

Improving Performance of MFC by Design Alteration and Adding Cathodic Electrolytes

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Abstract Performance of two microbial fuel cells (MFCs) was investigated under batch and continuous mode of operation using different cathodic electrolyte. The wastewater was supplied from the bottom port provided to the anode chamber in both the MFCs and the effluent left the anode chamber from the top port in MFC-1, whereas in MFC-2, the effluent exit was provided close to membrane. Stainless steel (SS) mesh anode was used in both the MFCs with surface area of 167 and 100 cm² in MFC-1 and MFC-2, respectively. Under batch mode and continuous mode of operation, these MFCs gave chemical oxygen demand removal efficiency more than 85% and about 68%, respectively. Under batch mode of operation, maximum power density of 39.95 and 56.87 mW/m² and maximum current density of 180.83 and 295 mA/m² were obtained in MFC-1 and MFC-2, respectively. Under continuous mode of operation, a reduction in power and current density was observed. Even with less surface area of the anode, MFC-2 produced more current (1.77 mA) than MFC-1 (1.40 mA). Among the cathodic electrolyte tested, these can be listed in decreasing order of power density as aerated KMnO₄ solution > KMnO₄ solution without aeration > aerated tap water > aerated tap water with NaCl.

Keywords Cathodic electrolytes · Design alteration · MFC · Power density

Introduction

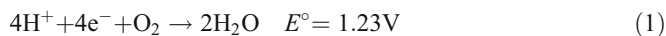
A microbial fuel cell (MFC) converts energy associated with bio-convertible organic substrate in wastewater directly into electricity using microorganisms as a catalyst [1]. Redox reaction of the substrate by microorganisms is the driving force of MFC. In bacterial cells, mitochondria serve as the energy storing units by accumulating or releasing chemical energy in the form of substances, like nicotinamide adenine dinucleotide (NADH) or

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nicotinamide adenine dinucleotide phosphate (NADPH), which act as electron transfer paths from the substrate to the metabolites [2]. Proper control of bacterial metabolism can convert most of the substrate to electroactive intermediates required for harvesting maximum energy from the substrate. The power recovery from the MFC is comparatively lower than other types of fuel cells. If power production and power recovery of this device could be improved, then using MFCs will be an economical method of electricity production, either by using artificially prepared feed from organic matters, or by using organic matter present in wastewater to achieve simultaneous treatment of wastewater.

In traditional MFC, substrate is oxidized by bacteria in the anode chamber, generating electrons and protons. According to principle of MFCs, protons from an anode chamber are allowed to flow to a cathode chamber through a proton-exchange membrane (PEM) with electrons going in the same direction via a conductive wire externally [3]. The electrons, transferred to the cathode through external circuit, and the protons diffused through PEM in cathode chamber are combined with oxygen to form water. Oxygen is usually supplied by aeration in cathode chamber to act as oxidant. The possible reaction in cathode chamber using aerated water is stated below [4–6]:



When, potassium permanganate is used as a cathodic electrolyte solution, the possible reactions in the cathode chamber are as follows [7]:



Performance of a MFC is affected by the substrate conversion rate, overpotentials at the anode and at the cathode, the proton exchange membrane performance, and internal resistance of the cell [1]. Performance of cathode, one of the governing factors in harvesting energy, is governed by the kinetics of reduction of oxygen, or other oxidant supplied, at the cathode [8]. Rate of reduction of oxygen at cathode is governed by the concentrations of proton, electron, and oxygen [9]. The proton transfer rate through the PEM is also affected by the concentration gradient across the PEM, which depends upon the reduction rate of oxygen, or other oxidant, supplied in the cathode chamber.

The main disadvantage of a two-chamber MFC is that the cathode solution must be aerated to provide oxygen to the cathode [10]. The power output of an MFC can be improved by increasing the efficiency of the cathode, e.g., power is increased by adding hydrogen peroxide, ferricyanide, hexacyanoferrate, oxygen, and permanganate to the cathode chamber. Using permanganate as the cathode's electron acceptor, the maximum power density of 3,986.7 mW/m² was achieved in the MFC [7].

The power output of MFCs can also be enhanced by proper spatial arrangement of inlet and outlet of feed solution with respect to position of membrane and electrode to optimize the mass transfer. Optimization of MFCs requires extensive exploration of the operating parameters that affect 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 culture, etc. However, the effect of reductive strength of cathodic electrolyte is one of the governing parameters, which has not been given enough attention so far. Cathodic reaction is a serious limiting factor in a MFC performance [11].

This study was aimed to investigate the performance of MFC, under batch and continuous mode of operation, by modifying configuration of MFC such as placing of electrode and spatial arrangement of effluent exit with respect to electrode and membrane. The performance was evaluated for organic matter removal and electricity production in terms of the power density and current density while treating synthetic wastewater. In addition, it was decided to conduct comparative study of reduction strength of different cathodic electrolytes, such as aerated tap water, tap water with KMnO_4 , and tap water with NaCl . The power production using these cathodic electrolytes was evaluated in this study.

