Electrochemistry Communications xxx (2008) xxx–xxx

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Effect of anodic pH microenvironment on microbial fuel cell (MFC) performance in concurrence with aerated and ferricyanide catholytes

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ARTICLE INFO

Article history:
Received 24 October 2008
Received in revised form 19 November 2008
Accepted 19 November 2008
Available online xxxx

Keywords:
Bioelectricity
Mixed consortia
Chemical wastewater treatment
Cell potentials

ABSTRACT

The performance of dual chambered microbial fuel cell (MFC, Nafion 117, non-catalyzed graphite electrodes) in concurrence with anodic pH microenvironment was evaluated based on bioelectricity generation and wastewater treatment efficiency. Experiments were carried out at different anodic pH microenvironments (acidophilic (6), neutral (7) and alkaline (8)) using both aerated and ferricyanide catholytes with mixed consortia as anodic biocatalyst employing chemical wastewater. Acidophilic pH in anodic chamber showed effective performance with respect to power output compared to the corresponding neutral and alkaline operations. However, substrate degradation was observed to be higher at neutral condition followed by alkaline and acidophilic operations. Ferricyanide as catholyte showed positive influence on the power output parameters compared to aerated catholyte. Nature of the catholyte did not show any visible influence on the wastewater treatment efficiency.

1. Introduction

Microbial fuel cell (MFC) is being viewed as a potential bio-electrochemical device capable of producing energy in the form bioelectricity apart from wastewater treatment [1–12]. MFC generates electrical energy through the oxidation of organic matter in the presence of fermentative bacteria under mild operating conditions. The potential (biologically mediated) developed between the bacterial metabolic activity (series of oxidation-reduction reactions generating electrons (e^-) and protons (H^+)) and electron acceptor conditions generate potential to make bioelectricity. Microorganisms extract energy required to build biomass (anabolic process) from redox reactions (catabolism) through electron donor/acceptor conditions. Anodic operating conditions play a significant role on the overall performance of MFC. Anodic pH microenvironment is one of the important factor influences substrate metabolic activity and inturn influence the e^- and H^+ generation mechanism. Generally, bacteria respond to changes in internal and external pH by adjusting their activity associated with many different processes, including proton translocation, amino acid degradation, adaptation to acidic or basic conditions and virulence [13]. Depending on the organism and growth conditions, changes in the external pH can bring about alterations in several primary physiological parameters, including internal pH, concentration of ions, membrane potential and proton-motive force [14,15]. We therefore focused our study to investigate the influence of anodic pH microenvironment on the performance of MFC employing mixed consortia as anodic biocatalyst during chemical wastewater treatment.

2. Methods

2.1. Wastewater and anodic mixed consortia

Chemical wastewater aggregated from bulk drugs, chemical intermediates, dye and dye intermediates, pharmaceuticals, pesticides and various chemical processes was used in the experiments. Characteristically, the wastewater was complex in nature with low-biodegradability (BOD/COD~0.3) (pH 7.82; suspended solids (SS) 0.98 g/l, total dissolved solids (TDS) 25.5 g/l, total alkalinity (TA) 0.12 g/l, chlorides 7.71 g/l, chemical oxygen demand (COD) 12.1 g/l and biological oxygen demand (BOD) 3.63 g/l). Anaerobic mixed consortia from laboratory scale biofilm reactor producing fermentative H_2 was used as parent inoculum in the anode chamber of MFC as biocatalyst as stated previously [16].

2.2. MFC configuration and operation

Dual chambered MFC separated by proton exchange membrane (PEM; Nafion 117) after pretreatment was fixed between clamps of anode and cathode chambers [4,16]. Non-catalyzed graphite plates (5×5 cm; 10 mm thickness) were used as electrodes (cathode 70 cm^2; anode (provided with nine uniform size holes of 0.1 cm diameter) 83.56 cm^2). Prior to use electrodes were soaked in deionized water and positioned at a distance of

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doi:10.1016/j.elecom.2008.11.038

