Preparation of a fouling-resistant sustainable cathode for a single-chambered microbial fuel cell

Pritha Chatterjee and M. M. Ghangrekar

ABSTRACT

Two different binder materials of varying water affinity, viz. poly vinyl alcohol (PVA) and poly-tetrafluoroethylene (PTFE), and biocide vanillin were tested for cathode fouling in a single chamber air-cathode microbial fuel cell (MFC) constructed with a low-cost baked clayware cylinder and operated under fed-batch mode. PVA and PTFE loadings of 0.5 mg/cm^2 were used for MFC-1 and MFC-2, respectively as a binder; and a 1:1 mixture of PVA + PTFE was used as binder in MFC-3 with same binder loading. Vanillin was mixed with PVA and also applied at a loading of 0.5 mg/cm^2 for MFC-4. Results showed organic matter removal efficiencies around 90% for all MFCs both before and after fouling. Coulombic efficiency was, however, found to decrease 50% after fouling in the MFC-3 coated with both PVA and PTFE. After 5 weeks of operation, due to fouling 56, 40 and 69% reduction in power densities were observed in MFC-1, MFC-2 and MFC-3, respectively. In the MFC-4 having PVA and vanillin, the least fouling was observed. A consistent volumetric power of 233 mW/m^3 was observed for MFC-4, thus potentially offering a suitable solution to alleviate the problem of fouling in the making of single-chamber air-cathode MFCs.

Key words | air-cathode, cathode fouling, microbial fuel cell, power density, wastewater treatment

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INTRODUCTION

Microbial fuel cell (MFC) technology has developed from a double-chambered aqueous cathode MFC to a single-chambered air breathing cathode MFCs (Logan 2008). Large-scale practical applications of MFC are yet to be achieved due to high cost and low energy conversion efficiency (Li *et al*. 2010; Zhang *et al*. 2010). Membrane costs account for around 37% of the total cost of a laboratory-scale MFC (Rozendal *et al*. 2008). Behera *et al*. (2010a, b) used clayware as a separator to reduce production costs of a MFC and obtained a maximum power density of 16.8 W/m^3. This MFC with manufacturing costs less than US$1 showed better performance compared to other MFCs prepared using expensive materials.

Using a graphite felt anode Ajayi & Weigele (2012) prepared a low-cost membrane electrode assembly with electrodes placed on both sides of the membrane by coating a terracota pot with graphite paint, and obtained a maximum power density of 33.13 mW/m^2. Our previous research efforts on sustainable power generation in an earthen pot air-cathode MFC have shown promising results giving higher power density as compared to a similar-volume aqueous cathode MFC (paper submitted). Although a high power density was achieved in air-cathode MFCs, they suffered from cathode fouling after a long run, which eventually reduced the overall performance of the MFCs in terms of power output.

Membrane fouling is a problem in almost all membrane processes, which needs an immediate solution, and though performance of fouled membrane in other membrane processes can be partially restored by appropriate cleaning methods, it will cause operational difficulties in a MFC and also add to the overall operational cost of the system (Ang *et al*. 2006; Creber *et al*. 2010; Kang & Cao 2012). Xu *et al*. (2012) observed a 32.3% decrease in power production due to fouling of the membrane. Therefore solutions are sought to remove fouling. Surface modifications by changing the water affinity of the material surface used for cathode preparation could be an option to reduce fouling in MFCs.

With this view, the present study aimed to evaluate the potential response of different binder materials, based on their water affinity, to cathode fouling. Using hydrophobic and hydrophilic binder materials for preparation of cathodes, the performance of a MFC was evaluated in

doi: 10.2166/wst.2013.760

response to drop in power production due to fouling. In addition, the effect of vanillin, being a biocide, was investigated for inhibition of biofouling in an air-cathode single-chamber MFC prepared using a clayware ceramic separator.

