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Performance of microbial fuel cell subjected to variation in pH, temperature, external load and substrate concentration

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ABSTRACT

During field application, the microbial fuel cell (MFC) will be exposed to variations in operating parameters. Hence, the performance of MFC, exposed to variation in temperature, pH, external resistance and influent chemical oxygen demand (COD), was investigated in the terms of coulombic efficiency (CE) and COD removal efficiency, while treating a synthetic wastewater. The performance was analyzed under two temperature ranges such as 20–35 °C and 8–22 °C. Operation under higher temperature range favored higher COD removal efficiency of 90% and lower current (0.7 mA) and CE (1.5%). At lower temperature range, although the COD removal efficiency of MFC decreased (59%), it gave higher current (1.4 mA) and CE (5%). The highest current was generated at pH of 6.5 in the anodic chamber with CE of 4%. Higher pH difference between anodic and cathodic electrolyte favored higher current and voltage. Within the range of COD tested (100–600 mg/l), linear correlation was observed between the current and substrate removed.

1. Introduction

The high energy intensive conventional wastewater treatment systems invites for the development of alternative treatment technology. There is a tremendous need to develop suitable and reliable technology for the treatment of wastewater. Such treatment technology should be cost effective, requiring less energy for its efficient operation and should generate less sludge. In addition, the treatment system should recover energy to make overall operation of wastewater treatment self sustainable.

Microbial fuel cell (MFC) provides new opportunity for the sustainable production of energy, in the form of direct electricity from biodegradable compounds present in the wastewater, achieving simultaneous wastewater treatment. MFC is a device that converts chemical energy to electrical energy with the aid of the catalytic reaction of microorganisms (Allen and Bennetto, 1993). In a MFC, substrate (organic matter or biomass) is oxidized in the anode chamber producing carbon dioxide, protons and electrons (Rabaey and Verstraete, 2005). Microorganisms here fulfill the role of catalysts in analogs to chemical fuel cells. The electrons and the protons produced in the anode chamber ends up at the cathode, via the external electrical circuit and through the proton exchange membrane (PEM), respectively. In the cathode, an oxidant (normally oxygen) is being reduced. Eqs. (1)–(3) illustrates the basic reactions occurring in MFCs, in the case of a sucrose fed wastewater in anode and oxygen as electron acceptor in cathode.

$$\text{Anode}: C_{12}H_{22}O_{11} + 13H_2O \rightarrow 12CO_2 + 48H^+ + 48e^- \quad (1)$$

$$\text{Cathode}: 48H^+ + 48e^- + 12O_2 \rightarrow 24H_2O \quad (2)$$

$$\text{Overall reaction}: C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O$$

$$\Delta.G^{\circ} = -5792.2\text{kJ/mol} \quad (3)$$

Performance of a MFC is affected by the substrate conversion rate, over-potentials at the anode and at the cathode, the PEM performance, and internal resistance of the cell (Rabaey and Verstraete, 2005). The optimization of MFCs requires extensive exploration of the operating parameters that affect the power output. A sound body of literature supports the exploration of different parameters such as surface area of electrode, different materials as electrodes, use of special aerobic culture of *Shewanella oneidensis* DSP10 as the active electrochemical species in the anode chamber (Ringeisen et al., 2007), *Geobacter sulfurreducens* (Dumas et al., 2008), sedimentary bacterium (Zhang et al., 2006); spatial arrangement of effluent with respect to PEM (Jadhav and Ghangrekar, 2008); electrode distance (Ghangrekar and Shinde, 2007); cathode performance with different electron acceptor such as a permanganate, oxygen (Jadhav and Ghangrekar, 2008; You et al., 2006); and Hexacyanoferrate (You et al., 2006); cathode surface area and cathode mediator (Kim et al., 2007), etc.

All the literature review supports performance of MFC under controlled conditions using different cultures. Enough attention has not been paid so far on evaluating performance of MFC

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exposed to changes in operating temperature and pH, which are among the important aspects for field application of the MFCs. The present study was aimed to investigate the performance of MFC subjected to variation in operating temperature, anodic pH, cathodic pH and external resistance. In addition, it was aimed to develop simple correlation for prediction of current based on the substrate removal. The performance of the MFC was evaluated subjected to temperature variation, as per the ambient temperature variation of 20–35 °C and 8–22 °C, and under different anodic pH, cathodic pH and external load as a power production unit with simultaneous treatment of wastewater.

2. Methods

2.1. Microbial fuel cell

Dual chambered MFC was constructed from acrylic sheet, with stainless steel anode having surface area of 170 cm^2. The stainless steel was used as a cheaper replacement to the graphite electrode, and as an easily available material in mesh form, to offer more surface area per unit volume (Jadhav and Ghangrekar, 2008). The wastewater was supplied from the bottom port provided to the anode chamber, and the effluent left the anode chamber from the top port (Fig. 1). Total working volume of each anode and cathode chamber was 1310 ml. Proton exchange membrane of 0.007 inches thickness (Nafion® 117, Aldrich) having surface area of 24.01 cm^2 was used to separate both the chambers. Three graphite rods having total projected surface area of 150 cm^2 were used as cathode. Electrodes were connected externally with concealed copper wire through external load resistance.

