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Generation of Electricity from Mango pulp Waste Water using Single Chamber Air Cathode Microbial Fuel Cell

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Abstract: **Electricity generation from an Air Cathode Microbial Fuel Cell (ACMFC) was investigated in treating real mango pulp waste water. In this study novel ACMFC with combined advantages for simultaneous waste water treatment and energy recovery. ACMFC was operated in batch mode with various external resistances. The mango pulp waste water varied concentration in the range of 50,000 mg COD^{-L} to 1,60,000 mg COD^{-L}. At pH range of 6.5–7.2, the cathode open circuit potential (OCP) was achieved as 1.18 V. The maximum voltage obtained was 1.133 V, with an overall chemical oxygen demand (COD) removal of 95 %. To estimate the performance of the ACMFC, the electro chemical measurements were carried out these results showed that the air cathode microbial fuel cell produced stable power and a high CE 31.09 %, making it useful for treatment of actual wastewaters. High power density and successive performance as a power generator was characterized based on polarization behavior. The results of recent studies suggest that in future ACMFCs will be of practical use will become a preferred option among sustainable bioenergy processes.**

Keywords: **Air Cathode Microbial fuel cell; mango pulp waste water; self-sustainable waste treatment process; Electricity generation; external resistances.**

1. INTRODUCTION

Microbial fuel cell (MFCs) are a promising approach for treating wastewater, as electricity is produced directly from the process of organics biodegradation [1], [2]. Single-chamber, air cathode MFCs have the advantages of a simple design, improved power generation, and the ability to use passive air for oxygen reduction [3]. Microbial Fuel cells are an alternative source of generating electricity from microorganisms for satisfying the high demand of energy. Because of their high power output, simple structure and low cost, single-chamber air-cathode MFCs hold great promise for large scale applications in waste water treatment [4], [5]. In MFCs, microbes play crucial roles in energy output and organic contaminants removal [6]. The ability of microbes to transfer electrons in the anode can significantly affect the performance of MFCs. Compared with traditional two-chamber MFCs, hybrid MFCs or membraneless SCMFCs have simple configurations, compact structure, and low internal losses, which are all essential criteria for scaling-up the MFC technology [7].

Several types of MFCs, such as double chamber MFCs [8], single chamber MFCs [9], tubular MFCs [10], up flow MFC [11] and multi-anode/cathode MFCs [12] have been developed. However, single chamber microbial fuel cells (SCMFCs) are believed to be superior because of their simple design, flexibility, low internal resistance, and relatively low cost [13].

Air-cathode MFCs have been shown to produce higher power output when operated without Proton Exchange membrane (membrane-less MFC), which has been attributed to higher cathode potential [14], [15]. MFC technology has not yet been applied to practical waste material treatments. This is primarily because it is an emerging technology and much time is required for technical maturation [16]. Electrodes materials play an important role in the cost and performance of MFCs.

The anode electrode materials should possess a good electrical conductivity, low resistance, strong biocompatibility, chemical stability, large surface area and an appropriate mechanical strength [17]. Carbon cloths are widely used in MFCs because of their higher porosity and mechanical strength in comparison with other electrode materials. [18]. MFC performance was evaluated in terms of maximum power output, columbic efficiency, and COD removal. To accelerate the catholic oxygen reduction reaction (ORR), catalysts (e.g. noble metals, platinum) are quite often used in MFCs. Even though the efficiency of the Platinum (Pt) based cathodes have been reported to be high in acidic solutions, it is known to be significantly lower in the neutral/mildly alkaline solutions [7]. PTFE coating on cathode improves the power density/Columbic efficiency and has been used as a diffusion layer in most of the air cathode studies [19, 20, 21, 22]. PTFE is a highly hydrophobic material, which is used to prevent water leakage in MFCs and it has good oxygen transfer efficiency [23]. PTFE coatings control the oxygen diffusion into the anode. However, PTFE may limit effective proton transfer to the Internal resistance can be reduced by decreasing the electrode spacing or increasing the solution conductivity [24]. Carbon brush anodes are ideal for scaling up MFCs as they have large porous surface areas, relatively non-corrosive, have low resistance, good electrical conductivity and show a compact and structured distribution of the bristles that helps to avoid bio fouling [25]. The anode electrodes is immersed in mango pulp waste water containing organic compounds and the anodophillic bacteria, growing on the anode surface and oxidize the organic substances through their metabolic processes. In the cathode, oxygen is normally used as the final electron acceptor. In a MFC, a microbial biofilm oxidizes organic matter and transfers these electrons from reduced compounds to an anode which accepts electrons. The bacteria grow on the anode and form a biofilm which helps to carry out the oxidation of organic substances into carbon dioxide, hydrogen-ions and electrons, in the absence of oxygen [26]. The electrons then pass through a circuit and combine with a terminal electron acceptor (oxygen) and protons and gets liberated as water at the cathode [27]. Treatability studies are therefore needed to evaluate a specific wastewater in a MFC, in terms of power generation and the extent of organics removal [28]. MFCs are able to generate power and at the same time remove organic wastes [18]. In MFCs, microbes play crucial roles in energy output and in the removal of organic contaminants. The ability of microbes to transfer electrons in the anode can significantly affect the performance of MFCs [6]. In spite of the attractive feature of power production with wastes and a cheap apparatus, this technology needs a deeper study of the involved mechanisms [29].

