



### The use of mixed algae species as biocathode in membrane-less microbial fuel cell

Karışık alg türlerinin membransız mikrobiyal yakıt hücresinde biyokatot olarak kullanımı

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#### Abstract

Membrane-less microbial fuel cell (MLMFC) is one of the most promising technologies for energy generation from organic wastes. The use of biocathode in the MLMFC system reduces the operation cost and provides many benefits. In an algal MLMFC system, the photosynthetic microorganism facilitates the oxygen reduction in the cathode chamber and improves overall cell performance. However, the assessment of the long-term stability of biocathode is a primary concern. In the current study, the electricity generation of algal MLMFC using mixed-algae as a biocathode was investigated. The results showed that the electricity generation of algal MLMFC increased during the light cycle because of the photosynthesis of algal cells in the cathode. During the light cycle, the maximum power density and lowest cathode charge transfer resistance of algal MLMFC were 215.71 mW/m<sup>2</sup> and 29.73  $\Omega$ , respectively. The electrochemical analysis demonstrated that the anode biofilm of algal MLMFC has high bioelectrogenic activity. This study plays a crucial role in determining the applicability of this technology.

Keywords: Membrane-less microbial fuel cell, Biocathode, Mixed algae, Power density.

#### Özet

Membransız mikrobiyal yakıt hücresi (MMYH), organik atıklardan enerji üretimi için en umut verici teknolojilerden biridir. MMYH sisteminde biyokatot kullanımı işletme maliyetini düşürür ve birçok fayda sağlar. Algal bir MMYH sisteminde, fotosentetik mikroorganizma, katot bölümünde oksijen azalmasını kolaylaştırır ve genel hücre performansını iyileştirir. Bununla birlikte, biyokatodun uzun vadeli stabilitesinin değerlendirilmesi birincil endişe kaynağıdır. Mevcut çalışmada, biyokatot olarak karışık alg kullanan algal MMYH'nin elektrik üretim performansı araştırılmıştır. Sonuçlar, katottaki alg hücrelerinin fotosentezi nedeniyle ışık döngüsü sırasında algal MMYH'nin elektrik üretiminin arttığını gösterdi. Işık döngüsü sırasında, algal MMYH'nin maksimum güç yoğunluğu ve en düşük katot transfer direnci sırası ile 215.71 mW/m<sup>2</sup> ve 29.73  $\Omega$  idi. Elektrokimyasal analiz, algal MMYH'nin anot biyofilminin yüksek biyoelektrojenik aktiviteye sahip olduğunu göstermiştir. Bu çalışma, bu teknolojinin uygulanabilirliğinin belirlenmesinde çok önemli bir rol oynamaktadır.

Anahtar kelimeler: Membransız mikrobiyal yakıt hücresi, Biyokatot, Karışık alg, Güç yoğunluğu.

# 1. Introduction

Microbial fuel cells (MFCs) are reactors that generate bioelectricity by converting chemical energy into electrical energy. [1]. MFCs can produce electricity and wastewater treatment simultaneously. In an MFC, the bacteria in the biofilm on the anode electrode produce electrons (e<sup>-</sup>) by consuming organic wastes fed in anode and transfer to the anode electrode [2]. These electrons move to the cathode on the external resistance and are used by a reduction reaction [3]. The reduction of oxygen in the cathode can produce a theoretic open-circuit voltage of 1.16V [4]. However, the low cathode performance, energy loss, low electrode activity, and low oxygen transfer from the atmosphere to the cathode liquid limits cathode performance [5]. Different cathode catalysts are generally used to improve the cathode performance of MFCs to provide effective oxygen reduction in the cathode chamber. The platinum (Pt) is a commonly used catalyst used in the cathode of MFC, which has a substantial reduction activity to provide a high cathodic potential [6]. In some previous studies, the

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 $MnSO_4$ ,  $MnO_2$ , and catalysts of carbon nanotube-supported  $MnO_2$  are cheaper than platinum, were used instead of platinum [7]. In addition to this, the cost and disposal of chemical catalysts still restrict the improvement of MFCs [8].

In addition to the use of chemical catalysts in the cathode of MFCs, the development of biocathodes has a significant potential for wastewater treatment and large-scale applications of the MFCs [9]. In particular, photosynthetic oxygen generation is quite interesting to provide oxygen as an electron acceptor and eliminate the energy requirement [10]. Recent studies using pure culture as biocathode suggest that the electron transfer mechanism of various strains could be critical. [8, 11]. Many algae species have been used as biocathode in MFCs, such as *Scenedesmus acutus* [12], *Chlorella vulgaris* [10], *Chlorella* sp. [13]. Although the previous studies demonstrated the increase in cathode performance of MFCs using photosynthetic microorganisms, the implementation of the biocatalyzed biocathodes is still unclear, as many studies have been carried out for the short-term operation [8].

In this study, the mixed microalgae were used as biocathode in the cathode chamber of algal MLMFC. The performance of algal MLMFC was evaluated by electrochemical analysis and the concentration of DO measurement in the cathode chamber.

# 2. Material and Methods

# 2.1. Cultivation of mixed algae

The algal samples were collected from the Keban Lake (Elazig). It was then cultivated in a photobioreactor system described in our previous study using BG-11 medium [14]. The photobioreactor system was operated with 75  $\mu$ mol photons/m<sup>2</sup>s. The cultivated algal biomass was used in the cathode chamber of the MLMFC as a biocathode.