MATERIALS AND METHODS

MFC construction

This study was carried out with four laboratory scale air-cathode MFCs constructed using clayware cylinders of 1,200 ml liquid volume (Figure 1). A stainless steel (SS) mesh having surface area of 500 cm^2 was used as anode, occupying the inner circumference of the cylinder, in all these MFCs. Both the outer surface and the inner surface of the MFCs were coated with Vulcan XC-72R carbon powder at loadings of 0.5 mg/cm^2. To hold this carbon powder on the surface of the separator a binder is required. Polyvinyl alcohol (PVA) and poly-tetrafluoroethylene (PTFE) were used as a binder at loadings of 0.5 mg/cm^2 for MFC-1 and MFC-2, respectively (Table 1). A 1:1 mixture of PVA and PTFE was used as binder in MFC-3, maintaining the same binder loading (Table 1). Vanillin (4-hydroxy-3-methoxybenzaldehyde) was mixed with PVA at a loading of 0.5 mg/cm^2 in the cathode preparation of MFC-4. The inner surface of the separator of MFC-4 was coated with vanillin-free ink. The ink was prepared and applied as described by Duteanu *et al.* (2010). The approximate cathode surface area of the MFCs was 720 cm^2. Four strands of SS wires were used as the cathodic current collector to ensure proper distribution of electrons and to reduce ohmic losses of the cell. Electrodes were connected through concealed copper wires through an external resistance of 100 Ω.

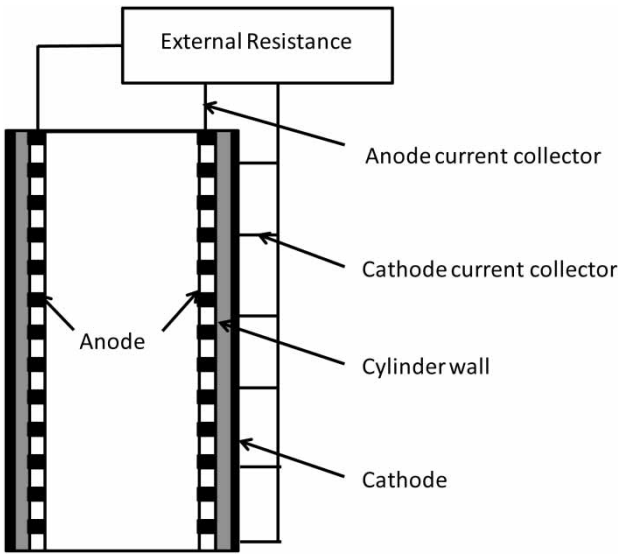

Figure 1 | Schematic of the air-cathode microbial fuel cell used.

Table 1 | Binders and biocides used for cathode preparation

MFC	MFC-1	MFC-2	MFC-3	MFC-4
Binder	PVA	PTFE	PVA + PTFE (1:1)	PVA + vanillin

MFC operation

Each MFC was inoculated with 60 ml of heat-treated anaerobic sludge with a volatile suspended solids (VSS) concentration of 23 and 35 g/L total suspended solids (TSS). A feed solution containing sodium acetate as a source of carbon and a chemical oxygen demand (COD) of 3,000 mg/L was used. The acetate medium also contained (per gram of COD) $NaHCO_3$, 1,500 mg; NH_4Cl, 318 mg; $CaCl_2.2H_2O$, 250 mg; $MgSO_4.7H_2O$, 64 mg; K_2HPO_4, 27 mg; and KH_2PO_4, 9 mg. Trace metals were added as $FeSO_4.6H_2O$, 10.00 mg/L; $MnSO_4$, 0.526 mg/L; $ZnSO_4.7H_2O$, 0.106 mg/L; H_3BO_3, 0.106 mg/L; $CuSO_4.5H_2O$, 4.5 μg/L, $CoCl_2$, 105.2 μg/L, and $(NH_4)_6Mo_7O_{24}.4H_2O$, 105.2 μg/L (Behera *et al.* 2010a). Fresh feed was given to the MFCs every fifth day after withdrawing about half of the anolyte volume.

