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# Microaerophilic microenvironment at biocathode enhances electrogenesis with simultaneous synthesis of polyhydroxyalkanoates (PHA) in bioelectrochemical system (BES)

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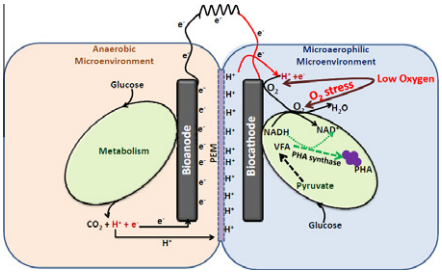
## HIGHLIGHTS

- Microaerophilic microenvironment was evaluated as terminal electron acceptor in BES.
- Microbial accumulation of polyhydroxyalkanoates (PHA) at biocathode was observed.
- Electron losses reduced due to synergistic association between anode and biocathode.
- Gradual substrate degradation was observed due to controlled microbial metabolism.
- Redox catalytic currents and bio-electro kinetics supported the bio-electrogenesis.

## GRAPHICAL ABSTRACT

Considering the microaerophilic microenvironment at biocathode in bioelectrochemical system (BES) will enhance the electrogenesis and reduce the losses due to the controlled microbial metabolism and simultaneously provides a chance to harness polyhydroxyalkanoates (PHA). The electrogenic activity (512 mV; 15.2 mW/m$^2$) was extended for longer periods (144 h) which might be attributed to the lowering of losses due to the controlled microbial metabolism. Growth limiting stress at cathode due to lower oxygen levels and its effective utilization by the protons and electrons coming from anode, might have diverted the microbial metabolism towards PHA synthesis instead of oxidation. PHA accumulation (19% of dry cell weight (DCW)) was observed with higher hydroxy butyrate (HB) (89%) concentration at 48th h in the cathodic biocatalyst and was re-utilized by the end of experiment. Bio-electro kinetics studied through voltammetry and Tafel analysis further supported the observed electrogenesis in microaerophilic reduction microenvironment, in terms of redox catalytic currents, Tafel slopes, exchange current densities and polarization resistance.

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## ABSTRACT

Microaerophilic microenvironment at biocathode was evaluated for electrogenesis along with the polyhydroxyalkanoates (PHA) accumulation in bio-electrochemical system (BES). The electrogenic activity (512 mV; 15.2 mW/m$^2$) was extended for longer periods (144 h) which might be attributed to the lowering of losses due to the controlled microbial metabolism. Growth limiting stress at cathode due to lower oxygen levels and its effective utilization by the protons and electrons coming from anode, might

*Abbreviations:* AO, activation overpotentials; BES, bio-electrochemical systems; C, charge (Coulumbs); COD, chemical oxygen demand; Co-polymer, poly (β-OH) butyrate-*co*-poly (β-OH) valerate, P3 (HB-*co*-HV); CP, concentration polarization; CV, cyclic voltammetry; DCW, dry cell weight; DO, dissolved oxygen; DSW, designed synthetic wastewater; E, applied voltage (V); $e^-$, electrons; ED, electron discharge; Emf, electron motive force; $H^+$, protons; I, current (mA/A); $i_o$, exchange current density (mA/m$^2$); ln $i_o$, logarithm of the exchange current density; MFC, microbial fuel cell; OCV, open circuit voltage (V); OL, ohmic losses; OLR, organic loading rate (Kg COD/m$^3$-day); PD, power density (mW/m$^2$); PHA, polyhydroxyalkanoates; PHB, polyhydroxy butyrate (poly(β-OH) butyrate); PHV, polyhydroxy valerate (poly(β-OH) valerate); $R_{ct}$, charge transfer resistance (Ω); $R_p$, polarization resistance (Ω); SDR, substrate degradation rate (Kg $COD_R$/m$^3$-day); TDS, total dissolved solids (mg/l); TEA, terminal electron acceptor; TEAP, terminal electron accepting process; V, voltage (V); VFA, volatile fatty acids (mg/l); $\alpha_a$, electron transfer coefficient during oxidation ($\beta_a$RT/nF); $\alpha_c$, electron transfer coefficient during reduction ($\beta_c$RT/nF); $\beta_a$, oxidative Tafel slope (V/dec); $\beta_c$, reductive Tafel slopes (V/dec).

