

Electricity Production during Distillery Wastewater Treatment in a Microbial Fuel Cell Equipped with Low Cost PVA-Nafion-Borosilicate Membrane

B. R. Tiwari and M. M. Ghangrekar

Abstract—Microbial fuel cell (MFC) fabricated using Polyvinyl alcohol (PVA)-Nafion-borosilicate membrane was evaluated for distillery wastewater treatment at three different organic loadings of 2300 mgL⁻¹ (OL-1), 4200 mgL⁻¹ (OL-2) and 6300 mgL⁻¹ (OL-3) under 96 h batch mode of operation. The linear sweep voltammetry (LSV) study of the MFC revealed that anodic activity was enhanced when the amount of metabolite available was higher. The LSV results supported the power output achieved from MFC during polarization. Maximum power density of 4.3 Wm⁻³ was obtained at substrate loading of 6300 mgL⁻¹, which was 1.2 folds and 1.6 folds higher than that obtained at OL-2 and OL-1, respectively. Along with power output, MFC was capable of efficiently degrading organic matter present in wastewater in the range of 54.5 % to 64.25 %. Successful reduction of organic matter from distillery wastewater apart from power generation establishes MFC using PVA-Nafion-borosilicate membrane as a suitable low cost technology for real wastewater treatment.

Index Terms—Microbial fuel cell, distillery, power density, borosilicate.

I. INTRODUCTION

The term ‘waste’ can no longer be associated with effluents discharged from industries due to their inherent reserves of organic matter, which if treated using appropriate technology can be utilized to harvest energy. Microbial fuel cells (MFCs) are such a carbon neutral energy harvesting technology which use microorganisms to convert the chemical energy stored in the bonds of organic compounds to electricity [1]. The electricity produced is both sustainable as well as environment friendly. MFCs consists of an anode electrode which provides surface for bacteria to attach and carry out oxidation of substrate, while cathode electrode facilitates reduction of oxygen. Both the electrodes are separated by a proton exchange membrane (PEM), which impede the oxygen diffusion and promote proton transfer.

Distillery spent wash is the unwanted liquid waste generated during alcohol production, which is highly polluting in nature and can cause serious environmental issues if not properly treated [2]. The quantity i.e. 8 L effluent discharged per L alcohol produced, and the quality i.e. extremely high Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Suspended Solids (SS), inorganic solids, colour and low pH, are a matter of

concern for the environment. Various physico-chemical processes like coagulation, adsorption etc. and biological treatment methods such as aerobic and anaerobic digestion, which are mostly energy intensive, have been proposed to degrade the dissolved organic matter present in distillery effluent. In the present world where the demand for energy has increased, MFCs can upgrade the entire wastewater treatment scenario by demonstrating utilization of waste as an alternate source of energy. Considerable reduction in COD (72.84 %) and color (31.67 %) was exhibited in a batch mode MFC treating molasses based wastewater under acidophilic conditions [3]. MFCs, being a proton mediated process, their performance is most likely to get affected by the change in pH of electrolytes. Anolyte pH of 7-9 and catholyte i.e. potassium ferricyanide at pH of 2 were found to favour higher power production in a MFC treating post methanated distillery effluent [4]. High concentration and low pH, often make it imperative to dilute distillery wastewater before introducing it into a biological wastewater treatment system, which increases the water demand of the system. Sewage can be a viable alternative to fresh water for the dilution. Air cathode MFC treating molasses mixed sewage wastewater achieved a maximum power density of 5.3 Wm⁻³ at a total COD removal of 59.08 % after 122 days of operation [5]. Although various treatment options for distillery wastewater treatment are available, the desired effluent concentration to meet the discharge standards is difficult to attain. Hence, a combination of anaerobic digestion and MFC has been suggested to improve organic matter removal as well as current generation [6], [7]. MFC coupled with anaerobic fluidized bed reactor was utilized to treat alcohol distillery wastewater at an influent loading of 6.89 to 16.86 kg COD m⁻³d⁻¹ and achieved a COD removal in the range of 58.44 % to 88.38 %. Simultaneous molasses wastewater treatment and power generation were achieved in an integrated UASB-MFC-BAF system during a 60-day operation [6]. Power density was found to increase while COD removal decreased with increase in influent COD concentration.

