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SIGNIFICANCE OF SURFACE AREA OF ANODE IN GENERATION OF ELECTRICITY THROUGH MICROBIAL FUEL CELL FED WITH ANAEROBICALLY DIGESTED DISTILLERY WASTEWATER

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ABSTRACT

Microbial fuel cells (MFCs) convert chemical energy into electrical energy using microorganisms. Various factors influence electricity generation by MFC. Surface areas of cathode and anode have been reported as significant factors affecting the performance of MFC. Hence, in the present study, the above mentioned factors were investigated for understanding their influence on generation of electricity. It was observed that the surface area of cathode did enhance the energy generation but only up to a certain limit (18.42 cm^2). However, surface area of anode was found to be more important and critical in increase the capacity and sustainability of the MFC system. Hence, it can be concluded that in an MFC system, bacteria are solely responsible for generation of electrons and thus, electricity. Providing large surface area for bacterial growth at anode would thus be a key parameter to enhance the electricity generation.

KEYWORDS: Microbial fuel cell, cathode, anode, biofilm, distillery wastewater.

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INTRODUCTION

Microbial fuel cell (MFC) is a device which converts chemical energy directly into electrical energy by using microorganisms as biocatalysts[1,2]. In nature, abundant energy is stored in the form of a variety of carbohydrates, from simple sugars to complex biodegradable polymers which has been elaborated in a review by Pant *et al.*[3] In typical MFC configuration, bacteria at the anode metabolize such biodegradable matter, generating electrons and protons. Electrons and protons are transferred to cathode through external resistance and proton exchangers respectively. At the cathode, electrons are accepted by an electron acceptor, thus completing the circuit and generating electricity[1,4-5]. So, the biodegradable matter present in variety of sources such as agricultural wastewater, domestic wastewater and industrial waste water would be preferred as feed[4]; thus electricity can be generated simultaneously treating the wastewater. The electricity production from renewable sources is desirable without net carbon dioxide emission[6-7]. Albert Einstein had quoted "problems cannot be solved by the same level of awareness that created them"[8] and hence generation of electricity from wastewater is going to be the focus of MFC. Majority of work on MFC deals with the efficiency of the system as industrial wastewater yields very low energy[3]. Several factors have been reported to affect the generation of electricity in MFC system. Amongst these, surface area of anode and cathode, size of proton exchanger, type of electrode and catalyst used and efficiency electro-active bacteria have been considered as crucial[9-11]. It has been reported that all factors mentioned above are important in increase the efficiency of MFC system. However, few researchers have proposed that surface area of cathode plays a crucial role in increasing the efficiency of MFCs[1,12-14]. Conversly, others are of the opinion that surface area of anode rather than cathode is crucial as the microorganisms are active on anode[2,15-17]. The purpose of this study is to systematically examine and better understand the effects of surface area of anode and cathode and their relative importance on the power output by using a two chambered MFC system. In this study, anaerobically digested distillery waste water was used as feed. The results obtained by varying surface area of anode and cathode from 6.14 cm^2 to 55.26 cm^2 were used to analyze their relative significance in terms of total output of electricity in the MFC.

MATERIALS AND METHODS

(i) Materials

Customized Scott Duran glass bottles of 500 mL capacity used as reservoir in the preparation of MFC were acquired from Omega Glass Works, Mumbai, India. Graphite rods removed from exhausted Eveready AA batteries were used as electrodes. Electrical hardware like external resistance and copper wires were bought from a local vendor. Voltages for all experiments were recorded by Picolog 1216, bought from Picotech, UK. Anaerobically digested distillery wastewater used as feed was procured from a distillery near Nasik, India. Sag Tex PHD antifoam was obtained from Momentive, India. All other chemicals used were of ExcelaR grade, used without further purification and obtained from Qualigens (Fisher Scientific), India.

(ii) Wastewater analysis

Wastewater was transported and immediately stored at 4°C. Characterization of the wastewater was carried out using standard methods by APHA[18]. The wastewater characteristics are shown in Table 1.

