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Electrogenic Digestion of Wastewater from Ethanol Production Plant

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Abstract. The study of electricity generation was conducted in a membrane-less microbial fuel cell (MFC). Wastewater from ethanol industry was anaerobically treated in a fabricated bioreactor for electricity generation. The design of reactor was simple in order to easily scale up for industrial applications. Instead of membrane as a selective proton transfer system, a two-chamber bioreactor used in this work was separated into aerobic and anaerobic chambers connected together through the salt bridge and operated in a batch mode at room temperature (30°C). Influences of different electrodes, nitrogen purging and extra substrate on cell voltage, power generated and COD removal were investigated. From the study, we found that the cell voltage and power generated were substantially increased when using graphite as an electrode compared with carbon cloth, consequently, COD removal from the graphite system was much higher than that from the carbon cloth system. In this work, effect of purging nitrogen to maintain anaerobic condition after sampling considerably enhanced the cell voltage. Adding glucose as an additional substrate to the anaerobic chamber gave significant effect on COD removal, cell voltage and power generation. Maximum COD removal of 74.35%, maximum cell voltage of 623.5 mV and power generation of 1.11 W/m^3 were achieved from the system with extra glucose substrate (3 gL^{-1}) using graphite as electrode when potassium permanganate in a combination with oxygen was used as electron acceptor.

Keywords: Electricity generation, Membrane-less microbial fuel cell (MFC), Two-chamber microbial fuel cell, Wastewater treatment, Anaerobic digestion, Electrogenic digestion

1. Introduction

It has been widely known that chemical bonds of organic compounds are able to convert to electrical energy by fuel cells. Microbial fuel cell (MFC) is one type of fuel cells demonstrating high performance to catalyse an electrogenic digestion by microorganisms attaching onto the surface of the cell's anodes. One potential application of this kind of fuel cell is treatment of wastewater effluents due to the variety of organic matters. Anaerobic digestion has been utilized to treat high organic content wastewater represented in terms of biological oxygen demand (BOD) and chemical oxygen demand (COD) removals. To apply the MFC in wastewater treatment system, several advantages have been stated including 1) production of a useful product in the form of electricity, 2) lack of need for aeration, 3) reduced solids production and 4) potential for odor control [1,2]. Anaerobic digestion converts organic particulate substrates into soluble substrates through hydrolysis followed by acedogenesis to produce volatile solids and hydrogen that ultimately convert to methane through methanogenesis. However, anaerobic digestion is often limited by the production of acedogenesis step in which generated volatile acids dramatically reduce pH and subsequently inhibit methanogens. This problem was proposed to be solved by using microbial fuel cell where volatile acids are utilized for electrogenic digestion. Therefore, organic solids are converted to volatile acids and finally transformed directly to electricity by exoelectrogens [1].

Owing to the high cost of selective proton exchange membrane to fabricate microbial fuel cells (MFCs), the utilization of MFCs was limited only in laboratory scale. The constraints of using membrane-type MFCs were found when applied to high organic content wastewater treatment plant [3, 4, 5]. Thus, the authors have been interested in the study of electricity generation by membrane-less MFCs using a salt bridge as proton

transfer system. Moreover, another significant limitation of using MFCs to generate power at low temperature was the use of oxygen as electron acceptor that required a high performance catalyst e.g. platinum [6]. In MFCs, oxygen plays an important role to accept electron from conducting wire and meanwhile reacts with two proton (H^+) from proton transfer system at the electrode surface to form a molecule of water. In this study, we focused on investigating the performance of potassium permanganate in a combination with oxygen using an air sparking system to enhance the electron accepting capacity without using platinum, a very high cost catalyst. Alternative catalytic systems to replace platinum have been widely researched [7]. A great advantage of this design is to easily implement to wastewater treatment for industrial applications when anode is present in an anaerobic digestion system and cathode is immersed in an aerobic treatment system in which oxygen is conventionally supplied such as activated sludge and trickling filter.

2. Materials and Methods

2.1. Materials

Wastewater was kindly supplied from an ethanol production plant of Siam United Winery Co., Ltd., Nakorn Pathom, Thailand. Glucose, potassium chloride, potassium permanganate and chemicals for analyses were analytical grade purchased from Fluka and Merck.

