Performance of Low-Cost Microbial Fuel Cell Using Earthenware Separator

Sudhansu Behera and Manaswini Behera

Abstract The extensive use of fossil fuels and the associated problems of environmental pollution and global warming demand alternate renewable energy sources. Microbial fuel cells (MFCs) is an emerging technology which uses the chemical energy stored in the organic matter and generates society's most useful form of energy, i.e., electricity. MFC has the advantages of less sludge generation, low temperature operation, and omission of off-gas treatment. The performance of a dual-chambered low-cost MFC employing earthenware separator modified with montmorillonite was studied as a potential device for dairy wastewater treatment and simultaneous bioelectricity generation. The dual-chambered MFC with inner anodic chamber and concentric outer cathode chamber showed appreciable performance with a maximum power density of 33.44 mW/m^2 normalized to anodic electrode surface area while fed with synthetic dairy wastewater having chemical oxygen demand (COD) of 1920 $\pm$ 20 mg/L. The wastewater was treated anaerobically in the anode chamber and the effluent from the anode chamber was given aerobic treatment in the cathode chamber. The MFC has shown a maximum COD removal efficiency of 89%. The low-cost MFC showed promising performance, which can be employed as a treatment technology for organic wastewater simultaneously generating electricity.

Keywords Microbial fuel cell (MFC) · Earthenware separator
Chemical oxygen demand (COD) · Power density
Proton exchange membrane (PEM)

Introduction

Fossil fuel depletion and energy crisis drive attention worldwide to renewable energy sources. The microbial fuel cell (MFC) is a representative of new biocatalyzing technology that can directly produce electricity from oxidation of organic

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matters using bacteria (Chaudhuri and Lovely 2003). The transformation of chemical energy stored in the bonds of organic matter to useful electrical energy is governed by the microorganisms present in wastewater, which act as active biocatalyst in anaerobic condition. The direct electricity thus produced is devoid of pollutants as the net carbon emission in the process is zero. The simultaneous treatment of wastewater and bioenergy production in a noble device MFC overcomes many challenges in the development of such needs. The major challenges related to MFC are its high operational cost and potential upscaling of power output. Although extensive research is taking place for the development of such a low-cost noble MFC still there are many loop holes behind in the field of MFC materials.

Operating Principle of MFC

The MFC is operated by anaerobic degradation (oxidation) of organic matter by the anaerobes in anode chamber consequently producing electrons that travel through a series of respiratory enzymes in the cell and provide energy in the form of ATP (adenosine triphosphate). The electron transfer mechanism by the bacteria is so far known to occur through two ways: (i) by electron shuttle via self-produced mediator (Rabaey et al. 2004) and (ii) nanowires produced by both *Geobacter* and *Shewanella* species (Gorby and Beveridge 2005). Thus, the electrons transfer to cathode through external electric circuit and are accepted at cathode chamber by terminal electron acceptors (e.g., oxygen, nitrate, sulfate, and others). The protons pass through cation exchange membrane to cathode which further react with electron and oxygen forming water as a by-product. The schematic of a traditional MFC is represented in Fig. 1.

The present study focused on fabrication of a low-cost dual-chambered MFC reactor by introducing a ceramic-based composite membrane. The earthenware separator was studied with a thickness of 5 mm for a period of 45 days. The anodic substrate as synthetic dairy wastewater was continuously supplied at flow rate of 2.16 mL/min followed by continuous aeration at cathode. The MFC was studied without any addition of external mediator in the electron transfer mechanism.

