BIOELECTRICITY GENERATION in ANNULUS STRUCTURE OF SINGLE CHAMBER MEMBRANE-LESS MICROBIAL FUEL CELL USING WASTEWATER FROM CHOCOLATE INDUSTRY

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ABSTRACT

Microbial Fuel Cell (MFC) is an efficient system for generating low power where wastewater is substrate for the biocatalyst. In this work, Annular Single Chamber Microbial Fuel Cell (ASCMFC) with spiral anode was fabricated and tested. Carbon cloth and stainless steel 400 meshes were selected as cathode and anode electrodes, respectively. In order to enhance the conductivity of anode, the graphite coating was applied. A 40% platinum as catalyst was used on carbon based cathode in MFC. The carbon cloth was coated with 5% Nafion solution. In fact Nafion acts as Proton Exchange Membrane (PEM) in the fabricated MFC. For the first time, wastewater of Chocolate industry with COD 1400 mg/L was used as substrate in anode compartment. Also a mixture of anaerobic sludge from wastewater treatment plant (Qaem-Shahr, Iran) was introduced into MFC. Maximum voltage obtained in the ASCMFC system was 792 mV in an open-circuit mode. Also, Fabricated MFC operating at 30 °C, the maximum achieved power density using an external resistance of 500 Ω was about 4.8 W/m3. The upshots from single chamber MFC were compared to dual chamber MFC. The findings demonstrate that, due to the generated high power density and voltage by the cell, the ASCMFC has a great potential for COD removal and wastewater treatment.

KEYWORDS

ASCMFC, Power Density, Bio-electricity, Chocolate wastewater.

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1INTRODUCTION

As fossil fuel sources are depleted, alternative source of energy for replacement is required. Replacement and use of renewable energy may ensure safe and eco-friendly environment while air pollution and emission of toxic volatile compounds are eliminated. Energy derived from organic waste not only convert waste to energy but the advanced technology may be an attractive sustainable technology for alternative energy source [1-3].

Microbial Fuel Cell (MFC) has been developed for production of energy from biodegradable biomass. MFC has gained a lot of attentions to produce low voltage of electrical energy from natural substrates such as carbohydrates [4]. In MFC organic wastes and chemical oxygen demand (COD) are oxidized; in fact biological treatment may occur while living cells are generating electron in anode chamber; then transferred through electrical resistance [5]. In oxidation and reduction via biological processes electrons and protons are generated [6, 7]. transmission of proton trough proton exchange membrane (PEM) create an opportunity for electrons and protons to meet on cathode for generating stable product known as hydrogen; then oxidized to water molecule [8]. Anaerobic condition must be established in anode for reduction of organic molecule to donate electron while cathode has to be aerobic for oxidation hydrogen [2, 9, 10].

Microorganism are able to utilize nutrients present in aquatic environment such as domestic wastewater [11], food industry wastes such as chocolate [12], dairy, sewage baker and confectionery products [13-15], marine sediments [16], animal waste [17], anaerobic sewage sludge [18], and literally any biodegradable organic compounds. The performance of MFC can be altered by several factors such as inoculum, digestion rate of substrate, electron transfer rate, type of proton exchanger, proton mass transfer through liquid, internal and external cell resistance, ionic strength of the solution, electrode types and spacing [10, 19, 20].

In order to increase the cell output power, structural optimization is considered as the important parameter which has the highest influence on the cell efficiency. Most MFCs are operated at neutral pH for desired bacterial growth conditions. Due to lower proton concentration, MFCs have lower internal resistance than chemical fuel cells that incorporate alkaline or acid electrolytes. The internal resistance may decrease by increasing the conductivity of the solution and decrease in electrode spacing without any changes on the pH of system [21].

Considering the fact that temperature has a direct effect on the bacteria kinetic, the performance of MFC can be altered by temperature fluctuations as well. Investigations of FCs are normally accomplished at temperatures around 30 to 37 °C. The desired temperature ranges are based on growth activities of organisms even in room temperature 15-30 °C for mesophyll or at high temperatures 50-60 °C for thermophiles or at temperatures less than 15° C which is suitable for psychrophilic growth.

