Journal of Hazardous Materials 187 (2011) 591–595

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Short communication

Bioelectricity generation and microcystins removal in a blue-green algae powered microbial fuel cell

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ARTICLE INFO

Article history:
Received 7 April 2010
Received in revised form 20 July 2010
Accepted 11 January 2011
Available online 18 January 2011

Keywords:
Blue-green algae
Microbial fuel cell
Microcystin
Bioelectricity

ABSTRACT

Bioelectricity production from blue-green algae was examined in a single chamber tubular microbial fuel cell (MFC). The blue-green algae powered MFC produced a maximum power density of 114 mW/m^2 at a current density of 0.55 mA/m^2. Coupled with the bioenergy generation, high removal efficiencies of chemical oxygen demand (COD) and nitrogen were also achieved in MFCs. Over 78.9% of total chemical oxygen demand (TCOD), 80.0% of soluble chemical oxygen demand (SCOD), 91.0% of total nitrogen (total-N) and 96.8% ammonium–nitrogen (NH_3–N) were removed under closed circuit conditions in 12 days, which were much more effective than those under open circuit and anaerobic reactor conditions. Most importantly, the MFC showed great ability to remove microcystins released from blue-green algae. Over 90.7% of MC-RR and 91.1% of MC-LR were removed under closed circuit conditions (500 Ω). This study showed that the MFC could provide a potential means for electricity production from blue-green algae coupling algae toxins removal.

1. Introduction

Blue-green algae, technically termed as cyanobacteria, are omnipresent microorganisms found in various water bodies throughout the world. As they bloom, they can discolor the water or produce floating rafts or scums on the water surface, resulting in the production of taste-and-odor compounds that cause malodorous or unpalatable drinking water [1]. Moreover, some blue-green algae contain potent toxins that could pose a health risk to people and animals [2]. Thus, the effective methods for regulating the occurrence of cyanobacteria and removing their toxic metabolites are especially important to save healthy water environments. On the other hand, blue-green algae contain high levels of proteins, carbohydrates and lipids, representing a very important biomass for energy products. For example, some blue-green algae have been used as raw materials for producing bio-oil, methane, methanol, and hydrogen [3–5]. However, the fuels produced from blue-green algae must be stored, transported and further processed to produce electricity, which will obviously increase the cost of energy production.

Microbial fuel cells (MFCs), which are devices that convert organic substrates into electricity with the aid of microorganisms as catalysts, are considered to be a promising sustainable technology to meet increasing energy needs [6,7]. Due to the complexity of anodic biofilms, there exists a possibility to integrate diverse components which provide an opportunity to trigger multiple reactions such as bio-chemical, physical or electrochemical oxidations, in the anodic compartments of MFCs [8]. As a result, MFCs are capable of producing electricity from complex substrates and even particulate organic matter derived from biomass. For example, Reimers et al. tested the possibility of generating electricity from marine plankton in two-chamber MFCs [9]. They reported that ca. 80% of particulate organic carbon was removed within 57-d MFC operation and a maximum power density of 17.2 mW/m^2 was harvested at the same time. Velasquez-Orta et al. found that the MFCs using *Chlorella vulgaris* and *Ulva lactuca* as substrates produced maximum power densities of 980 and 760 mW/m^2, respectively [10]. However, the direct production of electric power has not been previously shown from an MFC device using blue-green algae.

In this study, we evaluated the feasibility of using blue-green algae as the substrates for electricity generation in a single-chamber MFC equipped with cloth cathode assembly. Coupled with the bioelectricity generation, the changes in concentrations and removal efficiencies of TCOD, SCOD, total-N and NH_3–N were monitored in the MFCs under a fed-batch mode. Meanwhile, investigations of the removal efficiencies for microcystins were carried out in the MFC reactors under open and closed circuit conditions and an anaerobic reactor. Finally, cyclic voltammogram was

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doi:10.1016/j.jhazmat.2011.01.042

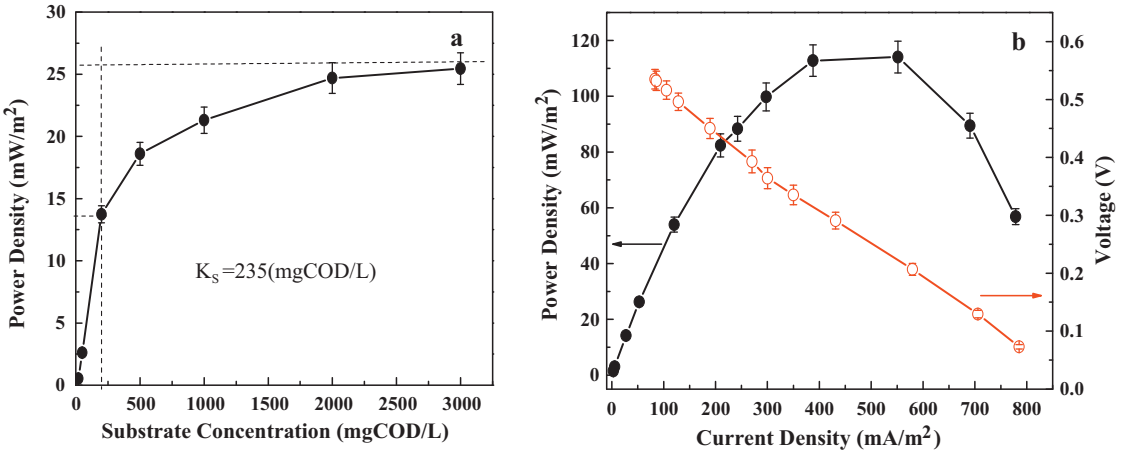

Fig. 1. Power densities as a function of initial blue-green algae concentrations (a), and power density vs. current density curve (b).

performed to characterize the anodic biofilm of the blue-green algae-fed MFCs.