Table 1
Characteristic of anaerobically digested distillery wastewater

Characteristics	Value
pH	7.96 ± 0.1[a]
Colour	Dark Brown
BOD (mg/L)	2330 ± 108[a]
COD (mg/L)	18560 ± 640[a]
TOC (mg/L)	6519 ± 89[a]
Total Solids (mg/L)	34658 ± 38.7[a]
Total Dissolved Solids (mg/L)	21914 ± 390.2[a]
Total Suspended Solids (mg/L)	12744 ± 135[a]

[a] values expressed as the mean ± the standard deviation (n=3).

(iii) Preparation of feed

250 mL of wastewater was diluted to 1 L with distilled water. 2% Dextrose along with 1 mL each of 0.1 M phosphate buffer of pH 7.2, 0.1 M $MgSO_4.7H_2O$, 0.2 M $CaCl_2.2H_2O$ and 0.01 M $FeCl_3.6H_2O$ were added to 1 L diluted anaerobically digested distillery waste water, to induce the growth of endogenous bacteria. To suppress foaming, 1.5 mL of Sag Tex PHD antifoam was added to 1 L of wastewater. This standardized wastewater was used as feed throughout the experiments.

(iv) Microbial fuel cell set-up and operational conditions

As explained in details in previous study[19], two chambered MFC was constructed appropriate for the batch operations. As shown in Fig1, the anodic and cathodic chambers of MFCs were joined by a salt bridge (15 mL) containing 10% KCl. Two identical cylindrical graphite rods were used as electrodes. Anodes and cathodes were connected through copper wires, connected to 1000 Ω external resistance. The anodic chamber was filled with 200 mL of standardized anaerobically digested distillery wastewater, while cathodic chamber was filled with 200 mL of 100 mM potassium ferricyanide prepared in 100 mM phosphate buffer of pH 7. Endogenous microflora from anaerobically digested distillery wastewater established at anode. All the experiments were carried out at room temperature (25°C to 30°C).

A typical MFC set-up

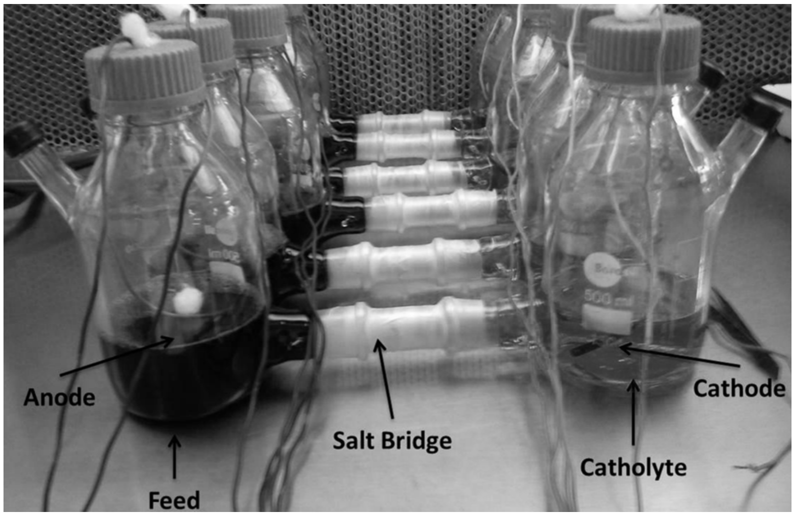

Figure 1
Anodic chamber contains anode immersed in wastewater while cathodic chamber contained cathode immersed in potassium ferricyanide; chambers are connected by a salt bridge

(v) Electrical measurements

All experiments were performed using Picolog 1216 data logger to determine the electricity generation. The voltage was recorded every 5 minutes. The current was calculated using Ohm's law V=I x R, where V is the voltage across resistance, I is the current generated and R is the external resistance. Other calculations used in the present study are as follows:

Power (W) = Voltage (V) x Current (A).

Area under Curve (Cumulative power) = 0.5 $\times(P_1+P_2)\times(t_2-t_1)$ (as mentioned by Pruessner *et al.*)[20]

(vi) Determination of relative significance of surface area of anode and cathode in MFC

Graphite electrodes were used as anode and cathode. Each electrode had a measured surface area of 6.14 cm^2. In the MFC system, the total surface area of anode and cathode respectively was varied from 6.14 cm^2 to 55.26 cm^2 by increasing the number of electrodes.

