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Closed circuitry operation influence on microbial electrofermentation: Proton/electron effluxes on electro-fuels productivity

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HIGHLIGHTS

- Novel hybrid reactor for harnessing bioelectricity and biohydrogen simultaneously.
- System buffering was critical factor during acidogenic–electrogenic processes.
- Influence of external resistance over anode potential.
- Voltammograms of closed circuitry operation deciphered electron delivery.

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ABSTRACT

A novel biocatalyzed electrofermentor (BEF) was designed which uncovers the intricate role of biocatalyst involved in cogeneration of electro-fuels (hydrogen and electricity). The specific role of external resistance (R_{ext}, electrical load) on the performance of BEF was evaluated. Four BEFs were operated separately with different resistances (25, 50, 100 and 200 Ω) at an organic load of 5 g/L. Among the tested conditions, external resistance (R_3) with 100 Ω revealed maximum power and cumulative H_2 production (148 mW and 450 mL, respectively). The competence of closed circuitry 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 electro-fuel productivity. Probing of electron kinetics was studied using voltammetric analyses wherein electron transfer by redox proteins was noticed. The designed BEF is found to be sustainable system for harnessing renewable energy through wastewater treatment.

1. Introduction

Currently, global circumstances of water and energy crisis have created a requisite in the research fraternity to capture energy from biological means along with treatment of negative valued waste (Sleutels et al., 2012). Bio-electrochemical system (BES) is recent green technology with multifaceted applications viz., harnessing energy, producing valuable added products, such as hydrogen, ethanol, fatty acids, etc. (Mohan et al., 2014; Chandrasekhar and Mohan, 2012; Cheng et al., 2009). A key advantage of BES is that these products can be generated from renewable waste materials with consequent remediation and lower greenhouse gas emissions compared to the conventional technologies (Mohan et al., 2014). The background work is carried out by the bacterial biocatalyst which has the special ability to efflux electrons to the solid electrode (Lin and Chou, 2004; McLean et al., 2010). Thus, process optimization will progressively enhance the understanding of the interdependence between electrochemical and microbial processes (Patil et al., 2012). Recently, research on BES is more focused on optimizing process parameters towards achieving improved performance with respect to power output and product recovery (Cheng et al., 2009; Huang et al., 2011). Among those parameters, anode potential (E_{anode}) showed significant influence since; it regulates the theoretical energy gain for microorganisms, which closely relates to their growth rate and electron affinity. Regulation of E_{anode} is usually carried out by poising external potential; alternatively, it can also be controlled by applying external resistance (R_{ext}). Studies have reported that amending R_{ext} is more feasible than poising E_{anode}; since, it aids in enriching electroactive bacteria (EAB) for biofilm formation without any external energy input. Changes in microbial composition and biochemical metabolism were also noticed due to the differences in anode affinity and substrate utilization rate. In addition, the

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cellular electron transfer rates responsible for overall biofilm development were affected by applying R_{ext} (Patterson et al., 2011).

Biohydrogen production from BES is a promising green alternative biofuel. Utilizing wastewater as dark fermentative substrate for H_2 production is gaining importance due to the fact that it has dual benefits of H_2 production as well as wastewater treatment (Oh and Logan, 2005). However, a typical acidogenic dark fermentation posses certain process impedes during operation viz., low substrate conversion due to process inhibition by acid-rich compounds (volatile fatty acids, VFA) (Mohan et al., 2007; Pham et al., 2006). These VFA at high concentrations affects the buffer capacity of the system leading to cessation of microbial growth (Mohan et al., 2008a; Mohanakrishna et al., 2010; Srikanth et al., 2009; Zheng and Yu, 2005).

Therefore, different strategies are reported to harness electricity and H_2 production by integrating with wastewater treatment processes (Babu et al., 2013; Mohanakrishna et al., 2010; Srikanth et al., 2009; Venkateswar Reddy et al., 2014). However, the main challenge of combining the two processes is the different microenvironments required by two types of microbial consortia for maximizing energy output. Presence of electrode assembly would increase the rate of hydrolysis of the substrate that paves way for higher energy recovery during the treatment process (Cheng et al., 2009; Mohan et al., 2014; Oh et al., 2010; Patil et al., 2012).

Keeping in view of the contemporary energy scenario, a novel biocatalyzed electrofermentor (BEF) was designed as a hybrid prototype with the functional properties of both MFC and acidogenic fermentation in a single entity (Nikhil et al., 2015). This facilitated a potential synergy between the two processes; since 'acidogens' produce H_2 by fermenting sugars into VFA while 'electrogens' (EAB) produce power by assimilating these VFA. By this way, two forms of energy are harnessed, simultaneously along with waste remediation. The earlier study evaluated BEF at different circuit conditions wherein closed circuit with an external load showed interesting results. Therefore, in the present study, optimization of load was carried out with four different external resistances. The variations in electrochemical and bioprocess parameters were studied to decipher the biocatalyst behavior and electron transfer kinetics involved during power and biohydrogen production.