The aim of the study is to generate electricity from mango pulp waste water using air cathode microbial fuel Cell. Also the performance of the Air cathode Microbial fuel Cell (ACMFC) was evaluated based on the characteristics of power density, columbic efficiency and chemical oxygen demand (COD) removal.

2. MATERIALS AND METHODS

Air cathode MFC setup:

In this study Air cathode Microbial fuel Cell with 240 ml anode chambers and air-cathodes are used. The Schematic diagram of proposed Air cathode Microbial fuel Cell (ACMFC) is shown in Fig 1.

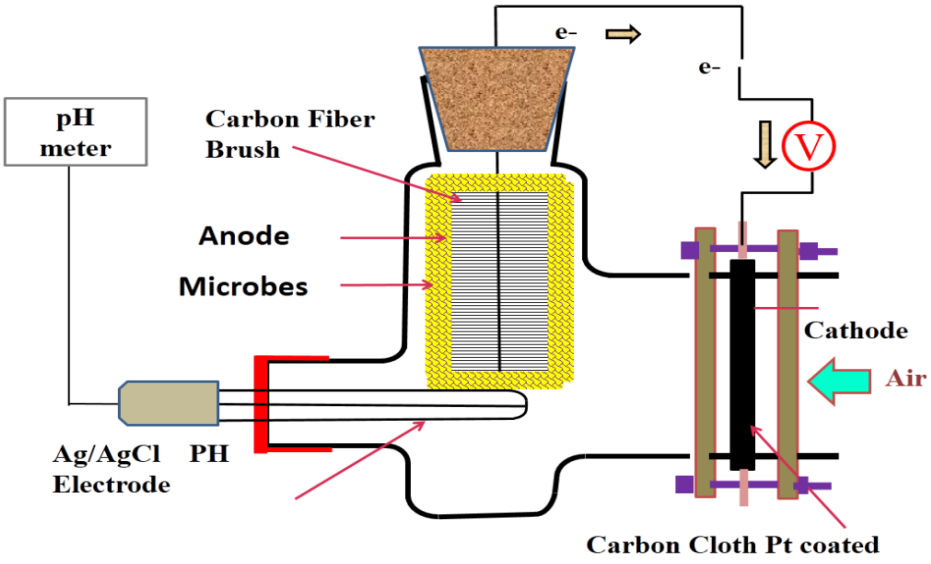

Fig.1. Schematic diagram of single chamber air cathode microbial fuel cell

Initial characteristics of mango pulp waste water:

The initial characteristics of mango pulp waste water sample has been carried out by the method detailed in APHA, 2005 [30] (Table 1).

Anode electrode:

The anode electrode was a carbon fiber brush size 7.62 X 3.81 cm as projected area, with a core of two twisted 17 gauge titanium wire current collector [31] and its overall length of brush is 15.24 cm. The carbon fiber brush fill 4,00,000 tips per inch and offers a large surface area for bacterial growth and higher power densities in microbial fuel cells (MFCs). The carbon fiber brushes are non-corrosive.

Enzymatic cathode electrode:

Carbon cloth is cut to the size of 9.625 cm2 as surface area (3.06 cm X 3.06 cm) with 30% wt. PTFE treated (Fuel Cell Earth), was used as current collector and cathode support. Teflonized carbon black (Vulcan XC72R with 35% wt. PTFE) was utilized as a gas-diffusion layer (GDL). The carbon base layer was prepared by applying a mixture of carbon powder (Vulcan XC-72) and 30 wt.% PTFE solution (20 mg of carbon power) onto one side of the carbon cloth, air-drying at room temperature for 2 h, followed by heating at 370 0 C for 0.5 h. The carbon loading in this DL was chosen to be 2.5 mg cm-2 [32], [19]. Pt catalyst (0.5 mg cm_2) was then applied to the water-facing side of the carbon cloth as previously described using Nafion as a binder [23]. Wet-proofed (30%) carbon cloth (type B, ETEK, Somerset, NJ, USA; 7 cm2) was coated with carbon/poly (tetrafluoroethylene) (PTFE) layers on the air-facing side and platinum (0.5 mg/cm2 cathode area) with Nafion as binder on the water-facing side, and used as the cathode (Fig. 2). The inner side of the teflonized carbon black (XC 35) was treated with isopropanol to achieve a gradient of hydrophobic to hydrophilic properties across the GDL, with XC 35 and isopropanol loadings of 60 mg cm–2 and 40μLcm–1, respectively. [8]. The micro porous layer (MPL) conductive ink layer was capable of enhancing oxygen transfer inside cathode structures and also increase the electrical conductivity of cathodes [20].