(vii) Aeration at cathodic chamber

An aeration pump (flow rate of 3 L/min) was used as an aerator in the experiment. Aeration was provided continuously in the cathodic chamber throughout the experiment, while anodic conditions were kept unchanged.

(viii) Statistical analysis

Results are expressed as Mean ± S.D. with experiments being conducted in triplicate. The statistical significance was determined by one-way analysis of variance (ANOVA) to determine if the data obtained was significantly varied from one another. Statistical significance between different columns (surface area) was determined by post-test Tukey using Graph Pad Prism software version 5.0 (Graph Pad Software, San Diego, CA, USA).

RESULTS AND DISCUSSION

1. Effect of surface area of cathode

MFC was constructed in the form of two chambers separated by salt bridge. Standardized anaerobically digested distillery wastewater was used as feed as well as source of inoculum[19]. In the first instance, the surface area of cathode was increased from 6.14 cm^2 to 55.26 cm^2 (at intervals of 6.14 cm^2) whereas surface area of anode was kept constant at 6.14 cm^2. As can be seen from Table 2, the voltage increased proportionally with increase in surface area of cathode till it reached 18.84 cm^2 (one way ANOVA followed by Tukey's test). From Table 2, it is evident that voltage and power produced increased with increase in the surface area of cathode till 18.42 cm^2. Statistical analysis by one-way ANOVA followed by Tukey's post-test confirmed that the voltage and power for surface area of 18.42 cm^2 and 30.7 cm^2 is statistically non-significant and any further addition of the cathodic surface area remained ineffective. This proves that electron generation at anode is an important factor and the acceptance of electrons at cathode depends on the number of electrons reaching the cathode. In the present study, the capacity of MFC was also evaluated by calculating cumulative generation of power as the area under curve as per the formula given by Pruessner et al.[20]. The lowest voltage was considered as baseline; thus any rise in the voltage was considered as a reflection of bacterial activity. The cumulative or total power generated evaluates the sustainability and capacity of the system over a period of time. The sustainability (total power) of the system was statistically significant when compared with surface area of 6.14 cm^2 and reached a plateau, once the surface area of cathode reached 18.42 cm^2 (Table 2).

Table 2
Effect of surface area of cathode

Surface area of cathode (cm^2)	Voltage (V)[a]	Time (h)[a]	Power (µW)[a]	Cumulative power (mW)[a]
6.14	0.031±0.003	29.5±0.7	0.97±0.16	0.055±0.02
12.28	0.041±0.002	30.6±0.9	1.66±0.17	0.078±0.01
18.42	0.051±0.003	30.1±0.4	2.61±0.37[b]	0.095±0.01[b]
30.7	0.053±0.001	29.9±1.1	2.75±0.07	0.08±0.004
55.26	0.05±0.006	29.9±0.3	2.49±0.08	0.08±0.019

[a] ***values expressed as the mean ± the standard deviation (n=3).***
[b] ***Surface area of 18.42 cm^2 showed maximum power and cumulative power generation when analysed by One way ANOVA followed by Tukey's test ($p<0.05$)***

2. *Effect of surface area of anode*

In the next set of experiments, the surface area of anode was increased in the range of 6.14 cm^2 to 55.26 cm^2 (at intervals of 12.28 cm^2) while the surface area of cathode was kept constant at 6.14 cm^2. Results showed linear increase in the voltage with increase in the surface area of anode (Fig2) unlike previous experiment related to surface area of cathode. When the surface area of anode is increased, the microbial community present in anaerobically digested distillery wastewater get exposed to larger surface area to adhere and transfer large number of electrons to anode, thus increasing the voltage. The results emphasizes the fact that bacteria in the biofilm are responsible for electron generation and its transfer to anode[2,17,22]. The energy stored in the chemical bonds of organic biodegradable compounds is converted into the electrical energy through enzymatic reactions carried out by microorganisms. Hence, electricity generation is associated with the metabolism and growth of bacteria[22]. Biofilms on the anode have been demonstrated to increase the current because of the direct transfer of electrons to the anode[23]. From Fig2, it can be observed that the time required by the system to achieve highest voltage also increased with increase in the surface area of anode. The slope of time-line, 4.6889 as compared to the slope of voltage line, 0.0125 (Fig2) suggests that the increase in time is not proportional to voltage; because adherence of bacteria on the surface of anode is a slow process as compared to the generation of highest voltage. The capacity (total power) of MFC was found to increase with increase in anodic surface area as shown in Table 3. Statistical analysis showed anodic surface area of 55.26 cm^2 could produce maximum cumulative power when compared with 6.14 cm^2 (one-way ANOVA followed by Tukey's test)

