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Rice mill wastewater treatment in microbial fuel cells fabricated using proton exchange membrane and earthen pot at different pH

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ABSTRACT

Performance of microbial fuel cells (MFCs), fabricated using an earthen pot (MFC-1) and a proton exchange membrane (MFC-2), was evaluated while treating rice mill wastewater at feed pH of 8.0, 7.0 and 6.0. A third MFC (MFC-3), fabricated using a proton exchange membrane (PEM), was operated as control without pH adjustment of the acidic raw wastewater. Maximum chemical oxygen demand (COD) removal efficiencies of 96.5% and 92.6% were obtained in MFC-1 and MFC-2, respectively, at feed pH of 8.0. MFC-3 showed maximum COD removal of 87%. The lignin removal was 84%, 79%, and 77% and the phenol removal was 81%, 77%, and 76% in MFC-1, MFC-2, and MFC-3, respectively. Maximum sustainable volumetric power was obtained at feed pH of 8.0, and it was 2.3 W/m^3 and 0.53 W/m^3, with 100 Ω external resistance, in MFC-1 and MFC-2, respectively. The power was lower at lower feed pH. MFC-3 generated lowest volumetric power (0.27 W/m^3) as compared to MFC-1 and MFC-2. More effective treatment of rice mill wastewater and higher energy recovery was demonstrated by earthen pot MFC as compared to MFC incorporated with PEM.

1. Introduction

Considerable attention has been paid to develop microbial fuel cells (MFCs) as a sustainable technology in recent years because of their capability to simultaneously generate electricity and treat organic wastewaters. The working principle of a MFC is based on the catalytic activity of microorganisms to oxidize organic substrate in an anaerobic anode chamber to generate electrons and protons. Electrons are transferred from the anode to the cathode through an external circuit, and protons are transferred towards the cathode through the internal membrane which separates anodic and cathodic chambers. On the cathode, electrons reduce the final electron acceptor, typically oxygen or an alternative electron acceptor.

MFCs have been operated successfully on a variety of organic matter varying from pure chemicals to complex wastes. Wide varieties of substrates have been tested such as glucose, acetate, butyrate [1], cysteine [2], proteins [3], and lignocellulose [4]. However, to make MFCs competitive with other technologies in renewable energy production, wastewaters are being considered to be the most promising electron donors for MFC systems because it is free and sustainable [5]. MFCs have been developed to generate electricity directly from complex organic wastewater such as food processing wastewater [6], brewery wastewater [7], domestic wastewater [8–11], chemical wastewater [12], starch wastewater [13], swine manure slurry [14,15], manure waste [16], landfill leachate [17], meatpacking wastewater [3], palm oil mill effluent [18], paper mill effluent [19] and for denitrification of domestic wastewater [20]. Recently Hong et al. [21] has reported better humification of sediment organic matter using sediment MFC system, which can have a potential for the energy-efficient remediation, monitoring, and/or management of the geo-environment in association with microbially catalyzed electricity generation. Cao et al. [22] demonstrated effective removal of azo dye (Congo Red) in anodic chamber of the MFC with the addition of readily metabolizable co-substrates such as glucose, acetate and ethanol.

Wastewaters coming from different industrial operations contain high concentration of organic and inorganic substances as well as soluble and insoluble materials causing significant polluting phenomena. The rice milling industry does not only mill rice but also carries out many other essential functions such as procurement, drying, storage, quality control, and utilization of by-products. Parboiled rice production generally requires a large amount of water for soaking of the paddy. The wastewater yield is about 1.0–1.2 L/kg of paddy [23]. To the best of our knowledge the feasibility of rice mill wastewater treatment and electricity generation has not been tested in the MFC, although few studies have been reported for its anaerobic treatment using upflow anaerobic sludge blanket (UASB) reactor [23].

The power production in the MFC mainly depends on the reactor configuration and electrode material; performance of proton exchange membrane (PEM); specific source of substrate; and operating conditions such as temperature and pH. Many improvements are being carried out to enhance the power production level of MFC. Many

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more improvements in the materials used for MFC construction will be necessary before practical implementation of the MFC, to make it economically competitive with the presently used treatment systems.

