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Terracotta Separator based Plant Microbial Fuel Cell for Bioelectricity and Catholyte Production

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Abstract

In this study two plant microbial fuel cells sharing common anodic chamber were evaluated in terms of power generation, biomass production and catholyte recovery. Dual chambered Plant Microbial Fuel Cell (DcPMFC) setup with internal cathode chamber and external terracotta separator- air cathode electrode assembly was constructed. Household terracotta pots were used as reactors and were coated outside with ink prepared from Vulcan (XC-72R) carbon base mixed with low-cost activated carbon catalyst at 1:1 ratio on which cathodic reduction takes place. Internal cathode chamber was constructed by placing finely fired terracotta tubes inside the terracotta pot. Graphite felt reinforced with a mesh of 316L stainless steel and activated carbon catalyst ink was used as electrodes in this experiment. Paddy (*Oryza sativa*) was used as model plant. Maximum voltage of 550 and 580 mV across 1000 Ω were observed in PMFC with terracotta separator-electrode assembly and internal tubular PMFC. The maximum volume of 259 ml per week of catholyte was recovered from the cathode chamber of PMFC. Catholyte collected was in basic pH with ammonium and potassium cations in higher concentrations. This can be attributed to the power production which drives the excess nutrients from the plant growing anode matrix to the cathode chamber through the ceramic membrane. Catholyte produced can be seen as the better water management strategy and recovery of excess applied fertiliser.

Keywords: Microbial Fuel Cell, Paddy, Terracotta Pot, Activated Charcoal, Catholyte.

INTRODUCTION

Plant microbial fuel cell (PMFC) is an engineered bioelectrochemical system where biomass production occurs along with simultaneous generation of green energy as co-product. In PMFC, light energy is converted into electrical energy mediated by photosynthesis of the plants and metabolism of exo-electrogenic bacteria. Plants synthesise chemical energy from light energy by photosynthesis and part of chemical energy synthesized by plants is released into the rhizosphere by its roots. This chemical energy released into root rhizosphere in the form of root exudates acts as the fuel in PMFC. Exoelectrogens inhabiting in rhizosphere utilise this chemical energy for their metabolism and simultaneously release electrons to outside of their cell which is captured by the anode of the electrical component of PMFC placed at rhizosphere followed by flow of electrons through the circuit, generates the current [1]. This integrated technology has many advantages like easy and anywhere installation and has the potential to address the long-lasting food and sustainable energy crisis of mankind without competing with the staple crop cultivation for land.

Although researchers are working on the optimisation of PMFC, till date scale-up of PMFC for practical application has not been achieved. This is due to the lack of optimised design, cost of electrode material [2] and lower rate of energy conversion [3]. Different designs and configurations of PMFCs were tested which includes single chambered air cathode PMFC [4], tubular PMFC [1] and flat-plate PMFC [5]. Among all configurations, flat-plate PMFC showed better performance with lower internal resistance [6]. Low-cost configuration is crucial to bring technology to pragmatic use. In this context, clay and earthenware based materials and ceramics are the better options to reduce the economics of reactor construction [2]. Conventionally, terracotta pots have been used as containers to grow household plants. Incorporating the PMFCs into household pot can provide a win-win situation where low-cost configuration along with concurrent biomass and electricity production can be achieved.

Search for low-cost electrode material is inevitable for upscaling the PMFC technology. Conventional electrode materials like carbon cloth, carbon felt and cathode catalyst like platinum are very expensive. Materials like activated charcoal [7] and carbon fibre [8] were used as anodes to reduce the cost and there is an urgent need for cost effective, biocompatible and optimal performing electrode materials. Water saturated environments are ideal for PMFC installation [9] and plant selection should be done on basis of tolerance of plant towards salinity, waterlogged condition, well developed rhizosphere and photosynthetic pathway [6]. In this study a novel design of dual chambered PMFC setup was constructed in which anode chamber is equipped with outer terracotta separator-air cathode electrode assembly, and inner cathode chamber.

The objectives of this study are (1) Developing the cost effective design for terracotta separator based PMFC and evaluate the performance of the design. (2) Study the feasibility of incorporating terracotta separator- air cathode electrode assembly in PMFC. (3) Recovery of catholyte from PMFC by incorporating internal cathode chamber.

