Dokuz Eylül Üniversitesi Mühendislik Fakültesi Fen ve Mühendislik Dergisi
Dokuz Eylul University Faculty of Engineering Journal of Science and Engineering

Basılı/Printed ISSN: 1302-9304. Elektronik/Online ISSN: 2547-958X

Wastewater Treatment and Electricity Generation with Different Cathode Solutions in MFC

MYH'de Farklı Katot Çözeltileri ile Atıksu Arıtımı ve Elektrik Üretimi

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Geliş Tarihi / Received: 20.11.2022 *Araştırma Makalesi/Research Article*
Kabul Tarihi / Accepted: 09.01.2023 *DOI:10.21205/deufmd.2023257420*
Atıf şekli/ How to cite: EKER,S.(2023). Wastewater Treatment and Electricity Generation with Different Cathode Solutions in MFC. DEUFMD, 25(74), 513-523.

Abstract

A microbial fuel cell (MFC) with cathode and anode chambers was utilized to generate power while simultaneously removing COD from wastewater. By utilizing various oxidant solutions, it is possible to increase the generated voltage. The anode chamber was used for anaerobic treatment of synthetic wastewater (approximately 1000 mg/L), whereas the cathode chamber contained various oxidant solutions such as dilute hydrogen peroxide (300 mg/L), $KMnO_4$ (300 mg/L), $K_2Cr_2O_7$ (300 mg/L) and Fenton reagent (H2O2/Fe(II), 300/20 mg/L). Aerobic wastewater treatment and intermittent ozonation were also tested in the cathode chamber. With intermittent ozonation of the cathode chamber, the highest power output (382 mW/m^2) was obtained. At the conclusion of the operation period, the COD concentration in the anode chamber decreased from 1170 mg/L to 650 mg/L, resulting in nearly 45% COD removal. In the cathode chamber, the use of diluted $KMnO_4$ and H_2O_2 solutions produced high power densities of 35 and 23 W/m^2, respectively, while the other oxidants produced low power densities. At the end of 72 hours, the COD content of the anaerobic chamber decreased from 800 mg/L to nearly 333 mg/L, resulting in nearly 59% COD removal for the $KMnO_4$ solution. Considering the high cost of ozonation, it is recommended that either aerobic wastewater treatment or dilute $KMnO_4$/H_2O_2 solutions should be used in the cathode chamber for high power generation.

Keywords: *Cathode Solution; Electricity Generation; Microbial Fuel Cell (MFC); Wastewater Treatment*

Öz

Eş zamanlı olarak atık sudan KOİ giderimi sağlanırken güç üretmek için katot ve anot odalarına sahip bir mikrobiyal yakıt hücresi (MYH), kullanılmıştır. Çeşitli oksidan çözeltileri kullanarak üretilen voltajı artırmak mümkündür. Anot bölümünde sentetik atık suyun (yaklaşık 1000 mg/L) anaerobik arıtımı sağlanırken, katot bölümü seyreltik hidrojen peroksit (300 mg/L), $KMnO_4$ (300 mg/L), $K_2Cr_2O_7$ (300 mg/L) ve Fenton reaktifi (H_2O_2/Fe(II), 300/20 mg/L) gibi çeşitli oksidan çözeltiler içermektedir. Aerobik atık su arıtma ve aralıklı ozon da katot bölümünde test edilmiştir. Katot bölümünün aralıklı ozonlanması ile en yüksek güç çıkışı (382 mW/m^2) elde edilmiştir. Çalışma periyodunun sonunda, anot odasındaki KOİ konsantrasyonu 1170 mg/L'den 650 mg/L'ye düşmüş ve yaklaşık %45 KOİ giderimi sağlanmıştır. Katot odasında seyreltilmiş $KMnO_4$ ve H_2O_2 çözeltilerinin kullanımı sırasıyla 35 ve 23 W/m^2'lik yüksek güç yoğunlukları üretirken, diğer oksidanlar düşük güç yoğunlukları üretmiştir. 72 saatin sonunda, anaerobik bölümün KOİ içeriği 800 mg/L'den yaklaşık

333 mg/L'e düşmüş ve $KMnO_4$ çözeltisi için yaklaşık %59 KOİ giderimi ile sonuçlanmıştır. Ozonlamanın yüksek maliyeti göz önüne alındığında, yüksek güç üretimi için katot odasında ya aerobik atıksu arıtımı ya da seyreltik $KMnO_4/H_2O_2$ çözeltilerinin kullanılması önerilmektedir.