PEM influences the power output of the MFC. Nafion is the most popularly used PEM in the MFCs because of its highly selective permeability of protons. However, Nafion is quite expensive, which results in upraised production cost of the MFCs. Nafion is also subjected to fouling in long run, which makes the operation and maintenance cost very high. Salt bridge [24], Ultrex [25], and porcelain septum made from kaolin [26] have been used as an alternative to Nafion, but the power production was an order of magnitude lower than that with Nafion.

Behera et al. [27] have demonstrated the performance of a low cost MFC, made of earthen pot without employing the commercially available expensive membrane. This earthen pot MFC, with total production cost for anode chamber less than 1.0 US$, was reported to give maximum power output of 16.8 W/m^3, while treating synthetic wastewater. This MFC demonstrated competitive performance as compared to MFCs incorporated with polymer membrane and MFCs provided with expensive catalyst on cathode.

In the present study, the feasibility of using rice mill wastewater as a substrate to the MFC for electricity generation with simultaneous accomplishment of wastewater treatment has been investigated. The study was carried out in a MFC made of earthen pot without using PEM and dual chambered MFCs incorporating PEM (Nafion). As the raw wastewater is acidic in nature, pH adjustment of the wastewater is necessary for biological treatment and in this study the effect of different operating pH on performance of MFC was evaluated using oxygen as an electron acceptor in the cathode. The maximum power production capacity of these MFCs was evaluated using permanganate as cathodic electron acceptor instead of aerated tap water after achieving steady state in these MFCs.

2. Methods

2.1. MFC construction

MFC-1 was made up of an earthen pot anode chamber having working volume of 400 mL. The wall of the earthen container (4 mm thick) itself was used as the medium for proton exchange. Stainless steel (SS) mesh having a total surface area of 190 cm^2 was used as the anode, and a graphite plate (projected surface area = 231 cm^2) was used as the cathode. This earthen pot anode was placed in the plastic bucket working as a cathode chamber. Two identical dual chambered MFCs (MFC-2 and MFC-3), incorporating Nafion as PEM, were also used for the treatment of rice mill wastewater. These dual chambered MFCs were made up of polyacrylic plastic with working volume of both anodic and cathodic chambers of 560 mL each. SS mesh having a total surface area of 190 cm^2 was used as the anode and graphite plate having a surface area of 130 cm^2 was used as the cathode. The anode and cathode compartments were separated with PEM (Nafion® 117, Sigma Aldrich, USA) having dimensions 2.54 cm × 2.54 cm. Electrodes were connected externally through concealed copper wire through an external resistance of 100 Ω, except when stated otherwise.

2.2. MFC operation

These MFCs were inoculated initially with anaerobic sludge collected from a septic tank bottom. The inoculum sludge was given heat pre-treatment [28] and 50 mL of sludge was added to the anode chamber of MFC-1 and 70 mL of sludge was added to the anode chamber of MFC-2 and 3, because of slightly higher volume of anode chamber in later MFCs. The rice mill wastewater was collected from a local rice mill situated in the Midnapore district, West Bengal, India. The characteristics of raw rice mill wastewater were: pH, 4.0–4.3; COD, 2200–2250 mg/L; lignin, 80.3–87.6 mg/L; and phenol, 14.8–16.5 mg/L. The collected wastewater was stored in the deep freeze before feeding to the MFCs. These MFCs were operated under fed batch mode. MFC-1 and MFC-2 were operated at anodic feed pHs of 8.0, 7.0, and 6.0 using 50 mM phosphate buffer. MFC-3 was operated with raw wastewater as feed without any pH adjustment. To compare the performances of these MFCs in terms of wastewater treatment and electricity generation, a reaction cycle time of 288 h was maintained and fresh feed was given after decanting the supernatant from the anode chamber. Reactors were fed twice at each operating pH. Initially, for acclimation of the culture the rice mill wastewater was diluted about four times and feed was given to the MFCs for two weeks with an interval of 7 days (results not shown). Later, two times diluted wastewater (COD = 1100–1125 mg/L) was fed to the reactors. After two feed cycles, wastewater without dilution was fed. Aerated tap water was used as cathodic electrolyte. Permanganate was used at the concentration of 0.2 g/L as cathodic electron acceptor at the end of the study to evaluate the maximum power production capacity of the MFC by overcoming the cathodic limitations.