In spite of serving the dual purpose of waste reduction and simultaneous energy harvesting, this technology is still eclipsed by the high cost of materials like catalyzed electrodes (such as platinum, palladium and other novel metals) and PEM (Nafion), which is popularly used as separator to separate anodic and cathodic chamber. Membrane separator almost accounts for one-third of MFC's manufacturing cost [8]. Recently, a low cost PVA-Nafion borosilicate membrane was developed and successfully used as a separator in MFC fed with acetate wastewater [8]. Use of this low cost separator in MFCs can reduce the manufacturing cost of MFCs and pave the way for their real

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The authors are with Indian Institute of Technology, Kharagpur, India, PIN-721302 (e-mail: brtiwari21@gmail.com, ghangrekar@civil.iitkgp.ernet.in).

field application. This work is an attempt to treat distillery wastewater and simultaneously harvest energy in the form of electricity in a MFC incorporated with PVA-Nafion borosilicate membrane.

II. MATERIALS AND METHODS

A. MFC Construction and Operation

A Polyvinyl alcohol-Nafion-borosilicate membrane was fabricated as mentioned elsewhere [8] and used as separator in the dual chambered MFC made of polyacrylic sheet (Fig. 1). Both anode and cathode chambers were of 19 mL capacity. The anode chamber was completely closed to maintain anaerobic microenvironment. Carbon felt (Panex® 35, Zoltek Corporation) having area of 12.5 cm² was used as anode. Nickel foam (12.5 cm²) coated with conductive carbon ink prepared from Vulcan XC-72R carbon powder, at a carbon loading of 0.5 mg cm⁻² with platinum catalyst at 10 % of carbon loading, was used as cathode. Mixed anaerobic sludge (VSS, 15 gL⁻¹) collected from a septic tank at IIT Kharagpur was used as inoculum in the anode chamber. The cathode chamber did not receive any microbial addition. Aerated tap water was used as catholyte and air was supplied by an aquarium pump (SOBO Aquarium air pump, China). Anode and cathode were connected by concealed copper wires across an external resistance of 100 Ω. MFC was operated for 60 days at three different organic loads of 2300 mgL⁻¹ (OL-1), 4200 mgL⁻¹ (OL-2) and 6300 mgL⁻¹ (OL-3) under batch mode with reaction time of 96 h. Feed pH was adjusted to around 6.0 by adding PBS buffer to suppress the growth of methanogens in the MFC.

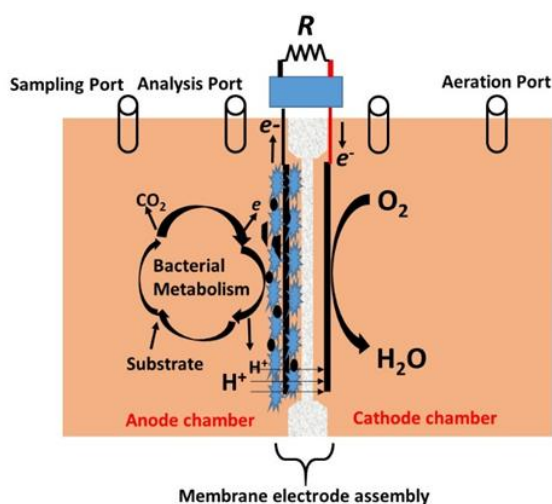


Fig. 1. Schematic diagram of the MFC set up used in this experiment.

B. Analysis and Calculations

Influent and effluent COD was measured by closed reflux method and VSS of the inoculum was determined as explained in Standard Methods [9]. pH was measured using a digital pH probe equipped with a data logger (Thermo Scientific Co., USA). Voltage and current readings for the MFC were measured using data acquisition unit (Agilent Technologies, Penang, Malaysia). Polarization studies were carried out by changing the external resistance stepwise from 40000 Ω to 50 Ω using the resistance box (GEC 05 R Decade Resistance Box, Renown Systems, Kolkata, India). Power

was calculated as the product of voltage and current. Volumetric power density was calculated by normalizing the power to the volume of the anolyte. Cathode and anode potentials were measured during polarization using Ag/AgCl reference electrode (Bioanalytical Systems, Inc., West Lafayette, IN, USA).