Anahtar Kelimeler: *Katot Çözümü; Elektrik Üretimi; Mikrobiyal Yakıt Hücresi (MFC); Atık su arıtma*

1. Introduction

Due to high aeration requirements and large wastewater volumes, the treatment processes require considerable capital investment and operating costs. In order to reduce the high cost of wastewater treatment operations, the generation of energy from some industrial wastewaters or the formation of commercial products have received considerable attention in recent years. One promising approach is to generate electricity from wastewaters during biological treatment using microbial fuel cells (MFC) which consist of anode and cathode compartments separated by a proton exchange membrane (PEM) or a salt bridge [1-11]. In the anode chamber, anaerobic organisms degrade organic compounds present in wastewater, generating electrons and protons while removing COD, where the electrons are transferred to the cathode through an external circuit and protons diffuse through the membrane or the salt bridge. Electrons and protons transferred to the cathode combine with oxygen to form water in the cathode compartment.

Mediator-containing and mediatorless fuel cells are the two major types of microbial fuel cells [12]. Some of the MFCs are electrochemically inactive, requiring mediators such as thionine, methyl viologen, and humic acid to transfer the electrons from the anode to the cathode compartment [13,14]. Mediatorless MFCs utilize electrochemically active bacteria such as *Shewanella putrefaciens* [15], *Aeromonas hydrophila* [16], *Geobacteraceae* [17, 18], and *Rhodoferax ferrireducens* [1] to generate electricity from organic acids and glucose. In studies, activated sludge bacteria were shown to produce electricity from domestic wastewater using MFCs with no mediators and electrochemically active special bacteria. Different substrates such as glucose, proteins, and organic acids were used for electricity generation by MFCs [8,10,18-20].

Some of the factors affecting the performance of a MFC are the type, concentration, and energy content of the substrate (carbohydrates, organic acids, proteins, lipids, and hydrocarbons), the type and surface area of anode and cathode materials, the type and surface area of the proton exchange membrane or the salt bridge, the resistance of the circuit, the pH and oxidation-reduction potential (ORP) of the cathode and anode chambers, and the proximity of the electrodes [21-25]. Anodes were typically graphite or carbon paper, with Pt-graphite cathodes [8,10,19-21]. Early studies [21,27] used an agar-salt bridge to separate the chambers and transfer proton, but this was later replaced by proton exchange membranes (PEM) due to high internal resistance. The most widely used PEM has been Nafion 117 (DuPont, Delaware, USA). Different wastewaters were used in MFCs for electricity generation [8,20,24]. The generation of electricity from sludges and marine sediments was investigated recently by using graphite foil electrodes [28]. MFCs originally had poor power production efficiency, but subsequent adjustments to their design, components, and operation have significantly increased their power output, allowing them to be used in wastewater treatment, biosensors, and bioremediation [29]. MFC converts waste into usable energy, but its practical applications are restricted to labs and research. Thus, MFCs are being designed to maximize their performance for removal of pollutants and electricity production. Biocatalytic cathode responses in the MFC cause voltage inversion and ionic shorting. In biocathodes, microorganisms play an active role in the chemical reactions that take place. Increasing MFCs' strength and variety will boost commercial utilization. High-performance MFCs that generate high power without limitations need much work. Synergy with other wastewater treatment innovations may accelerate MFC use. [30,31].

In the light of the literature reports, the major objective of this study is to compare different oxidant solutions in the cathode chamber with the possibility of improving the power generation by the MFC. The composition of the synthetic wastewater in the anaerobic (anode) chamber was kept constant while the type of oxidant solutions in the cathode was varied throughout the study. Instead of using classical graphite electrodes as reported in the literature, copper (Cu) and gold-covered copper (Cu-Au) wires were used as anode and cathode, respectively, with a surface area of 68 cm^2 for each electrode. Also, a salt (2% w/v)-containing agar (10% w/w) layer was used between the anode and cathode chambers instead of a proton exchange membrane (PEM). Chemical oxygen demand (COD) reduction and energy generation were performed on synthetic wastewater, including diluted molasses.

2. Materials and Methods

2.1. Experimental Set up

Figure 1 depicts a diagram of the experimental studies' microbial fuel cell, which consisted of two chambers separated by a salt-bridge. Each chamber measured 10 x 12 x 12 cm and contained a total volume of 1440 ml and a liquid volume of 1300 ml. The anode and cathode electrodes were copper (Cu) and gold-coated copper (Cu-Au) wires, each measuring 120 cm in length, 0.18 cm in diameter, and 68 cm^2 in external surface area. A copper wire containing 100 ohms of resistance was used to connect the electrodes.

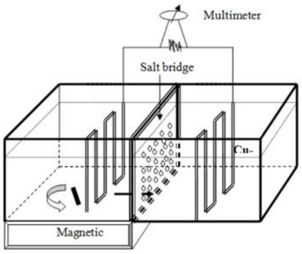

Figure 1. A schematic diagram of the microbial fuel cell used in experimental studies

Şekil 1. Deneysel çalışmalarda kullanılan mikrobiyal yakıt hücresinin şematik diyagramı

Using a multimeter (avometer), the voltage difference (mV) between the ends of the resistance was measured. The anaerobic chamber (anode) was separated from the cathodic chamber (cathode) by a salt bridge comprised of a salt-containing agar layer placed between two perforated plexiglass plates. Using silicone sealant, the plexiglass plate was attached to the reactor to prevent wastewater from leaking between the chambers. In each chamber, the electrodes were completely submerged in the wastewater.

