



# Biodiesel Wastewater Treatment and Power Generation Using Earthen Membrane Microbial Fuel Cell

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## ABSTRACT

Addressing the global energy needs and limited resources in the form of sustainable technologies should be ideally non-combustion based and have reduced net CO<sub>2</sub> emissions. Microbial Fuel Cells or MFCs can be part of this sustainable development and in the process support the water infrastructure as well. MFC research is evolving rapidly as a promising alternative. In this study, an attempt has been made to produce low cost MFC without involving any costly membrane. The wastewater used in this MFC was biodiesel based, the intention being the feasibility to treat wastewater from biofuel processing. The total dissolved solids or TDS of the wastewater initially was 4420±30 ppm on the first day which decreased to 3360±20 ppm after nearly three weeks of operation. Open circuit voltage or OCV was recorded around 800±10 mV, and the electricity production using a 100 Ω resistor produced around 0.0041±0.0003 mA, power density peaked at 0.15±0.03 mW/cm<sup>2</sup>. System architecture included graphene as a conductive anolyte, aluminum mesh as cathode and a commercially available earthen pot structure as membrane. XRD analysis of membrane showed feasibility of operation, which can be essential for future designs wherein low cost membranes can be integrated for sustainable power generation and wastewater treatment.

## INTRODUCTION

Emissions from combustion processes have increased the rate of climate change over the years as more erratic climate events continue to occur (Santoro et al. 2017). The CO<sub>2</sub> emissions from conventional methods of harvesting energy are not only affecting our present generation, but also the generation yet to come. Researchers believe that climate change is our single greatest security threat. Therefore, the need to find alternatives for the production of energy which is not only emission-free but feasible too is of interest. One such infrastructure can be fuel cells, as it has the ability to run thermal utilities, automobiles and power electronics (Banham et al. 2017). A fuel cell converts the chemical energy from a fuel (such as hydrogen) to electrical energy and being a non-combustion process does not have significant emissions.

Microbial fuel cell or MFC is a part of this infrastructure where the fuel is wastewater; such systems are also referred as biological fuel cell and use bio-electrochemical means to produce the electricity by microbial metabolism (Liu et al. 2004, Bose & Bose 2016). The decomposition of the organic constituents present in the wastewater leads to

exchange of ions leading to generation of electricity; in this context known as bioelectricity.

Present work reports the evaluation of low cost earthen pot membrane for microbial fuel cell which uses biodiesel wastewater present in the anode. The system developed, produces electricity by removing the organic load in the wastewater. Biodiesel regarded as the future fuel produces a lot of wastewater which requires additional setup and capital for its treatment. Present work focuses on the feasibility of such wastewater in MFCs in terms of sustainability and a scalable architecture for future usage.

## MATERIALS AND METHODS

The setup used for this study was designed in SOLIDWORKS™ software, as shown in Fig. 1, the anode will consist of the wastewater and the cathode will have a conductive solution for ease of ion transfer. The membrane will act as a separator between the two electrodes.

Based on the design conceived, there were two anodes made, initially with aluminum (surface area of 80 cm<sup>2</sup>), and from graphene (having surface area of 100.48 cm<sup>2</sup>). Both the anodes for separate studies were maintained at a dis-

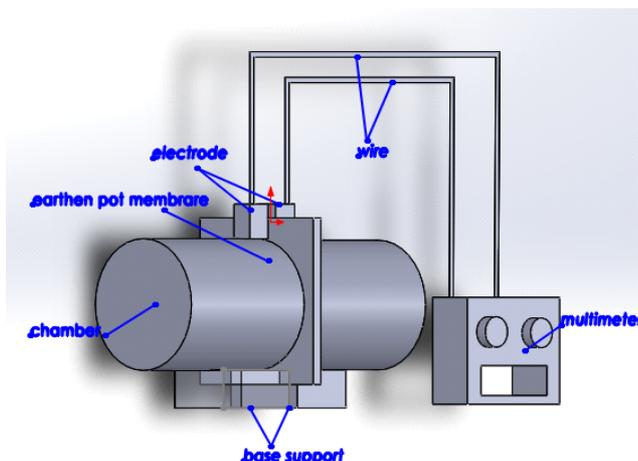


Fig. 1: The design of MFC reactor, with the electrodes and the membrane, the wires from the electrodes have been connected to the multi-meter which acts as a data acquisition system.

tance of 3 cm from the membrane. Anode chamber volume was 1 litre, with working capacity of half a litre. For the proton exchange, earthen pot membrane is used (having surface area of 144 cm<sup>2</sup>), this was fabricated using regular earthen pot material which is cheap and readily available (Behera et al. 2010). The cathode for all the evaluations was a stainless steel mesh. The system thus formulated is shown in Fig. 2.

