Effect of carbon materials as cathode on wastewater treatment and bioelectricity generation in a double chambered microbial fuel cell

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Abstract. Microbial fuel cell (MFC) is a promising and sustainable technology that has high efficiency to produce renewable energy and treat wastewater simultaneously. The effect of carbon materials on the removal of synthetic wastewater in the anodic chamber and electricity generation were investigated using a double chambered MFC. In this study, a double chambered reactor made up of anodic and cathodic chambers separated by proton exchange membrane has been developed. Carbon plate and carbon felt were characterized using scanning electron microscopy. Results revealed that 1.20 times higher chemical oxygen demand removal of synthetic wastewater using carbon felt (50.90\%) as compared with that of carbon plate (43.52\%). The maximum voltage output produced by carbon felt (280.20 mV) was 20.70\% higher than carbon plate (222.20 mV) as cathode in MFC. The surface morphology of carbon materials has significant effect on the oxygen reduction reaction reactivity at cathodic chamber.

1. Introduction

Over the past decade, environmental pollution and resource scarcity have caused adverse effects to the human life and development. Wastewater containing industrial waste materials is the major cause of environmental pollution in surface and ground water bodies [1]. Conventional wastewater treatment methods such as coagulation and sedimentation are mostly required a huge amount of energy and high cost of investments [2]. Therefore, development of alternative cost-effective methods has gained extensive interest from researchers worldwide.

Microbial fuel cell (MFC) has been considered as a promising technology which was capable to convert organic waste directly into electricity through microbial electrochemical reactions [3, 4]. A conventional MFC for energy recovery from wastewater is made up of anodic and cathodic chambers. The chambers are separated by a proton membrane exchange (PEM) that prevents the transfer of oxygen from anode to cathode. The main mechanism of MFC is the oxidation of the organic substance in the wastewater such as acetate, glucose, and lactase by the anaerobic microorganisms at the anode to
generate electrons and protons [5]. These electrons will be transferred from anode to cathode through the external circuit for the voltage generation.

Recently, research efforts have been made to improve the power output of MFC. The type of substrate, the configuration of reactor, the anode and the cathode materials and the external resistance are the primary factors that affect the power output [6]. Numerous electrode materials such as carbon felt, carbon paper and carbon cloth have been extensively explored for MFC. The electrodes in the MFC should be made up of materials that possess high specific area, good conduction, good chemical stability, high mechanical strength and low cost [7].

Since the electrode is the key factor in determining the performance and cost of MFC, the effect of carbon materials as cathode on the wastewater treatment and power output in MFC has been investigated in this study. These performances were evaluated in terms of chemical oxygen demand (COD), nitrate removal, coulombic efficiency (CE) and power density.

2. Material and methods

2.1. Materials

The following chemicals were supplied by HmbG Chemicals: ethanol (C\textsubscript{2}H\textsubscript{5}OH, 95%), sodium acetate (CH\textsubscript{3}COONa), ammonium chloride (NH\textsubscript{4}Cl), dipotassium phosphate (K\textsubscript{2}HPO\textsubscript{4}), potassium dihydrogen phosphate (KH\textsubscript{2}PO\textsubscript{4}), potassium chloride (KCl), sodium chloride (NaCl) and magnesium chloride hexahydrate (MgCl\textsubscript{2}•6H\textsubscript{2}O). Hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}, 35%) from Bendasen and sulfuric acid (H\textsubscript{2}SO\textsubscript{4}, 98%) from Fisher Scientific (M) Sdn Bhd were used for pre-treatment of PEM. All chemicals were employed without further purification.

2.2. MFC setup and operation

A double chambered reactor was made up by using two identical acrylic plates (10 cm x 10 cm x 20 cm). Both anodic and cathodic chambers were separated with Nafion 117 (Ion Power Inc, USA) PEM. The membrane was treated using hydrogen peroxide and sulfuric acid according to Mostafa et. al (2013) [8]. The net volume of each compartment was 1.4 L. A 2 cm thick carbon felt (SG-222, Maido Corporation, Japan) with a dimension of 9 x 5 cm was ultrasonically cleaned using ethanol. A carbon rod was inserted into the cleaned carbon felt as anode.