Type, size and fabrication routes of electrodes can also affect the performance and output power of FCs. Most used electrodes are carbon based such as carbon felt [22], carbon cloth [23], carbon paper [24], graphite granule [25], graphite brush [26], granular activated carbon [27], graphite rod [28], graphite fiber, graphite foam, RVC [29, 30]. The cathode

performance plays a pivotal role in overall cell performance. Platinum as an effective catalyst is widely utilized in the cathode electrode to compensate for the poor kinetic of oxygen reduction and promote the output power. The main disadvantage of platinum is its higher cost compared to other catalysts. However, a 0.5mg/cm² loading of Pt is used in most commercially available cathode electrodes and their performance have been investigated [19, 20].

Confectionery industries are an important sector of the food industry in terms of effluent and wastewater management. The effluents of these units are complex organic compounds such as polysaccharides, proteins, fatty acids and lipids. Normally COD is very high; for instance, a study conducted by Ozturk et al [31] the COD of wastewater for a confectionery factory in Turkey was 19900 mg/L . Consequently, the effluents of confectionery industries are highly prone to biodegradation and can serve as suitable substrate for MFCs.

The purpose of present work is to fabricate and test an especial design of MFC known as annular single-chamber microbial fuel cell (ASCMFC) using wastewater as source of energy. The unit may be used as pretreatment unit for waste water treatment. In order to reduce manufacturing costs of ASCMFC, special configuration of anode with spiral geometry was chosen. Also to enhance efficiency of the MFC, graphite –coated stainless steel was applied in anode compartment.

2 MATERIALS AND METHODS

2.1 ASCMFC design and construction

2.1.1 Fabrication of MFC body

To construct the cell, a transparent Plexiglas plate with thick of 3 cm was used to fabricate the MFC.

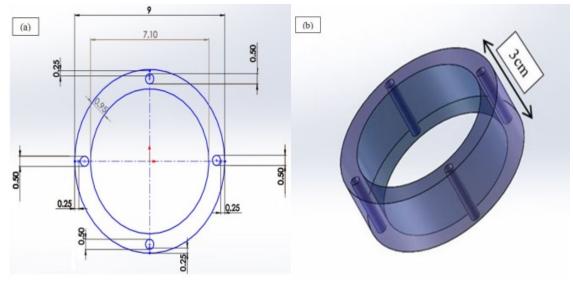


Figure 1. (a) 2D, (b) 3D scheme of SCMFC body

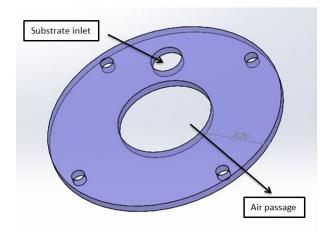


Figure 2. Top lid of ASCMFC

A circle with diameter of 9 cm was made on the surface of the specimen using Laser Cutter. The schematic diagram of MFC frame is shown in Figure 1. In order to serve as the main chamber of MFC, another hole with diameter of 7.1 cm was made on surface of the outer circle to have a chamber with inner and outer diameters of 7.1 and 9 cm, respectively. Finally, 4 holes with diameter of 5 mm were placed on the edge of the chamber, offering spaces for screw placement (see Figure 1).

Top and bottom lid of the cell are the other parts of the body which were made out of a 3 mm thick transparent Plexiglas plate. In addition, 4 holes with diameter of 5mm were located on the sides for screw insertion to connect lids to the chamber. It is important to note that the central hole was made to pass the air (see Figure 2).

2.1.2 Design and construction of cathode holder

A circle with outer diameter of 3.4 cm and inner diameter of 2.1 cm was made on the surface of a 3 mm thick Plexiglas plate. Four rectangular pillars with 3 cm height and 6 mm² Cross section were cut from a 6 mm thick plate. Each of these pillars includes 3 holes to pass the wire. As shown in Figure 3, rectangular pillars were fixed between the circular plates (Figure 3).

In order to provide conductivity between the cathode electrode and the outer part of the cell, one meter-long cupper wire was used. As shown in Figure 4, the wire was wrapped around the cathode holder through the embedded holes. Finally, the cathode holder was encrusted with a black strip of improved cathode electrode.