6 cm on either side of the PEM. Copper wires were used for contact with electrodes and the contact area was sealed carefully with 'epoxy' material. Each chamber was designed to have sample port, wire point inputs (top), inlet and outlet ports and anode chamber was sealed with washers to ensure anaerobic microenvironment. Two MFC (total volume, 0.75 l; working volume, 0.65 l) were operated separately with ferricyanide (MFC_{FC}; $K_3Fe(Cn)_6$ in phosphate buffer (50 mM; pH 7.5)) and aerated phosphate buffer (MFC_{AC}; pH 7.5; 50 mM) as catholyte in fed-batch mode at room temperature (28 ± 2 °C). The anodic chambers were operated with enriched mixed microflora initially by feeding designed synthetic wastewater [4,16]. Anodic chambers were fed with chemical wastewater (substrate loading, 5.3 g COD/l) after obtaining the stable performance with respect to power output parameters and performance of MFCs were evaluated at acidophilic (pH 6), neutral (pH 7) and alkaline (pH 8) conditions after adjusting the feed pH to the desired value (orthophosphoric acid (88%)/1 N NaOH). Fresh wastewater was replaced once voltage started to decrease. Anolyte was recirculated at a rate (1 l/h) necessary to suppress the prevailing substrate gradient during operation. After every feeding event, the anode chamber was sparged with N_2 gas for 2 min to maintain anaerobic microenvironment.

2.3. Analysis

Current (I, parallel) and open circuit voltage (OCV, series) measurements were recorded using multi-meter by connecting 100 Ω as external load. Polarization curve was generated (parallel) during stabilized phase of MFC operation. Cell potentials were measured against a saturated Ag/AgCl (S) electrode. Power density (PD) and current density (CD) were calculated by dividing the obtained power and current with the surface area (m^2) of the anode, respectively. Specific power yield (SPY) was obtained by dividing power generated with the substrate (COD) removed. COD, BOD, SS, pH, TDS, chlorides and TA were determined according to the standard methods [17].

3. Results and discussion

3.1. Power output

Anodic pH microenvironment and nature of catholyte showed visible influence on the performance of MFC (Figs. 1 and 2). Relatively higher power output was observed in the case of ferricyanide catholyte compared to corresponding aerated catholyte. Acidophilic pH evidenced relatively higher power generation compared to the corresponding neutral and alkaline operations irrespective of the nature of the catholyte used. Interestingly, more or less uniform OCV values were recorded during MFC operation under all pH conditions studied. On the contrary, current registered marked variation with the function of pH where acidophilic operation showed higher efficacy while alkaline operation showed the lowest. Among the studied cases, acidophilic pH operation in combination with ferricyanide catholyte documented highest current output (5.18 mA (100 Ω); 0.632 V; 3.27 mW). Acidophilic pH condition with aerated catholyte also showed good performance (4.26 mA (100 Ω); 0.578 V; 2.46 mW). Lowest efficiency was recorded with basic operation (MFC_{FC} 4.12 mA (100 Ω); 0.576 V; 2.37 mW; MFC_{AC} 3.48 mA (100 Ω); 0.538 OCV; 1.87 mW). Neutral operation showed better performance (MFC_{FC} 4.4 mA (100 Ω); 0.591 V, 2.60 mW; MFC_{AC} 3.98 mA (100 Ω); 0.603 V, 2.0 mW) than the corresponding basic operation. A consistent improvement in voltage was observed with every additional feeding event in all the experimental variations studied. This might be attributed to the adaptability of the inoculated microflora to the anodic microenvironment. Immediately after feeding fresh wastewater upshot in OCV was observed during initial phase. MFC_{FC} system was operated between 9 and 11 days retention time, while MFC_{AC} was operated between 10 and 12 days.

3.2. Fuel cell behavior

3.2.1. Polarization behavior

Polarization behavior of MFC during operation was recorded at various external resistances (100Ω–30 kΩ) to visualize the e^-

