Bioelectrogenesis from Raw Algal Biomass Through Microbial Fuel Cells: Effect of Acetate as Co-substrate

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Abstract Algae are autotrophic organisms that are widespread in water bodies. Increased pollution in water bodies leads to eutrophication. However, algae growing in lakes undergoing eutrophication could be utilized towards the generation of added-value bio-electricity using microbial fuel cells (MFCs). In the present study, two methods of electricity generation using raw algae (RA) and RA + acetate (AC) as co-substrate were analyzed in single chamber air cathode MFCs. MFCs supplemented with RA and RA + AC clearly showed higher power density, greater current generation, and improved COD (chemical oxygen demand) removal, which demonstrated the feasibility of using AC as substrate for MFC. The MFC–RA + AC (0.48 mA) generated 28% higher current relative to that generated by MFC with RA alone. Notably, the maximum power densities generated by MFC–RA and MFC–RA + AC were 230 and 410 mW/m², respectively. MFC–RA and MFC–RA + AC exhibited TCOD (total chemical oxygen reduction) removal values of 77% and 86.6%, respectively. Despite the high influent TCOD (758 mg/l) concentration, the MFC–RA + AC exhibited an 8.5% higher COD removal relative to that of MFC–RA (525 mg/l). Our current findings demonstrated effective energy generation using algae biomass with a co-substrate.

Keywords Algae · Co-substrate · Microbial fuel cell · Voltage · Power density

Introduction

Recent years have witnessed a worldwide surge in energy demand and depletion in fossil fuels [1]. As a result, various efforts have been made for the production of alternative fuels that are sustainable and cost-effective. Microbial fuel cells (MFCs) have gained considerable research attention to produce energy in the form of bio-electricity based on the degradation of organic materials present in wastewater or in waste biomass [2]. MFCs are bioelectrochemical systems that convert chemical into electrical energy by bacteria as biocatalysts on anode electrodes. A typical MFC consists of an anode and cathode, wherein oxidation and reduction reactions occur, respectively. In the anode, bacterial biofilms oxidize the organic matter and generate protons and electrons. The protons diffuse towards the cathode through a separator or a proton exchange membrane, whereas the electrons are transferred by an external circuit. In the cathode, the electron and protons are combined with oxygen (electron acceptor) to generate electricity [3]. For the past few years, the use of different types of simple substrates in the anodes of MFCs, such as acetate, glucose, pentoses, phenol, cysteine, and alcohols, has been explored for promoting efficient microbial growth [4, 5]. These organics can be economically unviable for long-term and commercial applications. Alternatively, various wastewaters ranging from low biodegradable to recalcitrant wastewaters produced from several types of industries and domestic origins were additionally tested as substrates for improving the economics of the bioelectricity and simultaneous waste

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remediation [4, 6]. However, the use of wastewaters has some limitations, such as incomplete degradation of organics, strong methanogenic activity, diffusion of ions to the cathode, and aerobic growth of microbes [7]. Furthermore, several other processes have been explored for improving power generation and waste remediation. Therefore, there is a need to identify novel substrates and develop MFCs as highly efficient technologies to increase power generation [4].

Microalgae comprise a large amount of biomass that are found in polluted lakes and exhibit huge potential in providing energy via the treatment of microalgae from water bodies. Therefore, the use of microalgae as substrates in anode of a MFC can enable low-cost generation of electricity. Moreover, algae are a major cause of eutrophication in several lakes, and large deposits of algal residues are usually present in wastewater treatment systems [8]. These algal residues are often released to sewage systems without pre-treatment, thereby leading to increased pollution load in downstream wastewater treatment. Hence, algal residues should be removed before discharging the water into the environment [9]. As a result, several studies have evaluated the use of microalgae as substrates in MFC operations. However, these studies are limited to the powdered form of algae, dried algae, and pre-treatment algae [10–12]. Therefore, further studies should explore the use of raw algae (RA) that are directly acquired from water bodies. The present study evaluated the use of raw algae collected from wastewater as substrates in MFCs. Furthermore, we evaluated the effect of combining raw algae with acetate as co-substrate relative to raw algae alone on electricity generation. Considering that acetate has been identified as an optimal substrate for bioelectrogenesis, acetate supplementation of raw algae could improve process efficiency. Performance evaluation was analyzed in terms of current generation, power density generation, and substrate degradation rate/efficiency.