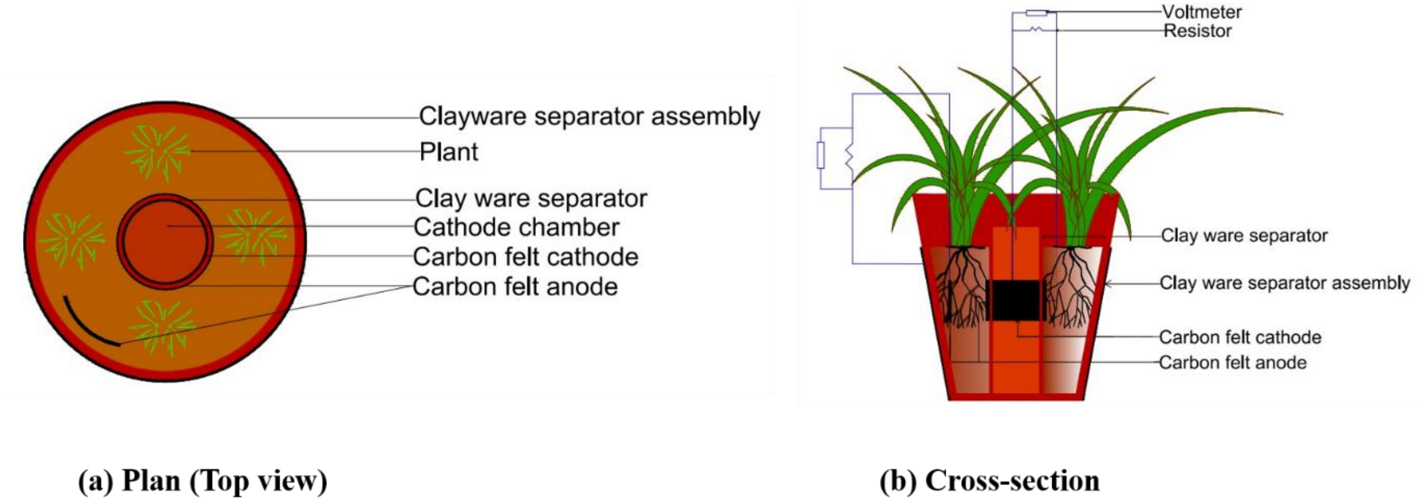

Figure 1. Graphical illustration of plan and cross-section of experimental set up of DcPMFC.

MATERIALS AND METHODS:

Construction of terracotta separator based PMFC

This research was carried out with two different setups, namely single chambered and dual chambered PMFC with terracotta separator-electrode assembly under ambient condition. Single chambered PMFCs (ScPMFC) were built by frustum shaped terracotta pots which are commonly used in India for the household plant growth. ScPMFC consists of air cathode separator-electrode assembly and anode chamber with anode and plant root zone. Dual chambered PMFCs (DcPMFC) were constructed by placing the terracotta cylinders in the household terracotta pots as shown in the figure.1b. The plan and cross section of DcPMFC is illustrated in figure.1 and it is equipped with an outer air cathode electrode-separator assembly, anode chamber with two anodes, plant root zone and an inner cathodic chamber with air cathode for the recovery of catholyte and nutrients.

Design of separator electrode assembly

Terracotta pots were coated with ink which was prepared by mixing Vulcan (XC-72R) carbon, commercial Activated charcoal, 60% PTFE, isopropyl alcohol and acetone. The loading rate of activated carbon, PTFE and carbon black, are 0.25, 0.5 and 0.25 mg Cm^{-2}. Catalyst ink was prepared and applied as explained by Duteanu et al. Sock net of 316L stainless steel (SS) was used as a current collector as described by P. Chatterjee et al., 2014.

Table. 1 gives the details of the electrode configuration. Graphite felt reinforced with 40 mesh 316L SS with dimensions 10 * 2 cm of L * B was used as the anode. Anodes were placed approximately 5 cm below the surface of the soil in both types of PMFC. Approximate cathodic surface area of the separator-electrode assembly of all PMFCs was 350 cm^2. Unmodified graphite felt with a projected surface area of 36 cm^2 was used as air cathode in the inner cathodic chamber of DcPMFC. Anode and cathode were wrapped around both sides of the inner terracotta cylinder of DcPMFC with copper wires which act as the current collectors and were connected through concealed copper wires and the circuit was completed with an external resistance of 1000 Ω.