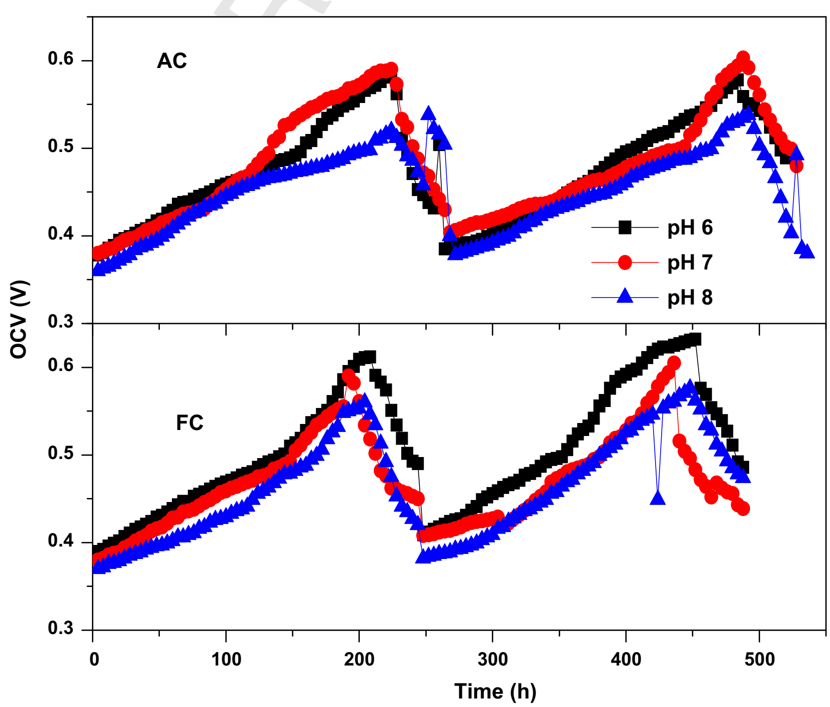

Fig. 1. Open circuit voltage (OCV) variation with the function of anodic pH microenvironment and catholyte nature during MFCs operation.

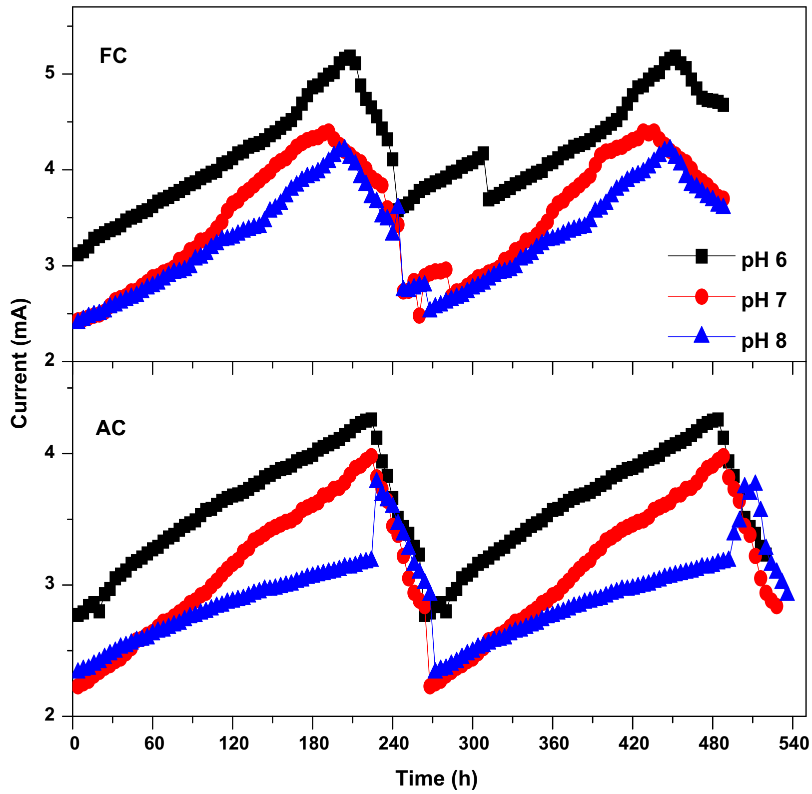

Fig. 2. Current (100 Ω; series) variation with the function of anodic pH microenvironment and catholyte nature during MFCs operation.