2.3. Analyses and calculations

The potential and current were measured using a digital multimeter with data acquisition unit (Agilent Technologies, Malaysia) and converted to power according to $P = IV$, where P = power (W), I = current (A), and V = voltage (V). Power density and power per unit volume were calculated by normalizing power with respect to anode surface area and net liquid volume of anode compartment, respectively. The influent and effluent COD concentrations, pH, conductivity, lignin and phenol contents were monitored according to APHA standard methods [29].

Polarization studies were carried out by varying the external resistances from 5000 to 10 Ω. Internal resistance of the MFC was determined from the slope of line from the plot of voltage versus current [30]. The anode and cathode potentials were measured using Ag/AgCl reference electrode (Bioanalytical Systems Inc., USA). Specific power yield (W/kgCOD$_\mathbf{R}$) was obtained by dividing power generated with the substrate (COD$_R$) removed [12]. The Coulombic Efficiency (CE) of the MFC was calculated by integrating the measured current over time relative to the maximum current possible based on the observed COD removal. The CE evaluated over a period of time t, is calculated as [31]:

$$CE = \frac{M\int_0^t Idt}{Fbv_{an}\Delta COD} \quad (1)$$

Where $M = 32$, the molecular weight of oxygen, F is Faraday's constant, $b = 4$ is the number of electrons exchanged per mole of oxygen, v_{an} is the volume of liquid in the anode compartment, and ΔCOD is the change in COD over time t.

3. Results and discussion

3.1. Treatment of rice mill wastewater

After initial acclimation with four times diluted rice mill wastewater for two consecutive feedings for the total duration of two weeks, these MFCs were operated with two times diluted wastewater having influent COD concentration of 1100–1125 mg/L. The anolyte pH was maintained at 8.0 in MFC-1 and MFC-2 by phosphate buffer addition. MFC-3 was operated with wastewater without any pH adjustment of the 50% diluted wastewater. After 288 h of reaction cycle, COD removal efficiencies of 93.2%, 85.1% and 70.5% were observed in MFC-1, MFC-2 and MFC-3, respectively. After two feed cycles with diluted wastewater, the MFCs were fed with rice mill wastewater without any dilution. The pH of the influent was

maintained at 8.0 in MFC-1 and MFC-2 for next two feedings for the reaction time of 288 h. Subsequently, these two MFCs were operated at pH of 7.0 and 6.0. At each pH the anode chamber was given feed twice with the reaction time of 288 h.

When operated at pH of 8.0 without dilution of the wastewater, MFC-1 and MFC-2 showed COD removal efficiency of 96.5% and 92.6%, respectively (Fig. 1). The pH inside the anode chamber was in the range of 7.5–7.8. After eliminating dilution and feeding actual wastewater, increase in COD removal efficiency was observed which can be attributed to the acclimatization of the anaerobic consortia inside the MFCs with the real wastewater environment. When MFC-1 and MFC-2 were operated at feed pH corrected to 7.0, the COD removal efficiency of MFC-1 and MFC-2 decreased to 92.3% and 88.5%, respectively. Further decrease in COD removal efficiency was observed with decrease in influent pH to 6.0. MFC-1 showed COD removal efficiency of 89.2% and MFC-2 showed removal efficiency of 85.4% at feed pH of 6.0. The pH inside the anode chambers was in the range of 5.9–6.3 during this operation. The optimum performance in terms of organic matter removal was observed when the feed pH was maintained at 8.0. The pH inside the reactor (7.5–7.8) might have favoured the anaerobic degradation of the wastewater, and this slightly alkaline pH is observed to be favourable for treatment of this complex wastewater with fermentable substrates.

Improvement in total COD removal is reported earlier when the operating pH of anolyte was changed from 6.8 to 7.2 while treating sewage sludge in the MFC [32]. However, slight reduction in the removal efficiency (6.8%) and marginal improvement in the power density is reported when the pH was further increased to 7.55. In the present experiments, when the anolyte pH was around 7.5 maximum COD removal efficiency has been observed in all these three MFCs. This could be due to partial phase separation expected under batch mode of operation, where actual pH within the biofilm on the anode is expected to be lower than the bulk liquid because of higher rate of acidification and slow rate of diffusion due to absence of mixing.