Analysis and calculations

The potential and current generated by the cells were measured by a digital multimeter with a data acquisition unit (Agilent Technologies, Malaysia). Power was calculated from these data according to the formula $P = IV$, where P is power in mW, I is current in A and V is voltage in mV. The volumetric power density was calculated by normalizing power to working volume of the anode chamber. Polarization studies were carried out by varying the external resistances from 10,000 to 1 Ω. The internal resistance of the MFCs was measured from the slope of the plot of voltage versus current (Behera *et al.* 2010a). The anode and cathode potentials were measured using a Ag/AgCl reference electrode. The coulombic efficiency (CE) evaluated over a period of time t was calculated as given by Logan (2008):

$$CE = M.I.t/(F.b.V.\Delta COD) \quad (1)$$

where M is molecular weight of oxygen (32), I is the produced current, F is Faraday's constant, b is the number of

electrons exchanged per mole of oxygen (4), V is the volume of liquid in the anode compartment, and ΔCOD is the change in COD over time t. Influent and effluent COD, pH, and VSS and TSS in the inoculum sludge were monitored according to *Standard Methods* (APHA 1998). A little portion of the cathode coating was scraped off, crushed and dried and the elemental composition of the cathode material was determined by energy dispersive X-ray analysis (EDX) in a scanning electron microscope with an Oxford EDX detector (JSM-5800, JEOL, Japan).

RESULTS AND DISCUSSION

Electricity generation

Operating voltage of all the MFCs, over an external load of 100 Ω, increased from around 20–40 mV to around 200 mV after the first week of operation. The maximum volumetric power obtained during polarization after 2 weeks of operation ranged between 250 and 275 mW/m^3 for the four MFCs. This suggests that hydrophilicity or hydrophobicity of the separator surface does not have any effect on the power generated for the initial few weeks.

Within 5 to 6 weeks of operation a reduction in power production and operating voltage was noted with maximum reduction in operating voltage (250 to 90 mV) and power (270 to 49 mW/m^3) for MFC-3, and almost insignificant decrease of the same occurred for MFC-4. Figure 2 shows the variation of operating voltage and open circuit potential for 50 days of operation. Power produced from the MFCs reduced to 117, 175, 49 and 233 mW/m^3, respectively, for the MFCs using PVA, PTFE, PVA + PTFE and PVA + vanillin as binder (Figure 3). This reduction in power and operating voltage may be the response to reduction in active cathode surface area, reduced oxygen diffusion, increased cell resistance (Vermaas *et al.* 2013), or decreased cation transfer (Rikame *et al.* 2012). As expected the power drop in MFC-2 using PTFE was less than that in MFC-1 using PVA, indicating that the level of fouling was less in the case of the hydrophobic binder (MFC-2) than the hydrophilic binder (MFC-1). The drop in voltage and power was almost negligible for MFC-4 using PVA + vanillin because of negligible fouling on the cathode, even after 49 days of operation.

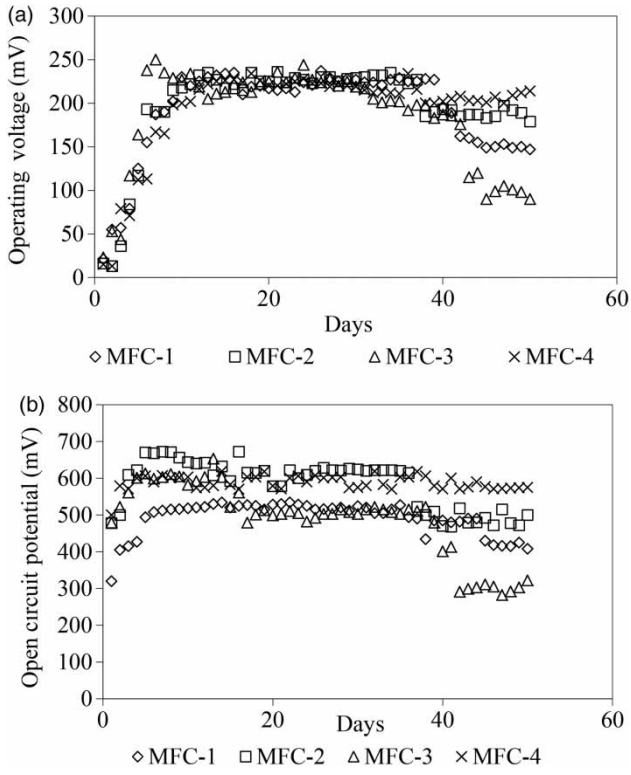

Figure 2 | Variation of (a) operating voltage and (b) open circuit voltage of the MFCs with time.