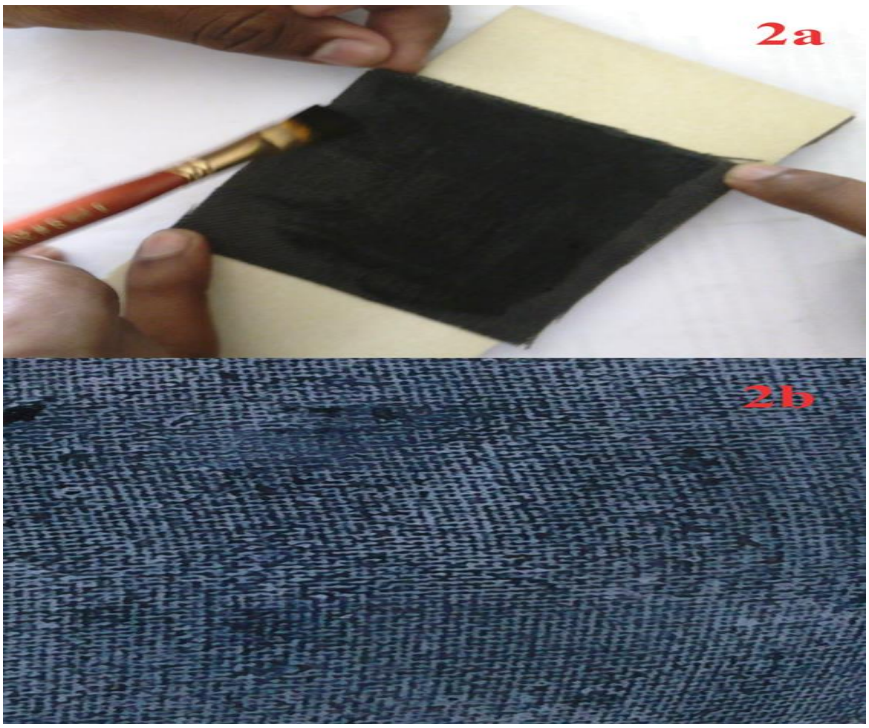

Fig. 2. (a) Carbon cloth coated with Nafion as binder on the water-facing side. (b) PTFE coated Carbon cloth micro porous layer (MPL).

Configuration of Air Cathode MFC:

A batch-mode membrane less SCMFCs, having a 240 ml cylindrical anode chamber was made of glass (Fig. 1). The anode electrode Carbon brush size 7.62 X 3.81 cm as projected area, twisted in titanium wire was obtained from Mill-Rose Company of USA. The anode electrode was inserted in the top inlet hole closed by screw cap lid.

The enzymatic cathode carbon cloth electrode having size 12.56 cm2 surface area (4 cm X 4 cm) is placed in the bigger hole of 50 mm dia with flange arrangement facing the carbon coated layer to air and Pt coated layer towards anode.

An Ag/AgCl reference electrode (Schott Inst., +0.197 V according to standard hydrogen electrode, SHE) was located in the anode chamber and connected to the electrodes to measure the anode and cathode potentials.

3. CALCULATIONS AND ANALYSIS

An external resistance (R) from 16,000 Ω to 60 Ω was connected between the anode and cathode in order to simulate a constant load and carry out discharge curves. The current variation was also monitored. The variation under closed circuit conditions were to obtain polarization and power density curves. Polarization curves were obtained by measuring the stable power generated. [30]. Cathodes and anode are electrically connected by an external resistor R. By the Ohm low (V = IR) the voltage V across the external resistor R is directly related to the current I generated in the MFC. Cell voltages across a resistor were recorded every 20 minutes at different loading rates were measured using a digital multimeter. The current production was calculated using ohms law; I = V/R, where I = Current (A), V = Voltage (V), is the voltage measured and R (Ω) is the external resistance applied. Power density (mW/m2) and current density (mA/m2) were calculated based on the anode surface area [2] power density (P) was calculated as P = V ×I. Both I and P were normalized to the projected area of cathode surface (4 cm X 4 cm).. The cells were periodically opened and an Ag/AgCl reference electrode was placed between cathodes and anodes (half way) in order to measure individual potentials (in open circuit) and to per-form polarization tests. Performances of the MFCs were assessed by power curves and polarization curves of anodic and catholic electrodes. The maximum power density was calculated by varying the external resistance up to 18000 in a single batch cycle or estimated from the polarization curve. The columbic efficiency can be calculated for a fed-batch system as [33]:

$CE = 8 \int I\, dt / (F\ V_{an}\ \Delta COD)$

Where ΔCOD depicts change in COD concentration over the batch cycle, F is Faraday's constant, I is the output current, and V_{an} is the volume of liquid in the anode compartment. The total columbic efficiency was obtained by dividing the sum of the charge produced by the four MFC units (the integration of current with respect to time) by the total charges consumed based on the observed COD removal. Polarization and power density curves were generated using the single-cycle method by measuring the open-circuit voltage (OCV).