Effect of surface area of anode on voltage and time

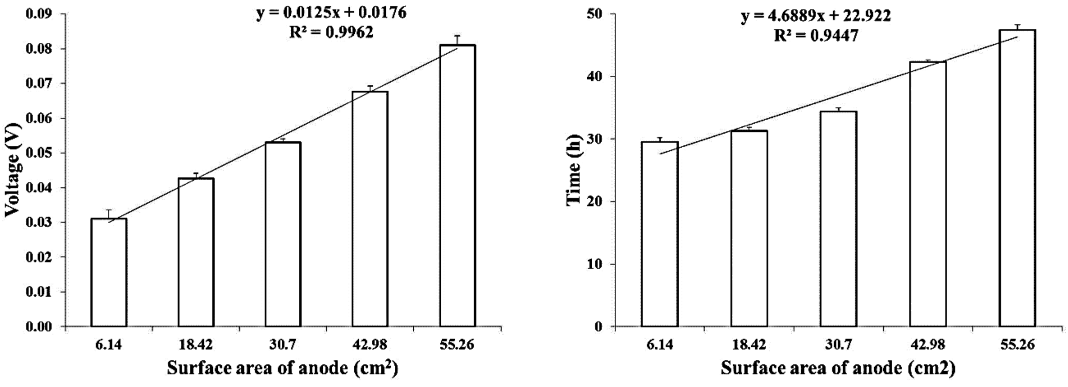

Figure 2
Highest voltage and time required to achieve highest voltage increased linearly with increase in the surface area of anode

Table 3
Effect of surface area of anode

Surface area of anode (cm^2)	Voltage (V)[a]	Time (h)[a]	Power (µW)[a]	Cumulative voltage (mW)[a]
6.14	0.031±0.003	29.5±0.7	0.97±0.16	0.055±0.02
18.42	0.043±0.001	31.31±0.55	1.8±0.13	0.14±0.019
30.7	0.053±0.001	34.39±0.61	5.6±0.0.1	0.2±0.02[b]
42.98	0.067±0.002	42.3±0.38	4.58±0.2	0.43±0.065[c]
55.26	0.081±0.002	47.44±0.83	6.6±0.4	0.65±0.35[c]

[a] values expressed as the mean ± the standard deviation (n=3).
[b] Surface area of 55.26 cm^2 showed maximum cumulative power generation when analysed by one way ANOVA followed by Tukey's test ($p<0.01$)
[c] Surface area of 55.26 cm^2 showed maximum cumulative power generation when analysed by one way ANOVA followed by Tukey's test ($p<0.0001$)