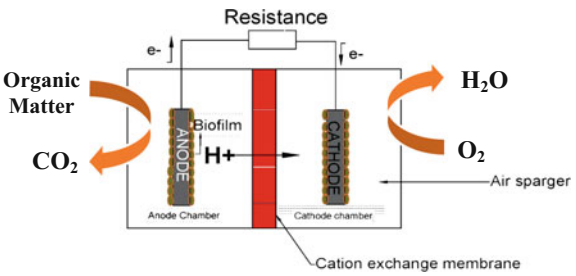

Fig. 1 A schematic of dual-chambered MFC

Methodology

MFC Construction

The dual-chambered MFC (Fig. 2) was fabricated using transparent poly acrylic material having inner cubical anode chamber inside a concentric outer cathode chamber. The anode chamber has a working volume of 780 mL while that of cathode is 6.6 L. Four grooves each having size of 6 cm × 8 cm were made for placing earthenware separator. Wastewater was fed to the anode chamber from the bottom. Two openings were made at the top of two opposite side walls of anode chamber for the passage of effluent from anode chamber to cathode chamber. Four earthenware separators having effective thickness of 5 mm were fixed on four sides of the anode chamber. Stainless steel (SS) mesh was used as anode electrode with total projected surface area 502.4 cm^2. Similarly graphite plates of size 6 cm × 8 cm having thickness of 0.5 cm were used as cathode electrode. The anode and cathode electrodes were placed very close to earthenware separator at a distance of 0.7 cm apart. Thin copper wire with full insulation was used in the electric circuit for conveyance of electricity. The anode chamber was kept airtight with a plate of poly acrylic material with stainless steel screws for tightening to maintain anaerobic condition.

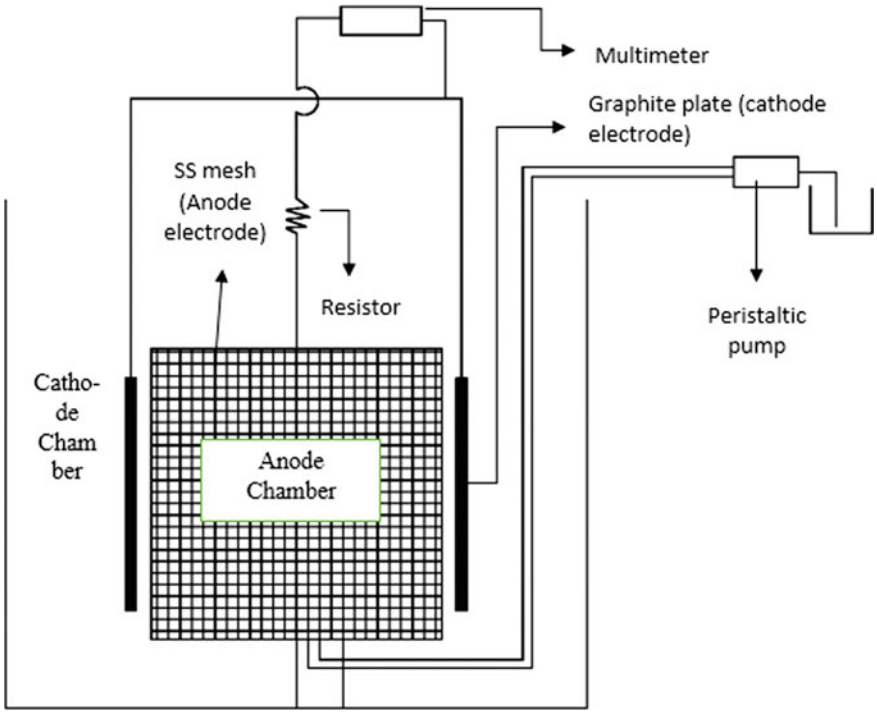

Fig. 2 A graphical presentation of the experimental setup of MFC

MFC Operation

The dual-chambered MFC was operated with a continuous supply of synthetic dairy wastewater having chemical oxygen demand (COD) of 1920 ± 20 mg/L. The substrate was supplied at a flow rate of 2.1 mL/min (hydraulic retention time, HRT = 6 h) by using a peristaltic pump. The constituents of synthetic dairy wastewater are milk powder, 1.6 g/L; $FeCl_3.6H_2O$, 15 mg/L; $MgSO_4.7H_2O$, 70 mg/L; $CaCl_2.H_2O$, 30 mg/L; $MnSO_4.7H_2O$, 15 mg/L; KH_2PO_4, 60 mg/L; NH_4Cl, 120 mg/L; $NaHCO_3$, 1 g/L (Raj and Murthy 1999; Zielinska et al. 2013). The substrate was given anaerobic treatment in the anode chamber then the effluent of anode chamber was given aerobic treatment in the cathode chamber with the help of active aeration. The anode chamber was inoculated with the bottom sludge of domestic sewer having volatile suspended solid (VSS) of 32.5 g/L. The anode and cathode electrodes were connected externally through insulated copper wire with a load of 150 Ω.