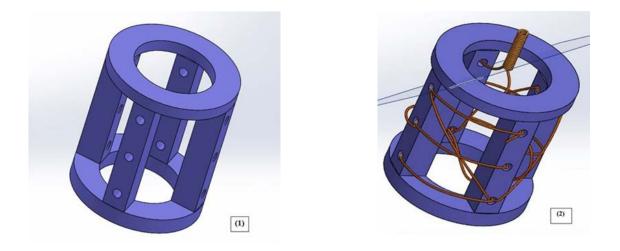


Figure 3. The central part of the ASCMFC, the cathode holder

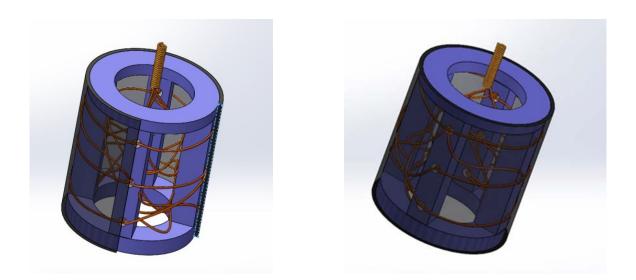


Figure 4. Holder covered by cathode electrode

2.1.3 Anode electrode

To fabricate anode electrode, a 2×57 cm² stainless steel mesh with 400 meshes was selected. Due to the high electrical resistance of stainless steel meshes, these meshes were coated with graphite to increase electrical conductivity. Use of steel mesh decreases operational costs dramatically compared with other types of electrodes. Furthermore, the mesh increases the possibility of growing the biological layer on its porous surface. On the other hand, flexibility and high ductility of steel along with its high mechanical resistance provides formability in a variety of geometries. In order to increase the surface area of anode and

simultaneously decrease the electrodes spacing and electrical resistance, spiral shaped mesh was used (see Figure 5).

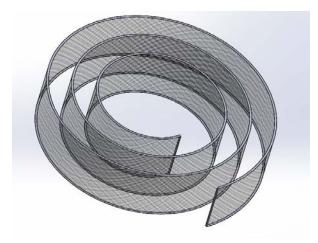


Figure 5. The metal strip used as anode

2.1.4 Cathode electrode

A 3.5×11 cm of carbon cloth was selected to fabricate cathode electrode. By creating diffusion layers on the surface of cathode using the structure introduced by Cheng et al [20], one can enhance MFC's power generation. To describe the structure, first of all, carbon is placed as the first layer. The inner surface under the exposure of air was coated with polytetrafluoroethylene (PTFE) solution as second layer. The outer surface was coated with catalyst ink which is the third layer. The used carbon cloth in this study (E-TEC- USA) was coated with PTFE by factory default, so only catalyst was coated on the outer surface.

2.1.4.1 Preparation of catalyst ink

A mixture of 40% carbon powder-platinum (Alfa Aesar), 5% nafion solution (Dupant), 99% isopropanol (Merck) and distilled water were used to produce the catalyst ink by the method described elsewhere [20]. A 0.5 mg of platinum for each cm² of carbon cloth was required. After weighing these components, they were sonicated for 4 minutes until a homogeneous suspension was obtained. It should be noted here that if these components are not mixed well or the amount of water is not enough, mixing of carbon-platinum and nafion can lead to combustion of the mixture. If nafion or isopropanol exceeds the optimum value, obtained ink will be diluted and will cross the carbon cloth. On the other hand, if it is less than optimum value, catalyst particles agglomerate and the catalyst ink may not form very well.

2.1.5 ASCMFC overall assembly

In the studied system, the dimensions of cathode and anode electrodes were $3.5 \times 11 \text{cm}^2$ and $2 \times 57 \text{cm}^2$, respectively. The volume of anaerobic chamber was 90 cm³. The anode surface area can be increased by the aid of spiral geometry. Furthermore, the substrate passes shorter route in spiral geometry and can diffuse through the biological layer which was grown on the porous surface of anode [32] (See Figure 6).

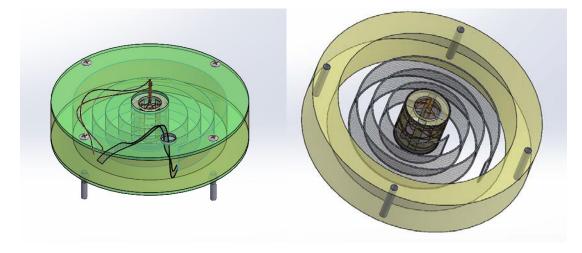


Figure 6. The scheme of the cell with circular structure and spiral anode

2.2 Inoculation and performance of the cell

In this study, wastewater of Farmand chocolate industry (Tehran, Iran) was used as substrate in the fuel cell. The oil phase of the wastewater was separated by physical treatment methods. The aqueous phase containing oily particulates and solid wastes were removed apart using coagulation processes. Consequently, the wastewater was majorly contaminated by hydrocarbons and water soluble fatty acids which were not separable by physical solutions but were strongly susceptible to biodegradation. Hence, biological processes were needed. Wastewater characterizations are given in Table 1.