4. RESULT & DISCUSSION

MFC performance:

The performance of the single chamber ACMFC in batch mode with mango pulp wastewater was examined under steady state condition. The pH of the mango pulp wastewater was about 6.2 and was maintained at 7 by 0.1 N NaOH during the operation period. MFC was operated at different organic loading 1000 mg/L to 4000 mg/L and results were studied.

Performance of air cathode MFC as a function of external resistance:

ACMFC Electricity generation potential was investigated with several external resistances [21]. The potential was recorded at different resistances from 60 Ω to 16 K Ω to analyze the MFC performance through the polarization curve method.

From the figure 3 (a) it was evident that as the cur-rent increases, the voltage decreases. The current and voltage recorded for resistance such as 16,000 ohms, 10000 ohms, 8,000 ohms, 5000 ohms, 3500 ohms, 1000 ohms, 700 ohms, 500 ohms, 300 ohms, 100 ohms, 60 ohms, under organic loading of 1000 mg/L, 2000 mg/L, 3000 mg/L and 4000 mg/L respectively. The maximum voltage obtained was 1.133 volt for the external resistances (16,000 Ω) and the maximum current obtained were 1.102 mA for the external resistances (60 Ω) at organic loading 2 g/L. With the same external resistance (16,000 Ω) the maximum voltage obtained were recorded to be 0.775 volt at organic loading 1 g/L, 0.947 volt at organic loading 3 g/L and 0.568 volts at organic loading 4 g/L respectively. Also the maximum current obtained were recorded to be 0.844 mA for the external resistances (60 Ω) at organic loading 1 g/L, 1.039 mA for the external resistances (60 Ω) at organic loading 3 g/L and 0.775 mA for the external resistances (60 Ω) at organic loading 4 g/L.

The figure 3 (b) illustrates the power density and current density evolution with load resistances ranging from 60 Ω and 16,000 Ω. From the figure it was evident that irrespective of loading there was an increase in power density with

corresponding increase in current density. The maxi-mum power density obtained was 356.02 mW/m2 for the external resistances (500 Ω) at organic loading 2 g/L. With the initial increase, there was a drop in power density with further increase in current density occurred. As the current density increased, the power density also increased and then decreased with increase in current density. For the rest of the organic loading the maximum power density obtained was 238.52 mW/m2 for the external resistances (700 Ω) at organic loading 1 g/L, 302.26 mW/m2 for the external resistances (500 Ω) at organic loading 3 g/L and 186.96 mW/m2 for the external resistances (700 Ω) at organic loading 4 g/L.

