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SHORT COMMUNICATION

Investigation into effects of cathode aeration on output current characteristics in a tubular microbial fuel cell

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Abstract This work is mainly focused on studying the effects of cathode aeration in a tubular mediator-less microbial fuel cell. COD removal efficiency and the effect of closing the circuit are among other parameters investigated. A new combination of electrodes, i.e., platinum-coated titanium as the cathode and chrome-/vanadium-coated stainless steel as the anode, is used in this work. Aeration of the cathode chamber is carried out by addition of oxygen, which plays the role of final electron-acceptor terminal. When the cathode chamber is aerated, the maximum achievable voltage and current are 630 mV and 1.06 mA, respectively. When the cathode operates under anaerobic conditions, COD reduced by only 40 % after 90 h, as opposed to 90 % achieved with cathode aeration, in which case more than 36 % of COD is removed in the first 8 h, while the rest of it is eliminated over a much longer period of time (i.e., 82 h). The best curve fitting for COD removal follows a logarithmic pattern, indicating higher removal levels when more substrate is available. Closing the circuit is followed by a plunge in voltage, which is attributable to the ohmic resistance.

Keywords Artificial wastewater · Cathode aeration · Chemical oxygen demand · Microbial fuel cell

Introduction

Microbial fuel cell (MFC) is an apparatus which transforms chemical energy into electrical energy by using catalytic reactions of microorganisms (Allen and Bennetto 1993). Most MFCs are structurally similar to other fuel cells; they are electrochemically inactive and require mediators to facilitate the transfer of electrons (Delaney 1984). Utilization of microbes which are electrochemically active was a major step in the manufacture and advancement of microbial fuel cell reactors (Kim et al. 1999a, b). First definitions of MFC were introduced in 1910, when electrical energy was produced from a culture (Du et al. 2007), but the idea of employing MFCs in municipal waste treatment did not grab researchers' attention until after 1990. Advances in output power of MFCs in the past several years are easily noticeable (Rabaey and Verstraete 2005).

A tubular microbial fuel cell consists of two chambers, one cathodic and one anodic, separated by an ion exchange membrane. It has been demonstrated that the efficiency of an MFC using a salt bridge is approximately 20 % of that using Nafion®, which is currently one of the most renowned ion exchange membranes (Min et al. 2005). In fact, Nafion® is a fluoropolymer-based sulfated tetrafluoroethylene compound (Heitner-Wirguin 1996). Anodic chamber contains

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microorganisms which oxidize the substrate (electron donor) available to them during an anaerobic process. The substrate used in an MFC can vary from sugar and organic acids, e.g., glucose and acetate, to complex polymers, namely cellulose and starch. The reaction of glucose as an electron supplier in the anodic chamber (oxidation reaction) is as follows:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \quad (1)$$

Anode plays the role of the external electron acceptor for microorganisms. Electrons arrive in cathode once they have generated a current passing through the circuit, and the following cathodic reaction (oxygen reduction) takes place. In addition, the corresponding protons travel through the membrane for the system to remain neutral.

$$6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O \quad (2)$$

There are two types of cathodic reductions, i.e., aerobic and anaerobic. In the former, oxygen is the final electron-acceptor terminal. Oxygen reduction is the electrochemical reaction predominant on the surface of the cathode. Thus, it follows that oxygen concentration influences both the kinetics of this reaction and the final power efficiency (Rismani-Yazdi et al. 2008). A number of limiting steps in a mediator-less MFC, as reported in previous research, include: (1) fuel oxidation in anode, (2) transfer of electrons from microbes to anode, (3) circuit resistance, (4) transfer of protons through the membrane, and (5) oxygen reduction in the cathodic chamber (Gil et al. 2003).

The efficiency of an MFC reactor is also assessed in terms of its ability to remove chemical oxygen demand (COD), which is defined as the amount of oxygen required to consume the organic materials. It is known that nearly all organic compounds can be fully oxidized to carbon dioxide with a strong oxidizing agent under acidic conditions. This provides the basis for a COD test, which indirectly measures the amount of organic compounds in water.

