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Effect of Catholyte Concentration on Current Production During Chocolate Industry Wastewater Treatment by a Microbial Fuel Cell

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Abstract

Microbial fuel cells (MFCs) use bacteria as a catalyst to oxidize organic and/or inorganic substrates and produce electric currents. Wastewater could function as an electron donor in the anode chamber and, thus, represents a very promising energy source. Catholytes, as electron acceptors, influence power production in MFCs by increasing the availability of electrons. The present research aims to determine the influence of catholyte concentration on current production in an aerobic two-chamber MFC. Aerobic treatment was carried out in the two-chamber MFC operated in an incubator at 37 ± 1 °C with and without aeration in the cathode chamber. Wastewater from the chocolate industry was used as a substrate and oxidized by using a bacterial consortium isolated from the sludge wastewater itself. The catholytes used were 0.01, 0.05, 0.1, and 0.3 N NaCl. In the presence of NaCl, the chemical oxygen demand (COD) removal efficiency in the cathode chamber of the MFC was approximately 65%–83% without aeration and 76%–89% with aeration after 72 hours. The current density increased as the catholyte concentration increased to 0.05 N, after which the oxidation process shifted from the anode chamber to the cathode chamber. Addition of O_2 to the cathode chamber influenced current production.

Abstrak

Efek Konsentrasi Katolit terhadap Produksi yang ada saat ini selama Pengolahan Air Limbah Industri Cokelat dengan Suatu Sel Bahan Bakar Mikroba. Sel-sel bahan bakar mikroba (MFCs) menggunakan bakteri sebagai suatu katalis untuk mengoksidasi substrat-substrat organik dan/atau anorganik dan memproduksi arus listrik. Air limbah dapat berfungsi sebagai suatu donor elektron di dalam ruang anoda dan dengan demikian, mewakili suatu sumber energi yang sangat menjanjikan. Katolit (catholytes), sebagai penerima elektron, mempengaruhi produksi daya pada MFC dengan meningkatkan ketersediaan elektron. Riset saat ini bertujuan untuk menentukan pengaruh konsentrasi katolit pada produksi arus di dalam suatu MFC dua ruang aerobik. Pengolahan aerobik dilaksanakan di dalam MFC dua ruang yang dioperasikan di dalam suatu inkubator pada 37± 1 °C dengan dan tanpa aerasi di dalam ruang katoda. Air limbah yang berasal dari industri cokelat digunakan sebagai suatu substrat dan dioksidasi dengan menggunakan suatu konsorsium bakteri yang diisolasi dari lumpur air limbah itu sendiri. Katolit yang digunakan adalah 0,01, 0,05, 0,1, dan 0,3 N NaCl. Dengan keberadaan NaCl, efisiensi pemisahan kebutuhan oksigen kimia (*chemical oxygen demand*/COD) di dalam ruang katoda MFC mendekati 65%–83% tanpa aerasi dan 76%–89% dengan aerasi setelah 72 jam. Kerapatan arus naik saat konsentrasi katolit naik ke 0,05 N, yang setelah itu proses oksidasi bergeser dari ruang anoda ke ruang katoda. Penambahan O_2 ke ruang katoda mempengaruhi produksi arus.

Keywords: Microbial fuel cell, chocolate wastewater, electron, catholyte, current

1. Introduction

Microbial fuel cells (MFCs) represent an alternative renewable energy source in which bacteria are used as catalysts to oxidize organic and/or inorganic matter and produce electricity. In an MFC, bacteria catalyze the oxidation process by reducing the substrate and release electrons from the respiration cell to the anode; electrons flowing through an external circuit loop to the cathode chamber produce currents. Each electron produces a proton that could be transferred through the electrolyte to maintain current continuity. Electrons and protons react with O_2 in the cathode chamber to form water under the action of a common catalyst, such as Pt.

According to previous research [1], electrons can be transferred to the anode by electron mediators or shuttles, direct membrane-associated electron transfer,

nanowires produced by bacteria, or undiscovered means [2]. Bacteria gain energy by electron transfer from substrate reduction at low potential (e.g., glucose) to electron acceptors at high potential (e.g., O_2).

Wastewater as an electron donor [3] may be placed in the anode chamber and function as an energy source [4]. Current production via nitrate reduction in a cathode chamber and glucose oxidation in an anode chamber with bacteria as the biocatalyst have been demonstrated, but further characterization of microbe communities in each compartment of an MFC is necessary [5]. Electric currents have also been produced in MFCs using *Clostridium* sp. with cellulosic waste [6]. Wastewater from the food industry contains high concentrations of organic. Thus, wastewater from chocolate, a popular industry in Indonesia, may be used as a potential substrate for MFC systems.

