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# Synergistic yield of dual energy forms through biocatalyzed electrofermentation of waste: Stoichiometric analysis of electron and carbon distribution



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### G.N. Nikhil, G. Venkata Subhash, Dileep Kumar Yeruva, S. Venkata Mohan\*

Bioengineering and Environmental Sciences (BEES), CSIR-Indian Institute of Chemical Technology (CSIR-IICT), Hyderabad 500 007, India

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#### ABSTRACT

A novel BEF (biocatalyzed electrofermentor) is designed by hybridizing the functional properties of both MFC (microbial fuel cell) and acidogenic fermentation process (AFP). This prototype facilitates potential synergy between the electrogenic and acidogenic processes to recover biohydrogen and bioelectricity with simultaneous wastewater treatment. The BEF was operated in three circuitry modes of operation viz., OC (open circuit), SC (short circuit) and CC (closed circuit) and the performance was compared with a control (without electrode assembly) with DSW (designed synthetic wastewater) having an organic load of 5000 mgL<sup>-1</sup>. In comparison with other test conditions, CC mode with fixed external resistance (300  $\Omega$ ) gave highest yields of power density (72 mW m<sup>-2</sup>) and biohydrogen production (343 mL). Besides, the BEF performance was sustained by the innate buffering capacity and the substrate-linked dehydrogenase enzyme activity. The CC mode comparatively excelled because it facilitates congenial ambiance for the enriched EAB (electroactive bacteria) resulting high rate of metabolic activity that paves way for higher substrate degradation and product conversion efficiency. The empirical analysis of electron and carbon distribution was in good agreement with the experimental results. The electron delivery kinetics studied using voltammetric technique confirmed electron transfer by the membrane bound redox mediators. The designed biocatalyzed electrofermentation unravels the scope to harness dual forms of energy along with waste remediation.

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#### 1. Introduction

Water and energy crisis have created an obligatory concern to the scientific community. Many reports are available on capture of renewable energy through biological routes with simultaneous wastewater treatment [1,2]. Recently, environmental research towards development of advanced BES (bio-electrochemical systems) for diverse applications is booming all around the world [3,4]. For instance, MFC (Microbial fuel cells) are exclusively designed for bioelectricity and MEC (microbial electrolysis cells) for biohydrogen (H<sub>2</sub>) production [1–7]. Synthesis of value added products such as polyhydroxyalkanoates (bio-plastics), acetate, etc. is another dimension of BES [8,9]. In MFC, electrons produced by microbial oxidation at the anode get reduced at the cathode chamber in closed circuit operation. In MEC, the working electrode poised with certain voltage assists in selective biofilm enrichment for better substrate removal and hydrogen production. On the other hand, typical acidogenic dark fermentation also yields H<sub>2</sub>; but possesses certain process impedes *viz.*, low *substrate* conversion attributable to inhibition by acid-rich compounds (volatile fatty acids, VFA) [10]. High concentrations of VFA perturbs the system buffer capacity leading to cessation of microbial growth or metabolic malfunction [11]. Different strategies are reported to improve electricity and H<sub>2</sub> production by integrating with wastewater treatment processes [12–15]. The main challenge of combining the two processes is the different microenvironments required by two types of microbial consortia for maximizing energy output.

Keeping in view of these issues, a novel BEF (bio-electrofermentor) is designed which is a hybrid prototype with the functional properties of both MFC and conventional dark fermentation in a single entity. This facilitates potential synergy between the two processes; since 'acidogens' produce  $H_2$  by fermenting sugars into VFA while 'electrogens' (a group of electroactive bacteria, EAB) produce power by assimilating these VFA. By this way, two forms of energy may be harnessed, simultaneously along with waste remediation. The performance of BEF was evaluated using DSW (designed synthetic



<sup>\*</sup> Corresponding author. Tel./fax: +91 40 27191765. *E-mail address:* vmohan\_s@yahoo.com (S. Venkata Mohan).