The anodic chamber was filled up with 1.0 L synthetic wastewater that contained 0.375 g L\textsuperscript{-1} CH\textsubscript{3}COO\textsubscript{Na}, 0.31 g L\textsuperscript{-1} NH\textsubscript{4}Cl, 3.40 g L\textsuperscript{-1} K\textsubscript{2}HPO\textsubscript{4}, 4.00 g L\textsuperscript{-1} KH\textsubscript{2}PO\textsubscript{4}, 0.13 g L\textsuperscript{-1} KCl, 0.116 g L\textsuperscript{-1} NaCl, 0.10 g L\textsuperscript{-1} MgCl\textsubscript{2}•6H\textsubscript{2}O and inoculated plastic biofilm carriers. The plastic biofilm carriers were inoculated in the sludge collected from the wastewater treatment plant of a rubber gloves manufacturing factory for more than one month. The anodic chamber was sealed to maintain the anaerobic condition.

A carbon plate and a carbon felt with the same dimension of anode were used as cathodes. 1.4 L of distilled water was filled in the cathodic chamber. Aeration was supplied at the cathodic chamber by using an aeration stone and aeration pump. Copper wires were utilized to connect the anode and cathode across an external resistance of 1 k\textohm. MFC was operated in the fed-batch mode under ambient temperature for 168 h. The efficiency of carbon plate and carbon felt as cathodes in MFC were compared and investigated for the evaluation of effect of carbon materials as cathode on the performance of MFC in terms of wastewater treatment efficiency and electricity generation.

2.3. Analytical method

The synthetic wastewater samples from the anodic chamber were collected daily for COD and nitrate measurement. The samples were centrifuged using centrifuge (Cence L500, China) before COD analysis. The COD concentration of the samples was determined using Hach DR 2800 (Hach, USA). The measurement of nitrate in wastewater samples was carried out using Bante931-NO3 Benchtop nitrate ion meter, China. COD and nitrate removal efficiency (X\textsubscript{E}, %) for synthetic wastewater were evaluated using formula (1):
\[ X_E = \frac{x_o - x_t}{x_o} \times 100\% \]  

where \( x_o \) is the initial concentration in mg L\(^{-1}\) and \( x_t \) is the concentration at certain reaction time \( t \) (h) in mg L\(^{-1}\).

The voltage output was recorded using a data logger (midi Logger Gl820 Graphtec, China). Polarization study was performed by a resistor box for varying the external resistance from 20 k\(\Omega\) to 10 \(\Omega\). The power density was calculated based on formula (2) below:

\[ P_d = \frac{VI}{A} \]  

where \( P \), \( V \), \( I \) and \( A \) represents power density, voltage output, current and area of cathode, respectively.

CE was evaluated using the ratio of experimental coulombs to the theoretical coulombs in formula (3):

\[ CE = \frac{M}{\int_0^t I \, dt} (Fb v \Delta \text{COD})^{-1}, \]  

where \( F \) is the Faraday’s constant (96485 C mol\(^{-1}\)), \( b \) is the number of moles of electrons generated per mol of substrate, \( v \) is the volume of substrate in L, \( \Delta \text{COD} \) is the change in COD concentration over one batch in g L\(^{-1}\) and \( M \) is the molecular weight of substrate in g mol\(^{-1}\) [9].

3. Results and discussion

3.1. Scanning electron microscopy (SEM) analysis of cathodes

The morphology of carbon plate and carbon felt is demonstrated in figure 1. Based on figure 1(a), the porous and flaky surface of carbon plate is observed. There are several pieces of large flakes on the surface of the carbon plate. The surface of carbon felt with carbon fibre networks is observed in figure 1(b).

![Figure 1: SEM micrographs of (a) carbon plate and (b) carbon felt cathode with magnification at x500.](image)

3.2. Wastewater treatment performance

COD is an important index for monitoring organic pollution in water and defined as the number of oxygen equivalents required to oxidize organic materials into carbon dioxide and water [10]. The COD removal efficiency in the anodic chamber was mostly contributed by the microbes act as biocatalysts to
oxidize the acetate under anaerobic conditions [11]. Figure 2(a) demonstrates the COD removal efficiency of synthetic wastewater for two different carbon materials and the efficiencies were increased over the reaction time. The COD removal efficiency of carbon felt (50.90%) was higher than the carbon plate (43.52%). This could be due to the carbon materials. The cathode is the site for oxygen reduction reaction (ORR) reactivity which required protons and electrons. The organic matters were consumed by the electrochemical-active bacteria at the anodic chamber to produce electrons and protons [12]. The carbon felt with higher porosity could provide larger specific surface area for ORR reactivity. Thus, it promoted and increased the microbial oxidation activity when the carbon felt was used as the cathode.