An electron-acceptor catholyte influences power production in an MFC; specifically, increasing the availability of electron acceptors could increase current production. Salts such as NaCl exist not only in seawater but also in saline wastewater [7]. Salts can act as electron acceptors and enhance power production [8]. The present study aims to study the characteristics of current production in an aerobic two-chamber MFC using chocolate industry wastewater as the substrate with different catholyte concentrations.

2. Methods

Reactor configuration. The MFC reactor was composed of two 1-liter beakers. The anode chamber was filled with 900 mL of chocolate wastewater and 100 mL of a microbial suspension, and the cathode chamber was filled with the catholyte. Distilled water was used as the control, and the concentrations of NaCl as the catholyte were 0.01, 0.05, 0.1, and 0.3 N. Moreover, the cathode chamber was operated with and without aeration.

The chocolate industry wastewater used in this work came from the equipment washing process of PT X, Bandung, and had a chemical oxygen demand (COD) between 5000 and 6000 mg/L (pH 4.0–5.6). Adjustment to a neutral pH prior to reactor operation was achieved by using NaOH. An Fe sheet with a contact area of 65 cm^2 was used as the anode and cathode material. NaCl was chosen as the catholyte because previous salt characterizations revealed that this salt could corrode Fe.

The microbial suspension consisted of a consortium of microbes isolated from the wastewater treatment plant (WWTP) sludge of PT X, Bandung, using standard isolation methods by American Public Health Association (APHA) [9].

A sulphonated butadiene–styrene cation exchange membrane was obtained from the Research Center for Chemistry, LIPI, and clamped between the anode and cathode chambers.

The batch reactor was operated with aeration in the anode chamber and with or without aeration in the cathode chamber, in by using an incubator (CERTOMAT® BS-1; Germany) at a temperature 37 ± 0.1 °C. The electrodes were connected to a multimeter (SANWA PC510a), and the data were transferred to a computer with a Data Acquisition RS 232c system, as shown in Figure 1. Current data were collected every hour.

Seeding and acclimatization. Before the microbial suspension was applied to 100% wastewater in the anode chamber, seeding and acclimatization were conducted in duplicate 1-liter single chambers consecutively started from 25, 50, until 75%-wastewater to glucose media.

The ratio of glucose medium as a carbon source to the nitrogen and phosphor nutrition was 100:10:1 [6]. The volume of glucose medium or wastewater added was 90% of the total reactor volume, and the remaining 10% was made up of the microbial consortium.

Data collection. Data on dissolved O_2 (DO), pH, COD, and volatile suspended solids (VSS) were collected every 12 hours during the acclimatization stage and every 24 hours during MFC operation. VSS, which represents the extent of microbial growth in the suspension, was determined in terms of optical density (OD). pH was measured by using a pH meter (Lutron PH-208), OD (λ = 650 nm) was detected by using a spectrophotometer (LW Scientific V325XS), and COD was analyzed by using closed reflux titration (Standard Methods 5220 C). DO measurement was conducted under controlled aerobic conditions in the anode and cathode chambers.

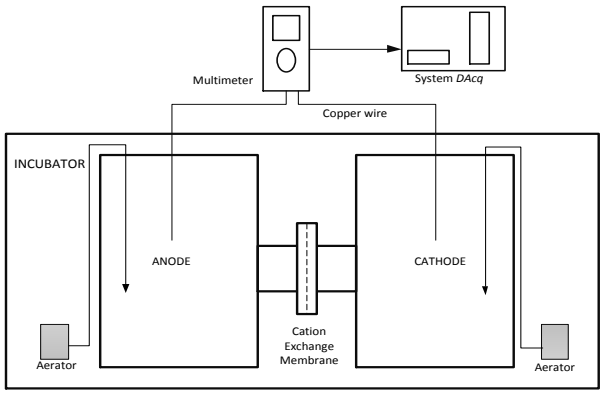

Figure 1. Scheme of the Proposed MFC with a Current Data Acquisition System

Microbe performance during acclimatization and MFC operation, COD efficiency removal, and current density (i.e. the current produced per unit area of the anode) were analyzed.

3. Results and Discussion

Seeding and acclimatization. Acclimatization occurred from the 60th to the 72nd hour after seeding at each stage, on the same temperature with MFC when 100% wastewater fed to the reactor.