2.2. Wastewater composition

In our studies, we used wastewater prepared from diluted molasses, urea, KH_2PO_4, and $MgSO_4$. The COD/N/P ratio in the aerobic chamber was 100/8/2, and in the anaerobic chamber, it was 100/2/1. When aerobic wastewater treatment was used, the COD level in the wastewater was around 1000 mg/L in both the anaerobic (anode) chamber and the cathodic chamber. Cathodic chamber contained one of the following solutions: (a) dilute H_2O_2 solution (300 mg/L); (b) dilute $KMnO_4$ solution (300 mg/L); (c) dilute $K_2Cr_2O_7$ solution (300 mg/L); (d) Fenton reagent (H_2O_2/Fe(III), 300/20 mg/L); (f) intermittent ozonation of water in the cathode; and (g) aerobic wastewater treatment. The initial pH of the wastewater in both chambers was constant at 7 ± 0.5 with phosphate buffer addition to both chambers. When aerobic wastewater treatment was realized in the cathode, the wastewater was aerated by using an air pump and diffusors to keep dissolved oxygen (DO) above 2 mg/L. The wastewater in the anaerobic chamber was mixed with 200 mg/L of Na-thioglycolate to keep the oxidation-reduction potential (ORP) below -200 mV. ORP values in the anaerobic chamber were between -200 and -300 mV, while ORP values in the aerobic cathode chamber were between +50 and +400 mV, depending on the solution used.

2.3. Microorganims

Mixed anaerobic culture used to inoculate the anodic chamber was obtained from the acidogenic unit of the anaerobic wastewater treatment plant of PAKMAYA Bakers Yeast Company in Izmir, Turkey. Aerobic chamber organisms were obtained from the aeration tank of the activated sludge unit of the same company.

2.4. Experimental Procedure

In the cathode chamber, a series of batch tests were conducted with various oxidant solutions. The agar-salt bridge was sandwiched between two perforated plexiglass plates and attached to the reactor using silicone sealant. The synthetic wastewater containing Na-thioglycolate was used to fill the anaerobic chamber (anode), which was then inoculated with an anaerobic inoculum culture. The cathode chamber contained dilute oxidant solutions or wastewater to be treated aerobically. The initial pH of the anaerobic chamber was adjusted to 7±0.5, and phosphate buffer was added to maintain a pH of 7 throughout the experiment. The initial pH of the cathodic chamber varied depending on the oxidant solution. The cathodic chamber was sometimes given ozone to keep the amount of ozone above a certain level. Dilute oxidant solutions were added to the cathodic chamber when necessary in order to keep the oxidant levels above the threshold. The batch experiments lasted 144 hours. Daily pH, ORP, and COD measurements were performed on samples taken from both chambers. Experiments were conducted at a temperature of 23±2 ^oC.

2.5. Analytical Methods

Samples withdrawn from each chamber everyday was centrifuged at 8000 rpm (7000g) to remove organisms from the aqueous phase and the analysis were carried out using the clear supernatants after centrifugation. According to Standard Methods, COD analysis was conducted using the closed reflux technique [32]. A multimeter (New Digital, Model MY62) was utilized to record the voltage difference (mV) between the ends of the 100 ohm resistance, which was then converted to power (mW) using the equation $P = V^2/R$ or current intensity by $I = V/R$. pH and oxidation-reduction potential (ORP) measurements were done by using pH and ORP electrodes along with pH and ORP meters (WTW Scientific,Germany).

3. Results and Discussion

Seven sets of batch experiments were performed with different cathodic chamber solutions where the voltage differences were recorded four times a day along with daily COD measurements during the course of experiments.

3.1. Dilute hydrogen peroxide solution in the cathode chamber

The synthetic wastewater (COD_o = 1000 mg/L) in the anode chamber was treated anaerobically while the cathode chamber contained dilute H_2O_2 solution (300 mg/L) in this experiment. Figure 2 depicts time course of variations of current (mA), power density based on anode surface area (mW/m^2) and COD in the anodic chamber. The voltage difference decreased from an initial value of 125 mV to nearly 55 mV and remained constant for the last three days. The current and the power density also decreased from initial values of 1.25 mA and 23 mW/m^2 to 0.55 mA and 4.0 mW/m^2, respectively after three days of operation and remained almost constant for the last three days. The highest voltage difference (125 mV), current (1.25 mA) and power densities (23 mW/m^2) were obtained during the first day of operation. COD content of the anaerobic chamber decreased from 910 mg/L to nearly 60 mg/L at the end of 144 hours yielding 93% COD removal. Almost 50% of the total COD was removed during the first day of operation. The power density and the current reached almost constant levels of approximately 4.0 mW/m^2 and 0.55 mA after three days of operation. The ORP in the anaerobic chamber decreased from -200 mV to -300 mV while the pH decreased slightly from 7.2 to 6.8. ORP level in the aerobic chamber was around +200 ± 20 mV and the pH was around 7.5 ± 0.2 throughout the operation. The initial biomass concentration in the anode chamber was 1430 mg/L yielding a specific COD removal rate of 4.13 mgCOD/g biomass.h, for the whole operation.