Table 1. Electrode configuration of PMFC

	Outer PMFC with terracotta Separator-Electrode Assembly	Inner tubular PMFC
Anode	Graphite Felt reinforced with SS Mesh	Graphite Felt reinforced with SS Mesh
Cathode	Activated Charcoal + Carbon Black	Graphite Felt
Anode surface area	36 cm^2	36 cm^2
Cathode surface area	350 cm^2	36 cm^2

Experimental setup

Experimental setup consists of eight terracotta pots (Figure. 2.). Pot 1 and 2 represents ScPMFC with terracotta separator-electrode assembly. Pot 3, 4, 5, 6 and 8 represents DcPMFC. Pot 7 represents the dual chambered sediment MFC (SMFC) without plants to compare the electricity generation in presence and absence of plants and pot 8 was installed same as 4 but the circuit was left open to measure open circuit voltage (OCV). A number of control plants were cultivated without any electrodes to evaluate the influence of MFC on the growth behaviour of plants. After the initial start-up reactor number 3 was discontinued due to operational errors.

Figure 2. Experimental setup of terracotta separator based PMFC

The soil used in this experiment was collected from the Pondicherry University premises and classified as sandy loam soil. Table. 2 provides the basic soil properties. Rice plants used in this experiment were the variety of ADT 43. Paddy seedlings were transplanted into the pots on the 2nd day after germination and followed the traditional pot cultivation method. Nutrient management was done by applying commercial NPK fertilizer (40 kg/ha) at three different growth stages of paddy.

Table 2. Basic Characteristics of Soil

Parameter	Quantity
pH	6.3
Total Nitrogen	0.16 %
Total Carbon	0.18 %

Data collection and analytical techniques:

Open and closed circuit voltages were monitored manually during the entire experimental period by a digital multimeter (Sanwa CD772) at 12 PM daily. Ohm's law was used for converting voltage into current and power. Polarisation study was performed by using resistance box, by varying resistances (10000 Ω to 10 Ω for outer PMFC and 5000 Ω to 10Ω for inner PMFC) with a ten minutes time interval for each resistance. Power densities were normalised to the projected surface area of the anode. Power density curves and internal resistance were obtained as explained by Logan and Regan, 2006. Surface morphology of activated charcoal, microstructure analysis of terracotta pot and the ceramic tube was analysed by scanning electron microscopy (SEM) (Hitachi S-3400N). Soil characteristics were tested by standard methods. Throughout the experimental period, the catholyte was collected daily at 6 PM. The collected catholyte was analysed for pH, conductivity, and cations (ion chromatography). Paddy growth was monitored throughout the experiment with the help of a digital camera.

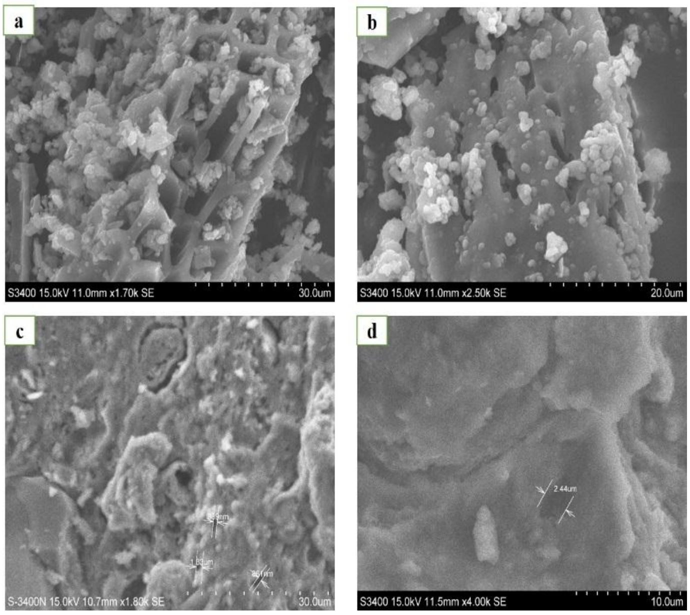

Figure 3. SEM image of Activated charcoal (a & b) Terracotta pot(c) and Ceramic Tube(d).

RESULTS AND DISCUSSION

Voltage output

Maximum open circuit voltage (OCV) of 716 mV and 801mV were recorded in outer and inner PMFC of reactor number 8. ScPMFC and outer PMFC of DcPMFC does not show any significance difference in terms of voltage output hence voltage obtained by ScPMFC was excluded. As pot 4, 5, and 6 were installed with the same configuration and all the reactors showed similar results. Hence only results obtained with reactor 4 is reported. Fig. 4 and Fig. 5 shows the voltage generated at 12 PM during the entire experimental period across 1000 Ω resistance in outer and inner PMFCs and SMFCs. The maximum working voltage generated in outer PMFC with separator-air cathode electrode assembly was 550 mV, and in inner PMFC associated with graphite felt was 580 mV across the resistance.

