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Enhanced performance of sulfate reducing bacteria based biocathode using stainless steel mesh on activated carbon fabric electrode

Mohita Sharma [a,b], Pratiksha Jain [a,b], Jhansi L. Varanasi [b], Banwari Lal [b], Jorge Rodríguez [c,d], Juan M. Lema [c], Priyangshu M. Sarma [a,b,*]

[a] TERI University, 10 Institutional Area, Vasant Kunj, New Delhi 110 070, India
[b] TERI, Darbari Seth Block, India Habitat Centre, New Delhi 110 003, India
[c] University of Santiago de Compostela, Santiago de Compostela, Spain
[d] Masdar Institute of Science and Technology, PO Box 54224, Abu Dhabi, United Arab Emirates

HIGHLIGHTS

- Anoxic biocathode was developed using SRB consortium and ACF.
- The effect of additional current collector over the electrode surface was assessed.
- DPV was explored as an additional tool for electrochemical analysis.
- Biocathode was used effectively to utilize VFAs from the fermentation effluent.

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ABSTRACT

An anoxic biocathode was developed using sulfate-reducing bacteria (SRB) consortium on activated carbon fabric (ACF) and the effect of stainless steel (SS) mesh as additional current collector was investigated. Improved performance of biocathode was observed with SS mesh leading to nearly five folds increase in power density (from 4.79 to 23.11 mW/m^2) and threefolds increase in current density (from 75 to 250 mA/m^2). Enhanced redox currents and lower Tafel slopes observed from cyclic voltammograms of ACF with SS mesh indicated the positive role of uniform electron collecting points. Differential pulse voltammetry technique was employed as an additional tool to assess the redox carriers involved in bioelectrochemical reactions. SRB biocathode was also tested for reduction of volatile fatty acids (VFA) present in the fermentation effluent stream and the results indicated the possibility of integration of this system with anaerobic fermentation for efficient product recovery.

1. Introduction

Microbial fuel cell (MFC) enables generation of bioelectricity along with treatment of wastewater using microbial catalysts. Conventional fuel cells make use of precious metal coating on the electrodes for the catalysis of chemical reactions taking place in the electrochemical cell. However, MFC makes use of biocatalysts that perform oxidation and/or reduction at electrodes. Here microorganisms transfer electrons from an electron donor at lower potential to a higher potential electron acceptor, which can be internal as in fermentation or external as in respiration. Additional use of biocathode, further reduces the operation cost and make the MFC operation more sustainable (Sun et al., 2012). The recent studies on MFC encompasses a wide range of applications including wastewater cleaning, nutrient removal, production of value added products, power production, microbial biomass production, production of biofuels like hydrogen and methane and implantable power source for bioelectronics including pacemakers and recently even for charging mobile devices (Rabaey et al., 2006; Zhang et al., 2008; Ieropoulos et al., 2013).

Despite the availability of abundant literature on MFC in the recent past, developments and related information on biological cathode is still in its infancy. The application of biocathodes not

Abbreviations: ACF, activated carbon fabric; CD, current density; CDP, cell design point; CEM, cation exchange membrane; COD, chemical oxidation demand; CV, cyclic voltammetry; DPV, differential pulse voltammetry; FS, forward sweep; GC, gas chromatograph; MFC, microbial fuel cell; OCV, open circuit voltage; ORP, oxidation reduction potential; PD, power density; R_p, polarization resistance; RS, reverse sweep; SRB, sulfate reducing bacteria; SS, stainless steel; TEA, terminal electron acceptor; VFA, volatile fatty acids.

* Corresponding author at: TERI University, 10 Institutional Area, Vasant Kunj, New Delhi 110 070, India. Tel.: +91 11 24682100; fax: +91 11 24682144.
E-mail address: priyanms@teri.res.in (P.M. Sarma).

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only has wide considerations related to electrode materials and solution chemistry, but engenders opportunities to convert electrical current into microbially generated reduced products (Huang et al., 2011). The versatility of biocathodes allows utilization of contaminants present in wastewater as possible electron acceptor other than oxygen which provides prospective for development of full biological MFCs in complete anoxic conditions by permitting the use of compounds such as nitrate, sulfate and iron as the terminal electron acceptors (TEA) in the process. With the potential application of sulfate reducing bacteria (SRB) in utilizing sulfate as its TEA, few researchers have started considering it for development of biocathodes (Cordas et al., 2008; Dutta et al., 2008; Sharma et al., 2013).

Another important parameter for developing biocathode in MFC operation lies in selection of electrode material. The ability of the microorganism to attach to the electrode material and form biofilm plays a key role in improving catalytic efficiency and power outputs of MFC (Rabaey and Rozendal, 2010). Zhao et al. (2008) reported the use of activated carbon fabric as a suitable electrode material for sulfide adsorption and oxidation, with significant potential for harvesting energy from sulfate-rich solutions in the form of electricity. Although several reports suggest the use of carbon based electrode materials for good bacterial adhesion (Liu et al., 2010; Zhang et al., 2012), such materials might not be able to transfer electrons at long distances as they lack electrical conductivity of metals. Hence in the present study, the combined effect of using SRB with an efficient ACF electrode material was studied with and without the presence of a current collector (SS mesh) to evaluate its effect on the overall performance of the biocathode.