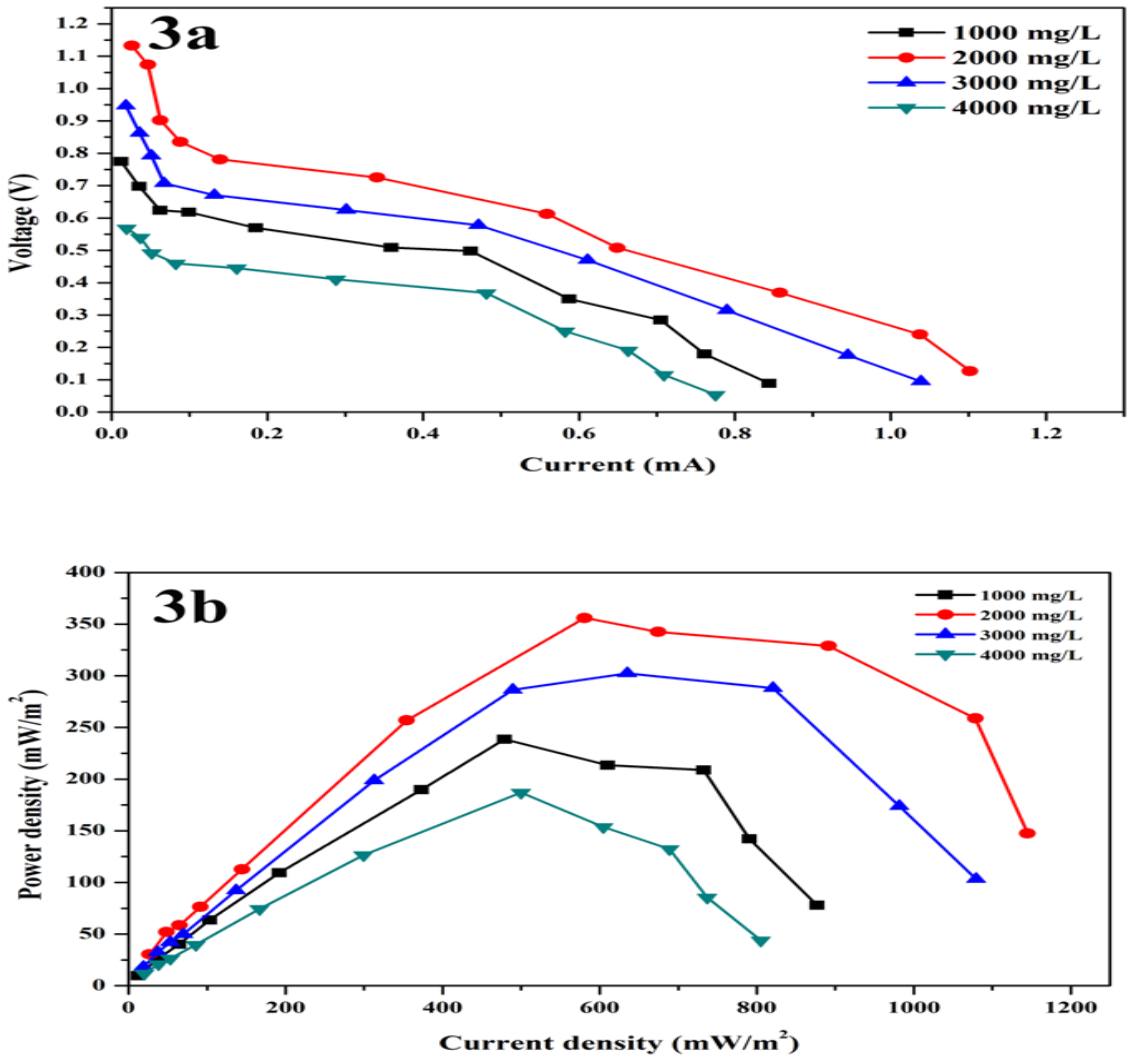

Fig. 3. (a) Current with Voltage under various organic loading. (b) Current Density and Power density evolution under various organic loading.

Open circuit voltage (OCV):

Fig. 4 (a) and (b) illustrates the open circuit voltage and closed circuit voltage during the study period. The open circuit voltage increased at an organic loading of 2g/L with increase in time and this trend last for 6 days. At day 6 MFC recorded highest OCV generation and was found to be 1179 mV. Further increase in treatment time causes decrease in OCV. For the rest of the organic loading the maximum generation of OCV for the other organic loading namely 1, 3 and 4 g/L are recorded to be 792 mV, 960 mV and 590 mV, respectively. It is confirmed that the catholic OCP (the initial point on LSV curve) increased drastically from Day 1 - Day 6 (Fig. 4 (a)) and decreased from day 7 onwards and this phenomenon continues till the end of the reactor aeration.