Open-circuit voltage (OCV) represented by  $V_{OC}$  is the difference of electrical potential between the two terminals of the reactor when there is no external load connected (Kim et al. 2002). Effectively, OCV shows how much a system can produce voltage when no load is connected.

Ohm's law is given by:

$$V = IR \quad \dots(1)$$

Where,  $V$  is the voltage recorded across the resistor,  $R$  is the resistance of 100  $\Omega$  that was connected parallel to the circuit to measure the voltage drop across it and  $I$  is the current computed in ampere.

Power is calculated from the equation:

$$P = VI \quad \dots(2)$$

Furthermore, for MFC power output characterization power density is computed by normalizing the power output with the anode surface area (Bose et al. 2018a). For the chemical characterization of the biodiesel wastewater, TDS and COD were evaluated. Total dissolved solutes or TDS give the measure of the dissolved impurities in the water stream and has profound implications for understanding efficiency of MFC systems (Shrestha et al. 2018). Chemical oxygen demand or COD is a measure of all the organics/complex



Fig. 2: The MFC reactor constructed from locally sourced material. Here the anode (graphene) is on the right side and has the biodieselwastewater (with aluminum/graphene as the electrode) and the cathode is on the left, the separator is the earthen pot membrane.

substrates present in the wastewater, which can be effectively used by the bacteria to generate power (Logan et al. 2006).

A low cost earthen pot membrane (58-68% kaolinite, 5-9% smectite, 15-26% illite) was used as the membrane between the electrodes to understand the membrane rheological characteristics; XRD analysis was done. X-ray powder diffraction (XRD) is a technique used for phase identification of a crystalline material and can provide information on unit cell dimensions (Ichihashi et al. 2012). The membrane material was powdered, homogenized, and average bulk composition was determined for the process. This evaluated the prospect of low cost membrane for on-site power generation.

Biodiesel is regarded as the automotive fuel of the next century, and the production process produces wastewater which is required to be treated with some input to it (Rosen 2014). Today, most of the wastewater treatment plants entirely focus on treating the wastewater with the use of expensive chemicals. The study in this paper shows how wastewater can be treated while producing some energy in the form of electrical power. The wastewater was taken from the Biodiesel Manufacturing Lab at the University itself and the MFC system was kept indoor at the room temperature, which varied between 22°C and 26°C.

## RESULTS AND DISCUSSION

Open circuit voltage for the system was observed for three weeks for which observations are shown in Fig. 3.

OCV of the whole system shows that how much voltage value, a given sample can attain. It is to be noted that after the attainment of peak value the voltage level drops as the time is increased, this shows that the decomposition of the contaminants of the wastewater via the bacterial interactions taking place in the system.

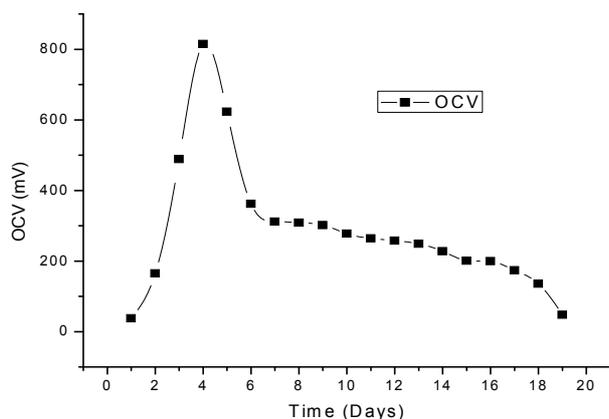


Fig. 3: OCV study peaked around  $800 \pm 10$  mV for the wastewater, this determines maximum possible voltage from such sources.