# 2.2. Construction of algal MLMFC and operation

The schematic diagram of the algal MLMFC system is shown in Figure 1. A cylindrical plastic container was used as the algal MLMFC reactor. The dimensions of the algal MLMFC were 7 cm in diameter and 18 cm in height. The platinum mesh and stainless steel mesh were used as cathode and anode electrodes [15].



Figure 1. The schematic diagram of algal MLMFC

A sand layer of 3 cm was filled on the anode chamber to physically separate the cathode and anode chambers and prevent the transport of anode medium to the cathode chamber. The height of the anode and cathode chambers was 8 cm. The anode and cathode electrodes were fixed with an external resistance of 1000  $\Omega$ . The wastewater treatment sludge obtained from the Elazig municipal wastewater treatment plant was used as a substrate for anode microorganisms. The anode chamber was covered with an aluminum folio to prevent growing photosynthetic microorganisms in the anode chamber of algal MLMFC. The cathode chamber of algal MLMFC was illuminated with a light intensity of 60  $\mu$ mol photon/m<sup>2</sup>.s using a fluorescence lamp.

### 2.3. Analysis

The voltage of algal MLMFC was measured using 34970A digital multimeter (Data Acquisition/Switch Unit) and saved to the computer. The electrochemical analysis of algal MLMFC was carried out Gamry Interface 1000 potentiostat (Gamry, Warminster, PA). The electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) analysis were carried out described in Taşkan [16]. The EIS data were fitted using a circuit model (Figure 4) given by Abazarian, et al. [13]. The concentration of dissolved oxygen (DO) was measured with a time interval of 15 min using a digital multimeter (Hach Lange HQ40D, Germany).

### 3. Results and Discussion

#### 3.1. The DO concentration in the cathode

The algal cells produce oxygen under light conditions by photosynthesis, and they use the oxygen under dark conditions for respiration. Figure 2 shows the change in DO concentration in a day under dark and light conditions. It was determined that the maximum DO concentration of the cathode reached 14.79 mg/L at the end of the light period and significantly decreased with the turn of the fluorescence lamp. Kakarla and Min [12] reported a maximum DO concentration of 15.7 in the cathode of the biocathode MFC using *Scenedismus obliquus* in the cathode. Abazarian, et al. [13] reported a maximum DO concentration of  $6.3 \pm 0.1$  mg/L in the cathode of MFC using mechanical aeration. The maximum DO concentration obtained in this study is more than two times the value obtained by Abazarian, et al. [13]. Additionally, a positive correlation between voltage and DO concentration was determined.



Figure 2. One-day DO concentration variation of the cathode chamber

#### 3.2. Power density

Figure 3 shows the power curve of algal MLMFC. The maximum power density of the algal MLMFC was determined to be 215.71 mW/m<sup>2</sup>. The maximum power density is relatively higher than literature values obtained by MFC with the algal cathode. The previous studies reported a positive correlation between power density and DO concertation in the cathode of MFC [17]. A maximum power density of 153 mW/m<sup>2</sup> was reported by a previous study, using *Scenedismus obliquus* in the cathode of MFC [12]. The obtained maximum power density of this study is higher than that obtained by Kakarla and Min [12]. In another study, the maximum power density produced by using *Chlorella* sp. as a photosynthetic biocathode in sediment-type MFC was reported to be 19.6 mW/m<sup>2</sup> [13].



Figure 3. Power density curve

#### 3.3. Electrochemical characterization of algal MLMFC

The circuit model and fitted EIS results are shown in Figure 4. The performance of cathodic oxygen reduction reactions in an MFC is relatively crucial to improving MFC's performance. The high DO concentration in the chamber of cathode promotes the electricity generation performance of MFC. The determination of constitution and distribution of internal resistance is required to increase MFC performance and obtain optimum power density [18, 19]. The performance of algal MLMFC can be increased by decreasing the components of internal resistance. The analysis of EIS was performed to investigate the components of the internal resistance of MFC. In the circuit model,  $R_{ct}$  is charge transfer resistance,  $R_{mt}$  is mass transfer resistance,  $R_s$  is solution resistance,  $R_o$  is other resistances in the cathode, and CPE is double-layer constant phase elements. The  $R_s$  and  $R_{ct}$  of the algal MLMFC were 51.55  $\Omega$  and 29.73  $\Omega$ . Consequently, biocathode in MFCs can make the distribution of electrons easy and improve the system performance incredibly.



Figure 4. Equivalent circuit model and nyquist plot

# 4. Conclusion

The current study used the mixed algae culture as biocathode in algal MLMFC. The electricity generation performance of algal MLMFC was investigated in detail. The results showed that the dark and light periods are very effective on the performance of algal MLMFC. The performance of reactor increased during the light period. Algal MLMFC produced a high-power density of 215.71 mW/m<sup>2</sup>. The results showed that the photosynthetic biocathode facilitates the oxygen reduction reaction at the cathode and the potential applicability of this technology.

# 5. Author Contribution Statement

In the study, Author 1 contributed (I) making the design and literature review, (ii) to form the idea, the analysis of the results, provision of the materials, and examination of the results, (iii) to checking the spelling and checking the article in terms of content.

#### 6. Ethics Committee Approval and Conflict of Interest

There is no need for an ethics committee approval in the prepared article. There is no conflict of interest with any person/institution in the prepared article.

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