The COD removal efficiency in MFC-3 increased from 75.4% during first feeding of undiluted wastewater to 87% in the last (sixth) feed cycle. The pH inside the reactor increased from 5.3 to 7.6 at the end of the experiment. This demonstrates the self buffering capacity of the wastewater and the adaptation of anaerobic consortia over a period of time. Enhancement in the organic matter removal with duration of operation was due to increase in the anodic pH which favoured the anaerobic degradation of this complex wastewater having fermentable organic matter.

The overall lignin removals in MFC-1, MFC-2 and MFC-3 were 84 ± 1.6%, 79 ± 1.8%, and 77 ± 2.6%, respectively. Lignin is a complex polymer that consists of various carbohydrates, oligomers, and monomers and has been considered to be relatively recalcitrant. Lignin is a bio-refractory material and is not degraded easily during treatment in conventional activated sludge process. The conventional treatment methods are also energy consuming and costly due to chemical consumption. Effective removal of lignin was observed in the MFCs throughout the study. Wang et al. [33] have shown lignin removal of 4 ± 1% and 11 ± 4% during treatment of raw corn stover and corn stover residual solids after steam explosion, respectively, in single chamber air cathode MFC inoculated with a mixed culture that was developed to have a high saccharification rate with corn stover. The lignin removal observed in the present experiment is significantly higher than the value reported earlier. With the present experimental conditions, the exact mechanism for the removal of the lignin could not be detected and detail investigations are required to know the mechanism. However, consistent high lignin removal in these three MFCs emphasizes utility of MFCs for treatment of wastewaters containing lignin.

These MFCs also demonstrated effective phenol removal. Overall phenol removal of 81 ± 0.8%, 77 ± 1.1%, and 76 ± 1.8% was observed in MFC-1, MFC-2 and MFC-3, respectively. The earthen pot MFC (MFC-1) showed higher lignin and phenol removal than MFC with PEM (MFC-2) throughout the experiments. Earlier Cheng et al. [18] have reported 100% phenol removal while treating palm oil effluent in an integrated system of two-stage MFCs and immobilized biological aerated filters. This study demonstrated effective treatment of recalcitrant contaminants like lignin and phenol in MFCs, which suggests the effectiveness of this technology in industrial wastewater treatment like rice mill wastewater with simultaneous generation of electricity.

3.2. Electricity harvesting

3.2.1. Performance of earthen pot MFC and MFC with PEM

The earthen pot MFC (MFC-1) generated a maximum power density (normalized to the anode surface area) and volumetric power (normalized to the working volume of anode chamber) of 12.5 mW/m^2 and 593 mW/m^3, respectively, with 100 Ω external resistance, when the influent COD was 1100–1125 mg/L. MFC-2 generated power density of 4.7 mW/m^2 and volumetric power of 158 mW/m^3 with 100 Ω external resistance at this influent COD. When the influent COD concentration was doubled and wastewater was fed without any dilution at an influent pH of 8.0, maximum voltages generation in MFC-1 and MFC-2 were 0.304 V and 0.172 V (Fig. 2), corresponding to the volumetric power density of

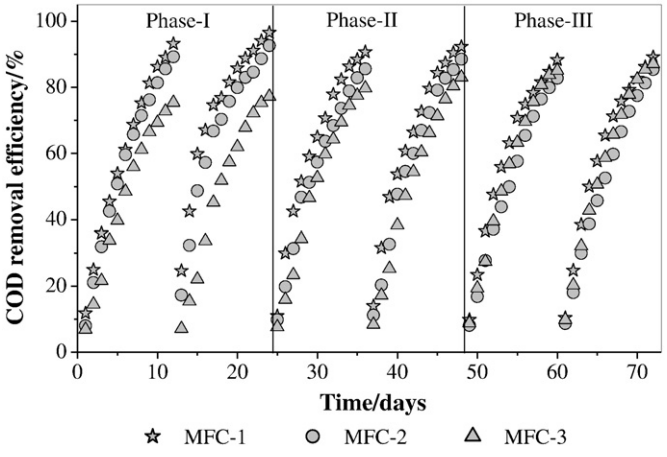

Fig. 1. COD removal efficiency of the MFCs during different phases. The operating feed pH was 8.0, 7.0 and 6.0 in MFC-1 and MFC-2 during Phases I, II and III, respectively, and in MFC-3, the anodic solution pH was 5.3 in the beginning and 7.6 at the end.