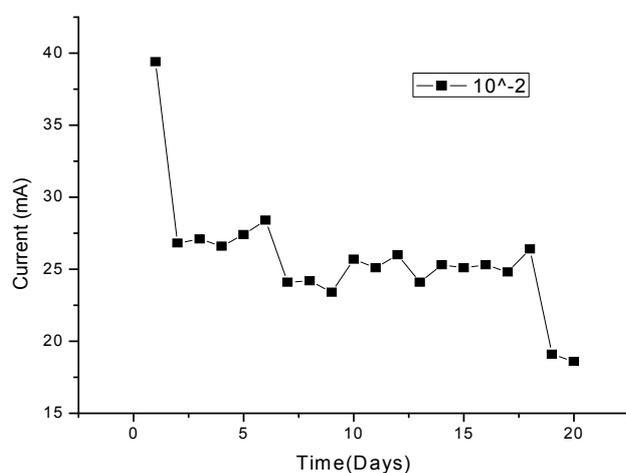


Fig. 4: Peak value current generated is reported at  $0.0041 \pm 0.0003$  mA. It is to be noted as when the time is increased the voltage decreases. This is consistent with the decomposition of constituents of biodiesel wastewater with respect to time. The minimal value recorded was  $0.0018 \pm 0.0004$  mA after two weeks of operation.

Following the study for OCV, suitability of system for current generation was conceived for the same timeline mentioned previously using a  $100 \Omega$  external resistor. System performance is shown in Fig. 4.

As shown in Fig. 5, it is to be noted that both power density and current density is calculated by normalizing the power generation and current generation to the anode surface area, thereby representing the values directly as a function of anode performance efficiency.

Biodiesel wastewater sample has been found to have an initial COD of  $800 \pm 30$  mg/L, while most studies have reported the organic load removal efficiency as a function of COD (Logan et al. 2015, Bose et al. 2018b, Yang et al. 2017). In the present work the same was evaluated in terms

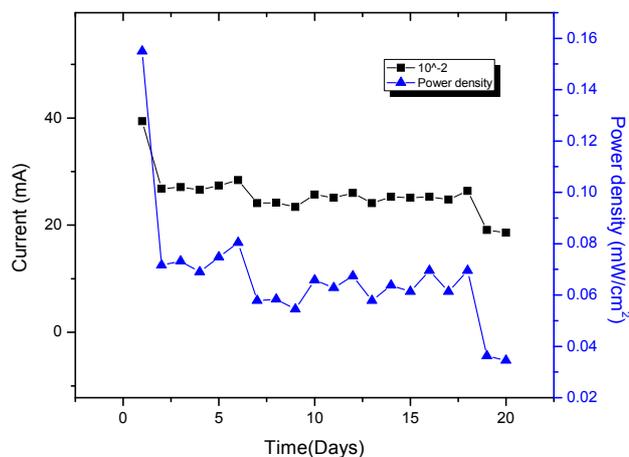


Fig. 5: Power generation in comparison with current and time of operation. Peak value for power recorded was  $0.15 \pm 0.03$  mW/cm<sup>2</sup>, a similar trend in decrease is observed which is consistent with current generation for the system.

of TDS, to see system performance for removing dissolved solids. The same is shown in Fig. 6 .

It is to be noted that the dissolved solids decreased as the time is increased. For the membrane, XRD analysis was done for determining the atomic and molecular structure of the crystals. Detailed diffraction designs comprise added substance influences of a few micro scale and macrostructural highlights of a defined sample. Peak position, cross section factors, space gathering, compound synthesis, macro stresses, or individual stage examination can be analysed by this method.

Earthen pot sample XRD analysis is also compared with other XRD analysis from the available literature. It is seen that the peak structure of the earthen pot sample would also contain silica ( $\text{SiO}_2$ ), margarite ( $\text{CaAl}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$ ), calcium silicate hydroxide ( $\text{Ca}_2\text{Si}_3\text{O}_7\text{OH}_2$ ), calcite ( $\text{CaCO}_3$ ), silicon (Si), calcium (Ca), aluminum (Al), iron (Fe), magnesium (Mg) and potassium (K). Fig. 7 shows the graph obtained from the analysis.