The nitrate removal efficiency in the anodic chamber under effect of carbon materials is illustrated in figure 2(b). Better performance (21.88%) was achieved in the removal of nitrate in the anodic chamber when carbon felt was utilized as cathode compared with that of carbon plate (17.60%). This phenomenon was in agreement with the findings in COD removal. The nitrate removal efficiency for the carbon plate could only increase slowly during the operation of 120 h to 168 h. This phenomenon was different when
carbon felt was used as cathode since nitrate removal efficiency increased steadily over the reaction time.

3.3. Power generation performance

In MFCs, electrodes are electron transferring sites and play the main role in maximizing the power output of the system [13]. The microbial oxidation of synthetic wastewater in the anodic chamber produced electrons and these electrons were transferred externally to the cathode which yielded voltage output. The voltage output of MFC with the application of carbon plate and carbon felt as cathodes is showed in figure 3(a). The results revealed that carbon felt (280.20 mV) produced higher maximum voltage output than carbon plate (222.20 mV). Larger specific area and porous structure of carbon felt offered a better electrochemical activity towards ORR compared with that of carbon plate [14]. The high porosity of carbon felt promoted sorption of oxygen in the pores and increased the ORR reactivity at cathodic chamber when carbon felt as cathode. Besides, the internal resistance has a significant effect on the voltage output [15]. The internal resistance of the carbon plate (600 Ω) was 1.5 times higher than the carbon felt (400 Ω). This indicated that the MFC system with carbon felt cathode offered larger power generation as compared to that of carbon plate cathode when run on the same operation condition [16].

Figure 3: (a) Voltage output and (b) power density curves for the MFC system using carbon plate and carbon felt as cathodes.
Figure 3(b) shows the power density curves for carbon plate and carbon felt as cathodes to access the maximum power density generated from MFC. The maximum power density obtained under carbon plate as cathode was 11.54 mW m$^{-2}$ which corresponded to the current density of 131.11 mA m$^{-2}$. However, MFC with carbon felt as cathode produced higher maximum power density of 21.28 mW m$^{-2}$ which corresponded to the current density of 228.89 mA m$^{-2}$ as compared with that of carbon plate. The difference of maximum power density between carbon plate and carbon felt was 45.77%. Higher porosity of carbon felt and better adsorption properties were beneficial for the ORR reactivity and led to the larger current density as compared to carbon plate with plain and smooth surfaces [17].

3.4. Columbic efficiency
CE is a quantitative measurement to determine the amount of COD that has been transferred as electrical current. It was calculated based on the voltage output and COD removal for both cathode materials along the operation. The CE for the MFC using carbon felt as a cathode (3.63%) was higher than the carbon plate (3.32%). This could be due to the carbon felt opposed higher oxygen reduction rate and promoted the rapid reactivity with oxygen. Therefore, it resulted in a high fraction of degradation of the organic substrate that contributed to electricity generation [18].

4. Conclusion
In conclusion, the cathode played crucial roles in the electron acceptance and ORR reactivity. Results revealed that COD and nitrate removal efficiencies of the MFC system which used carbon felt as the cathode were 50.90% and 21.88%, respectively and were higher than that of carbon plate (COD: 43.52% and nitrate: 17.80%). The MFC system which utilized carbon plate as cathode achieved maximum power density and current density of 11.54 mW m$^{-2}$ and 131.11 mA m$^{-2}$. The maximum power density and current density increased up to 42.72% and 45.77%, respectively, when carbon felt was employed as the cathode. This was attributed to the higher porosity, larger specific surface area and excellent adsorption characteristics of carbon felt. The application of carbon felt as a cathode significantly improved the removal of synthetic wastewater in the anodic chamber and bioelectricity generation of MFC simultaneously.

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