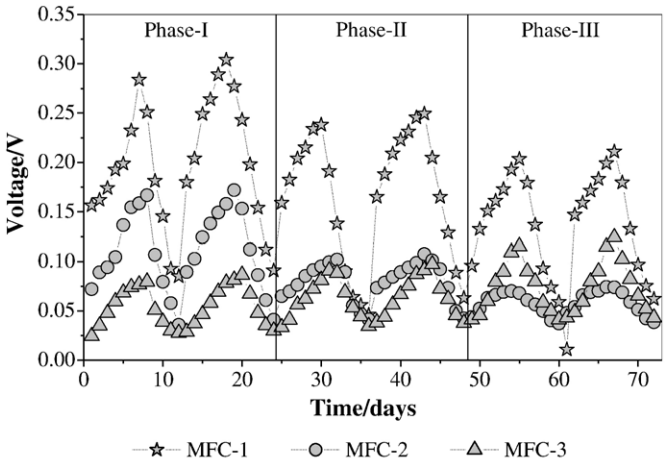

Fig. 2. Voltage generation in the MFCs across 100 Ω external resistance during different phases. The operating feed pH was 8.0, 7.0 and 6.0 in MFC-1 and MFC-2 during Phases I, II and III, respectively, and in MFC-3, the anodic solution pH was 5.3 in the beginning and 7.6 at the end.

2310 mW/m^3 and 528 mW/m^3, respectively, with 100 Ω external resistance. The power generation decreased in both the MFCs with decrease in influent pH. The volumetric power densities were 1550 mW/m^3 and 1113 mW/m^3 (Table 1) in MFC-1 and 204 mW/m^3 and 98 mW/m^3 in MFC-2, when operated with influent pH of 7.0 and 6.0, respectively. The volumetric power generation in MFC-1 was 11.4, 7.6 and 4.4 times higher than that of MFC-2 at feed pH of 6.0, 7.0, and 8.0, respectively. The difference in power generation between MFC-1 and MFC-2 decreased with increase in anodic pH and it was more pronounced at pH of 6.0.

The earthen pot MFC generated higher power than the MFC with PEM throughout the experiment under all the operating pH. The wall material of the earthen pot used was found to be effective for proton transfer as documented earlier by Behera et al. [27]. The surface of the earthen pot MFC provided larger area for proton transfer which contributed towards the higher power generation in the MFC-1. The catholyte pH in MFC-1 was in the range of 8.3–8.8 throughout the experiment. In MFC-2, the catholyte pH was in the range of 8.7–9.3. Higher proton transfer in earthen pot might have favoured the lower pH of the catholyte in MFC-1. The high rate of proton transfer in MFC-1 resulted in increased rate of proton harvesting in the anodic compartment, which increased the COD removal efficiency. Therefore, the COD removal efficiency was also higher in MFC-1 than that of MFC-2.

The volumetric power density in MFC-3 was 64 mW/m^3 (0.06 V, 0.6 mA), when diluted wastewater was fed. The electricity generation increased when wastewater without dilution was supplied. The electricity harvesting increased with each feed cycle (Fig. 2). The power generation in MFC-3 was always lower than that of MFC-1. During the last feed, the maximum volumetric power generation in MFC-3 was 274.6 mW/m^3 (0.124 V, 1.24 mA), which was higher than that generated in MFC-2, operated at anodic pH of 6.0 and 7.0.

With subsequent feedings over a period of 80 days the pH in the anodic compartment of MFC-3 increased from 5.3 to reach a stable value of 7.6, which favoured the anaerobic degradation of organic matter as well as power production. Although the anodic pH in MFC-2 when operated at influent pH of 8.0 and anodic pH of MFC-3 during the last feed cycle were in the same range, the power generation in MFC-2 (528.3 mW/m^3) was higher than that in MFC-3 (274.6 mW/m^3). This can be attributed to the higher conductivity of the anolyte in MFC-2 than that of MFC-3 due to buffer addition. The conductivity of anolyte was 13.56 mS/cm and 4.28 mS/cm in MFC-2 and MFC-3, respectively. This result demonstrates that phosphate buffer addition can substantially increase the solution conductivity and reactor performance. Feng et al. [34] showed that addition of a 50 mM phosphate buffer increased power output by 136% and 200 mM buffer increased power by 158%, while treating brewery wastewater in single chamber air cathode MFC.

