



Composite vegetable waste as renewable resource for bioelectricity generation through non-catalyzed open-air cathode microbial fuel cell

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ARTICLE INFO

Article history:

Received 17 July 2009

Received in revised form 31 August 2009

Accepted 1 September 2009

Available online 8 October 2009

Keywords:

Vegetable-based waste

Dark-fermentation

Anaerobic mixed consortia

Cyclic voltammetry

Substrate degradation

ABSTRACT

Single chambered mediatorless microbial fuel cell (MFC; non-catalyzed electrodes) was operated to evaluate the potential of bioelectricity generation from the treatment of composite waste vegetables (EWW) extract under anaerobic microenvironment using mixed consortia as anodic biocatalyst. The system was operated with designed synthetic wastewater (DSW; 0.98 kg COD/m³-day) during adaptation phase and later shifted to EWW and operated at three substrate load conditions (2.08, 1.39 and 0.70 kg COD/m³-day). Experimental data illustrated the feasibility of bioelectricity generation through the utilization of EWW as substrate in MFC. Higher power output (57.38 mW/m²) was observed especially at lower substrate load. The performance of MFC was characterized based on the polarization behavior, cell potentials, cyclic voltammetric analysis and sustainable resistance. MFC operation also documented to stabilize the waste by effective removal of COD (62.86%), carbohydrates (79.84%) and turbidity (55.12%).

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1. Introduction

A great deal of attention is being paid on bioelectricity generation employing microbial fuel cell (MFC) as an alternative and eco-friendly technology throughout the world and is gaining prominence due to its clean, efficient, and renewable nature (Lovley, 2006; Thygesen et al., 2009; Fu et al., 2009; Venkata Mohan 2008a, 2009a). Anaerobic microorganisms acts as biocatalyst in directly transforming the chemical energy to electrical energy by electrochemical reactions involving bio-chemical process under mild reaction conditions (ambient temperature and pressure) (Li et al., 2008; Huang et al., 2008; Venkata Mohan et al., 2008b,c,d). Recently considerable interest is documented in literature on using wastewater/waste as substrate for harnessing bioelectricity (Ghangrekar and Shinde, 2007; Aldrovandi et al., 2009; Sun et al., 2009; Kim and Chang 2009; Wen et al., 2009; Venkata Mohan et al., 2008b,c,d,e; Venkata Mohan, 2009).

Finding ways to produce useful products from waste has been gaining importance in view of environmental sustainability (Venkata Mohan et al., 2009b). Harnessing bioenergy from the organic matter present in the waste is one of the potential approaches which also accomplishes the simultaneous treatment. MFC enables the energy recovery out of waste while treating, limiting both the energy input and the excess sludge production. Exploiting the waste as a substrate to harness bioelectricity can be considered as sustainable and green approach and therefore reduces the cost

of treatment. MFC technology is both interesting and most promising innovation compared to conventional chemical fuel cells as it requires mild reaction conditions. Moreover, during MFC operation, there exists a possibility to integrate diverse components (biological, physical and chemical) which provides an opportunity to trigger multiple reactions (bio-chemical, physical, physico-chemical, electrochemical oxidation, etc.) cohesively termed as bio-electrochemical reactions occurring as a result of substrate metabolic activity and subsequent secondary reactions (Venkata Mohan et al., 2009a). These process integrations in anodic chamber will also have a definite positive influence on the overall wastewater treatment efficiency.

Vegetable-based composite solid waste available from vegetable markets is considered to have the potential to generate energy due to its higher organic composition and easily biodegradable nature. Huge quantities of these wastes are rich in carbohydrate content and are available throughout the world which can be beneficially used for retrieving energy by means of fermentation. The total amount of vegetable-based waste generated in India is reported to be 40.15% of the municipal solid waste (MSW, 22 × 10⁶ Tons/annum) (Palanichamy et al., 2002) which amounts to 8.83 × 10⁶ Tons/annum. This can generate 1086 kW h of electricity if treated in MFC [calculated based on the assumption of 50% energy conversion efficiency] (Logan, 2009) which accounts for a revenue of about \$109 × 10⁶ per annum (at a rate of \$0.1 per kW h) in the form of clean and renewable energy. Carbohydrate rich wastes such as food processing wastewater (Oh and Logan, 2005), starch processing wastewater (Lu et al., 2009) and chocolate-based wastewater (Patil et al., 2009) has been reported

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Nomenclature

C	charge (C)	OLR	organic loading rate (kg COD/m ³ -day)
CD	current density (mA/m ²)	PD	power density (mW/m ²)
COD	chemical oxygen demand (mg/l)	PEM	proton exchange membrane (Nafion 117)
C _s	COD/carbohydrate/turbidity concentration in outlet	RDAP	relative decrease in anodic potential (%)
C _{SO}	COD/carbohydrate/turbidity concentration in feed	RE	reference electrode (Ag/AgCl)
CV	cyclic voltammetry	SDR	substrate degradation rate (kg COD _R /m ³ -day)
DSW	designed synthetic wastewater	SPY	specific power yield (W/kg COD _R)
e ⁻	electron	UASB	upflow anaerobic sludge blanket reactor
emf	electro motive force (V)	VFA	volatile fatty acids (mg/l)
ECE	energy conversion efficiency (J/kg COD/m ³)	EWV	market-based vegetable waste extract
H ⁺	proton	VSS	volatile suspended solids (mg/l)
J	energy (J)	ξ _{COD}	COD removal efficiency (%)
MFC	microbial fuel cell	ξ _{Turbidity}	turbidity removal efficiency (%)
NTU	nephelometric turbidity units	ξ _{Carbohydrate}	carbohydrate removal efficiency (%)
OCV	open circuit voltage (V)		

in literature in the process of bioelectricity generation. Therefore, an attempt was made in this communication to evaluate the potential of composite vegetable-based waste as substrate to generate bioelectricity along with its stabilization.