3.2. Dilute hydrogen peroxide solution in the cathode chamber

The anode chamber contained synthetic wastewater (COD_o = 1000 mg/L) which was treated anaerobically while dilute $KMnO_4$ solution (300 mg/L) was used in the cathode as the oxidant solution. This experiment lasted for three days (72 h) due to operational problems. Time course of variations of current (mA), power density based on anode surface area (mW/m^2) and COD in the anodic chamber are depicted in Figure 3. The voltage difference decreased from an initial value of 154 mV to nearly 72 mV within the first two days which further decreased to 18 mV in the third day. The current and the power density also decreased from initial values of 1.54 mA and 35 mW/m^2 to 0.723 mA and 7.7 mW/m^2, respectively within the first two days which further decreased to 0.182 mA and 0.5 mW/m^2 at the end of 72 hours. COD content of the anaerobic chamber decreased from 800 mg/L to nearly 333 mg/L yielding nearly 59% COD removal at the end of 72 hours. The current and the power densities for the first two days were 0.72 mA and 7.7 mW/m^2. The ORP in the anaerobic chamber decreased from -200 mV to -290 mV while the pH decreased from 7.0 to 6.6. The ORP level in the aerobic chamber decreased from +490 to +230 mV and the pH was constant around 7.5 throughout the operation. High ORP levels (> 400 mV) or highly oxidative conditions in the cathode resulted in high power generation (35 mW/m^2) with dilute $KMnO_4$ solution. The initial biomass concentration in the anaerobic anode chamber was 1250 mg/L yielding a specific COD removal rate of 5.22 mgCOD/g biomass.h, for the whole operation.

3.3. Dilute $K_2Cr_2O_7$ solution in the cathode chamber

The synthetic wastewater (COD_o = 1000 mg/L) in the cathode chamber was treated anaerobically while the anode contained dilute $K_2Cr_2O_7$ solution (300 mg/L). The voltage difference decreased from an initial valu of 20 mV to nearly 4 mV at the end of the third day which further decreased to 3 mV at the end of 120 h (Data not shown). The current intensity and the power density also decreased from initial values of 0.20 mA and 0.59 mW/m^2 to 0.04 mA and 0.02 mW/m ^{2}, respectively which further decreased to 0.03 mV and 0.01 mW/m^2 at the end of the operation. COD content of the anaerobic chamber decreased from 900 mg/L to nearly 375 mg/L at the end of 120 hours yielding 58% COD removal. The ORP in the anaerobic chamber decreased from -216 mV to -345 mV while the pH decreased slightly from 7 to 6.8. ORP level in the aerobic chamber decreased from +180 to +50 mV and the pH was constant around 7.0 throughout the operation. $K_2Cr_2O_7$ solution in the cathode chamber resulted in the lowest power densities due to lower ORP levels in the cathode. The initial biomass concentration in the anaerobic anode chamber was 1010 mg/L yielding a specific COD removal rate of 4.33 mgCOD/g biomass.h, for the whole operation. Use of dilute dichromate solution is not recommended in the cathodic chamber due to low power generation.

3.4. Fenton reagent (H_2O_2/ Fe(II)) in the cathode chamber

Fenton reagent (H_2O_2 /Fe(II), 300/ 20 mg/L) was used as the oxidant solution in the cathode chamber with intermittent H_2O_2 (300 mg/L) addition while the anodic chamber contained anaerobically treated synthetic wastewater (COD_o = 1000 mg/L). Time course of variations of current (mA), power density (mW/m^2) and COD in the anodic chamber are depicted in Figure 4. The voltage difference decreased from an initial value of 75 mV to nearly 47 mV within the first two days and remained constant for the next 3 days which further decreased to 36 mV at the sixth day. The current and the power density also decreased from initial values of 0.75 mA and 8.3 mW/m^2 to 0.47 mA and 3.2 mW/m^2 after five days of operation, respectively which further decreased to 0.36 mA and 1.9 mW/m^2 at the end of 144 hours. COD content of the anaerobic chamber decreased from 1100 mg/L to nearly 176 mg/L at the end of 144 h yielding about 84% COD removal. The current (0.47 mA) and the power density (3.2 mW/m^2) reached almost a constant level for the time period between 48 and 120 hours. The ORP in the anaerobic chamber decreased from -300 mV to -320 mV while the pH was almost constant around 6.7. ORP level in the aerobic chamber decreased from +529 to + 250 mV and the pH increased from 3 to 5.5. Fenton reagent utilization in the cathode is not recommended due to low voltage and power generation. Intermittent H_2O_2 additions increased the power generation slightly. The initial biomass concentration in the anaerobic anode chamber was 1170 mg/L yielding a specific COD removal rate of 5.52 mgCOD/g biomass.h, for the whole operation.