The specific maximum power yield with respect to substrate removal was found to be 12.78 W/kg COD_R, 3.69 W/kg COD_R and 1.7 W/kg COD_R in MFC-1, MFC-2 and MFC-3, respectively. This specific power generation in these MFCs were higher than the reported values. Venkat Mohan et al. [35] reported maximum specific power yield of 0.231 W/kg COD_R, while treating composite vegetable waste in an air cathode MFC.

The Coulombic efficiencies of MFC-1 were 21.2%, 18.6% and 14.5% at influent pH of 8.0, 7.0 and 6.0, respectively. MFC-2 had CE of 8.5%, 6.3% and 4.8% at influent pH of 8.0, 7.0 and 6.0, respectively. In MFC-3, the CE increased with lapse of time from 4.1% in the beginning to 5.9% at the end of the experiment after 96 days of operation. The earthen pot MFC demonstrated higher CE throughout the experiment than the MFC employing PEM. Operation of all these MFCs also indicated that the CE decreases with decrease in anodic pH. This may be correlated to related thermodynamics of degradation of complex organic molecules, where more than one species are participating for oxidation of the complex substrate to final end product by electrogenesis in this case.

The maximum short circuit current (SC) of 6.25 mA and open circuit voltage (OCV) of 0.772 V was generated in MFC-1 at feed pH of 8.0. MFC-2 generated maximum SC of 3.86 mA and OCV of 0.670 V at feed pH of 8.0. In MFC-3, the SC and OCV generation increased with time and maximum SC of 2.76 mA and OCV of 0.665 V was obtained when the anolyte pH was 7.6.

The power generated in the earthen pot MFC is still low for practical application in rice mill; however, the MFC demonstrated effective treatment of the rice mill wastewater. MFC demonstrated effective removal of recalcitrant material like lignin, which is not degraded easily during treatment of this wastewater in conventional activated sludge process. MFCs will be able to economically treat the rice mill wastewater simultaneously generating electricity. In a rice mill, several MFCs are required to be installed to treat entire wastewater generated from that industry. These MFCs can be used in a combination of series and parallel connection, which will enhance the net power output for powering certain low power appliances.

3.2.2. Polarization

Polarization studies were carried out for the MFCs by varying the external resistance from 5000 Ω to 10 Ω. During polarization, maximum power densities of 50 mW/m^2 (163 Ω), 40.8 mW/m^2 (181 Ω) and 26 mW/m^2 (250 Ω) were obtained at the influent pH of 8.0, 7.0 and 6.0, respectively in MFC-1 (Fig. 3a). In MFC-2, maximum power densities of 16.3 mW/m^2 (325 Ω), 7.5 mW/m^2 (486 Ω) and 4.2 mW/m^2 (570 Ω) were obtained at the influent pH of 8.0, 7.0 and 6.0, respectively (Fig. 3b). The sustainable power generation increased with time in case of MFC-3. Initially, MFC-3 showed maximum power density of 3.2 mW/m^2 (828 Ω). At the end of the experiment, after about 96 days of operation, MFC-3 had maximum power density of 9.6 mW/m^2 (445 Ω).

Internal resistance of the MFC was determined from the slope of line from the plot of voltage versus current. The internal resistance of MFC-1 was 171 Ω, 195 Ω and 247 Ω and internal resistance of MFC-2 was 310 Ω, 465 Ω and 521 Ω when operated at the influent pH of 8.0, 7.0 and 6.0, respectively. In MFC-3, the internal resistance decreased from 832 Ω to 450 Ω with prolonged operation over a period of 96 days. Internal resistance increased with decrease in influent pH. This might be attributed to the anolyte conductivity at different pH. The anolyte conductivity was 13.96 mS/cm, 11.54 mS/cm and 8.64 mS/cm in MFC-1 and 13.56 mS/cm, 10.65 mS/cm and 7.83 mS/cm in MFC-2 at the influent pH of 8.0, 7.0 and 6.0, respectively. Decrease in anolyte conductivity with decrease in pH might have increased resistance to the flow of ions through the anolyte and thus, increased the ohmic losses. Slightly alkaline anodic pH might have helped in the establishment of electrogenic as well as other essential bacterial biofilm participating in the complete conversion of complex