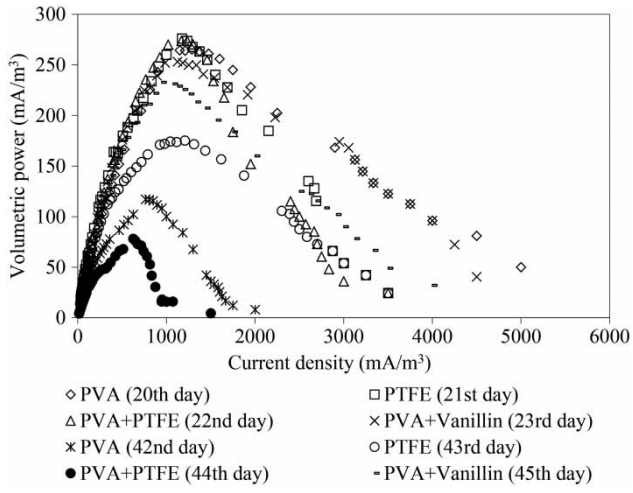

Figure 3 | Variation of power density of the MFCs before and after fouling.

Polarization analysis of electrode reactions

Variation of electrode potentials with current density obtained during polarization is presented in Figure 4. Up to the third week of operation, that is before fouling started to set in, electrode current densities in all the MFCs were stable. Anodic performance remained almost similar for the MFCs even after fouling started to set in. However, cathodic performance started to decline. The most stable performance was obtained for the MFC in which vanillin

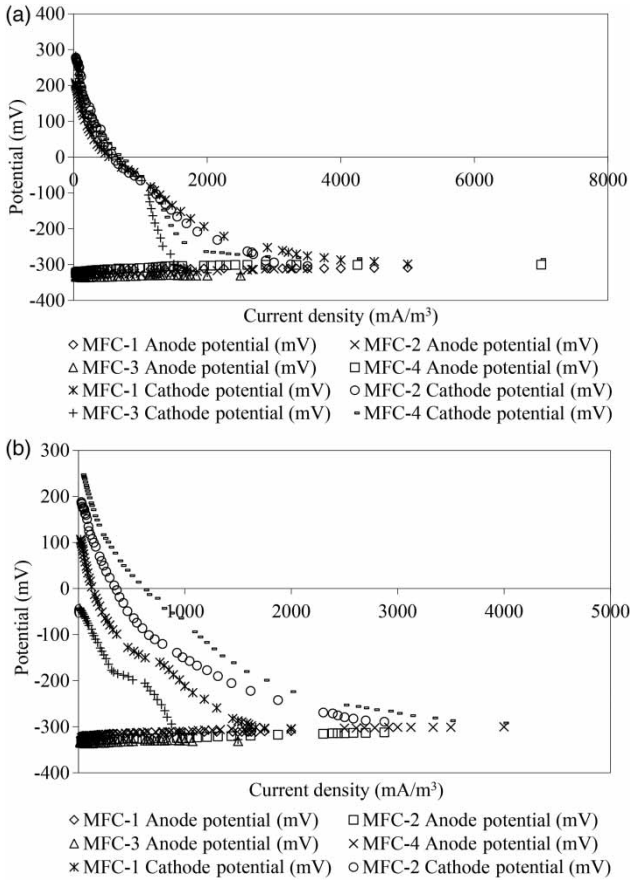

Figure 4 | Variation of electrode potentials with current density during polarization (a) before fouling and (b) after fouling.

was mixed with PVA. It did not allow any biological growth to form on the hydrophilic surface and the hydrophilicity of the surface did not allow any inorganic deposition to occur (Kwon *et al.* 2005). So, least fouling was observed in this MFC, which is reflected as better cathode performance. These results conform to that reported by Ponnusamy *et al.* (2010) who mentioned that vanillin, a well-known food flavoring agent, when used on a polystyrene reverse osmosis membrane, inhibited, biofilm formation by 46.3%.

Performance of the MFC using PTFE alone as a binder was also fairly good and its performance was better as a fouling-resistant material than PVA alone. This differs from the observations reported earlier by Rana & Matsuura (2010), Kang & Cao (2012), Liu *et al.* (2013), and Vermaas *et al.* (2013), stating that the hydrophilic membranes containing hydroxyl, carboxyl or ethylene oxide groups are more fouling resistant. PTFE, being hydrophobic, did not allow much biofilm formation on its surface as such, and only inorganic deposition was formed on this cathode surface. The MFC using PVA as binder showed remarkable reduction in cathode potential with time due to biofilm formation on its surface. Some researchers have reported that microbial biofilm formation on cathodes helps to produce a better cathodic reaction by improving the oxygen reduction reaction on the surface (Christiani *et al.* 2013); however, it is true only for electrochemically active bacterial growth and not for heterotrophic biomass growth and fungus growth as found on these cathodes.