Coulombic efficiency (CE) was estimated as the ratio of total coulombs actually consumed from the substrate for current production, to the maximum theoretical coulombs available in the substrate [10].

$$CE = \frac{M \int I dt}{Fbv\Delta COD} \quad (1)$$

where, $M = 32$, the molecular weight of the oxygen, F is Faraday's constant, $b = 4$ is the number of electrons exchanged per mole of oxygen, I is the current generated in the MFC, V is the volume of liquid in the anode chamber and ΔCOD is the change in COD over time t .

C. Electrochemical Tests for Cathodes

The anode reaction kinetics of MFC at three different organic loadings was evaluated by in situ study of linear sweep voltammetry (LSV) using potentiostat (AUTO LAB AUT58696, Metrohm. All measurements were carried out using three electrode system consisting of a working electrode (anode), an Ag/AgCl reference electrode and a Platinum (Pt) counter electrode. LSV was performed in voltage ranging from 0 V to 0.9 V (vs. Ag/AgCl) at a scan rate of 10 mVs⁻¹.

III. RESULTS AND DISCUSSIONS

A. Wastewater Characterization

The distillery effluent for this study was collected from the fermentation unit of a malt-based ethanol distillation plant in West Bengal, India. The wastewater had a very high COD of 57 ± 7 gL⁻¹, BOD of 26 ± 3 gL⁻¹, total solids of 33 ± 3 gL⁻¹ and acidic pH of 3.5 ± 0.1 . It was preserved at 4 °C prior to use. Once the solids were settled, the supernatant liquid was taken and diluted to achieve the desired feed concentration.

B. Electrochemical Analysis

LSV was performed in the voltage range of 0 V to 0.9 V and the corresponding anodic current responses in terms of current density were measured to evaluate the current generating capacity of MFC with varied substrate loadings of 2300 mgL⁻¹ (OL-1), 4200 mgL⁻¹ (OL-2) and 6300 mgL⁻¹ (OL-3). As the applied voltage vs Ag/AgCl was increased from 0 V to 0.9 V, the current density was also enhanced due to diffusion of the organic substrate to the anodic reaction interface and successive generation of electrons by the microorganisms (Fig. 2). In contrast, the highest amount of current density of 1.36 mA·cm⁻² was observed in case of OL-3 followed by OL-2 (1.20 mA·cm⁻²) and OL-1 (1.11 mA·cm⁻²), conforming highest amount of fermented product for direct conversion to electrons during electrogenic metabolic activity. Current response was enhanced at higher substrate loading as the electron donors were highest in number and the dilution was comparatively less, thus, decreasing the solution resistance.

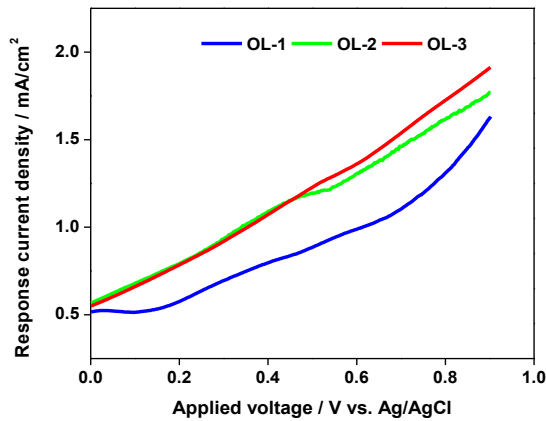


Fig. 2. LSV curves of MFC under different organic loading at a scan rate of 10 mVs⁻¹.

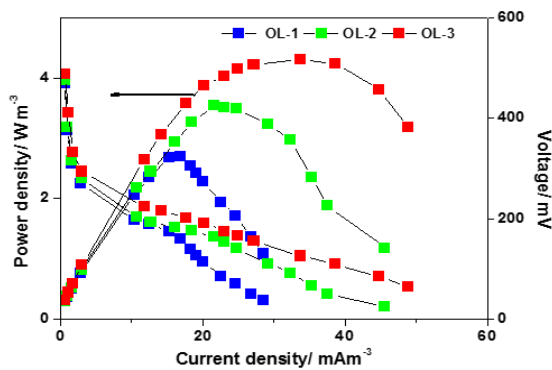


Fig. 3. Polarization curves for MFC at different organic loading.