discharge (current) phenomenon with respect to the experimental variations studied (Fig. 3). Generally higher e^- discharge is observed especially at lower resistances as a result of higher potential drop and slow stabilization tendency of the voltage in spite of higher current generation. Comparatively less current generation along with rapid stabilization of voltage was observed at higher external load (30 kΩ) due to low e^- discharge. This e^- flow towards cathode neutralizes the protons (H^+) present in the cathode chamber. The point at which maximum power density (PD_{max}) was observed on the polarization profile is generally considered as the cell design point (voltage change region) of that particular MFC system. Effective performance with respect to power output can be obtained on the right side of the cell design point. In MFC_{FC}, cell design point was observed at 400 Ω corresponding to PD_{max} at both acidophilic (65.82 mW/m^2) and neutral (49.26 mW/m^2) operations. Basic operation showed cell design point at comparatively low resistance (300 Ω) corresponding to a PD_{max} of 54.93 mW/m^2. Therefore, MFC_{FC} can be operated effectively at resistance below the cell design point with stable performance. In aerated catholyte operation, at acidophilic operation cell design point was observed at relatively higher resistance (500 Ω) with respect to PD_{max} (62.70 mW/m^2). Cell design point in alkaline and neutral operations was noticed at relatively lower resistance (300 Ω) corresponding to PD_{max} (47.24 mW/m^2 (pH 7); 48.56 mW/m^2 (pH 8)). However, higher CD was observed in the case of MFC_{FC} at acidophilic microenvironment (411.27 mA/m^2 (MFC_{FC}); 415.68 mA/m^2 (MFC_{AC})) compared to neutral (372.19 mA/m^2 (MFC_{FC}); 360.22 mA/m^2 (MFC_{AC})) and alkaline (388.94 mA/m^2 (MFC_{FC}); 380.56 mA/m^2 (MFC_{AC})) operations.

3.2.2. Cell potentials

Variation in cell emf (E_0), cathode potential (E_c) and anode potential (E_a) against external resistance (100Ω–30 kΩ) was recorded against saturated Ag/AgCl(s) electrode. Significant decrease in cell emf was observed when applied external resistance was less than 15 kΩ (MFC_{FC}) and 10 kΩ (MFC_{AC}). This indicated the possibility of effective e^- discharge during MFC_{FC} operation compared to MFC_{AC} operation especially at higher resistance. Higher cell emf was observed under acidophilic conditions (0.470–0.146 V (MFC_{FC}); 0.453–0.143 V (MFC_{AC})) compared to neutral (0.442–0.127 V (MFC_{FC}); 0.432–0.117 V (MFC_{AC})) and alkaline (0.452–0.136 V (MFC_{FC}); 0.441–0.112 V (MFC_{AC})) condition (Fig. 4). Cathode potential varied between a narrow range (0.242–0.02 V (MFC_{FC}); 0.13–0.02 V (MFC_{AC})) indicating that MFC performance was limited by anode condition and external resistance. Marked variation in anodic potential during MFC operation was noticed with the function of anodic pH microenvironment (Fig. 4). Acidophilic operation showed higher anodic potential (−0.228 to −0.126 V (MFC_{FC}); −0.323 to −0.141 V (MFC_{AC})) compared to the corresponding neutral (−0.200 to −0.107 V (MFC_{FC}); −0.302 to −0.115 V (MFC_{AC})) and alkaline (−0.210 to −0.116 V (MFC_{FC}); −0.311 to −0.110 V (MFC_{AC})) operations. Anode potential generally controls the kinetics of e^- transfer from the microorganism to anode.

3.3. Wastewater treatment

MFC also showed significant removal of substrate (COD) during operation apart from power generation irrespective of the experimental conditions used. Substrate removal efficiency was found to depend on the applied anodic pH rather than the nature of the catholyte. Cathloyte did not show any visible influence on the substrate degradation taking place in the anodic chamber. More or less the same COD removal efficiency (MFC_{FC}, 58.87–61.51%; MFC_{AC}, 56.98–60.38%) was noticed with both the catholytes. A gradual improvement in the substrate exhaustion was observed with every new feeding event irrespective of the applied pH. Contrary to the power generation, neutral feeding pH showed higher substrate removal efficiency (MFC_{FC}, 61.51%; MFC_{AC}, 61.89%) followed by