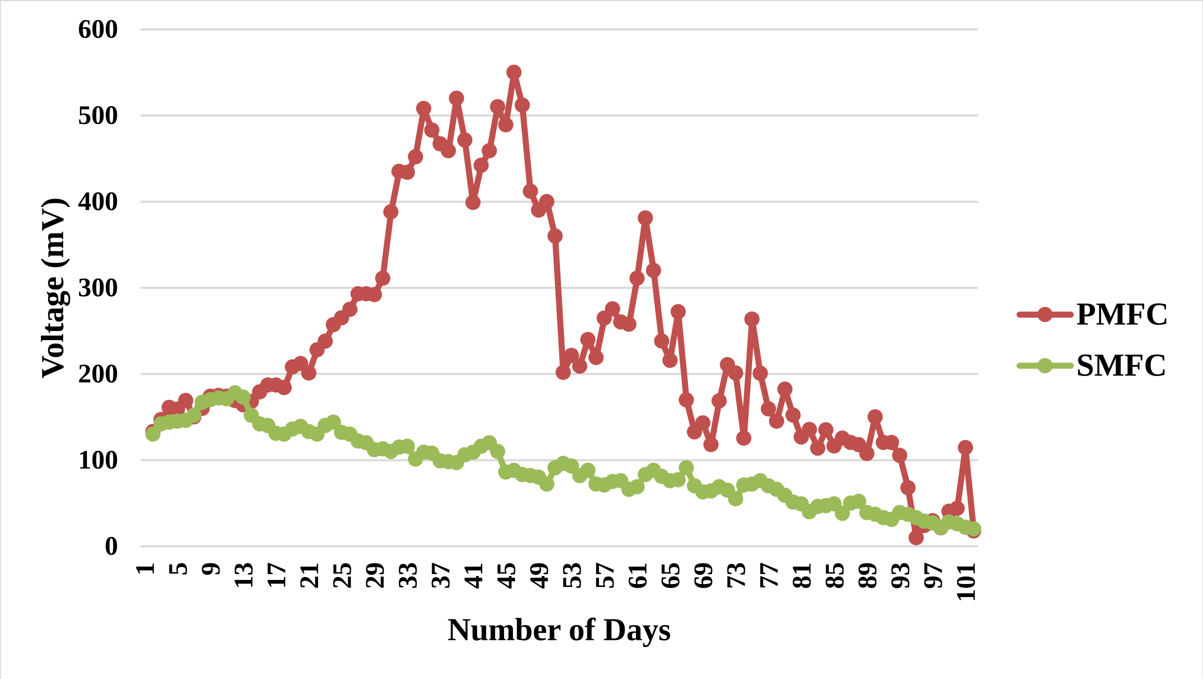

Figure 4. Voltage output from outer PMFC of DcPMFC and SMFC with separator-air cathode electrode assembly