3.5. Modified fenton reagent (H_2O_2/ Fe(III)) in the cathode chamber

Modified Fenton reagent (H_2O_2 /Fe(III), 300/ 20 mg/L) was used as the oxidant solution in the cathode chamber with intermittent H_2O_2 (300 mg/L) addition while the anode chamber contained anaerobically treated synthetic wastewater (COD_o = 1000 mg/L). Intermittent additions of H_2O_2 solutions increased the voltage difference and therefore, the power generation. The voltage difference decreased from an initial value of 55 mV to nearly 38 mV within the first two days and remained almost constant for the next four days. The current and the power density also decreased from initial values of 0.50 mA and 3.8 mW/m^2 to 0.38 mA and 2.1 mW/m^2, respectively within the first two days and remained constant for the last four days (Data not shown). COD content of the anaerobic chamber decreased from 910 mg/L to nearly 336 mg/L at the end of 144 h resulting in 63% COD removal. The final levels of current and the power density were 0.38 mA and 2.1 mW/m^2 for the last four days. The ORP in the anode chamber increased from an initial value of -235 mV to -170 mV and the pH increased from 6 to 6.6 at the end of operation. ORP in the cathode chamber decreased from +310 mV to +280 mV and the pH increased from 3.5 to 5.5. Modified Fenton reagent did not generate as much power as the Fenton reagent in the cathode due to lower ORP levels and is not recommended. The initial biomass concentration in the anaerobic anode chamberwas 1150 mg/L yielding a specific COD removal rate of 3.47 mgCOD/g biomass.h, for the whole operation.

3.6. Aerobic wastewater treatment in the cathode chamber

Before the aerobic biological wastewater treatment was tested in the cathode chamber, aerated water was used in the cathode with vigorous aeration to keep dissolved oxygen (DO) above 2 mg/L. The anode contained anaerobically treated synthetic wastewater with an ORP of -200 mV. The ORP in the aerated water of the cathode chamber was low (+25 mV). The generated power decreased from an initial value of 1 mW/m^2 to nearly 0.65 mW/m^2 within 96 hours. COD in the anode decreased from 1100 mg/L to 800 mg/L with only 28% COD removal at the end of 96 hours. Since the generated power was low with the aerated water in the cathode chamber, this set of data was not presented in details and this option was not considered further.

Aerobic biological treatment was considered as a viable option in the cathode where the cathode chamber contained aerobic activated sludge organisms treating wastewater (COD$_o$ = 1000 mg/L) while anaerobic treatment was taking place (COD$_o$ = 1000 mg/L) in the anode chamber. Aerobic chamber was aerated using an air pump and diffusors to keep DO level above 2 mg/L. Time course of variations of current (mA), power density (mW/m^2 anode) and COD in the anode and cathode chambers are depicted in Figure 5. Voltage difference increased from an initial value of 29 mV to 48 mV within the first three days and then decreased to 28 mV at the end of the sixth day. Accordingly, the current and power density increased from an initial levels of 0.29 mA and 1.2 mW/m^2 to maximum levels of 0.48 mA and 3.4 mW/m^2 after three days of operation which decreased further to 0.28 mA and 1.2 mW/m^2 at the end of operation. COD contents of the aerobic and anaerobic chambers decreased from initial levels of 915 and 840 mg/L to 50 and 470 mg/L, yielding 95% and 49% COD removals, respectively at the end of 144 h. The ORP in the anaerobic chamber decreased from -430 mV to -280 mV while the pH was constant around 7.2. The ORP in the aerobic cathode chamber increased from + 32 mV to +65 mV while the pH was almost constant at 7.4. The maximum power generated by the MFC with aerobic wastewater treatment in the cathode (3.4 mW/m^2) was lower than those obtained with H2O2 and KMnO$_4$ solutions. However, in this case COD removal was realized in the cathode along with the anode at the expense of aeration costs. The initial biomass concentration in the anaerobic and aerobic chambers were 930 and 1705 mg/L yielding specific COD removal rates of 2.74 and 3.53 mgCOD/g biomass. h, respectively.