Materials and Methods

MFC Inoculum and Algae Culture Development

Wastewater collected from a local wastewater treatment plant was used as inocula for electrogenic bacterial biofilm development in the anode and for producing the required mixed microalgal culture. The microalgae were isolated by illuminating the collected wastewater for a few days in the laboratory in a 3-L conical flask. Collected algae were supplemented with bold basal media (BBM) to promote algal growth [13]. In the BBM, microalgae were grown with a light intensity of 1600 l with filtered air to provide carbon dioxide (CO₂). [13]. The fully developed algal

biomass determined based on color development was harvested after 30 days of incubation by settling and filtering the BBM media with Whatman filter paper. Filtered raw algae were centrifuged and collected in pellet form. The microalgal pellet (0.4 g/L) was mixed with 20 ml of 100 mM phosphate buffer and used as a substrate in the MFCs.

MFC Assembly and Operation

Two similar single-chamber air cathode MFC reactors were operated, each having total and working volumes of 28 and 20 ml, respectively. The MFC reactor, operated with 0.4 g/L raw algae, was designated as MFC-RA, whereas the second MFC, which contained RA (0.4 g/L) supplemented with acetate (0.3 g/L), was designated as MFC-RA + AC. The plain graphite felt and platinum (0.5 mg/cm²)-coated carbon cloth served as the anode and cathode electrodes, respectively. Both electrodes were placed on opposite sides of the MFC. The anode and cathode chambers were partitioned by pre-treated proton exchange membrane [14]. Both MFCs were operated in a closed circuit with 1 K Ω as an external resistor. Both reactors were sealed with end plates to support the cathode and minimize the diffusion of oxygen from the cathode to the anode. All experiments were carried out in repeated cycles and used as replicates. Liquid samples collected from the MFCs were analyzed for total chemical oxygen demand (TCOD) and soluble COD (SCOD) concentration by Standard APHA Methods [15].

Analysis and Calculations

Voltage (V) generation was recorded across the external resistance of 1 K Ω using a digital multimeter. Polarization analysis was conducted by recording the current density and power density at varying external resistances from 30 K Ω to 10 Ω using a resistance box connected to each MFC. Voltage was calculated using Ohms law ($I = V/R$), and power was calculated by using the formula $P = I \times V$ [14]. The current density (mA/m²) and power density (mW/m²) were calculated based on the cathode surface area (7.05 cm²). The internal resistance (R_{in}) was calculated based on the I versus V curve of polarization [16].

During stable voltage generation, the MFCs were subjected to a turnover cyclic voltammetry (CV) analysis in a two-electrode system on a Bio-logic SP150 potentiostat (Bio-Logic Science Instruments, France). CV was carried out within a potential window of -1.0 to 1.0 V versus open circuit voltage (OCV) at a scan rate of 10 mV/s. The anode was connected as a working electrode, whereas the cathode served as both the counter and reference electrodes. The coulombic efficiency (CE%), TCOD, and

SCOD were calculated as previously described [15, 17, 18].

Results and Discussion

Current Generation from the RA and RA + AC MFCs

After the adaptation of MFC for 20 days, the system was able to generate a repeatable and stable voltage (Fig. 1). During initialization of the MFCs, RA and RA + AC in wastewater generated maximum current values of 0.28 ± 0.03 and 0.35 ± 0.02 mA, respectively. After recording the stable current generated, the wastewater media were replaced with buffer solution. MFC operation with RA with 1 K Ω of external resistance produced maximum current and OCV values of 0.36 ± 0.04 mA and 0.68 ± 0.02 V, respectively. For the MFC with acetate combined with raw algae, the maximum current and OCV values were higher by 13% (0.48 ± 0.04 mA) and 18% (0.82 ± 0.03 V), respectively. In both MFCs, the buffer solution along with substrate (RA and RA + AC) were replaced when the generated current decreased to < 0.18 mA. The observed difference in current generation between the MFC with RA and MFC with RA + AC could be explained by the difference in bacterial growth conditions/metabolism as a result of acetate supplementation. The average voltage generated from the MFC with RA + AC was found to be 2.0- and 1.2-fold higher compared to those reported in previous studies on MFCs that employed thermal treatment (0.24 mA) and sonication (0.40 mA) during pre-treatment of the algal biomass [11]. In repeated loading cycles, the current generation was found to be stable without any lag phase, thereby suggesting that the

use of simple carbon compounds, such as an acetate, could enhance power generation in MFCs [19].