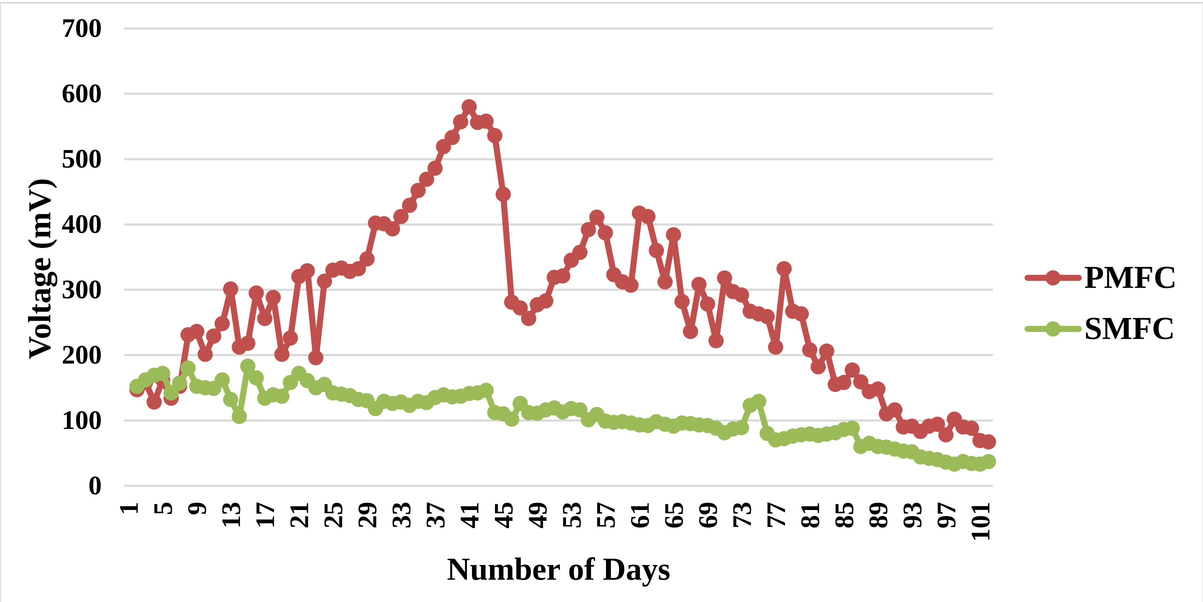

Figure .5. Voltage output from inner PMFC of DcPMFC and SMFC with graphite felt cathode

Since both PMFCs share a common anode chamber with paddy root matrix, both the PMFCs showed similar trends in voltage output. Voltage output gradually increased upto the fifth week of operation, reached a maximum and started to decrease in both PMFC. A similar trend in voltage output was previously reported by Moqsud et al., 2015 and Regmi and Nitisoravut, 2017. The reactor with out plants did not show this similarity in voltage output where both SMFCs initially showed some voltage and decresed gradually. Voltage output in paddy type PMFC is related to the growth stages of the paddy plant where different growth stages relese different amount of root exudates (Aulakh et al., 2001 , Regmi and Nitisoravut, 2017).

Polarisation study

Polarisation data was obtained at the end of the third and tenth week to evaluate the fuel cell behaviour of PMFCs and power densities were normalised to anode surface area. Fig. 6 and Fig. 7 represents the polarisation behaviour of both PMFCs sharing common anode chamber. Outer PMFC with separator-air cathode electrode assembly exhibited a power density of 42.9 mW/m^2 and 35.6 mW/m^2 in 3rd and 10th week respectively. Inner PMFC with graphite felt cathode showed a power density of 42.5 mW/m^2 and 32.3 mW/m^2 in 3rd and 10th week. Power densities obtained in this study are higher when compared to the power densities observed by De Schamphelaire et al., 2008. (26 mW/m^2) and TAKANEZAWA et al., 2010. (14.4 mW/m^2) with SMFC configuration and can be compared to the power density observed by Regmi and Nitisoravut, 2017. (60 mW/m2) with double chamber PMFC, terracotta separator and water cathode.