2.2. Microbial fuel cell

Microbial fuel cell used in the experiment was designed to be composed of two chambers, anaerobic and aerobic chambers, connected together by the salt bridge containing 1 $molL^{-1}$ KCl agar. Each chamber had 1-L capacity equipped with conducting wire and electrode and sealed tightly for the anaerobic chamber to prevent the air leak. In this work, graphite and carbon cloth as electrodes were investigated. Digital multimeter was connected to monitor the voltage alteration over the digestion period when the external resistor was 500Ω. Anaerobic chamber contained 700 mL waste water from ethanol plant with initial COD of approximately 330-340 mgL^{-1}, 3 gL^{-1} of glucose was dissolved in wastewater, and the chamber was continuously stirred using magnetic stirrer at 300 rpm. The anaerobic chamber was flushed with nitrogen gas for 5 min before starting up the system in order to maintain anaerobic condition and connected to an aerobic chamber equipped with electrode and conducting wire. Additionally air was supplied into the aerobic chamber with the flow rate of 20 mL min^{-1} when oxygen was tested as an electron acceptor. In some batches, potassium permanganate was added in an aerobic chamber as a combination with oxygen to act as an electron acceptor. The system was operated at room temperature (30°C) and the voltage change was monitored over the digestion period. Initial and final pH, COD, turbidity and total soluble solids of wastewater were determined.

2.3. Wastewater analyses

COD analysis was performed according to APHA standard method [8]. Initial and final pH of waste water was measured. The cell voltage change and the power generation over the resistor at a constant resistance (500Ω) were continuously monitored during the period of digestion using digital multimeter. Power generated was calculated based on working volume of wastewater. Scanning electron microscope (SEM) images of air-dried anode after the operation were taken after coating by thin platinum layer at 15kV (Hitachi S4800, Japan).

3. Results and Discussion

3.1. Influence of nitrogen sparging on cell voltage enhancement

The test of the MFC system's performance was carried out and represented in terms of cell voltage. In this experiment, graphite was used as electrode and the aerobic condition was maintained with 20 mL min^{-1} sparging air inlet since oxygen was used as an electron acceptor. However, the consumption of electron by microorganisms occurred during the first period of experiment from 0 to 85 hr showing the continuous reduction of voltage from 400 mV to 140 mV as illustrated in Fig. 1(A). This phenomenon besides happened as a result of microbial adaptation to a new environment. After a while, microorganisms started to grow together with digesting organic substances in wastewater and produce electrons simultaneously. Anaerobic digestion began with hydrolysis step where large complex molecules were degraded to small molecules. These monomers were subsequently converted to organic acids and volatile organic acids through

acedogenesis and finally biogas consisting of methane, hydrogen and carbon dioxide via methanogenesis. The pH decrease after digestion showed that some acids were generated during microorganism growth (data not shown).

Fig. 1(A) demonstrated the decrease of cell voltage after taking wastewater sample from anaerobic chamber. The reason of voltage reduction was presumably referred to the leak of oxygen into the anaerobic compartment. Oxygen leak into the chamber showed significant inhibition of microbial growth reflecting to either less electrons were generated or electrons generated were further reacted with oxygens and protons (H^+) to form water molecules. The latter was rather difficult to occur as the reaction of oxygens and hydrogens to produce water molecules at room temperature requires platinum or other particular catalysts [4]. Once purging the anaerobic chamber with nitrogen gas at 160, 180, and 210 hr, the cell voltage was substantially increased owing to the ongoing of anaerobic condition as shown in Fig. 1(A).