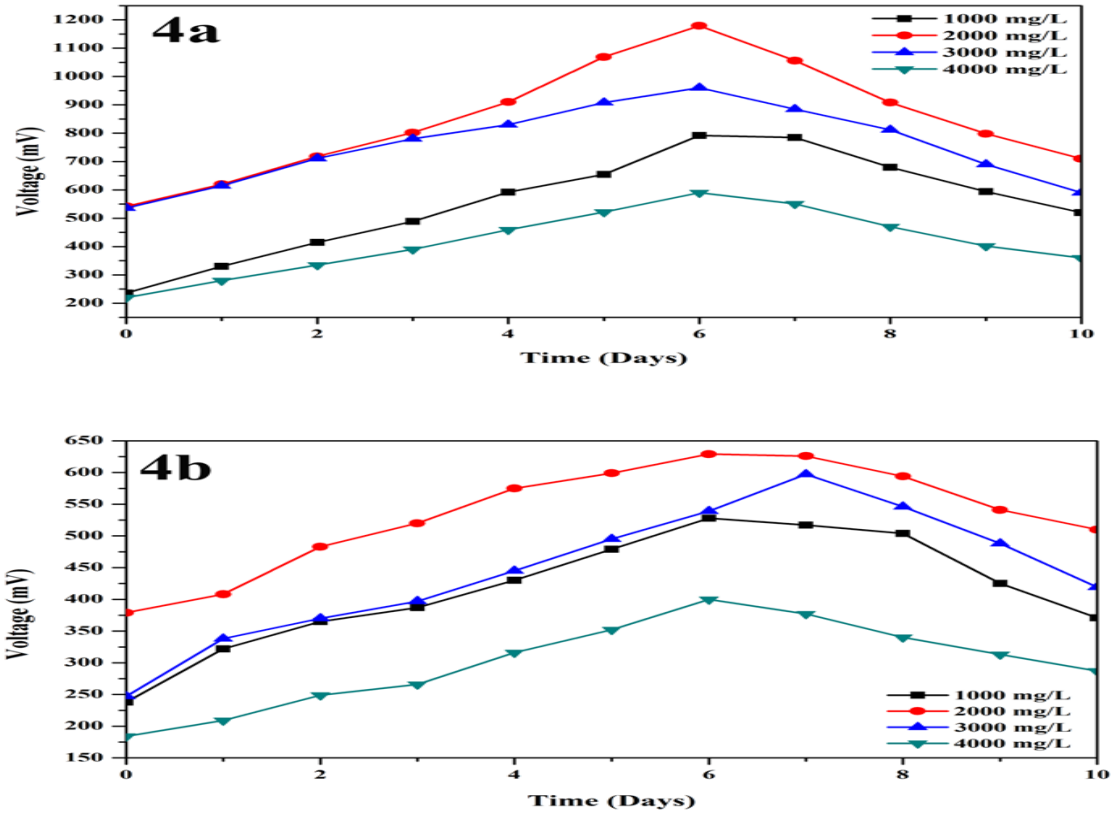

Fig.4. (a) Open circuit voltage with time (days). (b) Closed circuit voltage with time (days).

Closed circuit voltage (CCV):

The anode and cathode are closed with 700 Ω resistance. The maximum power density of 356.02 mW/m2 was obtained with the resistance 700 Ω. Hence this resistance is chosen for closed circuit voltage measurement. Fig. 4 (b) illustrates CCV during the operation period of the ACMFC. With an organic loading of 2 g/L the CCV was found to increase with increase in time and this procedure last for 6 days. At day 6 MFC recorded highest CCV generation and was found to be 629 mV. Further increase in treatment time causes decrease in CCV. For the rest of the organic loading the maximum generation of CCV for the other organic loading namely 1, 3 and 4 g/L are recorded to be 528 mV, 597 mV and 400 mV, respectively. It is confirmed that the catholic CCP (the initial point on LSV curve) increased drastically from Day 1 - Day 6 (Fig. 4(a)) and finally decreased from Day 7 onwards till the 10th day. Owing to various potential loses the OCV is considerably lower than the CCV. The energy loss is due to over potential accrued at the cathode and ohmic loses of the system [9].

Performance of air cathode MFC under various organic loading:

The figure 5 (a) shows the effect of organic loading on the power density in mango pulp waste water. From the figure it is evident that the maximum power density obtained was 356.02 mW/m2 at organic loading 2 g/L. For the rest of the organic loading the maximum power density obtained were recorded as 238.52 mW/m2 at organic loading 1 g/L, 302.26 mW/m2 at organic loading 3 g/L and 186.93 mW/m2 at organic loading 4 g/L respectively.

The figure 5 (b) shows the effect of organic loading on the columbic efficiency in mango pulp waste water. From the figure it is evident that the maximum columbic efficiency obtained was 31.09 % at organic loading 1 g/L. For the rest of the organic loading the columbic efficiency obtained were calculated as 18.59 % at organic loading 1 g/L, 14.29 % at organic loading 3 g/L and 9.42 % at organic loading 4 g/L respectively.

The columbic efficiency decreases with the increase in organic loading rate and in turn decreased contact time be-tween microorganisms in carbon fiber brush anode with mango pulp waste water in anode chamber. In this study it is observed that as the organic loading increased bacterial activity decreased and hence the columbic efficiency gets decreased.

