## 1. Introduction

Present global energy requirements are mostly dependent on fossil fuels, which are predicted to be depleted because of limited fossil energy sources. The combustion of fossil fuels also has serious negative effects on the environment due to $CO_2$ emission. Climate change, increased global demand for limited oil and natural gas reserves, and energy security have motivated the search for alternatives to fossil fuels [1]. A microbial fuel cell (MFC) is a device to treat wastewater and produce electricity. Microbes attached to the anode of the MFC oxidize substrates such as brewery wastewater and generate electrons and protons in the process. A MFC is a bioelectrochemical system that exploits the bacterial oxidation of biodegradable organic matter to generate electricity [2–4]. The microbial metabolism generates electrons ($e^-$) and protons ($H^+$) by the oxidation of organic substrates, which produces a biopotential. The electrons are transferred to the anode by the bacteria by several mechanisms, such as by a solid transfer matrix or electron shuttling. Electrons are then transferred to the cathode through an external circuit [5]. Brewery wastewater produced in cooling and washing units has a high chemical oxygen de-

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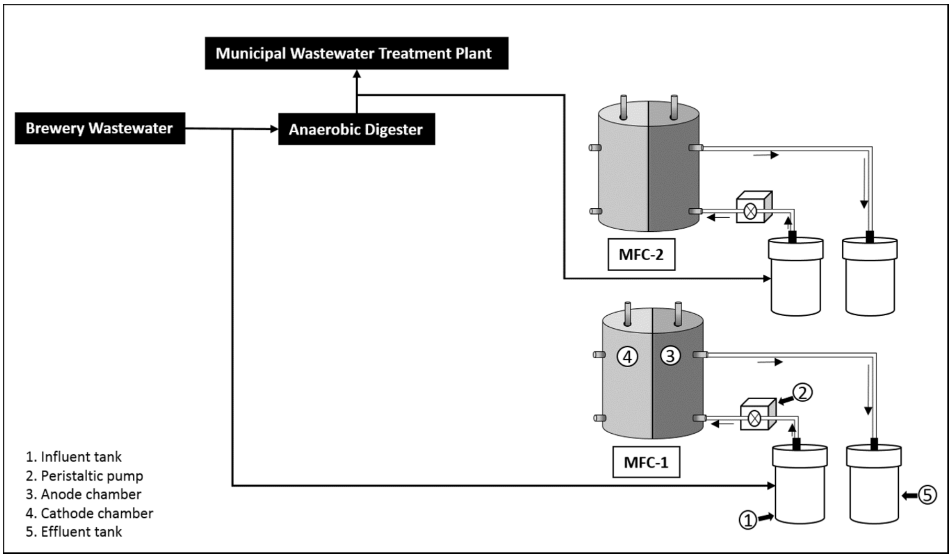


**Fig. 1.** Schematic of the brewery wastewater treatment plant and MFCs.

mand (COD) but is nontoxic. There are electrochemical limitations on the performance of the MFCs because of the discharge resistance, which results from ohmic, kinetic, and transport limitations [6,7]. A reverse correlation exists between the discharge resistance and power output [8,9]. Electrochemical impedance spectroscopy (EIS) is a technique that measures the resistance of a fuel cell [10]. There has been some research on resistance analysis by EIS using simulated artificial wastewater [11]. However, there are few reports using real wastewater.

In this paper, the possibility of continuous electricity production from brewery wastewater using dual-chamber MFCs was studied. The influences of the hydraulic retention time (HRT) on the voltage and power density and the effect of COD removal efficiency on the MFC performance were investigated. A basic electrochemical model of the MFC was set up using the polarization curve, and an elaborate analysis of the various voltage losses was conducted to obtain the net fuel cell *J*–*V* behavior. The surface morphology, dispersion, and functional groups were investigated by scanning electronic microscopy (SEM) and attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy.

## 2. Experimental

### *2.1. MFC construction and operation*

Two identical plexiglass dual-chamber MFCs were constructed on the basis of a previous study [12,13]. The reactors comprised a Nafion® 117 (Dupont) proton exchange membrane (PEM) to separate the partitions and tin-coated copper mesh as the anode and cathode electrodes. The PEM and tin-coated copper mesh had an effective area of 7 $cm^2$ and were fixed in the middle of the two chambers. The volumes of the anode and cathode chambers were 275 $cm^3$, and the effective volumes were 250 $cm^3$. Nafion® 117 was sequentially pretreated at 85 °C for 1 h in 5% $H_2O_2$, distilled water, 0.05 mol/L $H_2SO_4$, and distilled water as described in the literature [7]. The electrodes were in contact with the PEM and the outer surface of the cathode was exposed to distilled water. The electrodes were connected by a titanium wire across a decade resistance box with 500 Ω external resistance at start-up and 100 Ω thereafter, except during the power density and EIS analysis. The MFCs were fed with wastewater samples obtained from the inlet (called the inflow (MFC-1)) and outlet (called the outflow (MFC-2)) of the anaerobic digester of a brewery wastewater treatment plant (Fig. 1). Brewery wastewater was collected from a local brewing plant in Istanbul, which produces malt from barley. The characteristics of the two types of wastewater are given in Table 1.

The MFCs were continuously operated at room temperature (25 ± 2 °C) for approximately 87 d. $N_2$ was sparged to maintain anaerobic conditions in the anodic chamber. The wastewater in the MFC reactors was initially inoculated with a sediment sample obtained from the Golden Horn in Istanbul at a ratio of 1:10. The enrichment of microorganisms was carried out using a 250-mL serum bottle under anaerobic conditions. The enrichment medium was a composition of synthetic wastewater constituents with the following compounds (amount in 1 L deionized water): 9 g glucose, 4 g yeast extract, 4 g $NaHCO_3$, 0.6 g $NH_4Cl$, 9.3 g $NaH_2PO_4{\cdot}H_2O$, 3.2 g $Na_2H_2PO_4$, 0.125 g $K_2HPO_4{\cdot}3H_2O$, 0.1 g $MgCl_2{\cdot}6H_2O$, 0.11 g $CaCl_2{\cdot}2H_2O$, 3.92 g $NaHCO_3$, and trace amounts of metal ions (Fe, Zn, Co, Cu, and Ni) and vitamins [14]. The pH of the medium was 6.7. Cysteine (0.5 g/L) was included in order to keep the medium in an anaerobic condition. The medium (100 mL) was put into the bottle and flushed with nitrogen gas for 5 min to remove the air inside. Then the bottle was capped with a rubber stopper and stirred at 150 rpm with a magnetic stirrer. Each enrichment

**Table 1**
Characteristics of the brewery wastewater.

| Stage | COD (mg/L) | $BOD_5$ (mg/L) | TN (mg/L) | TP (mg/L) |
|---|---|---|---|---|
| MFC-1 | 2250 ± 80 | 650 ± 50 | 35 ± 2 | 33 ± 2 |
| MFC-2 | 480 ± 20 | 250 ± 20 | 10 ± 2 | 12± 4 |