Since mixed cultures cover a wide variety of microorganisms, they are very resistant to environmental fluctuations and are able to degrade wider ranges of substrates. In this study a mixture of anaerobic sludge from wastewater treatment plant in Qaem-Shahr was used as mixed culture. Organic and minerals materials are vital for bacteria nutrition and protoplasting purposes. Also, vitamin solutions are very useful for their growth and survival. Minerals and vitamins used in this work are given in Table 2.

Parameter	Values		
РН	5.02		
COD	1400 mg/L		
Turbidity	139.68 NTU		
Conductivity	3160 µS/cm		
TDS	1.57 ppm		
Salt	1.55 ppt		

Table 1. Wastewater Characterizations

Growth Media		Mineral Solution		Vitamin Solution	
Compound	Conc.	Compound	Conc.	Compound	Conc.
	(g/L)		(g/L)		(g/L)
KCl	0.13	CaCl ₂ .2H ₂ O	0.132	B-12	0.1
Na ₂ HPO ₄	4.09	CoCl ₂ .2H ₂ O	0.132	Biotin	1.96
NaH ₂ PO ₄	2.544	CuSO ₄ .5H ₂ O	0.0132	Folic Acid	2
NH ₄ Cl	0.31	FeSO ₄ .7H ₂ O	0.132	Panthothenic	
				Acid	
Mineral solution	12.5 mL	H ₃ BO ₃	0.0132	Pyridoxine HCl	3.6
Vitamin solution	5 mL	K_2SO_4	3.96	Riboflavine	3.06
Distilled water	1000 mL	MnSO ₄ .H ₂ O	0.66	Thiamin	3
		NaCl	1.32		

Table 2. Chemical composition of growth media added to MFCs [33]

As illustrated in Table 2, the growth media contains 12.5 ml of mineral solution and 5ml of vitamin solution in addition to several types of mineral salts that were mixed and diluted to 1 liter. In order to adapt the anaerobic sludge with chocolate wastewater, 10 ml of wastewater and 10 ml of growth media were mixed and introduced into sludge every 2 days for 3 month. After these injections, 3 ml of anaerobic sludge, 42 ml of growth media and 45 ml of wastewater were injected to the cell and the generated voltage was recorded. During the cell operation the pH of the media was dropped and sodium bicarbonate buffer solution, pH 10, was used to prohibit the acidification of anolyte.

2.3 Analytical technique

The cell potential was measured and collected every 15 minutes using a data acquisition system. Electrical current measurements were performed in different resistances applied by a variable resistor. The generated voltages were recorded in each resistance and electrical currents and power were calculated by Eq1 and Eq2, respectively. In order to normalize the results, power and current were divided to anaerobic chamber's volume. The ultimate upshots were reported in terms of W/m^3 and mA/m^3 for power and current, respectively.

I = V/R(1) $P = V \times I$ (2)

3 RESULTS AND DISCUSSION

3.1 Open-Circuit-Voltage (OCV)

The open circuit test was the first test which performed on the ASCMFC along with the microbial enrichment process.

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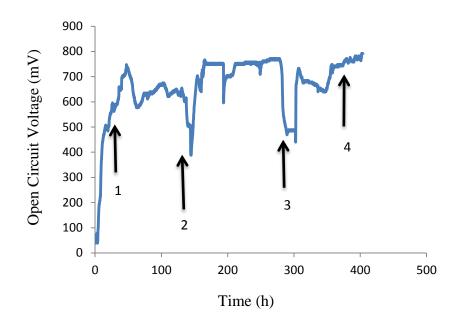


Figure 7.Measurement of ASCMFC opens circuit voltage. Addition of fresh substrate is indicated by arrows.