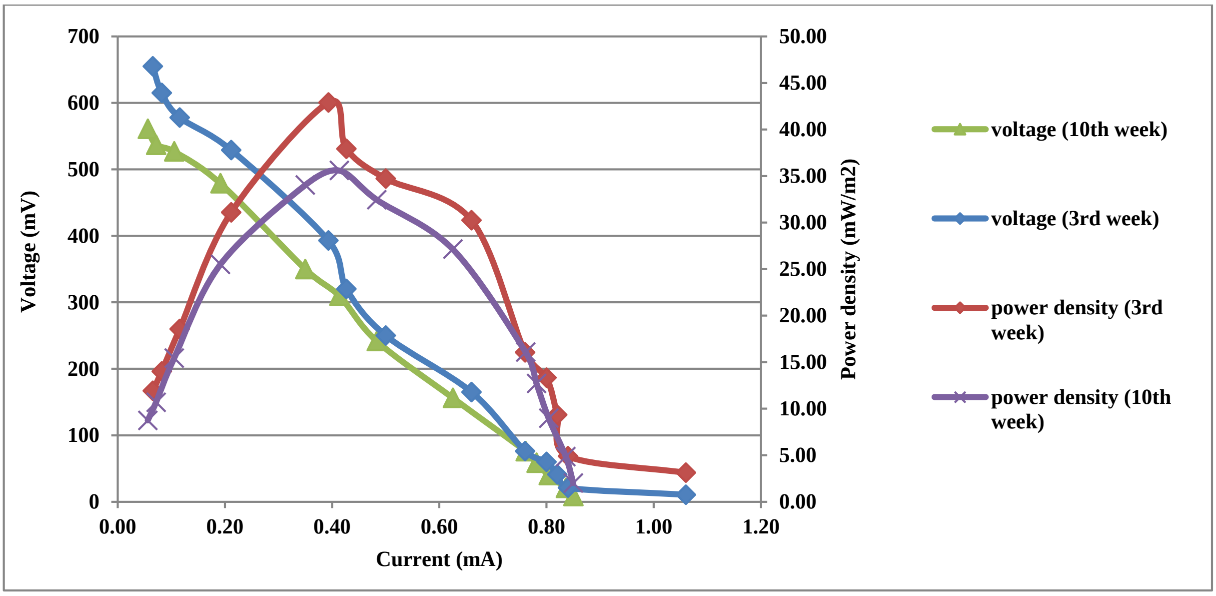

Figure 6. Polarisation curves of outer PMFC of DcPMFC reactor

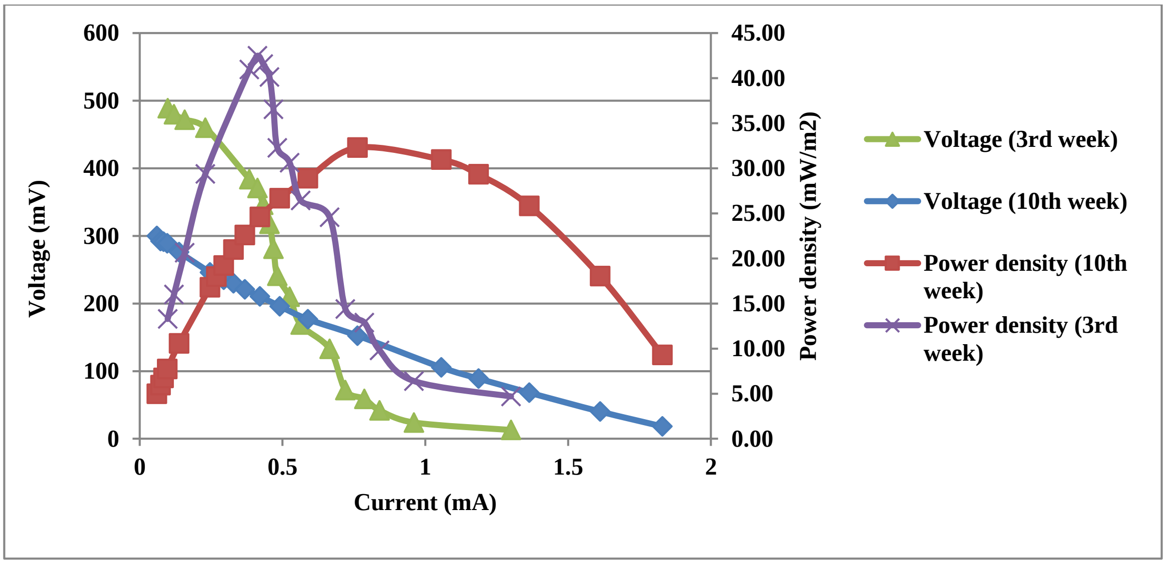

Figure 7. Polarisation curves of inner PMFC of DcPMFC reactor

The slope of voltage vs current curve represents the internal resistance of the system in PMFC studies. Table. 3 gives the details of power density and internal resistance obtained from both PMFCs. An internal resistance of 725 Ω and 692 Ω was observed by outer PMFC in 3rd and 10th week. Inner PMFC associated with cathode chamber showed the internal resistance of 513 Ω and 161 Ω in the third and tenth week. When the internal resistances obtained in the third and tenth week are compared it was observed that the internal resistance decreased during the time period in both the PMFCs and the decrese was prominent in inner PMFC with graphite felt cathode. Decrease in the internal resistance with the continuous operation of PMFC was previously reported by Kaku et al., 2008 and is associated with the enhanced activity of electroactive bacteria and stabilisation of the PMFC.

Table 3. Power densities and internal resistance obtained in polarisation study

PMFC type	Maximum Power density (mW^{-2})	Internal Resistance (Ω)
Outer PMFC with Separator-air cathode electrode assembly	42.9 (End of 3rd week) 35.6 (End of 10th week)	725 (End of 3rd week) 692 (End of 10th week)
Inner Ceramic tubular PMFC with the internal cathode	42.5 (End of 3rd week) 32.3 (End of 10th week)	513 (End of 3rd week) 161 (End of 10th week)

Catholyte recovery and analysis

Catholyte recovery from the microbial fuel cells treating wastewater gained importance in recent times but in plant microbial fuel cells is not yet reported. For the first time in PMFC research, this study reports the catholyte accumulation in addition to green electricity production. A total of 1456 mL and 2128 mL of catholyte was accumulated over 10 weeks' time period with a weekly maximum of 175 mL and 259 mL in the PMFC with the open and closed circuit condition. Operating PMFC produced 46.1 % more catholyte than the PMFC with OCV condition. This extra amount of catholyte produced (679 mL) with the closed circuit can be accounted for the PMFC performance. In open circuit condition, accumulation of catholyte is a function of osmotic pressure whereas in operating voltage condition accumulation is a function of electro-osmotic drag along with natural osmotic pressure [15]. Amount of catholyte recovery in the PMFC can be related to the growth stages of the plant and this requires further study.