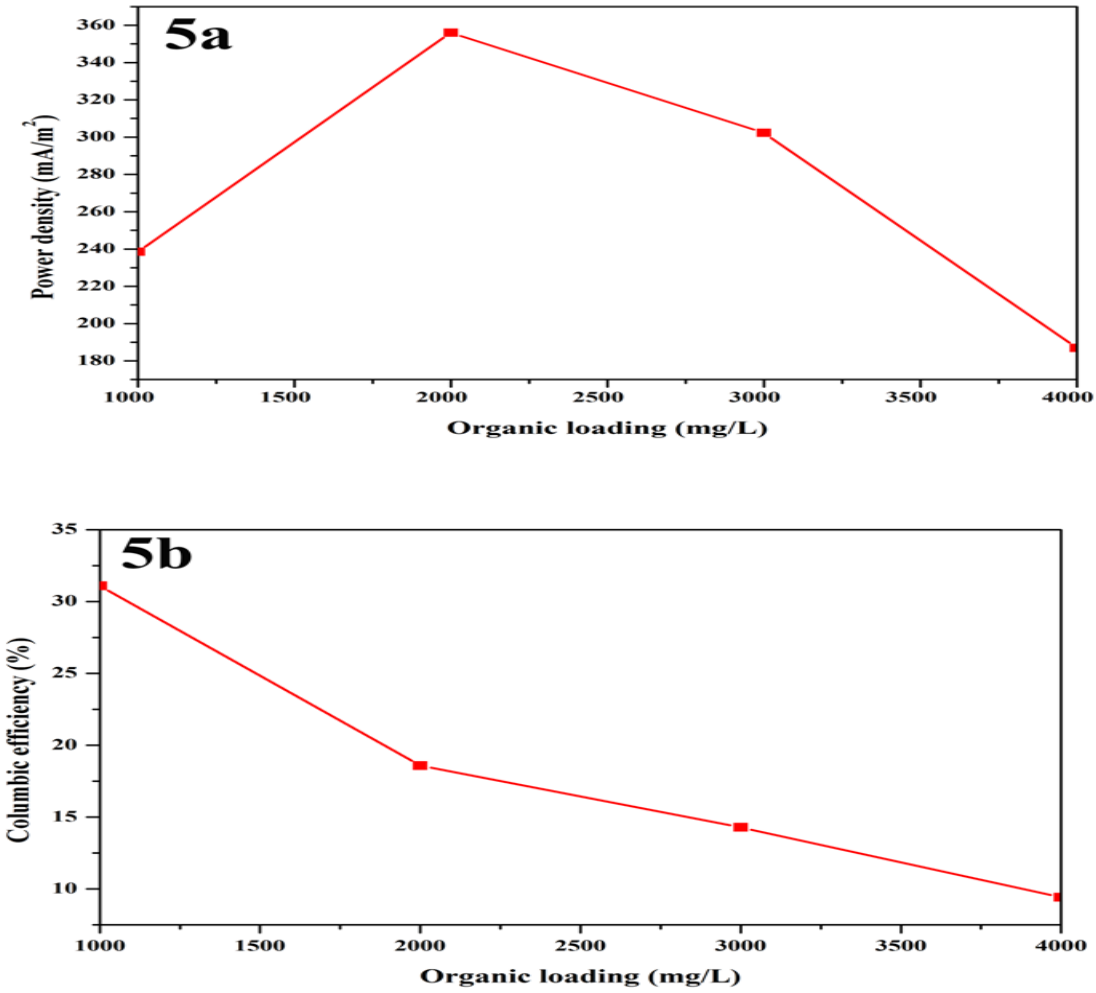

Fig.5. (a) Power density under various organic loading. (b) Columbic efficiency under various organic loading.

Table 1: Chemical parameters of mango pulp waste water (During sampling period)

Sl No	Parameter	Value	Unit
1	pH	6.5 +/- 0.2	
2	Total solids (TS)	37500 +/- 500	mg/L
3	Total suspended solids (TSS)	33100 +/- 250	mg/L
4	Total dissolved solids (TDS)	4400 +/- 50	mg/L
5	Chemical oxygen demand (TCOD)	162000	mg/L
6	Soluble chemical oxygen demand (sCOD)	86000	mg/L
7	Biological oxygen demand (BOD)	103000	mg/L

COD Removal Efficiency:

The COD removal efficiency of the mango pulp waste water was investigated in batch mode ACMFC under open and closed circuit condition. Fig. 6 (a), (b), (c) and (d) depicts COD removal efficiency of the ACMFC.

From the figure fig 6 (a) and 6 (b) it is evident that in ACMFC with mango pulp wastewater the TCOD removal efficiency increases with increase in operational period.

Under open circuit condition, the TCOD removal efficiency at organic load 1 g/L was 73 %. With the increase in organic loading the maximum TCOD removal efficiency was obtained to be 85 % at organic loading 2 g/L. Further increase in organic loading causes a decrease in TCOD removal efficiency. The TCOD removal efficiency of ACMFC was 81 % at 3 g/L and 79 % at 4 g/L organic loading. 85 % TCOD removal was achieved at 2 g/L, with the four different loading used.

In the same way TCOD removal efficiency was achieved for closed circuit mode. The TCOD removal efficiency achieved for closed circuit mode was found to be higher than open circuit mode for all organic loading used in this study. TCOD removal efficiency at organic load 1 g/L was 74 %. When the organic loading rate was increased to 2 g/L maximum TCOD removal efficiency was achieved as 87%, which is the maximum among the rest of the loading. Further increase in organic loading caused a decrease in COD removal efficiency. A TCOD removal efficiency of ACMFC 82 % and 83 % was achieved for organic loading 3 g/L and 4 g/L, respectively.

The SCOD removal efficiency of ACMFC at different organic loading for open and closed circuit condition were portrayed in figure 6 (c) and (d).