Table 1
Electricity generation in MFC-1 and MFC-2 under different anodic feed pH with 100 Ω external resistance.

pH	MFC-1 (Earthen pot MFC)				MFC-2 (PEM MFC)			
	Current (mA)	Voltage (V)	Power density (mW/m^2)	Power per unit volume (mW/m^3)	Current (mA)	Voltage (V)	Power density (mW/m^2)	Power per unit volume (mW/m^3)
8	3.04	0.304	48.64	2310.4	1.72	0.172	15.57	528.3
7	2.49	0.249	32.63	1550.0	1.07	0.107	6.03	204.5
6	2.11	0.211	23.43	1113.0	0.74	0.074	2.88	97.8

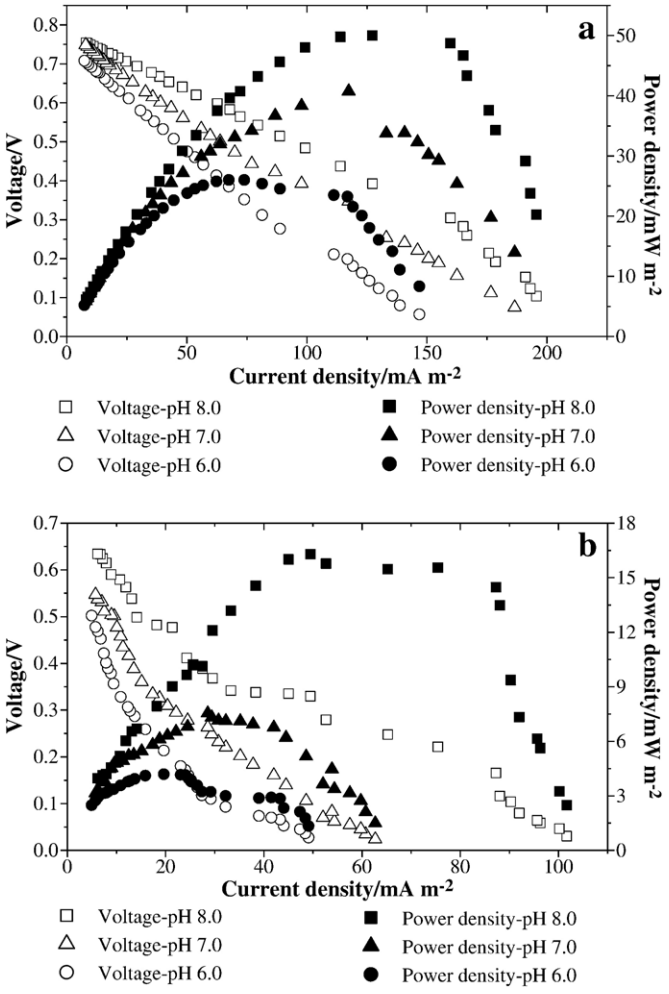

Fig. 3. Polarization curve for MFCs (a) MFC-1 (b) MFC-2.

substrate on the anode, which resulted in low activation losses. Therefore, the MFCs had lower internal resistance at higher operating anodic pH. This is evident from the operation of MFC-3, with same conductivity of the feed medium throughout, where the internal resistance was reduced considerably with increase in the anodic pH over a period of operation. The higher surface area available for proton transfer in MFC-1 helped in increased rate of reduction reaction on the cathode surface, resulting in reduced activation losses. Hence, MFC-1, made up of earthen pot, exhibited lower internal resistance than MFC-2, fabricated with proton exchange membrane due to lesser surface area of the membrane used.