2.2. Wastewater

The synthetic wastewater was prepared by adding 445 mg/l sucrose, 750 mg/l $NaHCO_3$, 159 mg/l NH_4Cl, 13.5 mg/l K_2HPO_4, 4.5 mg/l KH_2PO_4, 125 mg/l $CaCl_2{\cdot}2H_2O$, and 32 mg/l $MgSO_4{\cdot}7H_2O$. Trace metals like Fe, Ni, Mn, Zn, Co, Cu, and Mo were added as per the composition suggested by Ghangrekar et al. (2005). While evaluating the effect of temperature variation, the operating chemical oxygen demand (COD) of synthetic wastewater was in the range from 470 to 510 mg/l and influent pH was maintained in the range from 7.2 to 7.6. For evaluating the effect of pH, the pH of influent to the anode chamber was maintained in the range from 5.5 to 7.5 using 50 mM phosphate buffer as per the composition given in Table 1. For correlating substrate removal with current produced, the influent COD was varied between 100 and 600 mg/l.

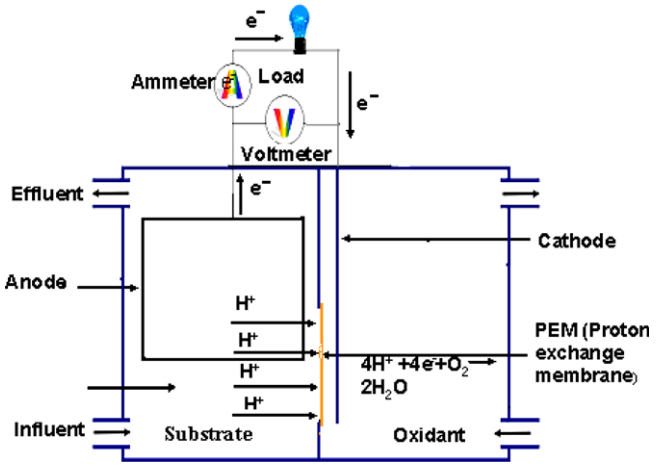

Fig. 1. Schematic diagram of microbial fuel cell.

Table 1
Composition of KH_2PO_4 and K_2HPO_4 used for maintaining different pH

pH	5.5	6	6.5	7	7.5
KH_2PO_4 (gm/100 ml)	0.653	0.599	0.475	0.288	0.128
K_2HPO_4 (gm/100 ml)	0.036	0.105	0.262	0.502	0.707

2.3. MFC operation

The MFC was inoculated with the adapted anaerobic culture collected from the anode chamber of the existing MFC under operation (Jadhav and Ghangrekar, 2008). This existing MFC was initially inoculated with preheated mixed anaerobic sludge and operated for four months. In the present experiments, MFC was operated initially under fed batch mode of operation for total 50 days, with aerated distilled water as cathodic electrolyte and using synthetic wastewater as a feed in anode chamber. The feed cycle time of 48 h was adopted throughout the batch mode of study. The MFC was exposed to ambient temperature changes. Initially the ambient temperature variation was in the range from 20 to 35 °C. Later, decrease in ambient temperature in the range from 8 to 22 °C occurred due to winter season. After 50 days of batch mode of operation, feed was not supplemented to the MFC for 35 days, to check the viability of MFC to sustain long duration of non feed conditions. After this shutdown period, during restart, the operation was shifted to continuous mode with same feed composition in anode chamber and aerated distilled water as cathodic electrolyte. The wastewater was applied at the rate of 1.3 l/d to the MFC making hydraulic retention time (HRT) of 24.55 h. Unless specified the external resistance of 50 Ω was used in the experiments.

The effect of anodic pH on the performance of MFC was studied in terms of COD removal efficiency and energy harvesting. The pH in the cathode chamber was maintained at 7.0 using 50 mM phosphate buffer; whereas, the pH in the anode chamber was varied in the range from 5.5 to 7.5 by suitable addition of KH_2PO_4 and K_2HPO_4 (Table 1). Effect of external load resistance was studied by varying external resistances in the range from 50 Ω to 100, 500, and 1000 Ω. The performance of MFC was evaluated under each external resistance for two days. Variation in the current produced was monitored under different organic loading rates in the anode chamber, and using aerated distilled water and distilled water with potassium permanganate (0.2 g/l) as cathodic electrolytes.

2.4. Analyses and calculations

The influent and effluent COD and pH were monitored according to APHA standard methods (APHA et al., 1998). The potential and current were measured using a digital multi meter (RISH Multi 15S, India) and converted to power according to $P = I{\cdot}V$, where, P = power (W), I = current (A), and V = voltage (V). Internal resistance of the MFC was measured from the slope of line from the plot of voltage versus current (Picoreanu et al., 2007). The coulombic efficiency (CE) was estimated by integrating the measured current relative to the theoretical current on the basis of consumed COD, $CE = (C_E/C_T) \times 100$. The theoretical current production 'C_T' was estimated as:

$$C_T = (F * n * w)/M \quad (4)$$

where 'F' = Faraday constant (96485 C/mol), 'n' = no. of moles of electrons produced per mole of substrate, $n = 4$ for wastewater COD, 'w' = daily COD load removed in gram, 'M' = molecular weight