Materials and Methods

Microbial Fuel Cell

Two dual-chambered MFCs were constructed from acrylic sheet, with difference of anode surface area, anode orientation, and position of effluent pipe (Fig. 1). MFC-1 was provided with stainless steel (SS) wire mesh square cage of side 7×7 cm and length of 7 cm as anode electrode, offering total surface area of 167 cm^2 , placed at the bottom of reactor (Fig. 1a). L-shaped SS mesh anode electrode, having surface area of 100 cm^2 , was used in MFC-2. The anode was placed in sludge and near to membrane (Fig. 1b). 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. The distances between the nearest face of anode and cathode electrodes in MFC-1 and MFC-2 were 2.0 and 0.5 cm, respectively. The wastewater was supplied from the bottom port provided to the anode chamber in both the MFCs and the effluent left the anode chamber from the top port in MFC-1, whereas effluent exit was provided near the membrane, wrapped with anode mesh in MFC-2. Total working volume of each anode and cathode chamber was 1,330 ml for MFC-1 and 1,310 ml for MFC-2. Proton exchange membrane of 0.007 in. thickness (Nafion[®] 117, Aldrich) was used to separate both chambers. Membrane surface area of 25.0 and 24.01 cm^2 was used in MFC-1 and MFC-2, respectively. SS mesh cathode electrode having surface area of 33.9 cm^2 was used in both the MFCs, placed close to the PEM. The electrodes were connected externally with concealed copper wire through external load resistance.

Wastewater

A synthetic wastewater containing sucrose as a carbon source was used throughout the study, as per the composition provided in Table 1 [12]. The chemical oxygen demand (COD) of synthetic wastewater was in the range of 480 to 510 mg/l for both the MFCs. Influent pH in both the MFCs was maintained in the range of 7.4 to 7.6 by suitable alkalinity addition.

MFC Operation

These MFCs were inoculated with anaerobic sludge collected from septic tank bottom. The inoculum sludge was sieved through 1-mm sieve, preheated at 100°C for 15 min to suppress the methanogens, cooled at room temperature and 300 ml of sludge was added to the anode chamber. This method was found effective to obtain an enriched culture of hydrogen producers [13]. MFC-1 and MFC-2 were operated in fed batch mode for a total of