The first-order kinetic reaction, as shown in Equation (1), can help determine the growth rate of the microbial consortium during the exponential phase; the relevant equation is:

$$[C] = [C_0]e^{-k.t} \quad (1)$$

Linearization of Equation (1) results in Equation (2).

$$ln\ \frac{[C]}{[C_0]} = k.t \quad (2)$$

where C_0 is the initial concentration of the biomass (expressed as VSS), C is the concentration of biomass at time t, k is a constant specific to the growth of the consortium (μ), and t is reaction time. Biomass growth as a function of time is shown in Figure 2.

As biocatalysts, microbes play an important role in MFCs; moreover, microbial consortia produce better results of organic decomposition compared with single cultures [10]. The microbial consortium in this study was obtained from an isolate of chocolate WWTP sludge. In previous research, [11], [12], and [13], seeding with a microbial consortium in the anode chamber of an MFC resulted in increased electricity production.

The first phase occurs when microbes are introduced to the glucose medium, the lag phase occurs without a sudden increase in microbe count over 5 hours of acclimatization in 25% wastewater, and the exponential phase occurs in 50% and 75% wastewater. These observations mean the consortium had adapted to the available nutrition.

The exponential or log phase is the step in which the microbial consortium develops and multiplies at maximum speed. The growth rate remained constant during the exponential phase, and microbes multiplied at regular intervals. If any increase in biomass concentration occurs at this phase, would not very extreme. Figure 2 reveals that the exponential phase lasts from the 20th to the 50th hour of acclimatization in 25% and 50% wastewater; during acclimatization in 75% wastewater, the exponential phase occurs during first 10–20 hours of seeding.

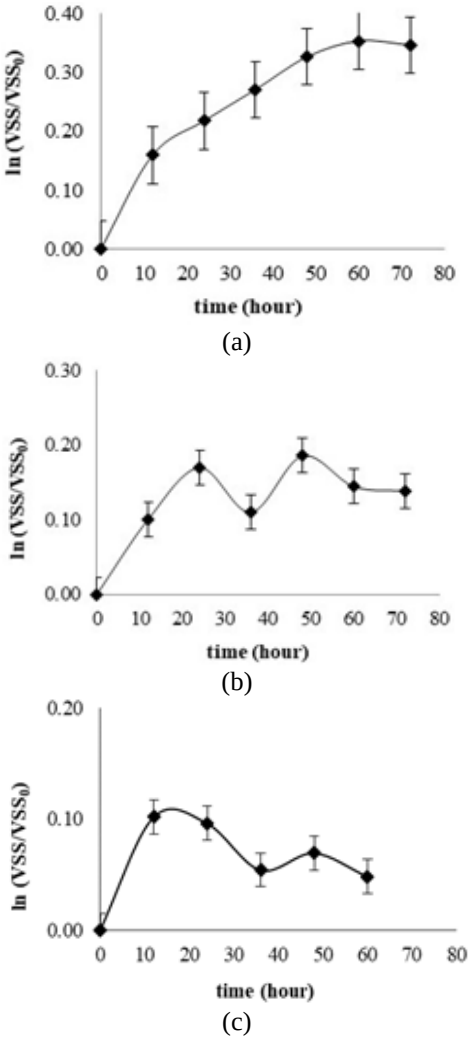

Figure 2. Curve of Microbe Growth during Acclimatization in the Wastewater: Glucose Medium at Ratios of (a) 25%:75%, (b) 50%:50%, and (c) 75%:25%. Counts are Expressed as Average and Standard Deviation

The stationary phase, in which the increase in microbial growth rate shows a horizontal trend, occurs from the 50th hour of acclimatization in 25% and 50% wastewater and then tends to decrease thereafter. During acclimatization in 75% wastewater, the stationary phase occurs after the 20th hour and remains constant after 50 hours.

The time range of the exponential phase in Figure 2(c) is shorter than those in Figures 2(a) and 2(b) likely because of more extensive microbial growth and adaptation of the microbes to the wastewater as a nutrition source.

The acclimatization stage occurred from the 60th to the 72nd hour in each stage at a temperature similar to that used during MFC operation. This finding is similar to previous studies in which 50 or more hours of

acclimatization was required to reach maximum electricity production [12].

Organic matter removal. The performance of the microorganisms in oxidizing substrates in the anode chamber is evidenced by a decrease in COD concentration during reaction. The minimum DO demand was 2 mg/L [14]. Aerobic bacteria could use DO concentrations as low as 0.1 mg/L in the anode chamber because of terminal oxidation O_2 transport system on aerobic respiration has very high affinity to the O_2 [10]. This means the anode chamber has aerobic conditions that conform to the minimum requirement of the microorganism consortium.