3.6. Ozonation in the cathode chamber

Water in cathode chamber was ozonated intermittently in this experiment by using an ozone generator to provide a highly oxidant media in the cathode while the anode chamber was used for anaerobic treatment of the synthetic wastewater (COD$_o$ = 1000 mg/L). Ozone loading rate was 5.8 g ozone/h when ozonation was applied. Time course variations of current (mA), power density (mW/m^2 anode) and COD in the anode chamber are depicted in Figure 6. Voltage difference increased upon introduction of ozone to the cathode chamber by intermittent ozonation which resulted in increases in current and power densities. Voltage difference varied between 160 and 50 mV depending on ozone concentration in the cathode. Accordingly, the current varied between 1.6 and 0.5 mA while the power density was between 38 and 3.6 mW/m^2. The average power density with ozonation was around 12.5 mW/m^2 between 48 and 120 h of operation which is considerably higher than those obtained with the other oxidant solutions. COD concentration in the anode chamber decreased from 1170 mg/L to 650 mg/L at the end of the operation period yielding nearly 45% COD removal. The ORP in the anaerobic chamber decreased from -300 mV to -410 mV and the pH increased from 6.0 to 6.6 at the end of operation. ORP level in the cathode chamber decreased from +100 mV to +30 mV and the pH increased from 7 to 7.4. The initial biomass concentration in the anaerobic anode chamber was 910 mg/L yielding a specific COD removal rate of 3.96 mgCOD/g biomass. h, for the whole operation. Highly negative ORPs obtained in anode and highly oxidative conditions in the cathode resulted in high power generations with ozonation. Both the maximum (38 mW/m^2) and the average (12.5 mW/m^2) power generations obtained with intermittent ozonation were considerably higher than those obtained with the other oxidants. However, considering the cost of ozone generation this option may not be economically favorable.

The maximum and the average power densities obtained with different oxidants in the cathode are summarized in Table 1 for comparison. The power generated by ozonation is much higher than the results reported in MFC literature using agar-salt bridge instead of PEM. This is because of highly oxidative nature of ozone. The highest power densities obtained with dilute KMnO4 (35 mW/m^2) and H2O2 (23 mW/m^2) solutions in the cathode are also higher than some of the literature reports indicating the effectiveness of the MFC configuration used in this study.

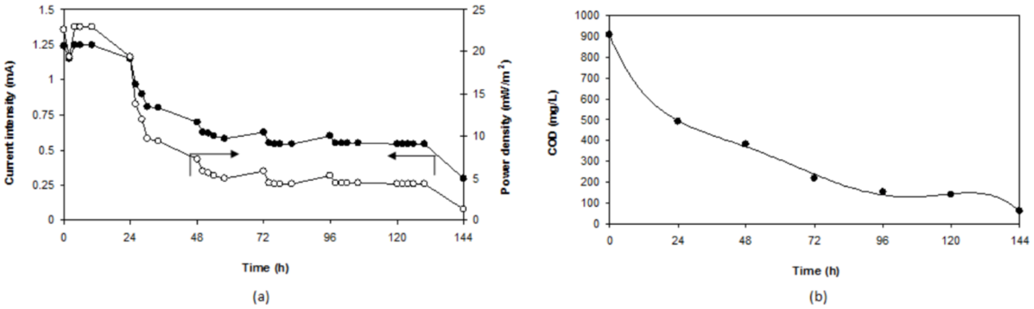

Figure 2. Variations of current (●) and power density (○)(a), COD(b) in the anode chamber with time when dilute H_2O_2 was used in the cathode

Şekil 2. Katotta seyreltik H_2O_2 kullanıldığında anot odasındaki akım (●) ve güç yoğunluğunun (○)(a), KOİ'nin (b) zamana göre değişimi

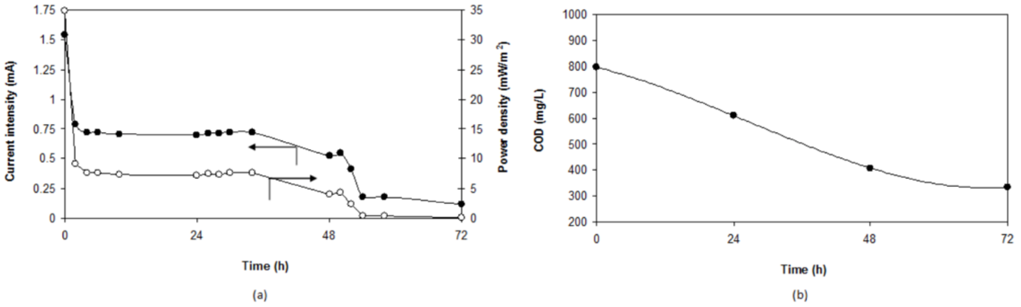

Figure 3. Variations of current (●) and power density (○)(a), COD(b) in the anode chamber with time when dilute $KMnO_4$ was used in the cathode

Şekil 3. Katotta seyreltik $KMnO_4$ kullanıldığında anot odasındaki akım (●) ve güç yoğunluğunun (○)(a), KOİ'nin (b) zamana göre değişimi