Oh and Logan specified in their research that power generation did not increase in proportion to surface area of anode[1].They added second electrode to the system but did not find any doubling of the overall voltage. After 90 h, the voltage of second electrode increased while that of first decreased. The possible explanation could be bacteria on anode require time for biofilm formation. When first electrode was added, bacteria started formation of biofilm on the electrode and over a period of time voltage was found to be increased. After some time, second electrode was added to the system. Thus it can be inferred that as there was no biofilm of bacteria on the added electrode, doubling of voltage did not occur. Once the biofilm was formed on second electrode at the end of 90 h, the voltage did increase. However by that time electricity generation capacity at first electrode had reached its limit thus voltage of first electrode was decreased over 90 h. Ishii *et al.* reported that the smallest anode surface area achieved anodic rate-limiting condition, as the bacteria responsible for generation of electrons were limiting[14]. Thus, the increase in surface area of cathode reached a plateau because of the limitation in generation of electrons at anode. In other words, the surface area of anode is critical because it is responsible for generation of electrons. Sadeqzadeh *et al.* also stated that surface area of anode is an important limiting factor for power generation. Electricity generation can be enhanced by anode material, anode structure and surface area of anode which ultimately increase performance of the MFCs[17]. Various reports suggest that power output increases with increase in surface area of cathode. Oh *et al.* reported 24% power increase with increase in surface area of cathode from 22.5 cm^2 to 67.5 cm^2 [24]. According to Cheng and Logan, doubling the surface area of cathode increased 62% power output while that of anode resulted in only 12% increase[12]. Even Call *et al.* showed reduction in performance of MFCs when cathode surface area was decreased by 75%[25]. Two significant observations were made in this study. (a) Increase in power generation was found to be 85.57% when surface area of anode increased from 6.14 cm^2 to 18.84 cm^2 while power increase was found to be 169.07% when surface area of cathode was increased from 6.14 cm^2 to 18.84 cm^2. (b) After further increase in surface area of anode from 18.84 cm^2 to 55.26 cm^2, 266.67% increase in power production was obtained but power produced did not increase at all when surface area of cathode was increased from 18.84 cm^2 to 55.26 cm^2 (Table 2 and 3). Considering the outcome of (a) and (b), the total power generation by surface area of anode is more than that of the surface area of cathode.

3. Effect of aeration at cathodic chamber

Literature has shown the importance of aeration at cathode in increasing the power generation of MFCs[26]. In one set of experiment, 200 mL of potassium ferricyanide was used as the catholyte and the experiment was carried out for 48 h, while in another, continuous aeration at cathodic chamber was provided with an aerator. It was observed that aeration did not increase power generation as compared with the normal MFC (Fig3). Thus electron generation became critical factor and hence, all the electrons generated at anode by bacteria were utilized immediately by potassium ferricyanide. The oxidation-reduction potential (ORP) of ferricyanide for MFC without aeration at the start of the experiment was found to be -121.3 mV, while it changed to +11.1 mV at the end of the experiment. While for MFC with aeration, ORP changed from -121.3 mV to + 11.4 mV. This showed that, aeration at cathode did not increase the accepting capacity of catholyte. Again this result showed that generation of electrons at anode was limited and enough for potassium ferricyanide to accept electrons at cathode alone, thus aeration did not affect the system for increase in power production. If generated electrons would have been in large number then possibly aeration would have increased the power production. This result also indicated that generation of electrons by is bacteria and hence surface area of anode becomes crucial and important factor in enhancing electricity generation[27].

Effect of aeration on voltage generation in MFC

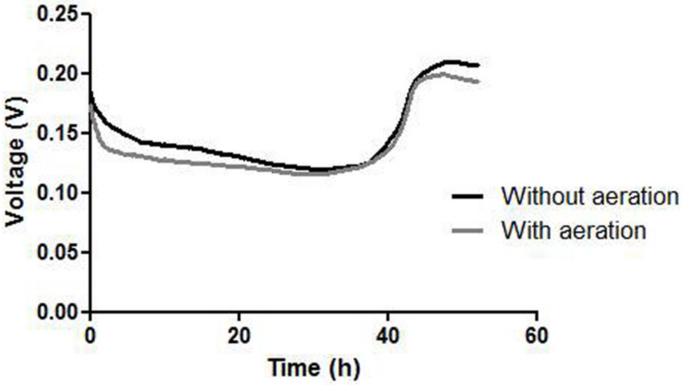

Figure 3
Effect of aeration in cathodic chamber

CONCLUSION

The results depict that the data from MFC system can be analysed by calculating area under the curve indicating sustainability and capacity of the system. The surface area of cathode definitely enhances the total power production of MFC system up to a certain limit after which there is no further increase in the power production. On the other hand, surface area of anode does not induce a plateau and is, thus, the critical factor. It is responsible for overall increase in the capacity of the system as anode is directly responsible for acquiring larger number of electrons through microbial metabolism. Hence, increase in surface area of anode is crucial to increase the power production in comparison to surface area of the cathode.

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CONFLICT OF INTEREST

Conflict of interest declared none.

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