The main goal of this work is to investigate the effect of cathode aeration in a tubular mediator-less microbial fuel cell, equipped with a membrane, on the output current and voltage. In addition, the overall efficiency of the reactor in terms of its ability to remove chemical oxygen demand (COD) is studied. The effect of opening and closing the circuit on the voltage value was studied as well. This work was conducted in Amirkabir University of Technology, Tehran, Iran, in 2013–2014.

Materials and methods

Tubular microbial fuel cell configuration

The microbial fuel cell used in this work was tubular, made of poly(methyl methacrylate) (PMMA), and consisted of five major and two minor sections, which allowed for membrane installation. The height of every section was 10 cm, giving the reactor an overall height of <60 cm, with a wall thickness of 10 mm. A multitask valve was devised in every section. The position of the electrodes was at the two ends of the reactor, with cathode and anode normally placed on the top and bottom end of the reactor, respectively. In this specific reactor design, different sections can be readily replaced by one another. An air pump (RS-510, China) was utilized to aerate the cathode chamber.

The inspiration for the design of this MFC was taken from a previous work (Du et al. 2008), but the following modifications were applied to it. Unlike Du's MFC which was membrane less, our design allows for a membrane separating the two chambers. The membrane used in this study was Nafion® (Germany), which had a thickness of 0.006 inch (Heitner-Wirguin 1996). In addition, Du carried out experiments with both rod and granular graphite electrodes, while the electrodes used in this work were chrome-/vanadium-coated stainless steel as the anode and platinum-coated titanium as the cathode. Furthermore, our design also allowed for the distance between the electrodes to be adjusted as desired.

Electrodes

Platinum-coated titanium and chrome-/vanadium-coated stainless steel were used as the cathode and the anode, respectively. The characteristics of the electrodes used in this work are listed in Table 1. The electrodes were cleaned with acetone and washed with distilled water several times prior to each experiment, to ensure the absence of any contamination, such as lipids. Both electrodes were then autoclaved in 121 °C for 15 min.

Wastewater and Inoculation

Mixed culture from anaerobic-activated sludge, obtained from Qeytarieh Refinery Plant (Iran), was used in this study. Artificial wastewater (AW) was prepared using glucose, according to the procedure described in the literature (Wei et al. 2012), and its composition is presented in Table 2. The initial COD of this wastewater was 1064 mgL^{-1}.

Table 1 Characteristics of electrodes placed in the MFC used in this study

Electrode material	Electrode cover	Electrode surface area (cm^2)	Electrode type
Stainless steel	Chromium-vanadium	65	Anode
Titanium	Platinum	70	Cathode

Table 2 Composition of artificial wastewater used in this study

Chemical name	Amount (g)	Composition (%)
$(NH_4)_2SO_4$	0.56	1.5
$MgSO_4{\cdot}7H_2O$	0.2	0.5
$CaCl_2$	15	40.3
$FeCl_3{\cdot}6H_2O$	1	2.7
$MnSO_4{\cdot}H_2O$	20	53.8
$NaHCO_3$	0.42	1.2

Experiments

First, 1 L of activated sludge was added to the anodic chamber for the first inoculation, and oxygen was removed by purging argon. The cathodic chamber was filled with distilled water and then closed, to initiate bacterial activities. The culture became compatible with the reactor after 4 days, and the produced voltage became virtually stable. The experiments were conducted at ambient temperature (32 ± 2 °C). Low PH values in the anode are due to the accumulation of protons in the cathode and their slow migration through the membrane. On the other hand, alkalinization is observed in the cathode as a result of continuous consumption of protons by the oxygen-reducing reaction as well as low proton replacement from the anodic oxidation reaction (Oliveira et al. 2013). The cathodic chamber was thus filled with phosphate buffer solution. Each liter of buffer solution contained 5.6 g of K_2HPO_4 and 4.4 g of KH_2PO_4. The circuit was established after the injection of buffer solution, and artificial wastewater was added to the anodic chamber as the nutrient. The experiments were conducted in two modes, i.e., with and without aeration, and the results were compared.