2. Experimental details

2.1. Experimental setup and reactor operation

Bio-electrochemical fermenter (BEF) with volume (total/working) of 0.8/0.6 L and gas holding capacity of 0.2 L was fabricated using perspex material. A multi-electrode assembly using non-catalyzed graphite plates (4×4 cm; 1 cm thickness with a projected surface area (PSA) of 40 cm^2) was integrated within the BEF. The anode was submerged completely in the anolyte and only one side of the cathode was exposed to open air. Both the electrodes (anode and cathode) were separated with a distance of 1.5 cm without using proton exchange membrane (PEM). The BEF was operated in closed circuitry with different external resistances viz., 25 Ω (R_1), 50 Ω (R_2), 100 Ω (R_3) and 200 Ω (R_4). Analogous system without electrode assembly was designed as control. Anaerobic sludge containing mixed microbial consortia was used as the biocatalyst, which was taken from an operating up-flow anaerobic sludge blanket (UASB) reactor. The mixed microflora was subjected to combined pretreatment to selectively enrich H_2 producers. The resulting enriched pretreated anaerobic mixed culture was used as inoculum (15% v/v of working volume) and designed synthetic wastewater (DSW (g/L): glucose: 5; NH_4Cl: 0.5; KH_2PO_4: 0.25; K_2HPO_4: 0.25; $MgCl_2$ $6H_2O$: 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) as feed to start-up both the reactors (BEF and control). Prior to start-up, pH of the feed was adjusted to 6 ± 0.1 using orthophosphoric acid (10% v/v) and the experiments were carried out in ambient room temperature (29 ± 2 °C). The reactors were operated in batch cycles with a hydraulic retention time (HRT) of 48 h under anaerobic microenvironment. Anolyte of the reactor was continuously re-circulated using a peristaltic pump to prevent substrate gradient.

2.2. Analysis

The performance of BEF was evaluated with different analytical parameters viz., chemical, electrical and electrochemical. The voltage–current (V–I) profile was assessed periodically and the product power ($P = V * I$) was calculated. At steady state, polarization study was carried out using a variable resistor box (30–0.05 kΩ). Further, anode potentials are measured along with relative decrease in anode potential (RDAP). The electron discharge pattern was obtained from various bio-electrochemical analyses viz., cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) using potentiostat–galvanostat system (Autolab-PGSTAT12, Ecochemie, Netherlands). The procedure and optimized parameters for operating bio-electrochemical station was well reported, previously (Raghavulu et al., 2012). For BEF, working electrode is anode and counter is cathode with Ag/AgCl as the reference electrode. The electrochemical kinetics was evaluated by Tafel slope analysis using GPES software (version 4.0). Moreover, chemical analyses such as pH, volatile fatty acids (VFA) and chemical oxygen demand (COD) were carried out according to the standard procedures. System buffering capacity (β) was estimated based on acid–base titrations reported by employing auto-titrator (Mettler Toledo, DL 58). The biohydrogen produced was measured using a H_2 sensor (ATMI GmBH Inc.) and the data was represented as cumulative hydrogen production (CHP), hydrogen production rate (HPR) and specific hydrogen yield (SHY). The bioprocess variation was monitored in terms of dehydrogenase enzyme activity based on reduction of 2,3,5-triphenyltetrazolium chloride (TTC) (Venkateswar Reddy et al., 2014).

3. Results and discussion

3.1. Electrogenesis

3.1.1. Power generation

The bioelectrogenic activity of BEF was monitored continuously in terms of power generation; which showed characteristic variation as a function of different external resistances (R_1–R_4). In control system, no bioelectrogenic activity was observed due to the absence of electrode assembly. During R_3 operated condition voltage (OCV) of 47 mV was observed during the initial phase of operation. A steady increase in OCV was noticed with time and approached a maximum of 147 mV. Maximum current of 0.92 mA (at 100 Ω external resistances) was observed during this phase of operation (Fig. 1). Power produced in R_3 increased gradually from cycle 1 and showed a highest stable power output in the cycle 3 (148.4 mW, 48 h) and thereafter declined till the end of the cycle. The power output in R_1 was noticed to be minimum because of less active biomass and higher extracellular polymeric substance (EPS) content in the biofilm. A maximum power output is obtained when the R_{ext} equals the internal resistance (R_{int}). An incorrect selection of R_{ext}, may lead to large losses in power output (Pinto et al., 2011). It was observed that changing the R_{ext} is more feasible than poising the E_{anode} because it regulates the faster and selective enrichment of the EAB and thereby resulting in maximum bioelectrogenic activity (Mohan et al., 2008b; Srikanth and Mohan, 2012; McLean et al., 2010).