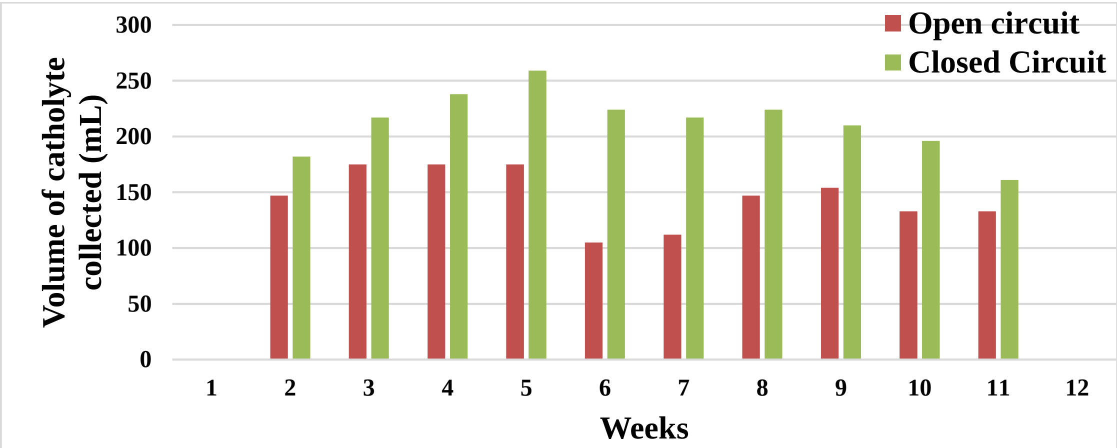

Figure 8. Amount of catholyte recovered from the open circuit and closed circuit PMFC.

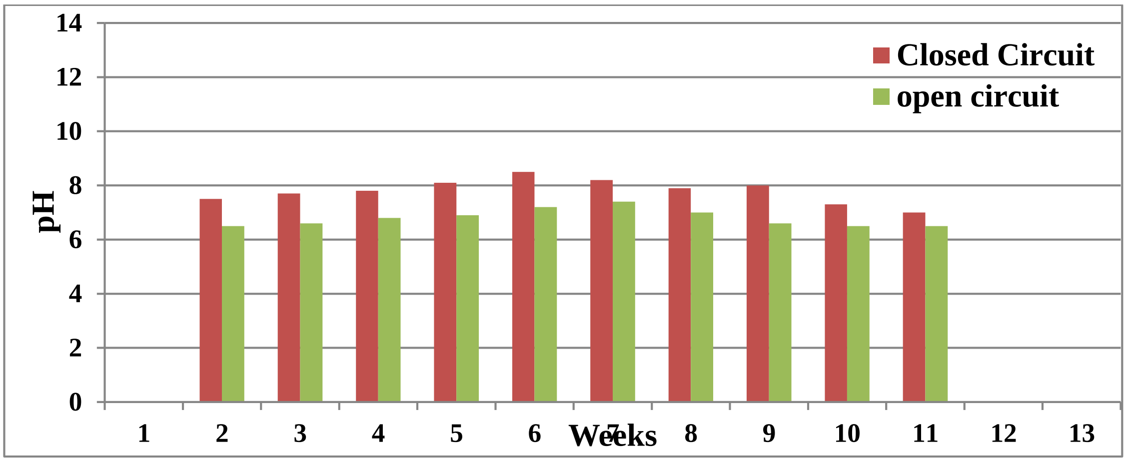

Figure 9. Variation in the pH of catholyte at open and closed circuit condition.