In view of the peak power, data about crystal structure (nuclear sites, temperature aspect, or possession) and in addition surface and quantitative stage investigations can be acquired. In comparison it is observed that the earthen pot sample contains: 1. Kaolinite  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , 2. Quartz, 3. Goethite ( $\text{FeO}(\text{OH})$ ), 4. Illite/mica: repeating units comprised of  $(\text{K}, \text{H}_3\text{O})(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}, \text{Al})_4\text{O}_{10}[(\text{OH})_2]$ .

The fermentative, anaerobic and aerobic processes are combined in the MFC reactor system. The complex organic compounds were digested to simple organic forms such as volatile fatty acid (VFA) via fermentation process by aerobic and anaerobic heterotrophic microorganisms. Heterot-

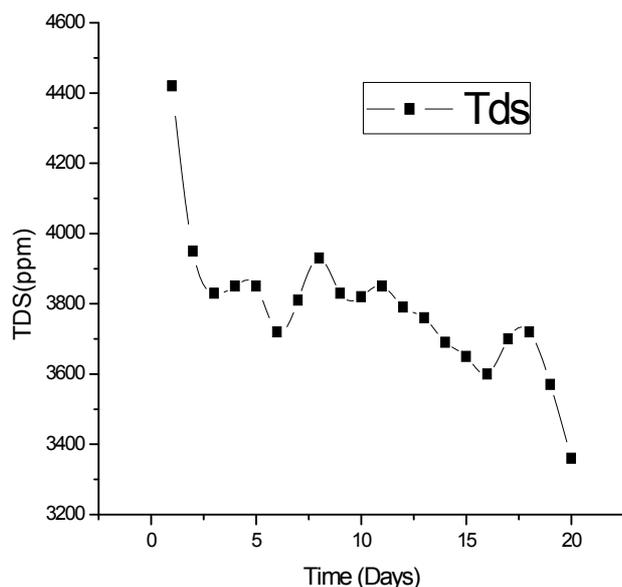


Fig. 6: TDS removal was evaluated for the same timeframe, consistent with previous analysis, peak value of  $4420 \pm 30$  ppm on the first day decreased to  $3360 \pm 20$  ppm after three weeks.

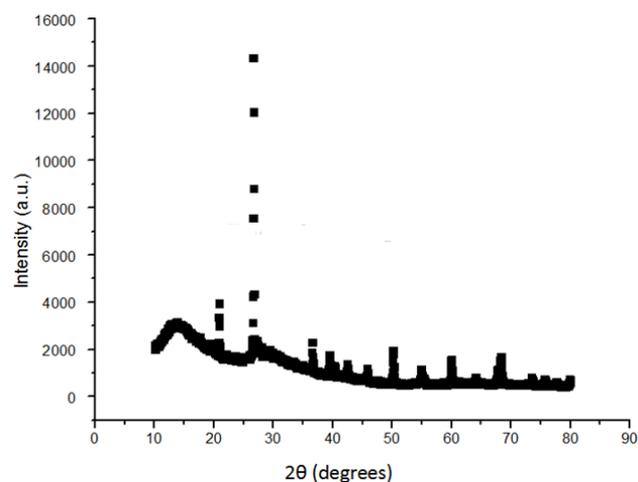


Fig. 7: XRD analysis of earthen pot membrane, comparing with conventional methodologies shows the elemental composition.

rophs consume organic carbon for the formation of new biomass. Through the process of respiration, aerobic microorganisms in cathodic compartment can further transform VFAs (and other bioavailable organic compounds) into carbon dioxide and water. Aerobic microbes can readily convert organic carbon into inorganic carbon and aerobic systems can provide high-rate wastewater treatment.

## CONCLUSION

The membrane used in the MFC is made of earthen pot, which is commercial and cheap in terms of availability, when

compared with other membrane available in the market. The wall material of the earthen pot used was found to be effective for proton transfer. This low cost earthen pot MFC, with reduced manufacturing gave a comparable performance with many sophisticated MFCs employing proton exchange membranes such as nafion, ultrex and related. Further to reduce the cost of the complete system other electrode material can be used instead of the graphene, however, developing such materials should be in line with reduced cost without compromising properties such as conductivity and stability. This represents a challenge and opportunity to fuel this sector of energy research.

Also, the production of biodiesel would generate significant quantities of wastewater which will require large inputs to get treated, so a viable and feasible method is required to treat this wastewater. MFCs is one of the example which not only treats the wastewater but generates usable value added products in the process i.e., bioelectricity.

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