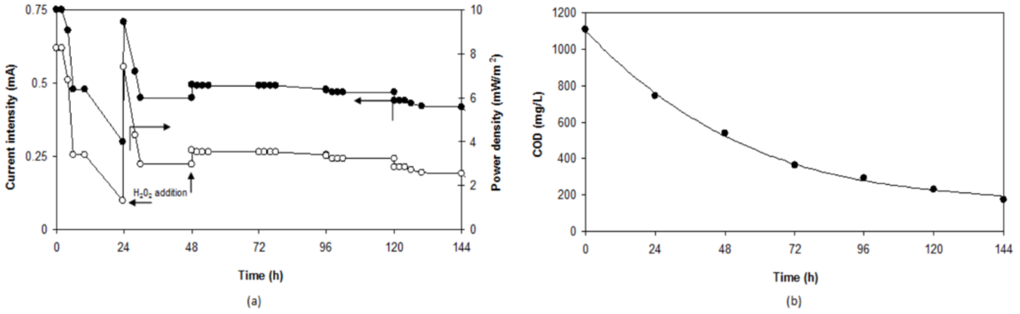

Figure 4. Variations of current (●) and power density (○)(a), COD(b) in the anode chamber with time when Fenton reagent (H2O2/ Fe(II)) was used in the cathode

Şekil 4. Katotta Fenton reaktifi (H_2O_2/ Fe(II)) kullanıldığında anot odasındaki akım (●) ve güç yoğunluğunun (○)(a), KOİ'nin (b) zamana göre değişimi

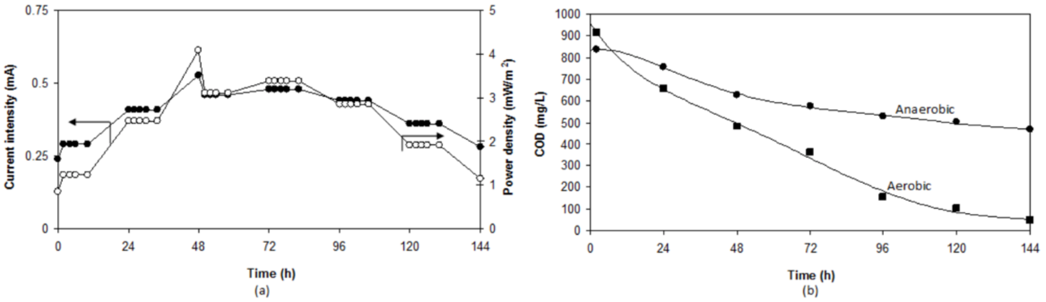

Figure 5. Variations of current (●) and power density (○)(a), COD(b) in the anode and cathode chambers with time when aerobic wastewater treatment was used in the cathode

Şekil 5. Katotta aerobik atık su arıtımında anot ve katot bölmelerindeki akım (●) ve güç yoğunluğunun (○)(a), KOİ'nin (b) zamana göre değişimi

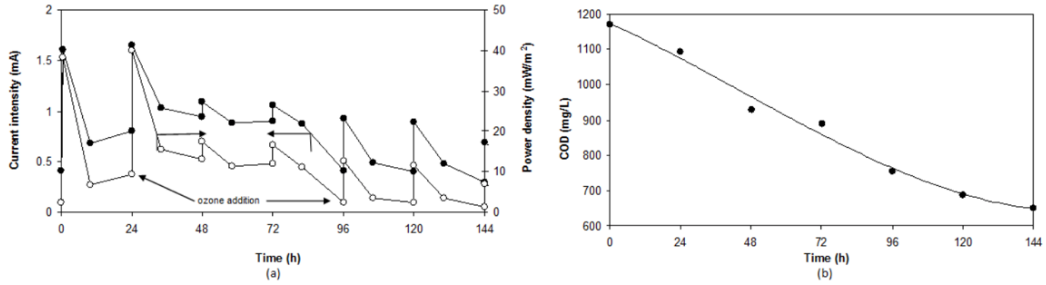

Figure 6. Variations of current (●) and power density (○)(a), COD(b) in the anode chamber with time when intermittent ozonation was used in the cathode chamber

Şekil 6. Katot bölmesinde aralıklı ozonlama kullanıldığında anot bölmesindeki akım (●) ve güç yoğunluğunun (○)(a), KOİ'nin (b) zamana göre değişimi

Table 1. Comparison of the highest and average power densities for different cathode solutions.

Tablo 1. Farklı katot çözeltileri için en yüksek ve ortalama güç yoğunluklarının karşılaştırılması.