Power Density from Polarization Analysis

The power density values generated using RA and RA + AC were recorded by varying the external resistance. The maximum power densities (PDs) of the MFCs with RA and RA + AC were determined to be 230 and 410 mW/m², respectively. For both MFCs, the maximum PD values were generated at a current density of 0.8 A/m² (Fig. 2). These power densities were found to be comparable with those reported in other studies on MFC systems using algal biomass subjected to alkaline pre-treatment (311 mW/m²) [11]. However, these values were lower than those obtained using algae biomass pre-treated via sonication, which was reported to produce 560 mW/m² [12]. This difference in power density could be attributed to many factors, such as differences in the algae used, pre-treatment, substrate concentration, electrode size, and internal resistance [20]. The maximum power density obtained in the present study using acetate as co-substrate (RA + AC) was 41 times higher compared to that obtained from MFC operation using dairy wastewater (10 mW/m²) [18]. Based on polarization analysis using the I–V curve, the maximum R_{in} of the MFC–RA + AC and MFC–RA were determined to be 280 and 325 Ω , respectively [16].

COD Reduction in the Anode of MFC

Substrate degradation in both MFCs were analyzed and presented graphically in Fig. 3. The TCOD and SCOD concentrations varied with changes in operational time. In the MFC–RA, the initial TCOD concentration of 525 mg/l was reduced to 120 mg/l, which is equivalent to a removal

Fig. 1 Current generation in Microbial fuel Cells using: (1) raw algae (RA; ■, black-filled squares), and (2) raw algae and acetate (RA + AC) co-substrates (●, red-filled circles) (color figure online)

Fig. 2 Voltage and power density generation in the Microbial fuel Cells during polarization analysis. Voltage-RA (■, black-filled squares), Voltage-RA + AC (●, red-filled circles), Power density-RA (▲, blue-filled up triangles), and Power density-RA + AC (▼, magenta-filled down triangles) (color figure online)

Fig. 3 Chemical oxygen demand reduction (Total COD and Soluble COD) noted in Microbial Fuel Cells as a function of time. T-COD-RA (■, black-filled squares), T-COD-RA + AC (●, red-filled circles), SCOD-RA (▲, blue-filled up triangles), and SCOD-RA + AC (▼, magenta-filled down triangles) (color figure online)

efficiency of 77% after 6 days of operation. Within the same operational period, the SCOD decreased from 258 to 51.2 mg/l with a removal efficiency of 80.2%. MFC operation with RA + AC produced initial SCOD and TCOD concentrations of 403 and 758 mg/l, respectively. These values were reduced to 42 (SCOD) and 101 mg/l (TCOD), with removal efficiencies of 89.4% and 86.6%, respectively. Despite the increase in the influent TCOD concentrations of MFC-RA + AC, we observed an 8.5% decrease in COD relative to that of MFC-RA. The above findings suggested that the use of acetate as co-substrate could improve COD reduction and energy generation.

On the basis of SCOD reduction, the CE values of MFC-RA and MFC-RA + AC were determined to be 19% and 26%, respectively. The CE of MFC-RA + AC was similar to those reported in other studies on MFCs using pre-treated algae as a biomass (23–28%) [10]. During the MFC operation with RA and RA + AC, the initial pH of 7.02 decreased to 6.1 ± 0.3 and 6.6 ± 0.2 , respectively. The reduction in pH with the MFC using RA alone can limit bacterial metabolic activity and can reduce the anode performance of MFC.

Cyclic Voltammetry (CV) Analysis of MFCs with RA and RA + AC

The electrochemical CV analysis was employed to investigate the electrochemical response of electrogenic biocatalyst [21]. The MFC with RA + AC exhibited improved redox current generation compared to the MFC with RA alone (Fig. 4). Marked differences were observed in terms of current generation and electron movement in forward and reverse sweep of CV analysis. The MFC with RA alone showed 61% (0.009 mA) lower oxidative current generation compared to the MFC with RA + AC

Fig. 4 Electrochemical (CV) response during operation of the Microbial Fuel Cells with: (1) RA (—, black solid line) and (2) RA + AC (·····, red dotted line) as substrate for electricity generation (color figure online)

(0.017 mA). The reductive current generation of the MFCs with RA and RA + AC were determined to be -0.011 and -0.047 mA, respectively. The larger difference in terms of redox current generation with the MFC with RA + AC suggested enhanced electrogenic biocatalytic growth in the anode [22, 23]. The results of CV analysis for the MFC with RA + AC as substrate were consistent with the results of current generation and polarization experiments.

Conclusion

Our findings suggested that the use of acetate as a co-substrate added to raw algae acquired from water bodies could improve MFC efficiency. The performance of the MFC with raw algae and acetate as co-substrate was like that observed from the MFC operated using pre-treated algal biomass. The MFC-RA + AC showed 8% higher TCOD removal compared to MFC-RA alone. Further studies are required to precisely evaluate the economics of electricity generation based on raw algae with co-substrate for feasible upscaling of the process and simultaneous control on eutrophication of water bodies.

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