Although the power generated from the MFCs before fouling was in a similar range, the maximum current densities supported by the MFCs varied considerably, indicating differences in performance. The cathodes coated with PVA and PVA + vanillin could support maximum current density up to 5,000 and 7,000 mA/m^3, respectively, followed by the cathodes coated with PTFE (3,500 mA/m^3) and PVA + PTFE (2,500 mA/m^3). The cathode potential was positive for lower current densities. However, as fouling started to appear on the cathode surface the maximum current density and also the range of current density supporting positive cathode potentials lowered to 2,000, 2,800, 1,500 and 4,000 mA/m^3, respectively for the four cathodes coated with PVA, PTFE, PVA + PTFE, PVA + vanillin. This observation indicates that, although initial performance of the MFCs is better using a hydrophilic binder (Rana & Matsuura 2010), to attain long-term stability either a hydrophobic binder is required or a biocide like vanillin should be used. Moreover, vanillin will not work on hydrophobic surfaces, because its action is antibiological (Ponnusamy *et al.* 2010) and biofouling is much less on hydrophobic surfaces.

Cathode fouling

Visual inspection of the cathodes showed appearance of random white patches on the surface after 3 to 4 weeks of operation. Maximum fouling was observed on the

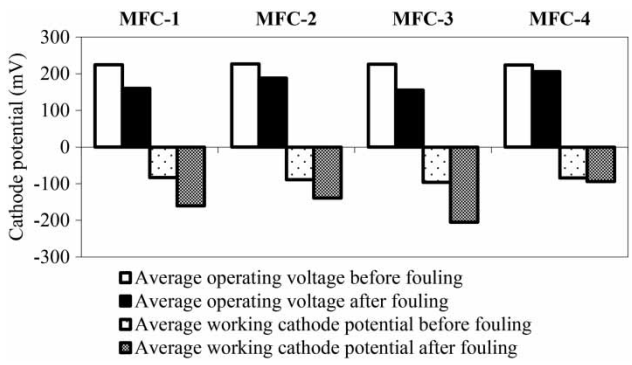

Figure 5 | Variation of operating cell potential and cathode potential with fouling.

Table 2 | Elemental composition of cathode material of the MFCs before and after 7 weeks of operation

	MFC-1		MFC-2		MFC-3		MFC-4	
Elements	**Before fouling**	**After fouling**	**Before fouling**	**After fouling**	**Before fouling**	**After fouling**	**Before fouling**	**After 7 weeks**
Carbon	35.26	45.35	29.84	21.77	37.99	14.29	35.99	36.91
Oxygen	64.54	50.22	69.72	58.81	61.64	56.93	63.64	62.36
Sodium	0.2	4.43	0.44	19.42	0.37	28.78	0.37	0.73

cathode that used a mixture of PVA and PTFE. Apart from the MFC using vanillin, least fouling was observed with the one that had only PTFE, with about 40% reduction in power density; while a 69% reduction in power was observed for the MFC-3 having both PVA and PTFE. Figure 5 shows the variation of operating cell potentials and operating cathode potentials before and after fouling for these four MFCs. During the initial days of operation the working potentials of the cathode ranged from −80 to −100 mV regardless of the cathode binder. Noticeable differences in cathode performance could only be observed after fouling started.

PVA, being of hydrophilic character, helps the formation of a water layer on the surface of the cathode. This attracts hydrophilic foulants, increasing fouling further (Kwon *et al*. 2005). Biological growth due to the hydrophilic surface also secretes extracellular polymeric substances which in turn deposits on the hydrophobic surface. Hence, instead of having an inhibitory effect on both hydrophilic and hydrophobic foulants, the combination of PTFE and PVA enhanced fouling by attracting both type of foulants. Vanillin acted as a biocide and even after few weeks of operation there was no fouling on the cathode coated with vanillin and PVA, resulting in reduction of power by only 8%.