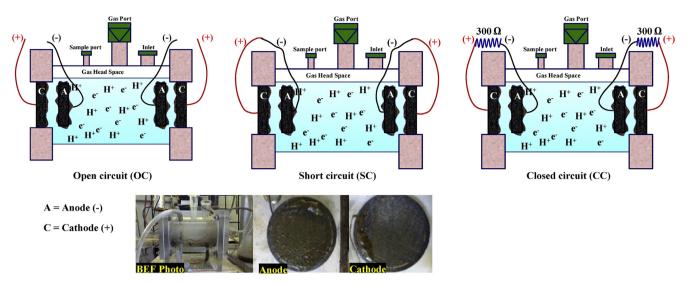


Fig. 1. Designed BEF reactor and different circuitry conditions for wastewater treatment with simultaneous bioelectricity and biohydrogen production.

wastewater) by operating under different circuitry conditions – OC (open circuit), SC (short circuit) and CC (closed circuit) with an external load of 300  $\Omega$ . A control was also operated without electrode assembly. In this study, carbon-electron flux balance was empirically carried out to gain more insights of acidogenic-electrogenic mechanism occurring concurrently during BEF operation.

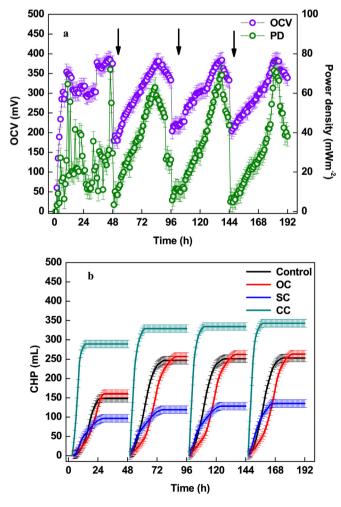
#### 2. Material and methods

#### 2.1. Bio-electrofermentor design

A membrane-less single chambered BEF is made of perspex material with a volume (total/working) of 0.8/0.6 L and gas holding capacity of 0.2 L (Fig. 1). The BEF comprises of two pairs of electrode assemblies on both the sides of BEF wherein each pair of anode and cathode is placed apart by a distance of 1.5 cm. The electrodes are non-catalyzed graphite (5 cm diameter; 1 cm thickness and PSA (projected surface area) of ~30 cm<sup>2</sup>) wherein the anodes submerge in the anolyte completely and the cathodes expose to open air. Analogous setup without electrode assembly is a control.

#### 2.2. Experimental design

Anaerobic consortia of about 10% of working volume was taken as inoculum from an operating UASB (up-flow anaerobic sludge blanket) reactor and was subjected to combined pretreatment to selectively enrich H<sub>2</sub> producers [16]. For all the experiments, DSW is used as feed with following composition (g/l): glucose: 5; NH<sub>4</sub>Cl: 0.5; KH<sub>2</sub>PO<sub>4</sub>: 0.25; K<sub>2</sub>HPO<sub>4</sub>: 0.25; MgCl<sub>2</sub> 6H<sub>2</sub>O: 0.3; FeCl<sub>3</sub>: 0.025; NiSO<sub>4</sub>: 0.016; CoCl<sub>2</sub>: 0.025; ZnCl<sub>2</sub>: 0.0115; CuCl<sub>2</sub>: 0.0105; CaCl<sub>2</sub>: 0.005 and MnCl<sub>2</sub>: 0.015. Use of DSW aids in optimizing influential parameters and improves the understanding of BEF functioning in a better way since; it has all the required macroand micro-nutrients required for specific microbial consortia enrichment. Besides, empirical and stoichiometric parameters may be calculated when known amount of substrate is fed into the BEF and the anticipated products are estimated. Before start-up, pH of the feed is adjusted to  $6 \pm 0.1$  using orthophosphoric acid (10% v/ v) and the experiments are carried out in ambient room temperature (30  $\pm$  2 °C). The reactors are operated in batch mode with a HRT (hydraulic retention time) of 48 h under anaerobic microenvironment. The performance of BEF is evaluated at different operating conditions based on external circuitry connection *viz.*, OC (open circuit), SC (short circuit) and CC (closed circuit) with an external load (300  $\Omega$ ). After operating for several cycles, the best results are graphical represented as an average of triplicate analysis along with standard deviation (±).



**Fig. 2.** a) Bioelectrogenic activity of BEF during open and closed circuitry; (b) cumulative hydrogen production (CHP) in different circuitry modes along with control during the operation period.

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