Solution	H_2O_2	$KMnO_4$	$K_2Cr_2O_7$	Fenton Reagent	Modified Fenton	Aerobic Treatment	Ozonation
Max power (mW/m^2)	23	35	0.6	8.3	3.8	3.4	38
Avg. power (mW/m^2)	4	7.7	3,5	3.5	2.1	2.8	12.5

In agreement with our study, You et al [28] also determined that the use of permanganate solution at low pH levels in the cathodic chamber improved the generated power considerably in a two-chamber MFC. With the recent developments in MFC technology and the use of single chamber, membraneless, air cathode MFC's the power densities increased considerably [3,7,9,33]. However, only anaerobic treatment is realized in single chamber MFC's while both aerobic and anaerobic wastewater treatments are possible with the two-chamber MFC configurations although the generated power is relatively low due to high internal resistance. Therefore, with the aerobic wastewater treatment advantage of two-chamber MFC's the selection of a suitable oxidant solution in the cathode is an important issue affecting the generated power density. The generated powers are somewhat lower than the single-chamber MFC's and PEM utilizing two-chamber MFC's. This is due to high resistance of the agar salt bridge and mass transfer limitations. However, our results should be compared with the two-compartment MFCs using agar-salt bridge instead of PEM. As compared to agar-salt bridge utilizing two-chamber MFC's [34], the power densities obtained in our study are much higher due to utilization of more effective oxidants in cathode chamber. Power densities can further be improved by using a PEM instead of an agar salt bridge and a permanganate or peroxide solution in the cathode chamber.

6. Discussion and Conclusion

Performances of microbial fuel cells with different cathode solutions were compared in terms of voltage differences, current and power densities. The anode chamber contained synthetic wastewater treated anaerobically for electron and proton generation while the cathode contained different oxidant solutions. The highest power generation was obtained with ozonation (38 mW/m^2) due to highly oxidative nature of ozone. $KMnO_4$ (35 mW/m^2) and H_2O_2 (23 mW/m^2) solutions also resulted in high power densities. Use of aerated water, Fenton or modified Fenton reagent did not improve the power generation over H_2O_2 and $KMnO_4$ solutions and therefore, are not recommended. The lowest power generation was obtained with the $K_2Cr_2O_7$ solution due to low ORP levels. Aerobic treatment by the activated sludge organisms in the cathode chamber also yielded comparable power densities (3.4 mW/m^2) with the added advantage of COD removal at the expense of aeration costs. Large ORP differences between the chambers resulted in high power densities when strong oxidant solutions were used in the cathode chamber. The ORP of the anode chamber varied between -200 and -300 mV while the cathode chamber ORP was quite variable (+200 and +50 mV) depending on the oxidant used. The highest current (1.65 mA) and power (38 mW/m^2) densities obtained with ozonation of the cathode chamber was much higher than those reported in MFC literature using a salt bridge instead of a PEM. However, due to high cost of ozone, utilization of peroxide or permanganate solutions may be preferred. The performance of the MFC used may be improved by using a PEM, high COD content wastewaters and concentrated oxidative solutions in the cathode chamber.

7. Tartışma ve Sonuç

Farklı katot çözeltilerine sahip mikrobiyal yakıt hücrelerinin performansları voltaj farklılıkları, akım ve güç yoğunlukları açısından karşılaştırılmıştır. Anot odası, elektron ve proton üretimi için anaerobik olarak arıtılmış sentetik atık su içerirken, katot farklı oksidan çözeltileri içermektedir. Ozonun yüksek oksitleyici özelliğinden dolayı en yüksek enerji üretimi ozonlama (38 mW/m^2) ile elde edilmiştir. $KMnO_4$ (35 mW/m^2) ve H_2O_2 (23 mW/m^2) çözeltilerinde de yüksek güç yoğunlukları elde edilmiştir. Havalandırılmış su, Fenton veya modifiye Fenton reaktifi kullanımı, H_2O_2 ve $KMnO_4$ çözeltilerine göre güç üretimini iyileştirmemiştir ve bu nedenle önerilmemektedir. Düşük ORP seviyeleri nedeniyle en düşük güç üretimi $K_2Cr_2O_7$ çözeltisi ile elde edilmiştir. Katot bölmesinde aktif çamur organizmaları tarafından gerçekleştirilen aerobik arıtma, havalandırma maliyetleri pahasına KOİ giderme ek avantajı yanı sıra karşılaştırılabilir güç yoğunlukları (3,4 mW/m^2) vermiştir. Katot bölmesinde güçlü oksidan çözeltilerin kullanılması ile bölmeler arasındaki büyük ORP farklılıkları, yüksek güç yoğunlukları ile sonuçlanmıştır. Anot odasının ORP'si -200 ile -300 mV arasında değişirken, katot odasının ORP'si kullanılan oksidana bağlı olarak oldukça değişkendi (+200 ve +50 mV). Katot odasının ozonlanmasıyla elde edilen en yüksek akım (1,65 mA) ve güç (38 mW/m^2) yoğunlukları, PEM yerine tuz köprüsü kullanılan MFC literatüründe bildirilenlerden çok daha yüksektir. Ancak ozonun maliyetinin yüksek olması nedeniyle peroksit veya permanganat solüsyonlarının kullanılması tercih edilebilir. Kullanılan MFC'nin performansı, katot odasında bir PEM, yüksek KOİ içerikli atık sular ve konsantre oksidatif çözeltiler kullanılarak iyileştirilebilir.

8. Ethics committee approval and conflict of interest statement

There is no need for an ethics committee approval in the current article.

There is no conflict of interest with any person/institution in the current article.

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