Preparation of Earthenware Separator

The earthenware separator was prepared by blending 80% of red soil (Laterite origin) and 20% of montmorillonite (cation exchanger) with the addition of small amount of water. Wet clay after achieving certain plasticity was filled in mould of size 7 cm × 9 cm × 0.5 cm. They are then exposed to open air for 5 days and dried in hot air oven at 150 °C for 2 h, and finally kept in muffle furnace at 650 °C for 30 min. Energy dispersive spectroscopy (EDS) analysis was carried out to find out the composition of earthenware separator. The composite membrane contained SiO_2—49.23%, Al_2O_3—21.6%, Fe—21.5%, K—2.15%, MgO—1.11%, Ti—1.45%, Na—0.95%, and Cu—2%. The photograph of clay mineral modified earthenware separator is shown in the following Fig. 3.

Analysis and Calculation

The COD concentrations of influent and effluent, dissolved oxygen (DO), pH, volatile suspended solid (VSS), and total solid (TS) were measured according to APHA standard procedure (APHA 1998). The current (*I*) and voltage (*V*) were measured by a true RMS professional multimeter (Extech, India). The power can thus be calculated as P = V * I. The open circuit voltage (OCV) and working voltage (external resistance of 150 Ω) were measured every day throughout a period of 45 days of working period. The power density and volumetric power were calculated normalized to anodic electrode area and net liquid volume of anode chamber, respectively. Polarization study was conducted after achieving a stable

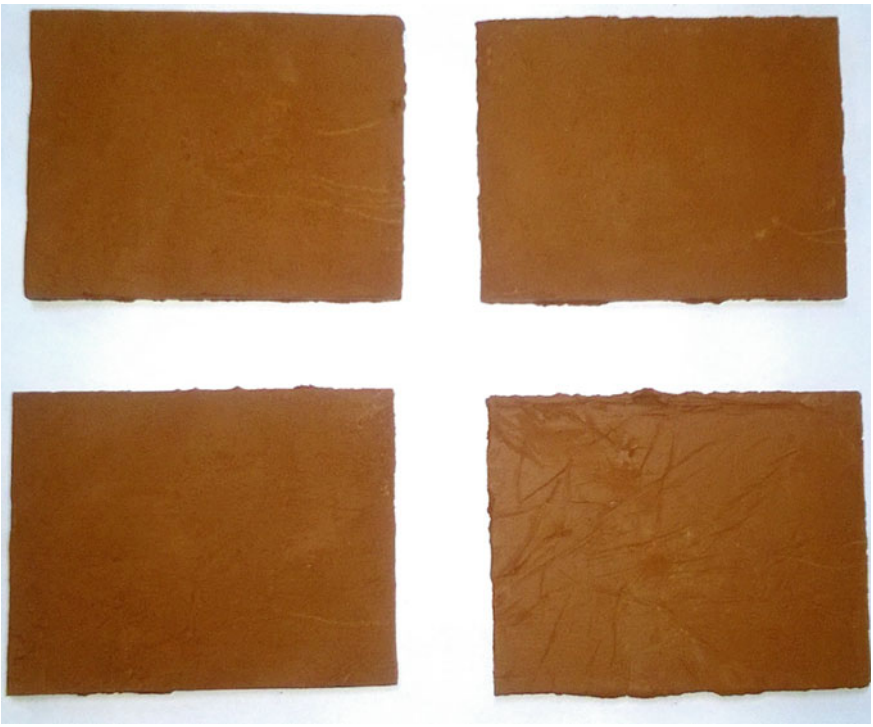

Fig. 3 Fabricated earthenware proton exchange membrane

performance by varying external resistances from 50 to 4500 Ω. The internal resistance associated with MFC was calculated from the slope of line plotted between current and voltage.