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## 1. Introduction

Biofuels present an exciting and sustainable alternative to the fossil fuels and can defend the existing energy crisis and environmental pollution problems. Microbial fuel cell (MFC) technology is representing a new and promising biological process for bioenergy generation (Venkata Mohan et al., 2008a; Rabaey and Rozendal, 2010; Huang et al., 2011). The possibility of using wastewater as anodic fuel in MFC is attracting the present research scenario, due to its dual benefits of energy (power) generation and waste management, making MFC as a sustainable technology (Aulenta et al., 2008; Oh et al., 2010; Venkata Mohan et al., 2008a; Venkateswar Reddy et al., 2010). In the recent past, the application of MFC was also extended for the recovery of some value added reduced end products apart from electrogenesis and waste remediation, by reinventing its efficiency as bio-electrochemical system (BES). The reduction mechanism at cathode helps to utilize the reducing equivalents [protons ($H^+$) and electrons ($e^-$)] effectively, for electrogenesis and also for the formation of reduced end products such as acetate, alcohols (e.g., methanol, ethanol, butanol, etc.), aldehydes etc., under *in situ* potential or mild applied potentials. Increase in the terminal electron acceptor (TEA) concentration or its efficiency at cathode helps to increase the electron transfer from anode and their effective utilization at cathode, resulting in decreased electron losses (concentration losses) and higher power output (Srikanth and Venkata Mohan, 2012). Apart from oxygen, various other catalysts viz, Platinum (Pham et al., 2004), specific metals such as $Mn^{2+}$, $Fe^{2+}$ (Park et al., 2000; Rhoads et al., 2005; Heijne et al., 2007; Venkata Mohan et al., 2008b), were studied as TEA at cathode to enhance the electrogenesis. Microbial metabolism is also found to be an effective TEA at cathode, in the recent past (Bergel et al., 2005; Rhoads et al., 2005; Hamid et al., 2008; Chen et al., 2008; Rabaey et al., 2008; Rosenbaum et al., 2011; Srikanth and Venkata Mohan, 2012). Application of microbial metabolism at cathode can also be extended to the removal of specific pollutants, viz., nitrates, sulfates, dye compounds and chloroorganics (Aulenta et al., 2008; Lefebvre et al., 2008; Hamelers et al., 2010; Venkata Mohan and Srikanth, 2011; Sanath and Min, 2012), and recovery of value added products (Rabaey and Rozendal, 2010). Increase in the electrogenic activity and substrate degradation along with the reduced internal losses during biocathode application was reported previously under aerobic and anaerobic microenvironments (Venkata Mohan and Srikanth, 2011; Srikanth and Venkata Mohan, 2012; Sanath and Min, 2012). However, the functional role of microaerophilic metabolism, switching between aerobic and anaerobic metabolic functions, as TEA is not yet reported.

On the other hand, there is a growing concern over the use of conventional plastics like polypropylene and polyethylene which depend on the depleting hydrocarbon sources (Rehm, 2010). These petroleum derived plastics takes several years to decompose and during degradation they produce harmful toxic compounds (Koller et al., 2010). Polyhydroxyalkanoates (PHA) production through biological route, is gaining importance in overcoming the adverse effects of conventional plastics degradation. PHA production from renewable sources like wastewater and mixed culture is gaining prominence and less reported (Sipkema et al., 2000; Salehizadeh and Van Loosdrecht, 2004; Venkata Mohan et al., 2010a; Pieja et al., 2011; Venkateswar Reddy and Venkata Mohan, 2012a). PHA synthesis and its accumulation as intracellular granules, usually occurs in presence of excess carbon source and associated growth limiting components such as nitrogen, phosphate, sulfur, oxygen or magnesium (Salehizadeh and Van Loosdrecht, 2004). Mixed culture utilization can lower the input costs, by allowing large scale fermentations to occur without overhead costs of sterilization. It also allows the utilization of a variety of substrates, due to the presence of several PHA producing organisms. A considerable effort has gone in the production of PHA's using mixed cultures and different wastewaters (Sipkema et al., 2000; Salehizadeh and Van Loosdrecht, 2004; Venkata Mohan et al., 2010a; Pieja et al., 2011; Venkateswar Reddy and Venkata Mohan, 2012a). Various factors influencing the microbial PHA accumulation have been optimized with pure as well as mixed cultures. It was reported that low oxygen levels in the system (microaerophilic) will divert the microbial metabolism towards accumulation of stored granules, among which PHA synthesis was proven to be a potential alternative (Sipkema et al., 2000; Pieja et al., 2011). Integrating the PHA synthesis under microaerophilic microenvironment with the microbial electrogenesis will have multiple benefits, viz., electrogenesis, PHA production and waste remediation. In this context, the present study was designed to evaluate the potential of PHA accumulating microbial metabolism as TEA condition at cathode, for enhanced electrogenesis and reduced internal electron losses, along with PHA recovery. Cathode was inoculated with aerobic mixed consortia under microaerophilic (growth limiting) condition and BES performance was evaluated in detail.

## 2. Experimental methodology

### 2.1. Biocatalyst

Anaerobic consortia acquired from an operating large scale anaerobic bioreactor [pH – 7.4, suspended solids (SS) – 66.02 g/l, volatile suspended solids (VSS) – 27.82 g/l, and total organic carbon (TOC) – 1.127 g/l] and aerobic consortia from activated sludge process unit [pH – 7.2, SS – 98.62 g/l, VSS – 46.64 g/l, and TOC – 1.548 g/l] were used as biocatalyst in the anode and cathode chambers (10% of the volume), respectively. Prior to inoculation, the parent culture was enriched in designed synthetic wastewater (DSW) [g/l; glucose-3.0, $NH_4Cl$-0.5, $KH_2PO_4$-0.25, $K_2HPO_4$-0.25, $MgCl_2{\cdot}6H_2O$-0.3, $FeCl_3$-0.025, $NiSO_4$-0.016, $CoCl_2$-0.025, $ZnCl_2$-0.0115, $CuCl_2$-0.0105, $CaCl_2$-0.005 and $MnCl_2$-0.015, chemical oxygen demand (COD) – 3.2)] under anaerobic and aerobic microenvironments at pH 6.0 and 7.0, respectively.

### 2.2. BES configuration and operation

Double chambered BES was designed and fabricated using perspex material in the laboratory, with equal volumes of anode and