C. Power Generation

Current is generated in a MFC due to the ability of electrogenic microbes to transfer the electrons released from oxidation of substrate to a solid anode through extracellular electron transfer. Polarization curves were plotted between current density against voltage and power density. Substrate metabolism as well as electron flow and eventually the current density during polarization increases with decrease in the external resistance [3]. The maximum power density was determined from the polarization curve obtained at each substrate loading once the MFC attained stable configuration. Power density of 2.69 W m^{-3} , 3.53 W m^{-3} and 4.3 W m^{-3} were achieved in the MFC at substrate concentration of 2300 mg L^{-1} , 4200 mg L^{-1} and 6300 mg L^{-1} (Fig. 3). Power output from MFC was found to increase with the organic loading due to the enhanced anodic activity as indicated by the current response from the LSV results. The carbon compounds present in the distillery effluent are the source of electrons to the anode, and as the availability of electron donors is enhanced, the electrical performance is improved. Previous study also supports the findings that increased substrate concentration led to higher power output [3]. Power output was less as compared to a study in which acetate was used as feed in the same MFC set up [8]. The reason is that acetate is non fermentable and the simplest form of carbon feed which can be readily utilized by the anodic microflora. But in case of real wastewater the substrate has a major fraction of highly complex macromolecules which undergo fermentation prior to being available to electrogenic microorganisms. Internal resistance of the MFC at different substrate conditions was calculated from the slope of the voltage versus current curve. With increase in dilution,

solution conductivity decreases and the internal resistance of the MFC increased from 334Ω to 276Ω [6]. The MFC system, if operated at an external resistance same as the internal resistance, would produce the maximum power under those conditions.

D. Organic Matter Removal and Coulombic Efficiency

The real wastewater contains complex macromolecules which are easier to degrade when varied groups of bacteria are present in the inoculum. The electrogenesis step is preceded by fermentation where complex macromolecules like polysaccharides, undergo degradation and get reduced to lower carbon chain compounds. Then, the simpler carbon compounds undergo electrogenesis. A part of the reduced substrate is utilized by microbes for the life supporting functions and the rest is converted into electrons and protons resulting in current output from MFC. COD removal efficiencies of $64.25 \pm 2.50 \%$, $58.0 \pm 1.4 \%$ and $54.5 \pm 1.3 \%$ were obtained at OL-1, OL-2 and OL-3, respectively (Fig. 4). COD reduction decreased at higher loading due to induced substrate inhibition at higher substrate concentrations [3]. Energy harvested was found to be 48.8 Wh/kg COD , 34.8 Wh/kg COD and 30.33 Wh/kg COD at OL-1, OL-2 and OL-3, respectively. As the MFC was inoculated with mixed anaerobic sludge, in addition to electrogenic bacteria, the anodic microflora also consists of other groups of microbes like methanogens, sulfate reducing bacteria, nitrifying bacteria etc. [1]. The non-electrogenic groups of bacteria compete with the electrogenic microbes for substrate as well as anodic space. Although the MFC exhibits COD reduction, only a part of the substrate utilized is converted to current, which is reflected in terms of coulombic efficiency. Coulombic efficiency was found to be $47.4 \pm 1.7 \%$, $40.9 \pm 1.7 \%$ and $37.6 \pm 1.1 \%$, decreasing in value with increasing strength of wastewater. The activity of electrogenic bacteria depends on the anodic surface area, which is fixed for this study. The decrease in CE with increasing substrate concentration was due to the rate saturation of electron conduction by electrogens resulting from the fixed electrode surface area [11].

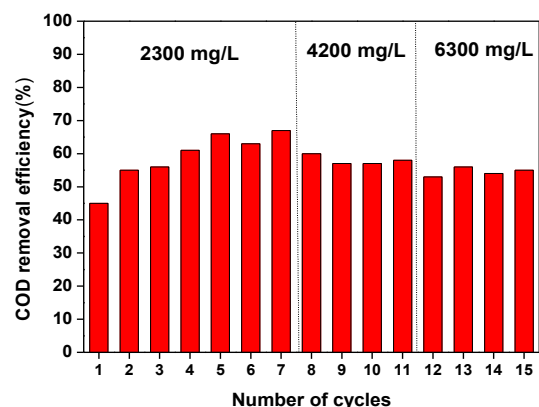


Fig. 4. COD removal efficiency achieved in the MFC at different substrate loading conditions.