3.2.3. Electrode potential

The anode potentials, versus Ag/AgCl reference electrode (3 M), of MFC-1 were −0.535 V, −0.510 V and −0.474 V and that of MFC-2 the anode potentials were −0.519 V, −0.492 V and −0.455 V when operated with feed pH of 8.0, 7.0 and 6.0, respectively. Lower anode potential in the MFCs at higher feed pH was due to the higher rate of substrate oxidation in the anode chamber at that pH. The maximum cathode potentials, versus Ag/AgCl reference electrode, were 0.237 V, 0.226 V and 0.221 V in MFC-1 and 0.164 V, 0.155 V and 0.147 V in MFC-2 at influent pH of 8.0, 7.0 and 6.0, respectively. Significant variations in cathode potentials were not observed in MFC-1 and MFC-2 with changes in anodic pH. The cathode potential in MFC-1 was always higher than that of MFC-2. In MFC-3, the anode potential decreased with each feed cycle. Initially the minimum anode potential of MFC-3 was −0.434 V (versus Ag/AgCl), when pH of anolyte was 5.3. It decreased to −0.478 V in the last feed cycle, when pH of anolyte was gradually increased to 7.6.

3.2.4. Effect of operating pH

The raw rice mill wastewater is acidic in nature and neutralization of the wastewater is necessary for biological treatment. Higher acidity or alkalinity of wastewater affects both wastewater treatment efficiency and the environment inside the reactor. The pH of wastewater needs to be maintained near neutral to protect micro-organisms to favour biological treatment processes. For acidic or alkaline industrial wastewaters, the pH is corrected to near neutral by suitable alkali or acid addition before biological treatment. The capacity of the anaerobic reactors to handle the loading rates depends on the feed pH and the alkalinity generating capacity of the wastewater to counteract the changes in pH. Therefore, in this study the performance of MFC was evaluated under different anodic pH. The experimental results clearly demonstrated that the MFC performance is dependent on the anodic pH. While treating such complex wastewater the optimum performance of MFCs, in terms of organic matter removal and electricity harvesting, was obtained at influent pH of 8.0. The COD removal and power generation decreased with decrease in feed pH and they were lowest when the feed pH was 6.0. The CE in the MFCs also decreased with decrease in influent pH. This result is in agreement with the result reported by Gil et al. [36] and He et al. [37]. All these studies observed that low pH (pH 5 and 6) resulted in lower electricity generation. The possible reason for higher current generation at pH 8.0 might be attributed to the effective extracellular electron transfer at this pH microenvironment, where electrogenic bacterial growth was favoured [38].

3.2.5. Performance of MFCs with permanganate as catholyte

The cathode potential of these MFCs in the present study using oxygen as cathodic electron acceptor was much lower than the theoretical value indicating the large energy loss occurring at the cathode, which limited the power output. Potassium permanganate was used as cathodic electron acceptor at the end of the study after 96 days of operation to evaluate the maximum power production capacity of these MFCs by overcoming the cathodic limitations. MFC-1 and MFC-2 demonstrated optimum performance in terms of electricity generation and organic matter removal at feed pH of 8.0. Therefore, the feed pH of MFC-1 and MFC-2 was adjusted to 8.0 and 0.2 g/L of potassium permanganate was added as catholyte. After, permanganate addition, the cathode potential in MFC-1 was increased from 237 mV to 500 mV (vs. Ag/AgCl reference electrode). Similarly, the cathode potential in MFC-2 was increased from 164 mV to 410 mV (vs. Ag/AgCl reference electrode). The higher redox potential of permanganate improved the cathode performance and overall power output of the MFCs. The volumetric power densities obtained across 100 Ω external resistance after permanganate addition were 5153 mW/m^3 (4.57 mA, 0.457 V) and 1273 mW/m^3 (2.67 mA, 0.267 V) in MFC-1 and MFC-2, respectively. The volumetric power density increased by 104% in MFC-1 and 141% in MFC-2. The addition of permanganate increased power output by 113% to reach to a value of 585 mW/m^3 in MFC-3.

4. Conclusions

The study demonstrated effective treatment of rice mill wastewater in microbial fuel cell, simultaneously generating bioelectricity. The earthen pot MFC demonstrated very good performance in terms of electricity harvesting and organic matter removal at all the operating feed pH, offering a low cost MFC fabrication option for treatment of industrial wastewaters. The wall material of earthen pot MFC proved to be cost effective alternative to Nafion, facilitating better proton transfer. The internal resistance of the earthen pot MFC was lower than that of MFC employing PEM. Slightly alkaline anodic pH (about

7.5) was observed to be favourable for higher power generation and organic matter removal in the MFCs.

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