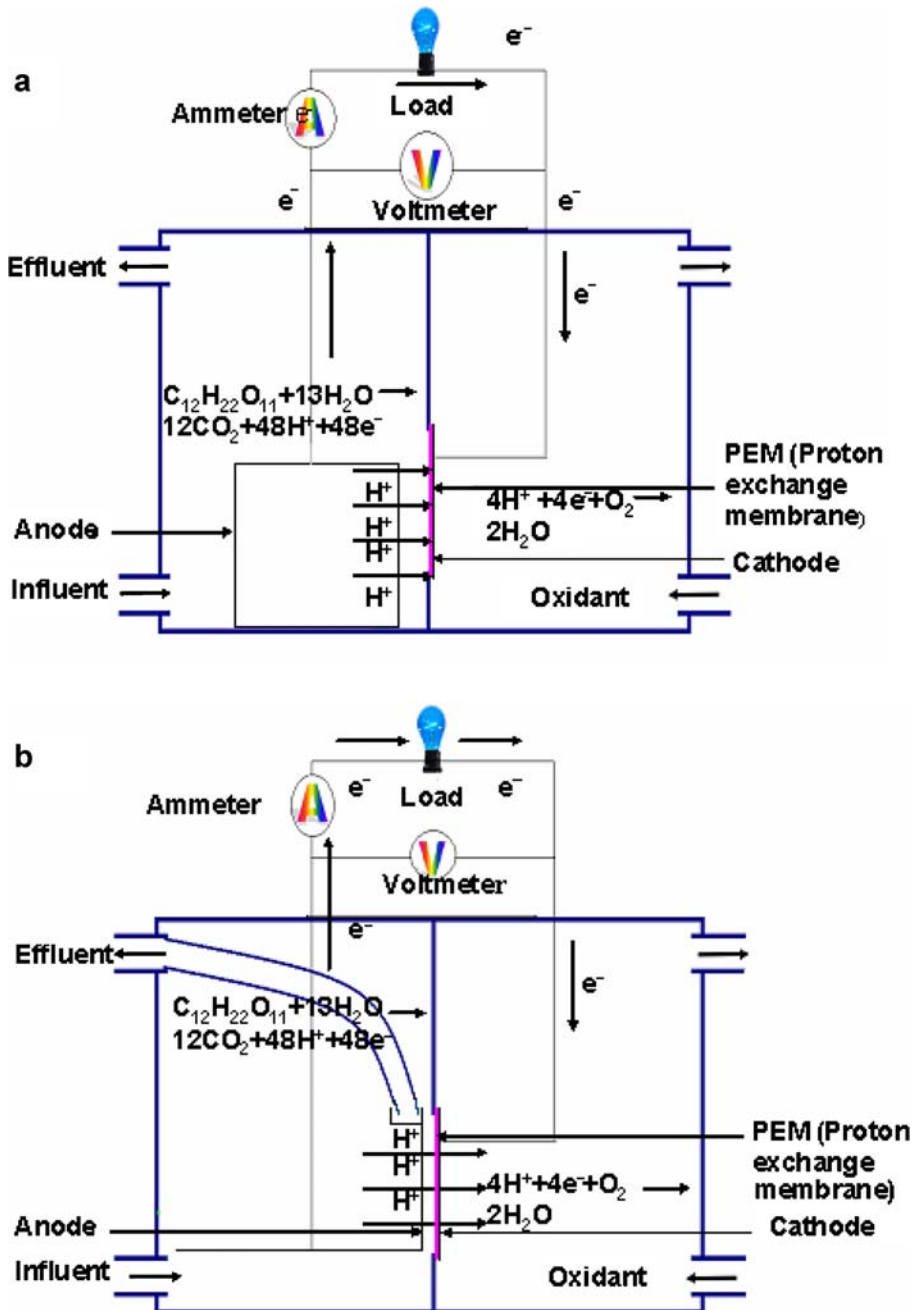


Fig. 1 Schematic diagram of microbial fuel cells: **a** MFC-1 and **b** MFC-2

40 and 30 days, respectively, with 0.5 g $KMnO_4$ per liter as cathodic electrolyte and using synthetic wastewater as a feed in anode chamber. Later, when the short current of both these MFCs reached to a stable value of around 2 mA, the mode of operation was shifted to continuous mode with same feed composition in anode chamber and 0.2 g $KMnO_4$ per liter

Table 1 The composition of the synthetic wastewater.

Component	Sucrose	NaHCO ₃	NH ₄ Cl	K ₂ HPO ₄	KH ₂ PO ₄	CaCl ₂ ·2H ₂ O	MgSO ₄ ·7H ₂ O
mg/l	445	750	159	13.5	4.5	125	32

Trace metals were added as FeSO₄·7H₂O=10 mg/l, NiSO₄·6H₂O=0.526 mg/l, MnSO₄·H₂O=0.526 mg/l, ZnSO₄·7H₂O=0.106 mg/l, H₃BO₃=0.106 mg/l, CoCl₂·6H₂O=52.6 µg/l, CuSO₄·5H₂O=4.5 µg/l, and (NH₄)₆Mo₇O₂₄·4H₂O=52.6 µg/l

as cathodic electrolyte. The wastewater was applied at the rate of 1.3 l/day to both the MFCs making hydraulic retention time (HRT) of 24.55 h in MFC-1 and 24.18 h in MFC-2. After reaching the steady state condition, the performance of these MFCs was evaluated for 2 days with different cathodic electrolyte such as aerated tap water, tap water with 0.2 g KMnO₄ per liter, aerated tap water with 0.2 g KMnO₄ per liter, and aerated tap water with 10 g NaCl per liter. All experiments were conducted at room temperature ranging from 27 to 33 °C. All the experiments were conducted with the external resistance of 50 Ω, unless specifically mentioned.

Analyses and Calculations

The potential and current were measured using a digital multimeter (RISH Multi 15S, India) and converted to power according to $P=IV$, where P =power (W), I =current (A), and V =voltage (V). The influent and effluent characteristics such as COD and pH were monitored according to American Public Health Association (APHA) standard methods [14]. Internal resistance of the MFC was measured from the slope of line from the plot of voltage versus current [15]. The coulombic efficiency was estimated by integrating the measured current relative to the theoretical current on the basis of consumed COD, $E=(C_E/C_T) \times 100$. The theoretical current production C_T was estimated as $C_T=(f \times n \times w)/M$, where f =Faraday constant (96,485 C/mol), n =number of moles of electrons produced per mole of substrate, $n=4$ for wastewater COD, w =daily COD load removed in gram, M =molecular weight of substrate in gram. The actual current production C_E was integrated as $C_E=I \times t$, where I =current (A) and t =time (s).

Results and Discussions

MFCs Performance Under Batch Mode

MFC-1 was operated under batch mode at feed cycle time of 72 h for first 15 days and later at feed cycle time of 48 h for next 25 days. For MFC-2, the feed cycle time of 72 h was adopted for the first 9 days, and later for next 21 days, it was operated at feed cycle time of 48 h. In early stage of batch mode of operation, the pH of anodic solution was decreased in both the MFCs. The short current, voltage, and power got increased with time, with subsequent decrease in internal resistance of cell. After reaching the peak, on 24th day in MFC-1 and 21st day in MFC-2, on later days of operation, slight decrease in current, voltage, and power density have been noticed in both the MFCs. This might be due to increase in internal resistance and increase in pH of anode chamber solution on later days of operation after reaching the peak.

During early days of operation, performance of these MFCs in terms of energy harvesting got improved with increase in COD removal efficiency. Maximum power

density of 39.95 mW/m^2 and coulombic efficiency of 6.15% was observed on the 24th day in MFC-1 with corresponding COD removal efficiency of 81.8%. The corresponding short current was 3.02 mA. The maximum current densities, with respect to anode and cathode surface area, were 180.83 and 890.85 mA/m^2 , respectively. MFC-2 exhibited the maximum power density of 56.87 mW/m^2 and coulombic efficiency of 6.10% on 21st day, with corresponding COD removal efficiency of 79.2%. At this peak, the short current in MFC-2 was 2.95 mA, with maximum current density of 295 and 870.20 mA/m^2 with respect to anode and cathode surface area, respectively. After reaching this peak value, a decrease in short current was noticed on the later days, although improvement in COD removal efficiency occurred. This reduction in current might be due to increased concentration of sludge in anode chamber and hence increased activity of methanogens with time, contributing to enhance COD removal. The current was stabilized at around 2 mA after 30 days in MFC-1 and after 26 days in MFC-2. After stabilization, at fed batch mode cycle time of 48 h, the COD removal efficiencies of 88% and 85% were observed in MFC-1 and MFC-2, respectively.