As illustrated in Figure 7, the open circuit voltage was examined for 403 hours. The initial voltage between anode and cathode was 68 mV, due to the chemical and biological differences. At the beginning of the process it showed a minor decline caused by incompatibilities between bacteria and the chamber conditions which named lag phase. Then, there is a substantial increase to 748 mV after 46 hours. This upward trend was named logarithmic phase. For stationary phase, it was remained constant approximately around 750 mV with some fluctuations and gradual rise to the end of the test. It was perceived from the graph that, substrate consumption and decrease in pH leads to diminish voltage in stationary phase. But the decline in voltage was retrieved, by each injection of substrate and pH adjustment with phosphate buffer (pH=7). After the last injection (the injection number 4 shown in Figure 7) maximum voltage obtained 792 mV and remained Table at this voltage without any noticeable differences. Finally it was found that, microbial enrichment was completed and further investigation was conducted.

3.2 Effect of external resistance on the performance of ASCMFC

With the application of external resistance, the system was switched to closed circuit mode and electrical currents were evaluated over time. External resistances of 500 and 300 Ω were

applied and potential variations were recorded with each resistance for 382 and 264 hours, respectively. During the test, fresh wastewater was injected to the cell 4 times. As illustrated in Figure 8 using resistance of 500 Ω , the maximum observed values for generated current and power density were 0.932 mA and 4.82 W/m3, respectively. Likewise, using resistance of 300 Ω the maximum obtained values for generated current and power density were 1.253 mA and 5.23 W/m3, respectively. Similar for OCV test, wastewater renewal at each decline causes abrupt ascends during the test.

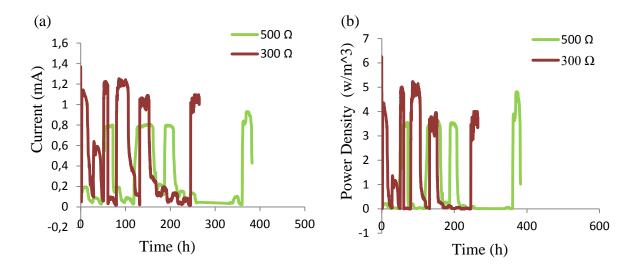


Figure 8. (a) Current and (b) Power density variations

These ascends were attributed to wastewater renewal and subsequently generation of electrons by oxidation/reduction processes. Investigations of system response to wastewater renewal at 300 Ω resistance showed that, the period of ascending phase was shorter, the stationary phase lased shorter and the period of decline phase was longer compared to 500 Ω resistance. Moreover the system response to wastewater renewal was faster at lower resistance. With the application of lower electrical resistance, more electrons were transferred toward the cathode and consumed in the proximity of oxygen. Since the substrate oxidation reaction is an equilibrium reaction, high consumption of generated electrons caused high amounts of substrate to be oxidized. Thus, high oxidation rates are expected at low electrical resistances. At lower resistances, the electron transfer rate was higher compared to the generation rate. As a consequence, the period of ascending phase was shorter and the stationary phase lasted longer.

3.3 COD removal

One of the most important methods to measure the high organic loading of wastewater is the COD test. It is defined as the amount of oxygen required to convert organic compounds to water and carbon dioxide. The value of measured COD is proportional to the level of organic contaminants. That is, the higher value for COD is an indication of high levels of available organic compounds. Figure 9 illustrates COD removal for ASCMFC. The COD of used

wastewater was 1400 mg/L which reduced to 123.2 mg/L after 96 hours and COD removal was 91.2%.

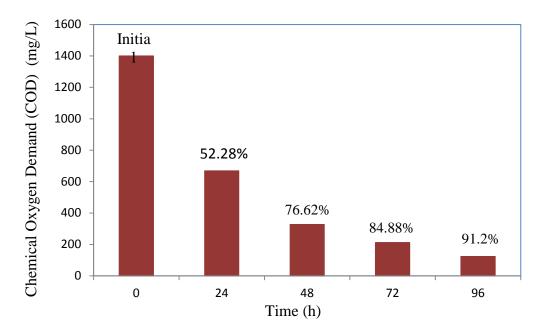


Figure 9. COD removal

4 CONCLUSIONS

In this work, an ASCMFC was fabricated for wastewater treatment and power generation. Chocolate wastewater was used as the substrate in the fabricated fuel cell. Different electrical resistances were applied to the system and the MFC responses were assessed. Investigations on electrical current using resistances of 300 and 500 Ω revealed that at low resistance, the system response was fast and the time period of ascending phase was short. Maximum reported value for OCV was 792 mV. The MFC was also highly capable of COD removal which reduced the COD value by more than 91%. This remarkable efficiency in COD removal envisages the use of this MFC for wastewater treatment in shorter short period of time.

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