IV. CONCLUSION

MFC with PVA-Nafion-borosilicate membrane successfully accomplished distillery wastewater treatment and simultaneous electricity generation. Higher substrate

loading (6300 mgL^{-1}) generated a higher anodic current response, which was eventually translated into higher power density of 4.3 Wm^{-3} . Although the COD removal efficiency was adversely affected by induced substrate inhibition at higher feed concentration, it can be improved by increasing the retention time further. This study can put forward reference for further achieving higher efficiency of distillery wastewater treatment and power generation at low cost.

REFERENCES

- [1] B. R. Tiwari and M. M. Ghangrekar, "Enhancing electrogenesis by pretreatment of mixed anaerobic sludge to be used as inoculum in microbial fuel cells," *Energy Fuels*, vol. 29, no. 5, pp. 3518-3524, April 2015.
- [2] U. S. Hampannavar and N. V. Pradeep, "Treatment of distillery wastewater using single chamber and double chambered MFC," *Int. J. Environ. Sci.*, vol. 2, pp. 114, April 2011.
- [3] G. Mohanakrishna, S. V. Mohan, and P. N. Sarma, "Bio-electrochemical treatment of distillery wastewater in microbial fuel cell facilitating decolorization and desalination along with power generation," *J. Hazard. Mater.*, vol. 177, pp. 487-494, December 2010.
- [4] A. Kaushik and A. Chetal, "Power generation in microbial fuel cell fed with post methanation distillery effluent as a function of pH microenvironment," *Bioresour. Technol.* 147, pp. 77-83, August 2013.
- [5] S. Sevdá, X. Dominguez-Benetton, K. Vanbroekhoven, H. D. Wever, T. R. Sreekrishnan, and D. Pant, "High strength wastewater treatment accompanied by power generation using air cathode microbial fuel cell," *Appl. Energ.*, vol. 105, pp. 194-206, January 2013.
- [6] B. Zhang, H. Zhao, S. Zhou, C. Shi, and C. W. J. Ni, "A novel UASB-MFC-BAF integrated system for high strength molasses wastewater treatment and bioelectricity generation," *Bioresour. Technol.* vol. 100, pp. 5687-5693, July 2009.
- [7] J. Huang, P. Yang, Y. Guo, and K. Zhang, "Electricity generation during wastewater treatment: An approach using an AFB-MFC for alcohol distillery wastewater," *Desalination*, vol. 276, pp. 373-378, May 2011.
- [8] B. R. Tiwari, Md. T. Noori, and M. M. Ghangrekar, "A novel low cost polyvinyl alcohol-Nafion-borosilicate membrane separator for microbial fuel cell," *Mater. Chem. Phys.*, vol. 182, pp. 86-93, July 2016.
- [9] American Public Health Association, American Water Works Association, Water Pollution Control Federation (1998) Standard methods for the examination of water and wastewater, 20th ed. American Public Health Association, Washington DC.
- [10] B. E. Logan, *Microbial Fuel Cells*, John Wiley and Sons, Inc., Hoboken, NJ, 2007, ch. 4.
- [11] P. T. Ha, T. K. Lee, B. E. Rittmann, J. Park, and I. S. Chang, "Treatment of alcohol distillery wastewater using a bacteroidetes-dominant thermophilic microbial fuel cell," *Environ. Sci. Technol.*, vol. 46, pp. 3022-3030, January 2012.



B. R. Tiwari was born in Odisha, India on January 13, 1986. He received his master degree from IIT Kharagpur in 2011. He later joined in the PhD research program in the same institution. His research area deals with microbial fuel cells, with major focus on achieving higher efficiency in treatment of industrial wastewater and improving power generation by implementing inoculum pretreatment, novel electrocatalyst and low cost separators.



M. M. Ghangrekar received his doctorate from IIT Bombay in 1996. Prior to this, he served NERI as a senior research fellow. Later he undertook and successfully accomplished different projects under AICTE and UGC Govt. of India and joined as lecturer in various Govt. engineering colleges from 1996 to 2003. He joined at IIT Kharagpur in 2004 as an assistant professor. He has authored and co-authored more than 90 peer reviewed papers and won various awards and recognition including Alexander Von Humboldt fellowship in 2013, Gandhian Young Technological Innovation Award, in 2014 and 2015. His research area is microbial fuel cell, UASB reactor design and wastewater treatment.