The internal resistance of these MFCs ranged from 210 to 380Ω for MFC-1 and 100 to 300Ω for MFC-2. The spacing between the electrodes and orientation of electrodes made this difference in internal resistance. During the early days of operation, the internal resistance of these MFCs decreased with time. For MFC-1, the internal resistance was 302, 259, and 210Ω on the 15th, 19th, and 24th day, respectively (Fig. 2), and for MFC-2, it was 189, 164, and 124Ω on 14th, 17th, and 21st day, respectively (Fig. 3). An increase in internal resistance was observed on later days, and it was 259 and 174Ω for MFC-1 and MFC-2 on the 40th and 30th day of operation, respectively.

MFCs Performance Under Continuous Mode

The mode of operation was shifted to continuous mode on the 40th and 30th day for MFC-1 and MFC-2, respectively. These MFCs were operated under continuous mode at average

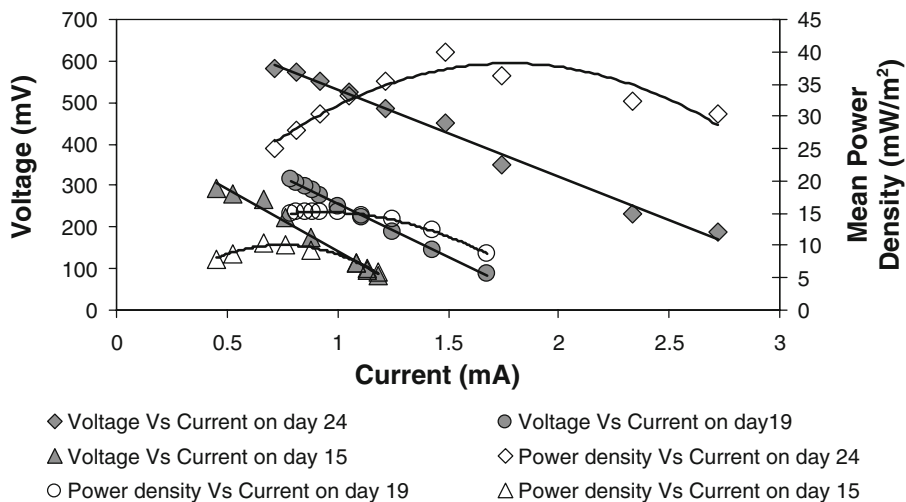


Fig. 2 Polarization curves for MFC-1 during batch mode operation and variation between current and voltage. Slope of the straight line plot between voltage and current gives the internal resistance of MFC on different operating days

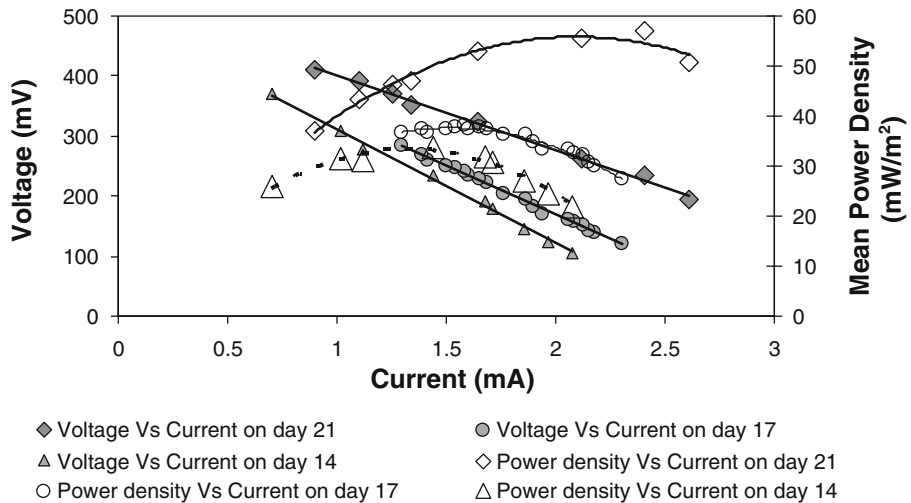


Fig. 3 Polarization curves for MFC-2 during batch mode operation and variation between current and voltage. Slope of the line gives the internal resistance of MFC

organic loading rate of $0.48 \text{ kg COD/m}^3 \text{ day}$. Tap water with 0.2 g/l KMnO_4 was used as cathodic electrolyte. Under continuous mode of operation, COD removal efficiencies were 68.13% and 67.11% for MFC-1 and MFC-2, respectively. The reduction in removal efficiency with change in operation mode could be attributed to the reduction in retention time and hence increase in organic loading to the MFCs. The pH of influent was maintained at 7.6 during continuous operation, whereas the pH of effluent from the anode chamber was 6.85 for MFC-1 and 6.80 for MFC-2.

After achieving stable performance within 4 days, comparative study of MFCs were conducted using different cathodic electrolytes such as aerated tap water with 0.2 g/l KMnO_4 , aerated tap water, and aerated tap water with 10 g/l of NaCl. It was observed that energy harvesting capacity of system improves with increase in reduction strength of cathodic electrolyte. In MFC-1, the short current got decreased from 1.401 to 1.194 mA when aerated tap water with KMnO_4 and aerated tap water with NaCl, respectively, were used as cathodic electrolyte (Table 2). In MFC-2, the short current got decreased to 1.376 from 1.772 mA (Table 3) when aerated tap water with NaCl and aerated tap water with KMnO_4 were used as cathodic electrolytes, respectively.