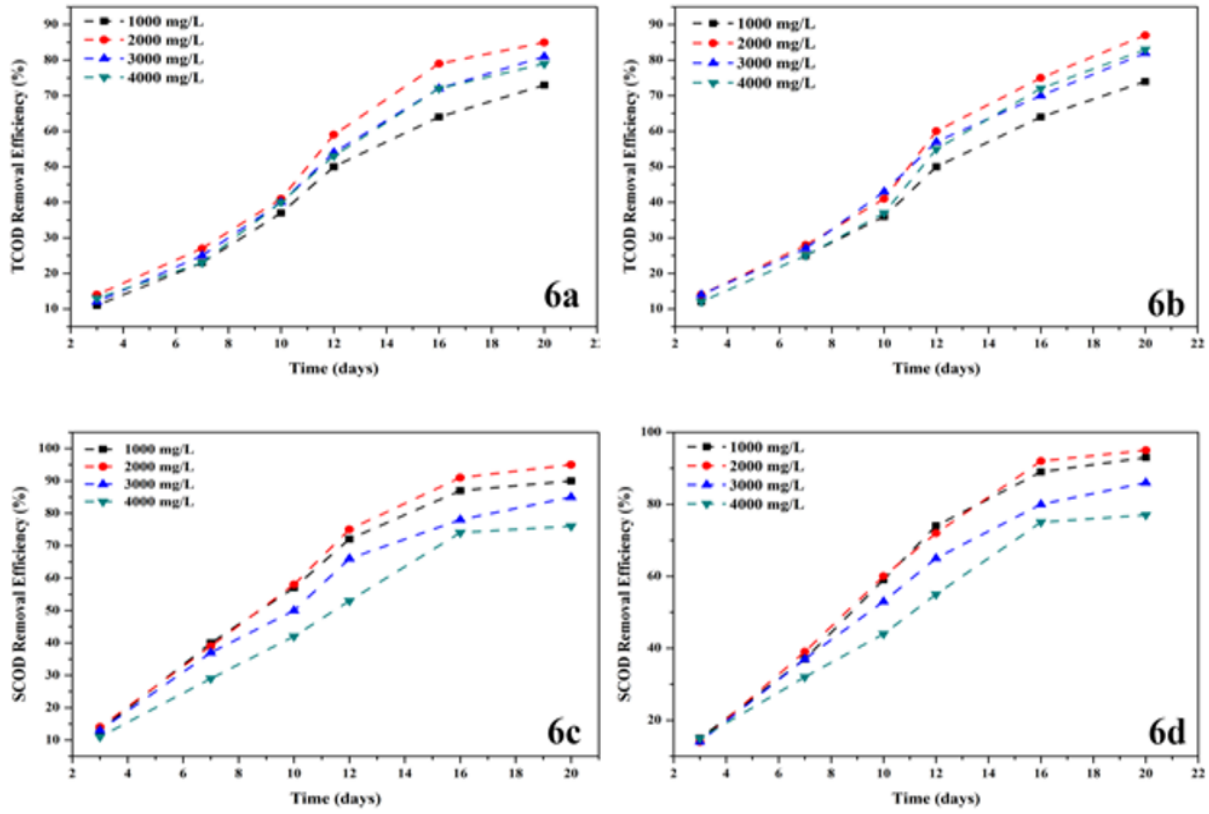

Fig.6. (a) TCOD removal efficiency with time in open circuit condition. (b) TCOD removal efficiency with time in closed circuit condition. (c) SCOD removal efficiency with time in open circuit condition. (d) SCOD removal efficiency with time in closed circuit condition

From the figure 6 (c) it was evident that the maxi-mum SCOD removal efficiency of ACMFC under open circuit condition for the organic load 1 g/L was 90 %. When the organic loading rate was increased to 2 g/L the SCOD removal efficiency increased and was found to be 95 %, which is the maximum among the rest of the loading. Further increase in organic loading causes a decrease in SCOD removal efficiency. At organic loading 3 g/L and 4 g/L the SCOD removal efficiency was achieved to be 85 % and 76 % respectively.

Similarly the SCOD removal efficiency was arrived for closed circuit mode and was shown in figure 6 (d). The SCOD removal efficiency of closed circuit mode was found to be greater than open circuit mode for all organic load used in this study. The SCOD removal efficiency at 1 g/L organic loading was 93 %. When the organic loading was increased to 2 g/L the SCOD removal efficiency was also increased and was found to be 95%, which is the maximum among the rest of the

loading. Further increase in organic loading causes a decrease in SCOD removal efficiency. The SCOD removal efficiency was 86 % at 3 g/L organic loading and 77 % at 4 g/L organic loading. The achievement of higher COD removal under closed state was achieved as there is no significant loss of biomass from the anode chamber [18].

Moreover, utilizing mango pulp water in ACMFC natural waste products enables to convert into electricity without any pretreatment, which is self-sustainable waste treatment process.

5. CONCLUSIONS

This study was the first in the field to investigate extensively the performance of real mango pulp wastewater to generate electric power using membrane less ACMFCs with Pt-based cathodes. With this concept the maximum COD removal efficiency of 86 % and maximum SCOD removal efficiency 96 % under closed circuit condition were achieved [22]. The maximum power density of 356.02 mW/m2 and maximum current density 1145 mA/m2 at 2000 mg/L OLR were also measured. The maximum voltage generated was 1.133 volts.

The study revealed that, the Air Cathode Microbial Fuel Cell (ACMFC) could also be used for substrate removal in real mango pulp waste water as well as electricity. The Chemical Oxygen demand removal efficiency demonstrates that ACMFC as an alternative wastewater treatment unit. These results demonstrates that the generated power can be increased by scaling-up the factors such as electrode spacing as well as to develop cost effective MFC systems.

For real time application the ACMFC can be used as simultaneous wastewater treatment and electricity generation real mango pulp wastewater.

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