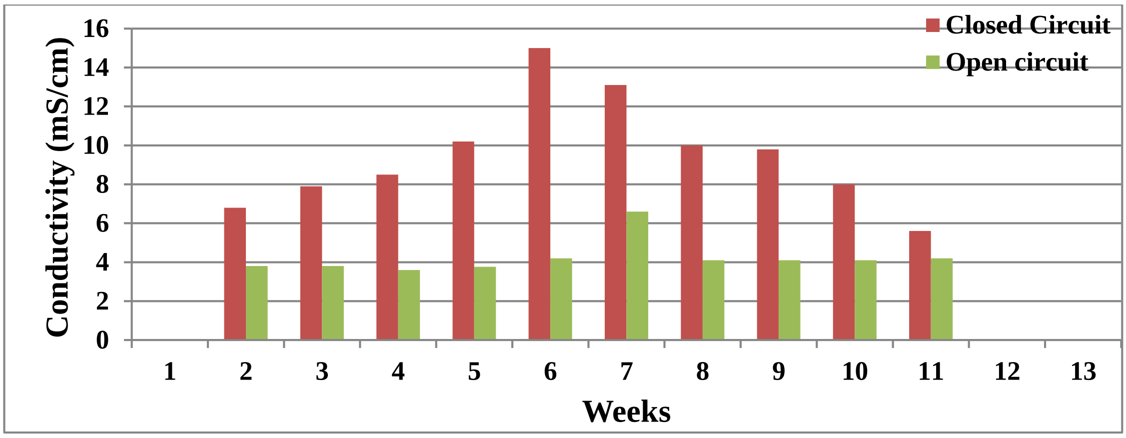

Figure 10. Conductivity of catholyte produced at open and closed circuit condition.

Fig.9 and Fig.10 give the details of variation in pH and conductivity of the catholyte accumulated over the experimental period. Catholyte produced at OCV showed acidic pH and low conductivity whereas catholyte produced under closed circuit showed basic pH with higher conductivity values. Caustic catholyte production was reported earlier [16] with MFC treating wastewater. The pH and conductivity of catholyte is a function of the presence or absence of the external load [17]. and better performance of the MFC resulted in more caustic catholyte accumulation [18]. Catholyte was further analysed for cations with ion chromatography and results showed the presence of Na, K, Mg, Ca and NH_3 cations with ammonium and potassium cations in higher concentrations (Fig. 11 and Table.4.).

Table 4. Details of concentration of cations obtained from ion chromatography analysis

No.	Retention time	Peak Name	Height	Area	Relative area	Concentration
	(min)		µS	µS*min	%	(ppm)
1	5.27	Na	2.026	0.457	6.91	53.026
2	6.10	NH4	11.995	3.879	58.64	903.030
3	7.90	K	5.998	1.830	27.66	348.712
4	14.25	Mg	0.115	0.073	1.11	4.759
5	18.48	Ca	0.441	0.376	5.68	37.585
Total:			20.574	6.616	100.00	1347.112

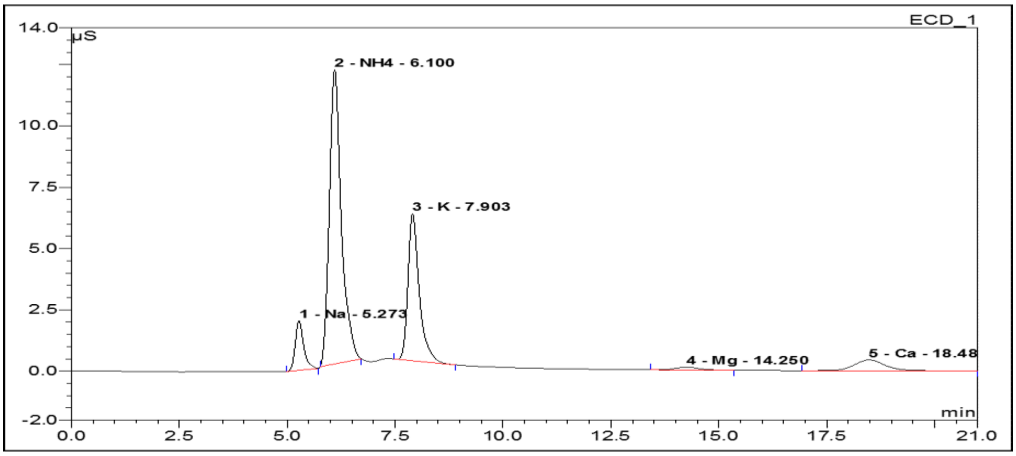

Figure 11. Cation analysis of catholyte of working PMFC by ion chromatography

CONCLUSION

This study provides the simple and cost effective design for household terracotta separator based PMFC. PMFC with separator-electrode assembly and PMFC with internal cathode chamber was first time evaluated. Integration of PMFC with external separator-air cathode electrode assembly and PMFC having internal cathode chamber by a common anodic chamber can solve the problem of the cost of electrode material and give additional benefit of water recovery and recycling. Approaches followed in this research can lead towards the sustainable biomass and bioelectricity production in the household terracotta pot based PMFC by balancing water-energy-food nexus. Further research should be focused on the nutrient recovery from the inner cathode chamber and the scale up.

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