Effect of Reduction Strength of Cathodic Electrolyte

The effect of reduction strength of cathodic electrolyte was studied for MFC-2. With an increase in reduction strength of cathodic electrolyte, an increase in the power density was noticed (Fig. 4). The power density was maximum (24 mW/m^2) when aerated tap water with KMnO_4 was used as the cathode solution, and it was minimum (11.52 mW/m^2) when aerated tap water with NaCl was used as cathode solution. Among the cathodic electrolytes used in this study, these can be placed in decreasing order of their reduction strength as aerated tap water with 0.2 g KMnO_4 per liter > tap water with 0.2 g KMnO_4 per liter > aerated tap water > aerated tap water with 10 g NaCl per liter.

The internal resistance of the MFC varied with the cathodic solution used (Fig. 5). For aerated tap water as cathode solution, the internal resistance of the MFC was maximum

Table 2 Current and power density observed in MFC-1 under continuous mode of operation.

Cathodic electrolyte	Current (mA; with load of 50 Ω)	Max current density with respect to		Power density at 1,000 Ω load resistance (mW/m ²)	Voltage at 1,000 Ω load resistance (V)
		Anode (mA/m ²)	Cathode (mA/m ²)		
Tap water with 0.2 g KMnO ₄ per liter	1.373	82.22	405.00	10.06	0.410
Aerated tap water with 0.2 g KMnO ₄ per liter	1.401	83.89	413.26	10.56	0.420
Aerated tap water	1.29	77.25	380.55	ND	ND
Aerated tap water with 10 g NaCl per liter (after 16 h)	1.194	71.50	352.22	ND	ND

ND Not determined

(273 Ω), and it was minimum (162 Ω) when aerated water with NaCl was used as cathodic electrolyte. Addition of KMnO₄, with or without aeration, resulted in similar internal resistance.

Electron harvesting rate at anode was affected by the reduction strength of cathodic electrolyte. The reduction strength of cathodic electrolyte governs the rate of consumption of electrons at cathode. The rate of consumption of electrons at cathode is governed by the formation rate of water (or MnO₂) following any of the Eqs. 1, 2, and 3 stated earlier. The formation rate of water (or MnO₂) is governed by the concentrations of reactants, i.e., proton, electron, and oxygen (or MnO₄⁻) available at cathode. After reaching a particular concentration of dissolved oxygen, increase in current was not observed with further increase in oxygen concentration due to limitation of proton transfer rate.

Performance of MFCs with different cathodic electrolyte and configuration, as reported in recent literature and observed in present experiments, is summarized in Table 4. The power density obtained in the present experiment is comparable with many of the MFCs provided with sophisticated electrodes or mediators. Power density value of 196.80 mW/m², with respect to cathode surface area, observed in the present study is more than the values reported by other researchers. The comparable power density using stainless steel as

Table 3 Current and power density observed in MFC-2 under continuous mode of operation.

Cathodic electrolyte	Current (mA; with load of 50 Ω)	Max current density with respect to		Power density at 1,000 Ω load resistance (mW/m ²)	Voltage at 1,000 Ω load resistance (V)
		Anode (mA/m ²)	Cathode (mA/m ²)		
Tap water with 0.2 g KMnO ₄ per liter	1.651	165.1	487.02	15.60	0.395
Aerated tap water with 0.2 g KMnO ₄ per liter	1.772	177.2	522.71	16.40	0.405
Aerated tap water	1.470	147.0	433.62	13.99	0.374
Aerated tap water with 10 g NaCl per liter (after 16 h)	1.376	137.6	405.89	6.35	0.252

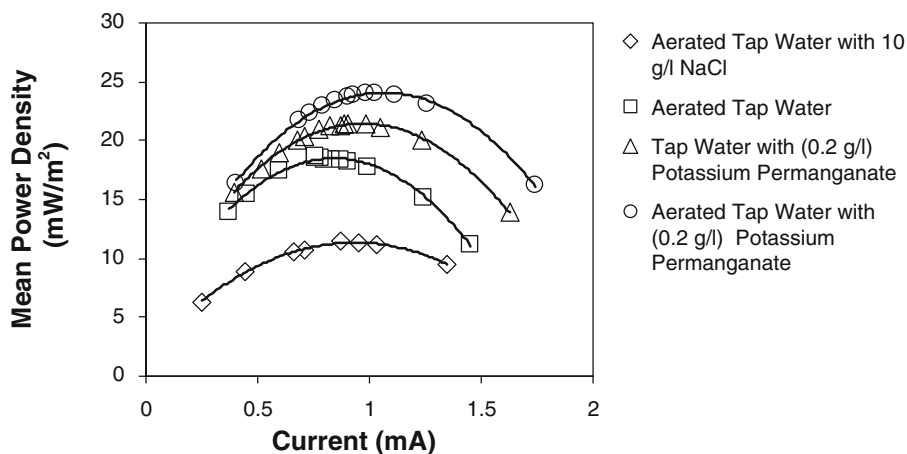


Fig. 4 Polarization curves for various cathodic electrolytes in MFC-2 under continuous mode of operation

electrode material also suggest that it can be successfully used as electrode material, without catalyst or mediator, which will be economical and provide more surface area with less volume occupation in the reactor.