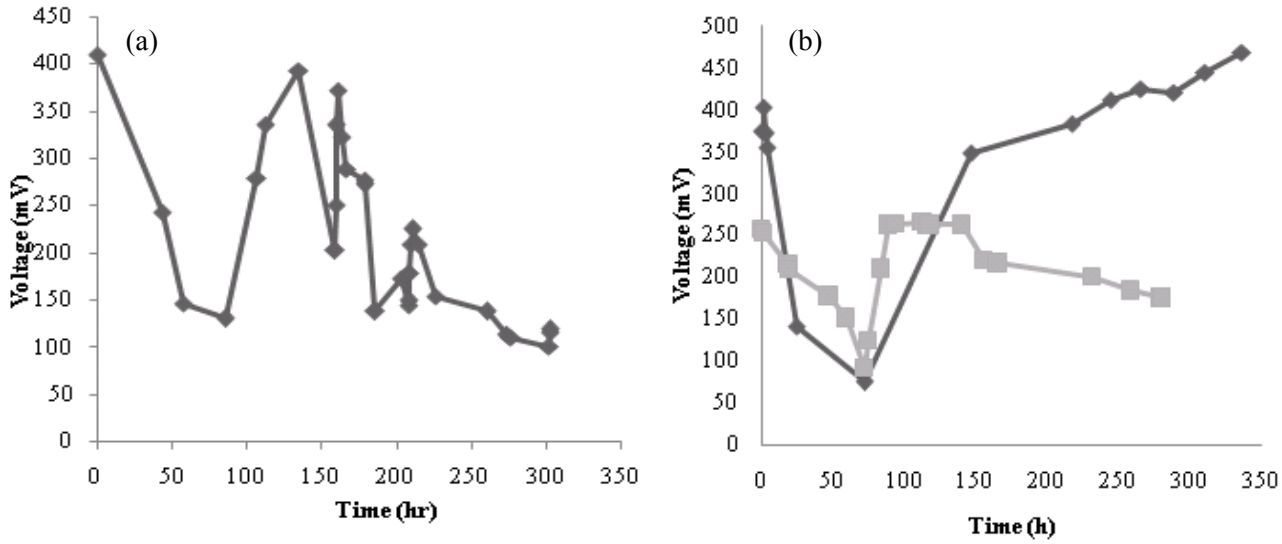

Fig. 1 : (A) Effect of nitrogen purging in anode chamber on the cell voltage at 160 hr, 180 hr and 210 hr, and (B) cell voltage of MFC when graphite (♦) and carbon cloth (■) were used as electrodes.

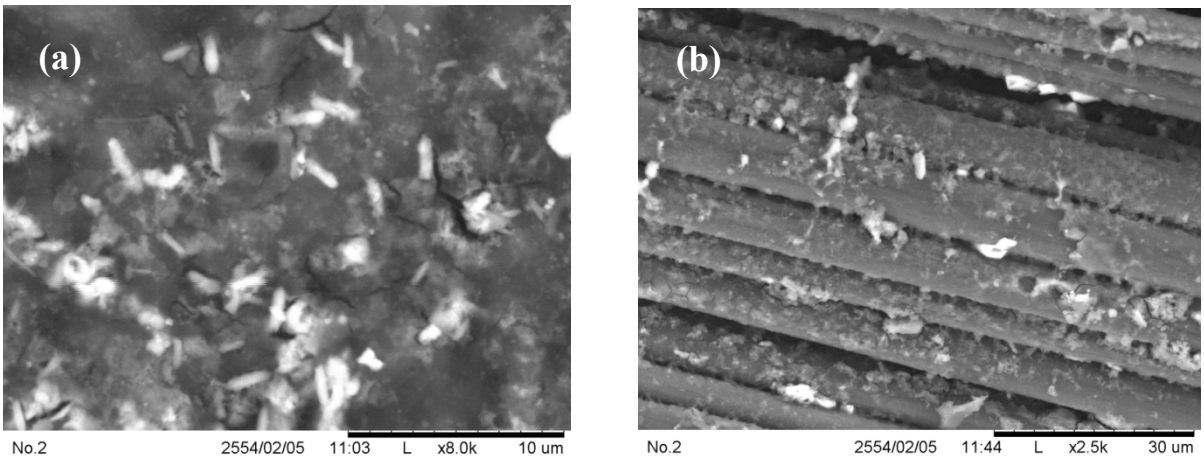

Fig. 2 : Scanning electron microscope (SEM) images of (a) graphite and (b) carbon cloth electrodes in anode chamber after electrogenic digestion for 12 days.

3.3. Influence of glucose on cell voltage

As illustrated in Fig. 3(a), adding glucose as an additional substrate into anaerobic compartment containing wastewater greatly enhanced cell voltage. Moreover, this was able to shorten the lag phase or adaptation period of microorganism from 75 hr to 50 hr relative to the control as glucose is monomeric substrate which is easily utilized by most anaerobic bacteria. The s-shape profile of microbial growth phase was able to observe by the curve of cell voltage change when glucose was used as a co-substrate. Therefore,

Fig. 3(a) illustrated the first exponential phase from 50 to 100 hr and afterward the microbial growth reached the stationary phase until the 150th hour. This was mainly due to the consumption of glucose which is easily utilized compared to organic matters in wastewater. Soon after, microorganisms started the exponential phase again from 150 to 250 hr by degrading complex organic matters in wastewater and utilized as substrate. The normal single growth profile was observed in the control containing merely wastewater as substrate.