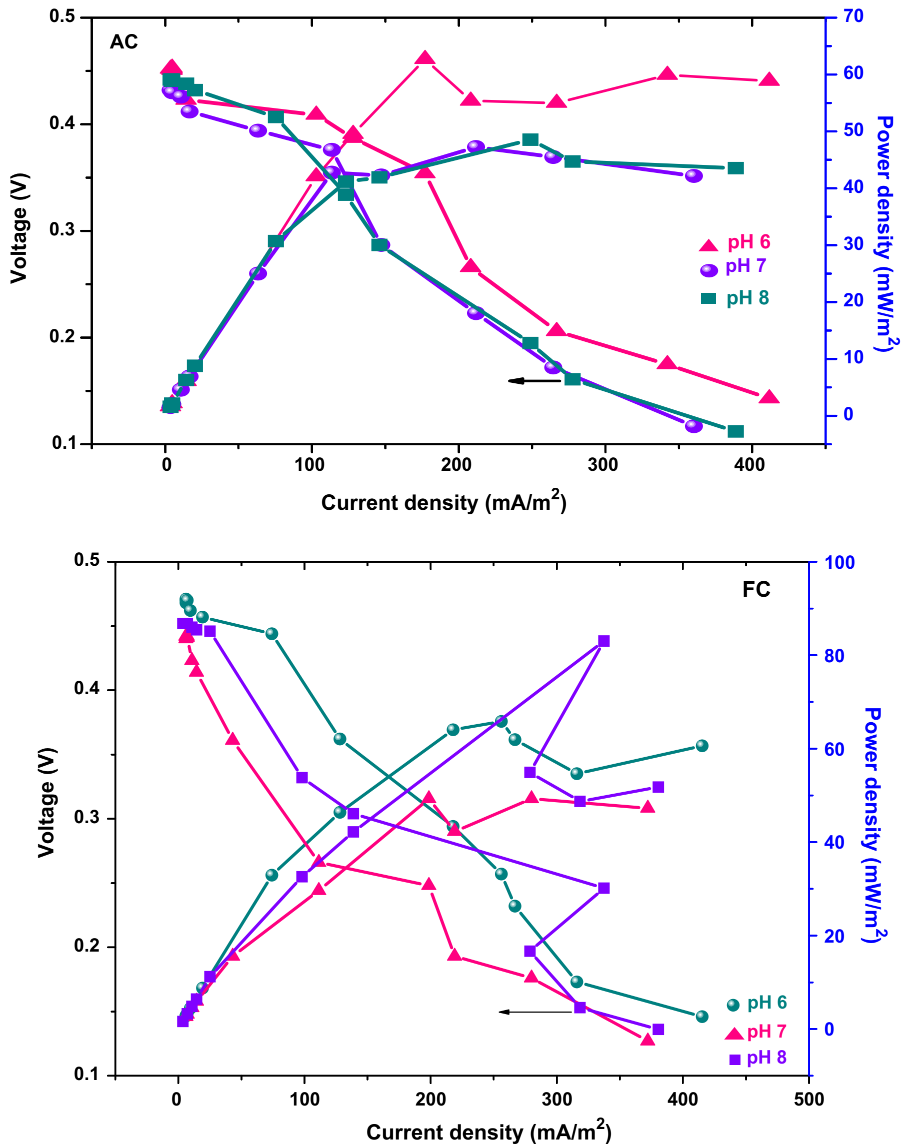

Fig. 3. Polarization behavior (parallel, 0.1–30 kΩ) of MFCs during operation with the function of anodic pH microenvironment and catholyte nature.

alkaline (MFC_{FC}, 60.75%; MFC_{AC}, 60.38%) and acidophilic (MFC_{FC}, 58.87%; MFC_{AC}, 56.98%) operations. Acidophilic pH conditions depicted relatively lower substrate degradation efficiency. However, high SPY was observed at acidophilic microenvironment (MFC_{FC}, 1.05 W/kg COD_R; MFC_{AC}, 0.81 W/kg COD_R) compared to corresponding neutral (MFC_{FC}, 0.80 W/kg COD_R; MFC_{AC}, 0.73 W/kg COD_R) and alkaline (MFC_{FC}, 0.70 W/kg COD_R; MFC_{AC}, 0.58 W/kg COD_R) operations. Effective substrate degradation efficiency observed under neutral conditions may be attributed to functioning of methanogenic bacteria (MB) resulting in complete metabolism of the substrate. However, acidophilic condition inhibits the MB function and creates conducive environment for proliferation of acidogenic bacteria (AB), where complete reduction of substrate was not feasible. Optimum range MB functions effectively near pH 7.0, while AB had lower pH optimum around pH 6.0 and are insensitive to acidic conditions [18].