Effect of Sodium Ions

After addition of NaCl in the cathode chamber, sudden increase in the current was observed in both MFCs. In MFC-1, the short current was increased from 1.29 mA with aerated tap water to 2.152 mA when aerated tap water with 10 g NaCl per liter was used as cathodic electrolytes, whereas in MFC-2, the respective short currents were 1.47 and 2.4 mA. However, the short current decreased gradually with time. After a lapse of 16 h, it maintained a more or less stable condition with increase in pH of cathodic electrolyte from 7.1 to 8.24 and 8.31 in MFC-1 and MFC-2, respectively. At stable condition, the short current of 1.194 and 1.376 mA was observed in MFC-1 and MFC-2, respectively. Increase in pH of the cathode solution indicates formation of alkalinity causing compounds as an

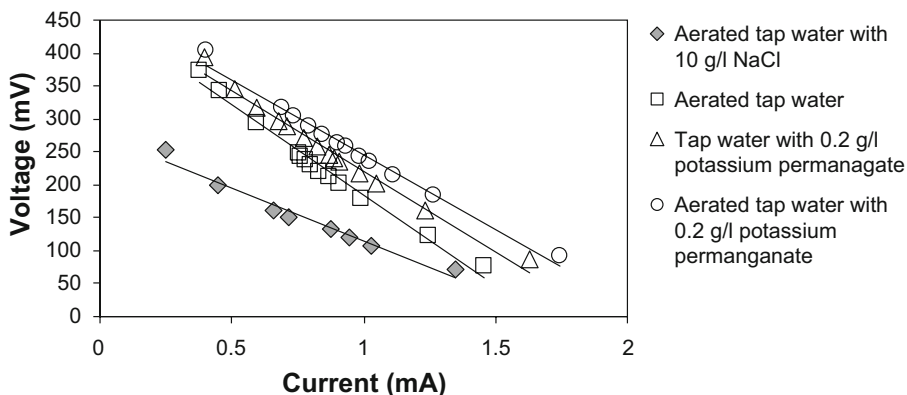


Fig. 5 Variation between current and voltage for MFC-2 with different cathodic electrolyte. Slope of the line gives the internal resistance of MFC

Table 4 Summary of performance of MFC with different cathode electrolytes.

Reactor type	Mode of operation	Cathodic electron acceptor	Cathodic mediator	Anode type and area	Cathode type and area	Power (anode surface area; mW/m ²)	Power (cathode surface area; mW/m ²)	Reference
Two-chamber MFC (membrane less)	Continuous	Oxygen Hydrogen peroxide	–	Graphite rods, 118.7 cm ²	Graphite rods, 118.7 cm ²	7.2 22	7.2 22	[16]
Two-chamber MFC	Batch	Ferricyanide	(K ₂ HPO ₄ as cathodic mediator)	Graphite plate 83.56 cm ²	Graphite plate 70 cm ²	119.31	142.42	[17]
Two-chamber MFC	Batch	Aerated cathode	–	Carbon paper (2.0 cm × 5.0 cm)	Carbon cloth (2.0 cm × 5.0 cm)	82.77	98.77	[7]
	Batch	Permanganate	–			115.60	115.60	
	Batch	Hexacyano-ferrate	–			25.62	25.62	
Single chamber	Batch	Oxygen	–			10.2	10.2	
	Continuous	Aeration	–	Graphite + PTFE	Graphite + PTFE	80 600		[18]
Two-chamber MFC	Continuous aerobic anode	Potassium ferricyanide	Phosphate buffer	Graphite felt	Graphite felt 611 cm ²	5.237	–	[19]
Two-chamber MFC	Continuous anaerobic anode	Potassium ferricyanide	Phosphate buffer	Graphite felt	Graphite felt 611 cm ²	1.8	–	[19]
Two-chamber MFC	Batch	Permanganate	–	Stainless steel 167 cm ²	Stainless steel 33.9 cm ²	39.95	196.80	Present work
Two-chamber MFC	Batch	Permanganate	–	Stainless steel 100 cm ²	Stainless steel 33.9 cm ²	56.87	167.75	Present work
Two-chamber MFC	Continuous	Permanganate + oxygen	–	Stainless steel 100 cm ²	Stainless steel 33.9 cm ²	24	70.79	Present work
	Continuous	Permanganate				21.4	63.13	
	Continuous	Oxygen				18.6	54.88	

end product of cathodic reaction. With increasing pH in the cathode chamber, lowering of the potential of cathode chamber is reported [11].

Sodium chloride dissociates in water and increases the ion concentration. With increase in ionic strength of anode solution, increase in power density was reported earlier [20]. This increase in power density is probably due to a reduction in internal resistance of the MFC. With lapse of time, the concentration of ion decreases with increase in pH, indicating precipitation of salts in cathodic electrolyte. Formation of carbonate salt film on the cathode is reported earlier [21]. In addition, as a result of the addition of NaCl, the solubility of oxygen in water also reduces due to reduction in saturation concentration. Hence, marginal decrease in current was observed with the addition of NaCl at stable condition, compared with the current produced when only aerated tap water was used as cathodic solution.