The removal efficiency of organic contents in the anode chamber, which is represented by COD, without aeration in the cathode chamber reached 65%–83% within 72 hours, as shown in Figure 3.

The COD removal efficiency in the cathode chamber with aeration reached 76%–89% after 72 hours, as shown in Figure 4.

As shown in Figures 3 and 4, aeration in the cathode chamber resulted in faster decreases in COD compared with that obtained without aeration. This result reveals that O_2 as the electron acceptor in the cathode chamber influences the performance of substrate removal by microorganisms in the anode chamber.

According to Figures 3 and 4, the 72-hour COD removal efficiencies obtained under difference catholyte concentrations without and with aeration reached 65%–83% and 76%–89% respectively. This removal efficiency is obtained within the similar time of acclimatization stage. Compared with previous research [15], which required 150–200 hours to achieve 75% COD reduction at 28 $\pm$ 2 °C, the reaction time in the present system is shorter. A recent study applied a relatively higher working temperature of 37 $\pm$ 1 °C and revealed that the biochemical reaction rate for biomass growth and substrate utilization increases with increasing temperature [14]. Previous research also demonstrated that decreasing the temperature from 32 °C to 20 °C could decrease power production by 9% because of the resulting low cathode potential ([16] in [17]). According to Jadhav et al. [18], the COD removal efficiency in MFC systems with mixed cultures would decrease as the operating temperature decreases.

Current density production. The current density produced in the proposed two-chamber MFC is shown in Figures 5 and 6.

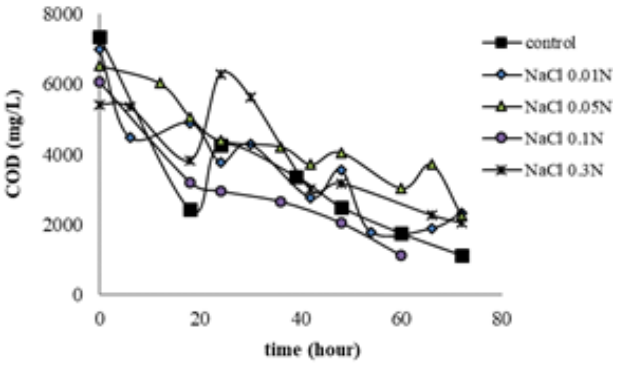

Figure 3. COD Removal Under Different Catholyte Concentrations without Aeration

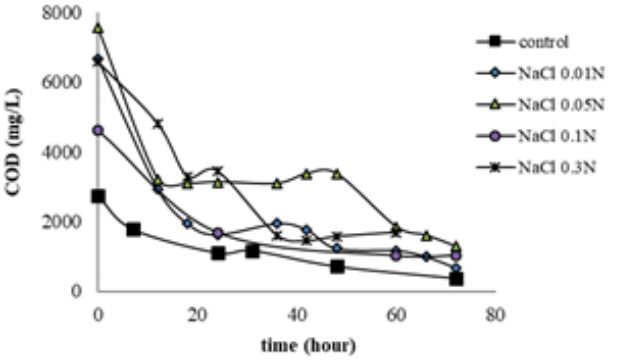

Figure 4. COD Removal Under Different Catholyte Concentrations with Aeration

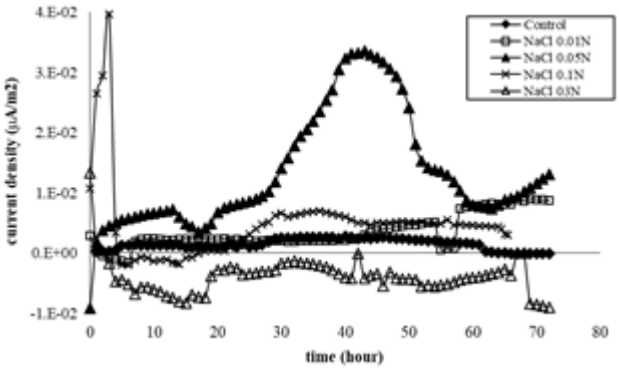

Figure 5. Current Density Under Different Catholyte Concentrations without Aeration