Moreover, the most prominent application for biocathode in MFCs lies in the production of value added products along with effective power generation. Complete energy recovery from dark anaerobic fermentation process is limited by thermodynamic constraints and accumulation of volatile fatty acids. Integration of such a process with MFCs for effluent polishing with simultaneous electricity recovery proves to be a promising technology (Premier et al., 2013). There are studies reported by few investigators in which volatile fatty acids (VFAs) were used as suitable carbon source for generation of electricity along with reduction in COD and production of other value added products (Liu et al., 2005; Mohanakrishna et al., 2010). Recently, Sharma et al. (2013) reported the bioelectrosynthesis of alcohols and acetone by electrochemical reduction of VFAs with SRB as a biocathode. Hence, an attempt was made in this study to develop an anoxic sulfate reducing biocathode using activated carbon fabric as electrode material and to investigate the role of an additional current collector in improving the performance of the biocathode. The study also reports the ability of developed SRB biocathode for reduction of VFAs from the fermentative effluents.

2. Methods

2.1. Source of inoculum and electrolyte

The SRB mixed consortium used to inoculate the cathodic chamber was taken from a laboratory scale anaerobic continuous reactor developed by inoculating mixed SRB strains isolated from different petroleum refineries and formation sites across India (Sharma et al., 2013). A volume of 10% (v/v) was taken from the reactor, centrifuged, washed and the pellet was used for subsequent enrichment in API RP-38 medium (4 g sodium lactate, 1 g yeast extract, 0.1 g ascorbic acid, 0.2 g $MgSO_4$, 0.01 g K_2HPO_4, 0.1 g KH_2PO_4, 0.2 g NH_4FeSO_4 and 10 g NaCl, for 1 L, pH-7.4) for developing the biocathode. The effluent to be used in cathodic chamber was acquired from a dark fermentative hydrogen production reactor running in the laboratory that initially had molasses as a carbon source. The characteristics of the effluent prior to its use in the MFC were: pH: 4.51; ORP (oxidation–reduction potential): 162 mV and total VFA: 3128 mg/L, characterized based on analytical methods provided below. The effluent was centrifuged (5000 rpm, 15 min) to remove bacterial biomass and other debris prior to use.

2.2. Development of biocathode

SRB biofilm was developed on ACF electrode material ($8 \times 5\ cm^2$; BET Surface area: $1500 \pm 150\ m^2/g$; Pore Volume: 0.6 cc/g; Density: 0.45 g/cc; Ash < 2%; Source: HEG Ltd, Madhya Pradesh, India) by submerging it in 300 ml of API-RP-38 medium with 10% SRB inoculum, in a 500 ml glass jar bottle after purging it with sterile nitrogen gas (Sigma Gases and Services, India) (Sharma et al., 2013). This set-up was incubated at 37 °C (80 rpm) for10 days in a fed batch mode by replacing 100 ml of the spent medium with fresh API-RP-38 medium after every 72 h. This developed biofilm on ACF material was anaerobically transferred to the cathode chamber of MFCs to act as biocathode in subsequent experiments.

2.3. Reactor design and operation

Three conventional H-shape dual-chambered MFCs with total/working volume 200/150 ml were designed and fabricated locally and cation exchange membrane (CMI-7000; Membranes International Inc., USA) was used for partitioning the chambers. The membrane was pretreated with 3% sodium chloride overnight and then dried before use as described by Rabaey et al. (2003). The cathode compartment of the three MFCs consisted of biocathode (as described above) as electrode while the anode compartment consisted of carbon rod electrode pre-treated with dil. sulfuric acid (0.001 M). Both the chambers were sealed using O-rings, clamps and fasteners after purging it with sterile nitrogen gas (Sigma Gases and Services, India) and sealed with butyl rubber stoppers. Fig. 1 shows the schematic of the reactor set up used for the experiments.

Three sets of experiments were conducted simultaneously. In the first set of experiment (MFC-1), the biocathode MFC was run in a fed-batch mode with sampling conducted at every 72 h for a total incubation of 30 days. During sampling, 50 ml of the medium in the working electrode chamber (cathodic chamber) was replenished by fresh medium of API RP-38. In the second set of experiment (MFC-2), the ACF electrode material of the biocathode was embedded onto SS mesh in sterile anaerobic conditions so as to study the effect of an additional current collector, while all other operating parameters were kept similar to MFC-1. In the third set of experiment (MFC-3), API RP-38 medium was replaced with fermentation effluent as electrolyte and the system was operated in batch mode for 30 days with SS mesh. All the other conditions of the reactor configuration and operation remained identical to MFC-2.

2.4. Analytical methods

Out of the total volume of the samples collected for each experimental set as described above, 5 ml of sample was centrifuged at 10,000 rpm for 10 min and supernatant was filtered and used for pH, ORP and VFA analysis. pH and ORP were measured using a pH/ORP meter with relevant probes (SevenMulti pH and conductivity meter, Mettler Toledo, India) as described previously by Tenca et al., 2012. VFAs in the liquid phase were analyzed with GC 6890N (Agilent, USA) equipped with flame ionizer detector and DB-WAXetr column ($30\ m \times 530\ \mu m \times 1\ \mu m$). The oven