Effect of Design Alteration

In MFC-1, maximum electrode surface area was immersed in the sludge present in the anode chamber, whereas in case of MFC-2, maximum surface area of anode was present in bulk solution that had more chances to come in contact with electrons. As a result, even with lower area of the electrode, MFC-2 gave same short current under batch mode of operation. Under continuous mode of operation, in case of MFC-2, the effluent pipe and electrode arrangement was made in such a way that all the effluent was forced to come in contact with electrode, hence enhancing the chances of electron trapping by the electrode. This arrangement of effluent exit in the proximity of anode also reduced the chances of proton loss through effluent, by repelling proton away from the anode, hence forcing it to diffuse through the membrane. In MFC-1, the effluent exit was away from the electrode and hence resulted in lower current due to loss of charges through effluent. The effectiveness of this arrangement can also be justified with reference to coulombic efficiency of 2.61% and 3.55% obtained in MFC-1 and MFC-2, respectively, under continuous mode of operation. The higher coulombic efficiency in MFC-2 supports higher electron harvesting capacity of this device due to arrangement of effluent exit close to the anode.

Internal resistance of a cell changed with cathodic electrolyte. For MFC-2, the internal resistance of the cell was 245, 228, 273, and 162 Ω for tap water with potassium permanganate, aerated tap water with potassium permanganate, aerated tap water, and aerated tap water with NaCl, respectively. For MFC-1, it was 364 and 359 Ω for tap water with potassium permanganate and aerated tap water with potassium permanganate, respectively. Under similar cathodic electrolyte solution, the MFC-1 showed higher internal resistance due to difference in configuration and location of electrode with respect to membrane.

Comparison between the short current observed in MFC-1 and MFC-2 is provided in Fig. 6. It was observed that during the batch mode of operation, the electron harvesting capacity of MFC-1 was higher than the MFC-2. Whereas in continuous mode of operation, under all the cathodic electrolytes used, MFC-2 showed higher current production. This was due to the higher electron harvesting capacity of MFC-2 than MFC-1 because of the position of the effluent pipe. In MFC-1, currents, with 50 Ω external load, were 1.194, 1.29, and 1.373 mA, and 1.401 mA for the cathodic electrolytes such as aerated tap water with 10 g NaCl per liter, aerated tap water, tap water with 0.2 g KMnO_4 per liter, and aerated tap water with 0.2 g KMnO_4 per liter, respectively. For MFC-2, the respective currents, with external load of 50 Ω , were 1.376, 1.47, 1.651, and 1.772 mA. With increase in reduction strength of cathodic electrolyte, the rate of increase in short current was less in MFC-1 than the MFC-2 (Fig. 7). As stated earlier, diffusion rate of proton in cathode chamber also governs rate of reaction in cathode chamber. The placement of effluent exit near the PEM in

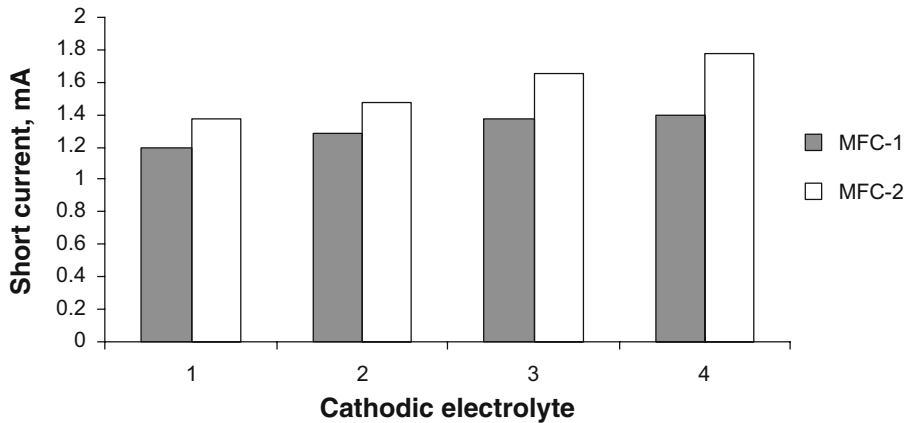


Fig. 6 Comparison of currents with different cathodic electrolyte for MFC-1 and MFC-2 at external resistance of 50 Ω . (1 aerated water with 10 g NaCl per liter; 2 aerated tap water; 3 tap water with 0.2 g KMnO_4 per liter; 4 aerated tap water with 0.2 g KMnO_4 per liter)

MFC-2 produced strong proton gradient across the membrane as compared to MFC-1, hence resulted in higher diffusion rate of proton in case of MFC-2.

Effect of Surface Area of Electrode

The open-circuit potential (OCP) difference developed in MFC-1 was 0.78 V, and for MFC-2, it was 0.68 V, when aerated tap water with KMnO_4 was used as a cathodic electrolyte. Though MFC-2 had more electron harvesting capacity than MFC-1, open-circuit voltage developed in MFC-1 was higher than MFC-2. Furthermore, it was observed that the rate of increase in voltage with respect to external load resistance was more for MFC-1 than MFC-2 (Fig. 8). However, with an increase in external resistance, rapid decrease in current was observed in MFC-2 as compared with MFC-1. It is known that increasing the electrode area could decrease the overpotential of the electrode due to the increase in area for bacterial attachment and growth. This observation conveys that the surface area of anode also affects the performance of MFCs.