Table 2 shows the elemental composition of the cathode material before and after fouling. Carbon content of MFC-1 (PVA) increased while it decreased for all the other MFCs, indicating biological or organic growth on the cathode surface in MFC-1. Initially, before fouling, sodium content was much less, ranging from 0.2 to 0.5%, which increased after fouling and a maximum increment was observed in MFC-3 (PVA + PTFE) followed by MFC-2 (PTFE), indicating the predominance of inorganic fouling in these two MFCs. Very negligible change in elemental composition of the cathode material occurred with time for MFC-4, which had vanillin mixed with PVA. This shows there were no foreign particles on the surface, thereby indicating no fouling and hence fouling was not observed.

Wastewater purification and CE

All the four MFCs, regardless of the binder used in the cathode, gave significant performance with respect to wastewater treatment, demonstrating COD removal efficiencies above 90% (Figure 6(b)); that is more than 0.5 kg COD/(m^3.day), which is comparable to the conventional activated sludge process (Logan 2008). As evident from Figure 6, the ability of the MFC to treat wastewater did not reduce even after fouling in the last few cycles. Coulombic efficiencies of the MFCs were around 4% for the initial few weeks. Afterwards, as fouling started, the CE decreased to a minimum of 1.88% for the MFC using both PVA and PTFE. However, as expected the MFC coated with vanillin (no fouling) had a

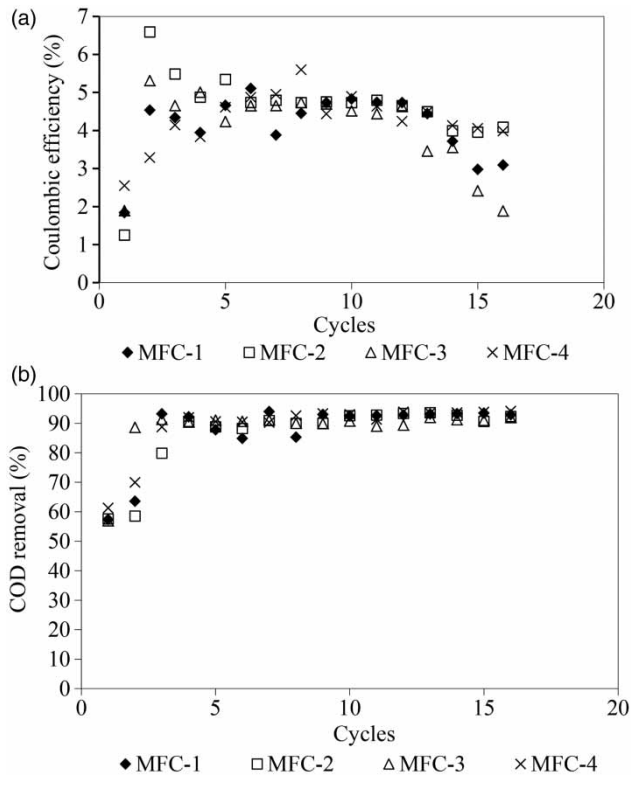

Figure 6 | Variation of (a) CE and (b) COD removal of the MFCs in different cycles of feeding.

consistent CE and the MFC using PTFE also showed very little decrease in CE. Although the COD removal efficiency was quite high, low values of CE indicate the presence of methanogenic bacteria and other non-electrogenic bacteria in the anode chamber, most likely because of anaerobic mixed sludge being used as inoculum (Behera *et al*. 2010b).

CONCLUSIONS

Presence of hydrophilic PVA on the cathode surface allows fouling because it provides favorable conditions for biological growth. Hydrophobicity of PTFE reduced fouling to some extent mainly by reducing water loss and inhibiting bacterial growth on the dry surface of the cathode; however, enough resistance to fouling was not observed and power produced by the MFC reduced with time of operation. A mixture of PVA and PTFE, though thought to perform better, actually enhanced fouling, because it attracted both hydrophilic and hydrophobic foulants and maximum fouling was observed in this MFC. Fouling in the MFC with PVA binder could be almost eliminated by use of the biocide vanillin, and a mixture of PVA and vanillin as cathode binder showed negligible fouling. Hence, vanillin can be successfully used as an antifouling agent in air cathodes without any compromise in their performance.

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First received 28 July 2013; accepted in revised form 11 November 2013. Available online 25 November 2013