The Coulombic efficiency (CE) is defined as the ratio of total coulombs recovered during the operation per total coulombs present in the substrate (Logan 2008). The CE of MFC operated in continuous mode of substrate supply can be found out from the formula:

$$\mathrm{CE} = \frac{8I}{Fq\Delta\mathrm{COD}}, \tag{1}$$

where, I is the measured electric current; 8 is a constant used for substrate measured in terms of COD based on molecular weight of O_2 as 32 g/mol; F is the Faraday's constant = 96485 C/mol; q is the flow rate of substrate in L/day; ΔCOD is the change in COD value of the influent and effluent in mg/L. The morphological characteristics of earthenware separator were studied by energy dispersive spectroscopy (EDS) analysis.

Results and Discussion

Physical Characterization of Separator

EDS Analysis

The microscopic analysis of earthenware PEM has shown an appreciable amount of silica and aluminum as the key inorganic elements in a typical soil sample. The chemical constituents of montmorillonite and the composite soil membrane are listed in Table 1.

The interpretation for the above elements present in the composite membrane shows abundant amount of oxides of silica which shows a potential membrane for proton exchange. The clay particles contain huge amount of silicon ion creating negative charge when combined with silicon–oxygen tetrahedron. Thus, the presence of silicon ions helps in retaining the positive ions, i.e., protons (H^+) ions on the surface of earthenware separator (Behera and Ghangrekar 2011).

The clay mineral montmorillonite is found to have highest cation exchange capacity (CEC) ranging about 70–100 meq/100 g among all minerals present in soil. The CEC is the number of exchangeable cations per dry weight that a soil is able to hold. Therefore, Blending low-cost and easily available cation exchangers could possibly enhance the performance. It was decided to blend different proportions of montmorillonite by weight with the parent material, i.e., red soil. Further, the clay minerals are very fine and by blending with soil having higher particle size could possibly reduce the voids. Thus, montmorillonite has the potential to acts as proton exchanger and plays a great role in the fabrication of earthenware separator.

Table 1 Composition of soil with their weight percentages

Elements	Montmorillonite (%)	Composite (Montmorillonite + red soil) (%)
Al_2O_3	19.68	25.64
SiO_2	51.42	45.78
K (Feldspar)	1.89	2.2
Fe	17.76	22.94
Cu	2.44	3.43
Ti	2.81	–
Na (Albite)	1.19	–
MgO	1.95	–
Ca (Wollastonite)	0.86	–

Table 2 Power production values

Working voltage (mV)	Power density (mW/m^2)	Volumetric power (W/m^3)	OCV (mV)
470 (max)	29.31	1.88	490
422 (average)	23.71	1.52	440

Power Production in MFC

The direct electricity production in MFC from organic substrates is a function of strength (COD) of organic matter. The more the rate of oxidation in anode chamber, the more would be the power density. A maximum open circuit voltage (OCV) of 0.49 V obtained on the 16th day of operation. The maximum and average power production values are shown in Table 2. The power was calculated by the formula P = V * I, where *P* is the power generated in watt, *V* is the working voltage and *I* is the measured current with a load of 150 Ω.

The volumetric power in the current study using a low-cost earthenware separator was found to be higher than the value 1.6 W/m^3 reported by Jana et al. (2010), used Nafion as potential PEM.

Coulombic Efficiency

The average CE during the period of stable performance was found to be 4.16%. The low CE shown by the MFCs might be due to utilization of large percentage of substrate by anaerobic microbes such as methanogenic archaea or sulfate-reducing bacteria other than anode-respiring bacteria (He et al. 2005).

Polarization Study and Internal Resistance

The polarization study is mainly conducted to know the effect of different external resistances on the performance of the system. Figure 4 shows the polarization curve as a function of current density, voltage and power density measured at variable external circuit load (50–4500 Ω). During polarization, current generation decreased with increase in external resistance, which indicated typical fuel cell behavior. The power density curve showed a maximum power density of 33.44 mW/m^2 at an external resistance of 200 Ω during polarization.

From the curve between current (*I*) and voltage (*V*), the slope of line represents internal resistance of the reactor which was found to be 108 Ω.