2. Experimental methodology

2.1. Vegetable-based waste

The vegetable-based waste was collected from the waste dump yard of local municipal vegetable market. The waste was composite in nature with different kinds of rotten vegetables viz., carrot, tomatoes, cabbage, brinjal, coccinia, potato, okra and beetroot. The composite waste was masticated in electrical food-mixer and the resulting liquid/slurry portion was separated by removing pulp through nylon filter. On an average 12% of pulp was removed from the masticated volume. The resulting extract was used in the experiment after diluting to required amount using tap water. Extracted waste (without pulp) has high concentrations of COD (52.0 g/l) and carbohydrates (14.2 g/l) (Venkata Mohan et al., 2009c).

2.2. Anodic mixed consortia

Anaerobic consortia from operating UASB reactor was used as parent culture (biocatalyst) for inoculating the anodic chamber (Venkata Mohan et al., 2008a). Parent culture was washed thrice (5000 rpm; 20 °C) in saline-phosphate buffer (50 mM) [17.2 mM KH₂PO₄ and 32.8 mM K₂HPO₄ in 0.85% NaCl solution] and enriched in designed synthetic wastewater (DSW) [glucose – 3 g/l, NH₄Cl – 0.5 g/l, KH₂PO₄ – 0.25 g/l, K₂HPO₄ – 0.25 g/l, FeCl₃ – 0.025 g/l, NiSO₄ – 0.016 g/l, MgCl₂ – 0.3 g/l, CoCl₂ – 25 mg/l, ZnCl₂ – 11.5 mg/l, CuCl₂ – 10.5 mg/l, CaCl₂ – 5 mg/l, MnCl₂ – 15 mg/l, and chemical oxygen demand (COD) – 3.2 g/l] at pH 7.0 under anaerobic conditions.

2.3. MFC configuration

Single chambered MFC (open-air cathode) was fabricated in laboratory using 'perspex' material. Anodic compartment of MFC was designed to have a total volume of 0.55 l (working volume 0.43 l). Non-catalyzed graphite plates (5 × 5 cm; 10 mm thick; surface area of 70 cm²) were used as electrodes. Prior to use electrodes were soaked in deionized water for overnight. Pre-treated PEM (Nafion 117; Sigma–Aldrich) was attached to bottom side of the

cathode. Top portion of the cathode was exposed to air while bottom portion was fixed to PEM and was in contact with wastewater. Both sides of the anode were submerged completely in the anolyte. Provisions were made in the design for inlet and outlet, sampling, wire input points (top), gas outlet, etc. Leak proof sealing was provided at the joints to maintain anaerobic microenvironment in the anode compartment and sealed carefully by epoxy sealant.

2.4. Operation

Prior to startup, the anodic chamber was inoculated with anaerobic mixed microflora (VSS, 3.6 g/l) by dissolving in DSW (0.5 l) at OLR of 0.98 kg COD/m³-day. After two cycles of operation the reactor was fed with three OLRs of the EWV (OLRs 2.08, 1.39, 0.7 kg COD/m³-day) and each OLR was operated for three cycles. The HRT was maintained for 96 h. Prior to feeding of the wastewater, the pH was adjusted to 7 using concentrated orthophosphoric acid (88%) or 1 N NaOH. Wastewater was fed to MFC from the inlet provided at the bottom of anode chamber to facilitate flow in upward direction passing through anode towards cathode. MFC was operated in fed-batch mode at room temperature (29 ± 2 °C). Anolyte was continuously re-circulated (0.32 l/h) in the same direction of flow to eliminate the concentration gradient formation during operation. Before every feeding event, inoculum was allowed to settle down (30 min) and exhausted feed (0.43 l) was removed (15 min) under anaerobic conditions. Settled inoculum (~50 ml by volume) was used for subsequent operations. Feeding, decanting, and recirculation operations were performed using peristaltic pumps controlled by electronic timer.

2.5. Bio-electrochemical analysis

Current output and substrate degradation rate (SDR) were considered as the two key parameters to evaluate the performance of MFC during operation. Potential difference/open circuit voltage (V) and current (I) (in series; 100 Ω) measurements were recorded using auto-range digital multi-meter. Power (mW) was calculated using $P = IV$. Current density (mA/m²) and power density (mW/m²) were calculated by dividing the obtained current and power with the surface area (m²) of the anode. Bio-electrochemical behavior of MFC during electricity generation was studied *in situ* by CV using potentiostat-galvanostat system (Autolab, PGSTAT12, Ecochemie) linked to a microcomputer data acquisition system during stabilized phase of operation. CV was performed by applying a potential ramp at a scan rate of 30 mV/s over the potential range from +0.5 to -0.5 V to working electrode (anode of MFC; graphite) against

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