In spite of more or less equal voltage output, marked change in current generation was observed with respect to pH microenvironment irrespective of the nature of the catholyte. The possible reason for this phenomenon may be attributed to the effective extracellular e^- transfer at acidophilic pH microenvironment compared to neutral and basic operations. The higher activity of intracellular e^- carriers (which will help in translocation of e^- from bacteria to the out side of the cell) might be the other possible reason for higher current generation at acidophilic pH operation. Moreover, reduction of H^+ during the degradation of substrate up to the final end product formation might be visualized in the case of neutral and basic operations. In the case of acidophilic operation all the H^+ might not get reduced which inturn led to the generation of e^- discharge (current). At acidophilic operation, dehydrogenase activity represents proton (H^+) shuttling between metabolic intermediates through electron carriers/redox mediators [19]. The higher dehydrogenase activity in basic operation represented the reduction of substrates to end-products instead of generating potential leading to lower e^- discharge (current). The lower substrate removal observed at acidophilic operation in this study corroborated the above observation. Moreover, the e^- generated might also be scavenged during further reduction of substrate prior to reaching anode in the case of basic and neutral operation. Hence, the current observed was low at neutral and basic operations even though, the voltage was more or less the similar.

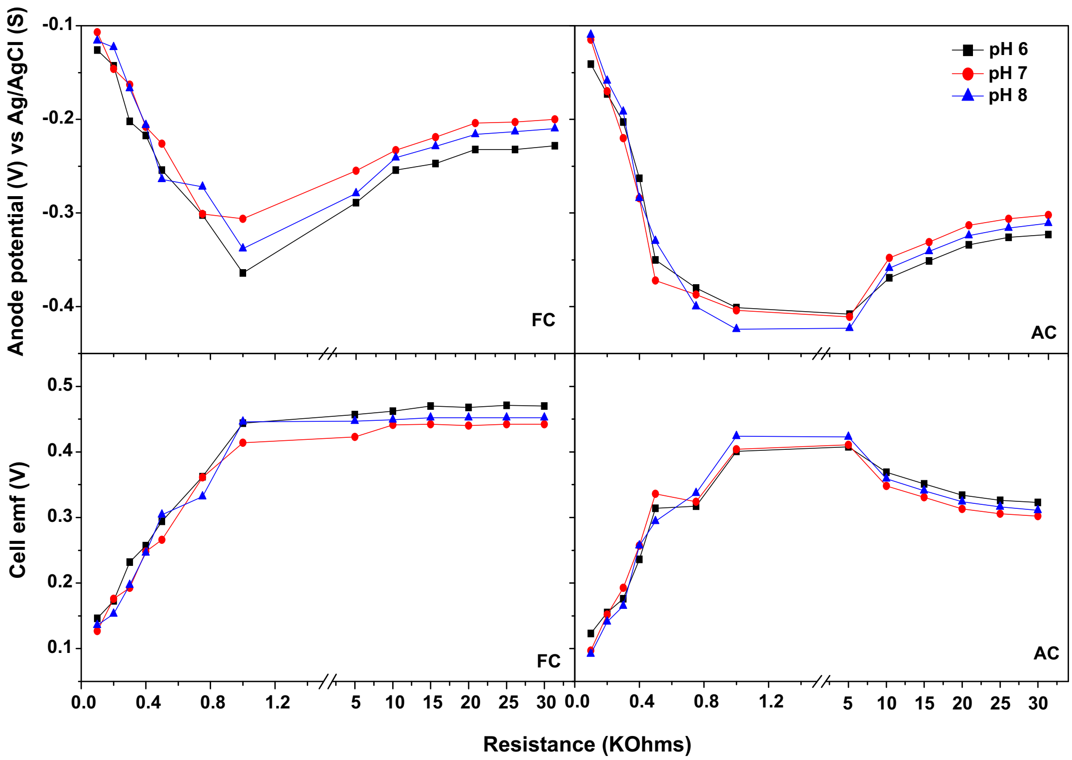

Fig. 4. Variation in cell emf and anode potentials (parallel, 0.1–30 kΩ) observed with the function of anodic pH microenvironment and catholyte nature.

4. Conclusions

Feed pH of the wastewater showed significant influence on the overall process performance of MFC. Experiments demonstrated the effectiveness of acidophilic operation of MFC anodic chamber on bioelectricity generation compared to neutral and alkaline operations. Substrate degradation was observed to be higher under neutral operating conditions followed by alkaline and acidophilic conditions. Ferricyanide catholyte responded effective power output compared to the corresponding aerated catholyte. However, nature of catholyte did not show any visible influence on the substrate degradation efficiency.

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Please cite this article in press as: S.V. Raghavulu et al., Effect of anodic pH microenvironment on microbial fuel cell (MFC) performance ..., Electrochem. Commun. (2008), doi:10.1016/j.elecom.2008.11.038