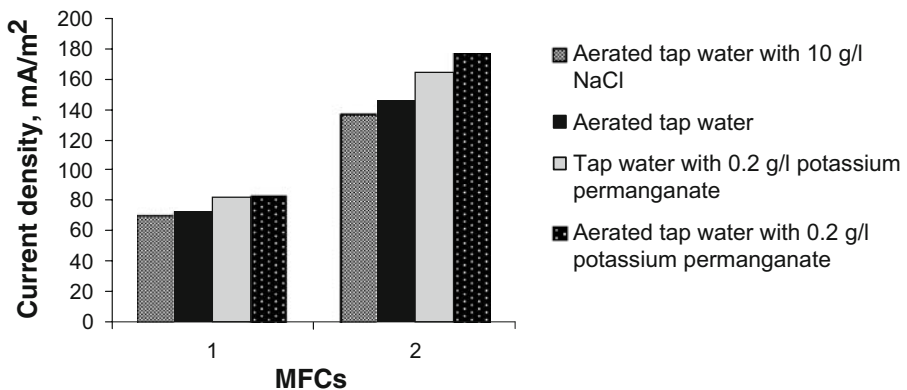
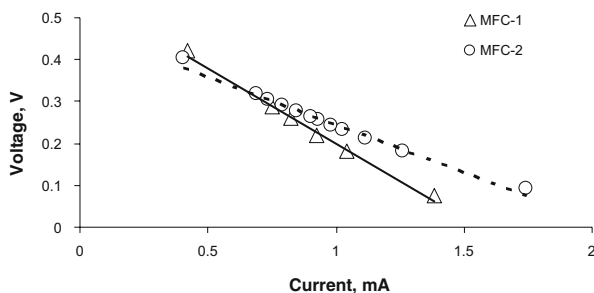


Fig. 7 Variation in current density (at 50 Ω resistance) with different cathodic electrolyte in MFC-1 and MFC-2

Fig. 8 Variation between current and voltage for MFC-1 and MFC-2 with aerated water with 0.2 g KMnO_4 per liter as cathodic electrolyte



Comparison of Observed Potential with Theoretical

OCP means the potential difference between the electrodes, anode and the cathode. The anode potential is affected by factors such as substrate conversion rate, electrons transfer rate from microorganisms to the anode surface, and characteristic of anode, while cathode potential depends on the types of cathodic electron acceptor used as well as the concentration and electrochemical reaction rates [7]. Assuming the redox potential of NAD^+/NADH in the anode as constant (-0.32 V) [1], the OCP will be dependent on the performance of cathode only. Different electron acceptors will give a different cathode potential on the basis of the redox potential of a particular electron acceptor. Therefore, the OCP value will depend on the type of electron acceptor used as cathodic electrolyte. As mentioned previously (Eqs. 2 and 3), permanganate gives a higher OCP in acidic conditions than in alkaline conditions. Based on Eq. 2, the cathode potential as a function of pH and permanganate concentration can be described by using Nernst equation, as below [7]:

$$E = 1.70 + 0.0197 \log[\text{MnO}_4^-] - 0.0787 \text{ pH} \quad (4)$$

Considering $[\text{MnO}_4^-] = 0.15$ g/l (9.495×10^{-4} mol/l) and pH 8.0 based on the results from this study, the cathode potential (E) could be calculated as 1.011 V from Eq. 4. The cathode potential as a function of pH when oxygen is used as electron acceptor can be described by using Nernst equation based on Eq. 1, as below:

$$E = 1.23 - 0.059 \text{ pH} \quad (5)$$

Redox potentials for different electron acceptors, used in the cathode chamber of a MFC, are presented in Table 5 along with the observed potential. The experimental potentials were in the range of 73% to 77% of the theoretical potential in MFC-1 due to lower overpotential because of higher surface area of the electrode. Whereas in MFC-2, the experimental observed potentials were in the range of 62% to 69% of the theoretical potential. The experimental potential is more close to the theoretical potential when aeration

Table 5 Comparison of observed potential with theoretical potential in the MFCs.

Oxidant	Theoretical potential (V)	Experimental OCP (V)	
		MFC-1	MFC-2
Oxygen	0.782	0.58	0.54
MnO_4^-	1.011	0.74	0.64
Oxygen+NaCl	0.740	0.54	0.50
Aeration+ MnO_4^-	1.011	0.78	0.68

is carried out in the cathode chamber. The mixing, induced in the cathode chamber during aeration, improved the proton transfer to the electrode, and as a result, more potential difference was obtained because of improved cathode reaction.

Conclusions

From the present study, it was observed that the performance of MFCs in terms of energy harvesting improves with increase in reduction strength of cathodic electrolyte. The internal resistance of cell differs with electrode orientation, distance between electrodes, and cathode solution. Internal resistance of cell decreases with a decrease in distance between electrodes. Electron harvesting capacity of anode is not only a function of surface area but also a function of overall design of MFCs, such as orientation of effluent pipe, place of anode, and distribution of anode surface area. When operated in the batch mode, the MFCs produced more power density as compared to continuous mode. When the performance of MFCs was tested with different cathodic electrolyte, these can be listed in decreasing order of power density as aerated tap water with 0.2 g KMnO_4 per liter > tap water with 0.2 g KMnO_4 per liter > aerated tap water > aerated tap water with 10 g NaCl per liter as a cathodic solutions.

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