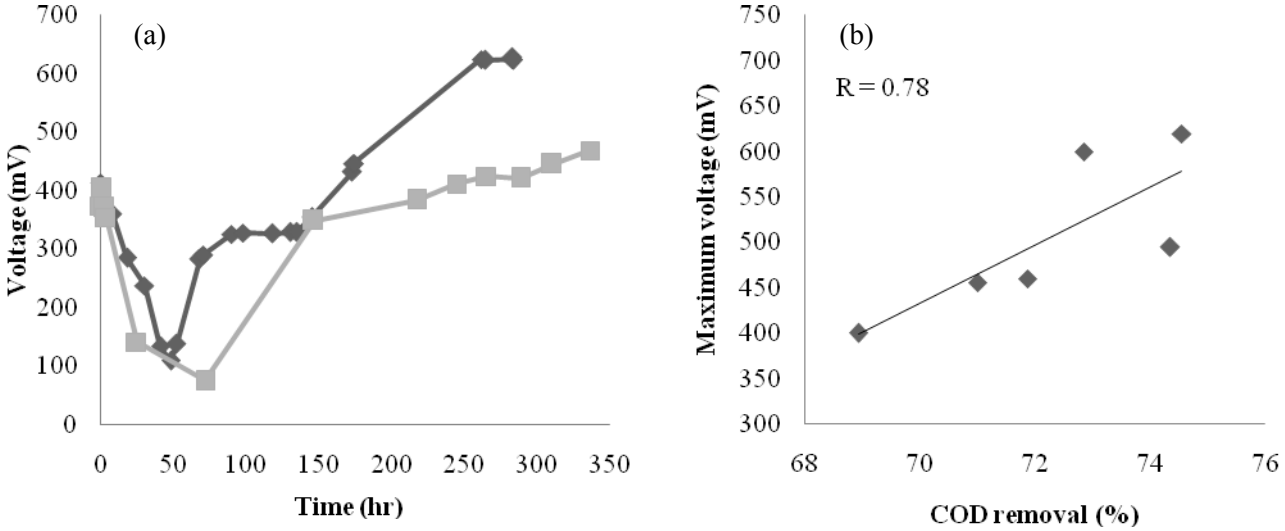

Fig. 3 : (a) Cell voltage of MFC when adding glucose as a co-substrate (♦) compared with the control (■) and (b) correlation between maximum MFC cell voltage and percentage of COD removal of the wastewater.

Final pH of the system with glucose as an extra substrate was lower than that of the control as demonstrated in Table 1. This was most likely due to the addition of glucose accelerating the acedogenesis during anaerobe's growth to produce volatile organic acids. The volumetric power generation of the glucose added system (1.11 W/m^3) was higher than that of the controlled system (0.63 W/m^3). Moreover, similar results were found for the maximum cell voltages of both systems; however, COD removals after the anaerobic digestion of these two systems were not significantly different. In summary, the cell voltage and power generation were enhanced for the system containing glucose as a co-substrate.

Table 1. Comparison of COD removal, pH, cell voltage, and power generated from the MFC

Substrate in anaerobic chamber	COD removal (%)	pH		Max. cell voltage (mV)	Power (W/m^3)
		Initial pH	Final pH		
Controlled (wastewater)	74.55	8.40	7.48	468.5	0.63
Adding glucose	74.35	8.30	7.39	623.5	1.11

3.4. Correlation of COD removal on maximum cell voltage

A good positive correlation between maximum cell voltages at the equilibrium state and percentages of COD removals was found from six experiments operated. As demonstrated in Fig. 3(b), the correlation coefficient (R=0.78) of these two parameters was acceptable. This particularly means the apparatus in addition can be used as a COD monitoring system to predict the COD reduction over the period of digestion from the increase of maximum cell voltage of the MFC. As a result, electrogenic digestion generated substantial amount of electrons which were transferred to aerobic compartment to react with oxygen from air sparging system. The higher the organic matters in wastewater were degraded, the greater the maximum cell voltage and the power generated were detected.

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