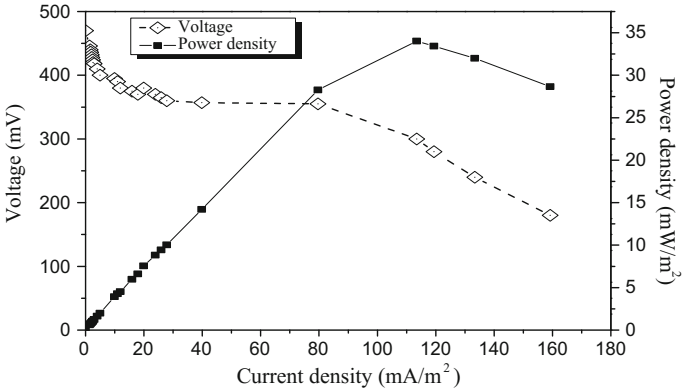

Fig. 4 Voltage and power density values as function of current density

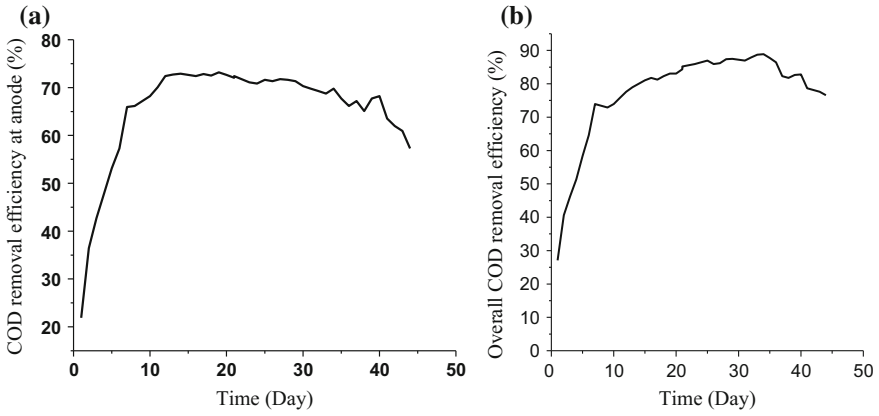

Fig. 5 **a** COD removal in anode chamber. **b** Overall COD removal

Wastewater Treatment

There has been a consistent increase in the COD removal efficiency after an acclimatization period of 12 days of operation. The average COD removal efficiency of anode chamber after attaining a stable removal rate was 69.7%. Similarly, the COD removal efficiency of cathode chamber was calculated to be 45.2% and finally the overall COD removal efficiency was calculated to be 83.3%. The COD removal efficiency decreased after 35th day of operation, which may be attributed to the decrease in the room temperature in the winter. The dual-chambered MFC was found to be efficient to treat synthetic dairy wastewater. The introduction of biocathode also helped in reducing the strength of organic matter of anode effluent by continuous aeration. Figure 5a, b shows COD removal at anode chamber and the overall COD removal of the reactor, respectively, as the time progresses.

The average pH in the anode chamber was 6.5 whereas an average pH of cathode chamber was 8.42 during stable period. The dissolved oxygen (DO) level in cathode chamber was found to be a major parameter for the biocathode. There is an average DO of 7.8 mg/L maintained at cathode which is sufficient to grow the aerobic bacteria. It was observed that anaerobic microbes at anode have self-buffering capacity, thus the pH at anode automatically comes to 7 without any external buffer addition. It was also observed that the high concentration of DO at cathode is very necessary for electron acceptor and also required for aerobic treatment of effluents. Oxygen was used as terminal electron acceptor in the cathode chamber because oxygen is freely available in the atmosphere and it does not produce any toxic by-products as the end product is water. The MFC has found to be a potential device for field application for effective wastewater treatment by the removal of organic matter from the wastewater. There were no other mediators like nitrate or permanganate solution added to the cathode chamber as an external agent for electron acceptor.

Conclusion

The current study on dairy wastewater treatment in the dual-chambered MFC employing low-cost earthenware separator demonstrated that the device is efficient in wastewater treatment with 89% COD removal efficiency and simultaneous electricity generation. The composite separator was efficient for cation exchange. The MFC employed with earthenware separator exhibited internal resistance of 108 Ω. The low-cost separator of 5 mm thickness has outperformed the most expensive Nafion membrane. The compositions of earthenware separator have confirmed the presence of silicon and aluminum which act as effective materials for proton exchange. The earthenware separator was found successful to withstand up to long period at such hydraulic load.

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