Analyses

Voltage (V) and current (I) were continuously measured and recorded using a multimeter (DT-830D, Liveton Co., Inc, China). pH was measured during the experiments using photometer equipment (9700 model, PalintestLtd., United Kingdom). COD test was conducted in accordance with procedures described in standards (APHA 1998).

Results and discussion

Effect of cathode aeration on voltage and current

Once the electrochemical activity of the bacteria had started and consequently, the voltage surpassed a minimum value, the circuit was established and the reactor was set to work in batch (discontinuous) mode. Aeration was constantly applied with a flow rate of 2 L min^{-1}. Output voltage had very little increase during the first 12 h and experienced a relative increase after the first injection of the feed (substrate). The decreasing slope observed in the voltage curve after 30 h is an indication of substrate consumption, and the voltage drops to the limiting value of zero if the substrate is completely consumed. As can be seen in Fig. 1a, b, the maximum voltage, i.e., 630 mV,

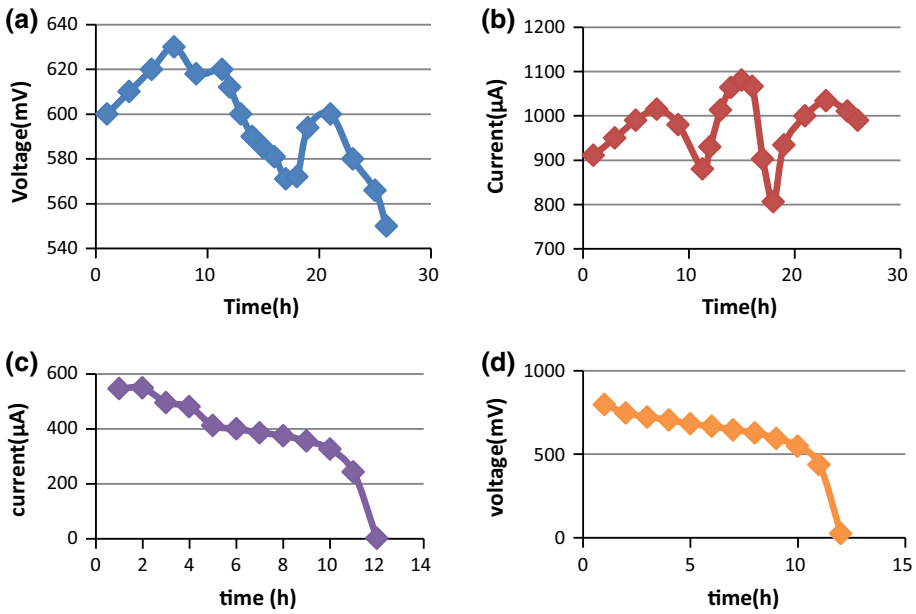

Fig. 1 **a** The voltage (V) and **b** the current (A) curves versus time (h) during aeration, **c** the voltage (V) and **d** the current (A) curves versus time (h) without aeration