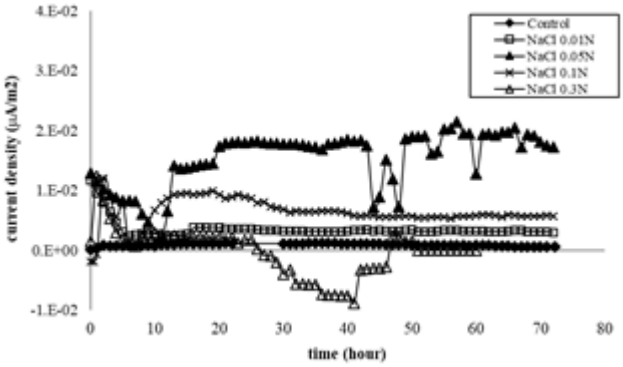

Figure 6. Current Density Under Different Catholyte Concentrations with Aeration

In the cathode chamber without aeration, as shown in Figure 5, the maximum current densities obtained by using the control and 0.05 N NaCl catholytes are 2.72×10^{-3} and 3.36×10^{-2} μA/m^2, respectively. The maximum current density in 0.1 N NaCl reached 3.97×10^{-2} μA/m^2 at the beginning of MFC operation but tended to decrease to a maximum value of 6.95×10^{-3} μA/m^2. The increase in current at the beginning of fuel cell operation with NaCl as the catholyte may attributed to salt ions increasing the conductivity between the anode and cathode chambers, which would increase electron transfer from microbes that had adapted to the substrate. Compared with the control, 0.1 N NaCl as a catholyte resulted in a 2-fold higher current within 22 hours and 2.6-fold higher current within 33 hours.

When aeration treatment is carried out in the cathode chamber, as shown in Figure 6, the maximum current densities obtained by using the control and 0.1 N NaCl catholytes are 1.18×10^{-3} and 1.20×10^{-2} μA/m^2, respectively. Compared with the chamber without aeration treatment, where the maximum current obtained by using 0.1 N NaCl reaches 6.95×10^{-3} μA/m^2, the maximum current obtained by aeration treatment is clearly higher. The ion availability of NaCl could increase the conductivity of the MFC system and facilitate proton transfer [19].

Operation of the MCF with 0.3 N NaCl without and with aeration treatment initially yielded maximum currents of 1.33×10^{-2} and 1.24×10^{-2} μA/m^2, respectively; however, these currents decreased until negative values were reached. This result may be caused by the formation of a high concentration of NaCl, which allows the oxidation rate of the Fe cathode to exceed that of microbes at the anode chamber so that the current flows from the cathode chamber into the anode chamber. Oxidation on the Fe electrode occurs quickly in the presence of Cl^- because of peptisizing performance that caused on passivation layer destruction of Fe [20].

Compared with the maximum current obtained in previous research [15], which reached 3.1 mA using O_2 as the catholyte, the maximum current obtained in the present study is lower. This variation may be attributed to the use of a graphite electrode, which is inert and does not react during cell operation, in the previous research.

O_2 functions as an electron acceptor in the dual-chamber MFC, which more economic and commonly used, due to O_2 high redox potential, +1.230 volt.

The theoretical current achieved from organic substrate (COD) removal could be calculated by using the equation below:

$$number\ electron = \frac{(i\ x\ t)}{96500}\ mol \tag{3}$$

Modification of Equation (3) yields an equation for $I_{stoichiometric}$ as follows [19]:

$$I = \frac{n\ x\ 96500}{t\ x\ 32}\ x\ r_{COD} \tag{4}$$

where n is the number of electron per mmol O_2, 32 (mg O_2/mmol O_2), t is 86400 s/day, and r is the substrate removal per day (mg/day). Assuming a substrate removal efficiency of 80%, according to Figure 3, the stoichiometric current could reach 223 mA under approximately 1600 mg O_2/day.

The lower current production obtained in the present study compared with the theoretical stoichiometric current could be explained by competition between O_2 in the anode chamber under aeration and O_2 in the cathode chamber for electron transfer. Electrons produced from substrate oxidation tend to combine with O_2 in the anode chamber rather than that in the cathode chamber due to the shorter travel distance in the former. Future work could focus on improving the MFC design to achieve aerobic conditions without direct aeration and modify the electrode surface area to attract electrons as quickly as they are produced.

4. Conclusion

A two-chamber MFC performance using chocolate industry wastewater as a substrate with different catholyte concentrations was examined in this work. The potential use of chocolate wastewater as a nutrition source in the anode chamber of MFC systems was also demonstrated. Result showed that the COD removal efficiency could reach 65%–83% without aeration and 76%–89% with aeration within 72 hours. During MFC operation, current production increased with increasing NaCl concentration in the cathode chamber, peaked at 0.05 N NaCl, and then decreased thereafter. The oxidation process shifted from the anode chamber to the cathode chamber as oxidation of the Fe surface occurred in the cathode chamber. Addition of O_2 as an electron acceptor via aeration in the cathode chamber also increased the current density. The use of inert electrodes may prevent this shifting of the oxidation process.

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