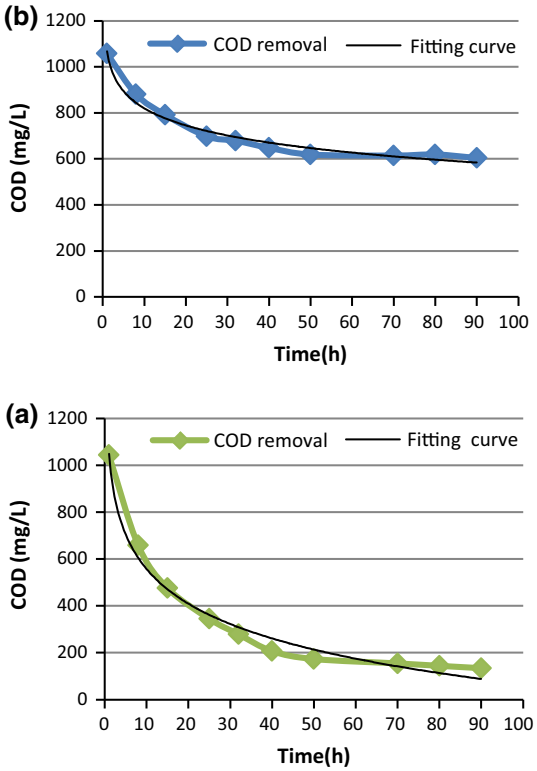

Fig. 2 COD (mg/L) removal as a function of time (*h*) and the logarithmic fitting for the MFC working **a** without aeration (*green curve*) and **b** under aeration (*Blue curve*). Curve fittings show good agreement with the experimental results

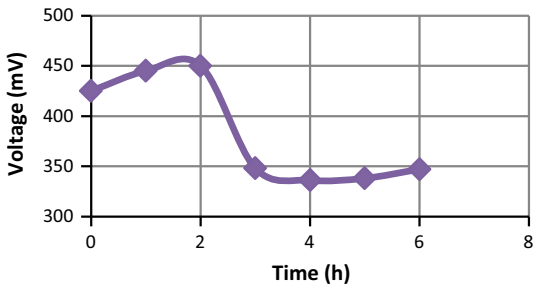

Fig. 3 Voltage variation versus time (the circuit is closed after 2 h)

relative to a current of 1.06 mA, corresponds to the second day (after the second injection). Presented in Fig. 1 is also the best curve fitting for current variations as a function of time.

In the second mode, where all the conditions were the same except that cathode aeration was stopped, the voltage and current dropped to zero after 12 h. As can be seen in Fig. 1c, d, this plunge in the current and voltage is in fact an indication of oxygen reduction (the final electron-acceptor terminal). Oxygen concentration affects both reaction kinetics and final power efficiency.

Effect of aeration on COD removal

Figure 2 shows how cathode aeration affects COD removal in the anode chamber over time. As it can be seen in Fig. 2a, under anaerobic conditions, i.e., without aeration, the COD decreased by only 40 % after 90 h of operation; however, when the cathode chamber was aerated, Fig. 2b, the reduction reached 90 %. According to Eq. 2, insufficient amounts of oxygen (the limiting reactant) in anaerobic conditions lead to the accumulation of H^+ species in the cathode chamber, which in turn hinders the progress of Eq. 1. Therefore, the consumption of the substrate and the reduction in the COD will not exceed a certain level. Thus, reduction–oxidation reactions account for the higher COD removal when aeration is applied to the cathode. On the other hand, higher amounts of oxygen promote the reduction reaction (Eq. 2), causing the H^+ concentration to drop in the cathode chamber, thereby enhancing the generation of electrons in the anodic chamber. The consequent progress of Eq. 1 is manifested in higher COD removal due to higher consumption of the substrate.

Effect of closing the circuit on voltage value

When potential difference remained quite constant, the circuit was closed to study its possible effects. In Fig. 3, which presents the effects of closing and opening the circuit, a jump is observed in the potential difference. This can be well attributed to the fact that the circuit, in its closed state, has a high ohmic resistance, which is due to the internal resistance. Closing the circuit, thus, gives rise to a sudden decrease in the potential difference.

Conclusion

A mediator-less tubular microbial fuel cell, equipped with a Nafion® membrane, was utilized in treating artificial wastewater. Using this system, operating with cathode aeration, it was demonstrated that maximum voltage of 630 mV relative to a current of 1.015 mA was achieved. COD values were shown to reduce from 1064 to 134 mg L^{-1} (90 %) in 90 h in this case, while the COD reduction achieved without aeration did not exceed 40 %. We also made a qualitative comparison between open- and closed-circuit modes, revealing the ohmic resistance of the circuit in the closed state.

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