2. Materials and methods

2.1. MFC assemblies and operation

A single-chamber tubular MFC was similarly constructed as previously described [11]. The tubular MFC was built with a 0.2 cm-thick polyvinyl chloride (PVC) plastic tube (23.0 cm long by 4.6 cm in diameter). Graphite felt as roll form was nested inside the chamber as the anode. The empty bed volume (i.e., liquid volume) of the reactor was 170 mL. The cathode consisted of a cloth cathode assembly (CCA) structure fabricated as reported by Zhuang et al. with a projected surface area of 187.5 cm^2 [11]. The catalyst loading of MnO_2 was 5.0 ± 0.1 mg cm^{-2}.

MFC reactors were inoculated using a pre-acclimated microbial community from another MFC that was initially inoculated with anaerobic sludge collected from local wastewater treatment plant (Liede wastewater treatment plant, Guangzhou, China) and was running in the fed-batch mode over 12 months by feeding domestic wastewater. The cell voltage output across the external load was monitored by a 16-channel voltage collection instrument (AD8223, China). All MFCs were operated in fed-batch mode at a fixed external resistance of 500 Ω (unless otherwise stated). To obtain polarization and power density curves as a function of current density, the external resistance was varied from 5 to 10,000 Ω when the voltage output approached the steady-state. At each resistance the steady-state voltage was recorded, and the current was calculated as $I = U/R$, or the current density normalized by the cathode surface area, where U is the measured voltage, R is the external resistance. The polarization curve was obtained by plotting voltage vs. current density. The power density was calculated from the measured voltage as $P = U^2/RA$, where A (cm^2) is the projected cathode surface area. The blue-green algae were sampled from the Taihu Lake located in Anhui province of China. The blue-green algae had total suspended solids (TSS) content of 0.91%, volatile suspended solids (VSS) content of 0.79%, ash content of 0.12%, pH 6.15, total chemical oxygen demand (TCOD) of 14050 mg L^{-1}, soluble chemical oxygen demand (SCOD) of 3100 mg L^{-1}. The diluted blue-green algae with various concentrations were amended with NaCl to maintain a constant ionic conductivity, and then filled to the anodic compartment of an MFC. As a control, anaerobic reactors were constructed similarly to that reported by Velasquez-Orta et al. [10], by sealing the MFC reactor in a plastic container. All reactors were conducted at least in duplicate at 30 ± 1 °C in a temperature-controlled chamber.

2.2. Electrochemical measurements

Cyclic voltammetries were carried out in a conventional three-electrode cell using CHI660A system (CH Instruments, Inc.). The anode of MFC was used as the working electrode and the reference electrode was an Ag/AgCl, while the cathode of MFC served as the counter electrode. The potentials were applied from −0.6 V to +0.6 V (vs. Ag/AgCl) at a scan rate of 1 mV/s with continuous monitoring of the current response.

2.3. Analyses

TSS and VSS of blue-green algae were determined at 105 °C (4 h) and 550 °C (2 h) with the standard methods [12], respectively. TCOD and SCOD were measured by the COD Digital reactor block (DRB200, HACH, USA) equipped with a spectrophotometer (DR2700, HACH, USA). NH_3–N and total nitrogen (total-N) were determined through the Hach test kits with a UV–vis Spectrophotometer (S53, China). Microcystins were measured using a HPLC (Shimadzu, Japan) equipped with a UV detector. Every set of assays was performed in duplicate, and the reported data were averaged.

3. Results and discussion

3.1. Bioelectricity generated from blue-green algae-MFC

Maximum power density increased with substrate concentration until reaching a plateau (Fig. 1a), which was in accordance with those using pure substrates such as acetate and glucose in an MFC. The half-saturation concentration (K_s) was 235 mg COD/L. When a saturating substrate concentration was fixed at around 1113 mg COD/L, a maximum power density of 114 mW/m^2 was achieved at a current density of 550 mA/m^2 (Fig. 1b). According to the linear fit of the polarization curve, the internal resistance was determined to be 31 Ω. Open circuit potential (OCP) of blue-green algae-fed MFC was 0.58 V. A Coulombic efficiency of 28.2% was achieved at the blue-green algae concentration of 1113 mg COD/L at 500 Ω loading. Experimental data illustrated the feasibility and sustainability of using blue-green algae as anodic substrate in MFC for bioelectricity generation. Microorganisms presented in anodic chamber served as biocatalysts and converted the energy stored in the chemical bonds of blue-green algae into electrical energy. It was worth noting that the maximum power density produced from blue-green algae was even higher than that obtained using brewery wastewater (86 mW/m^2) in the same reactor configuration, but lower than that obtained from glucose (172 mW/m^2) [11,13]. The

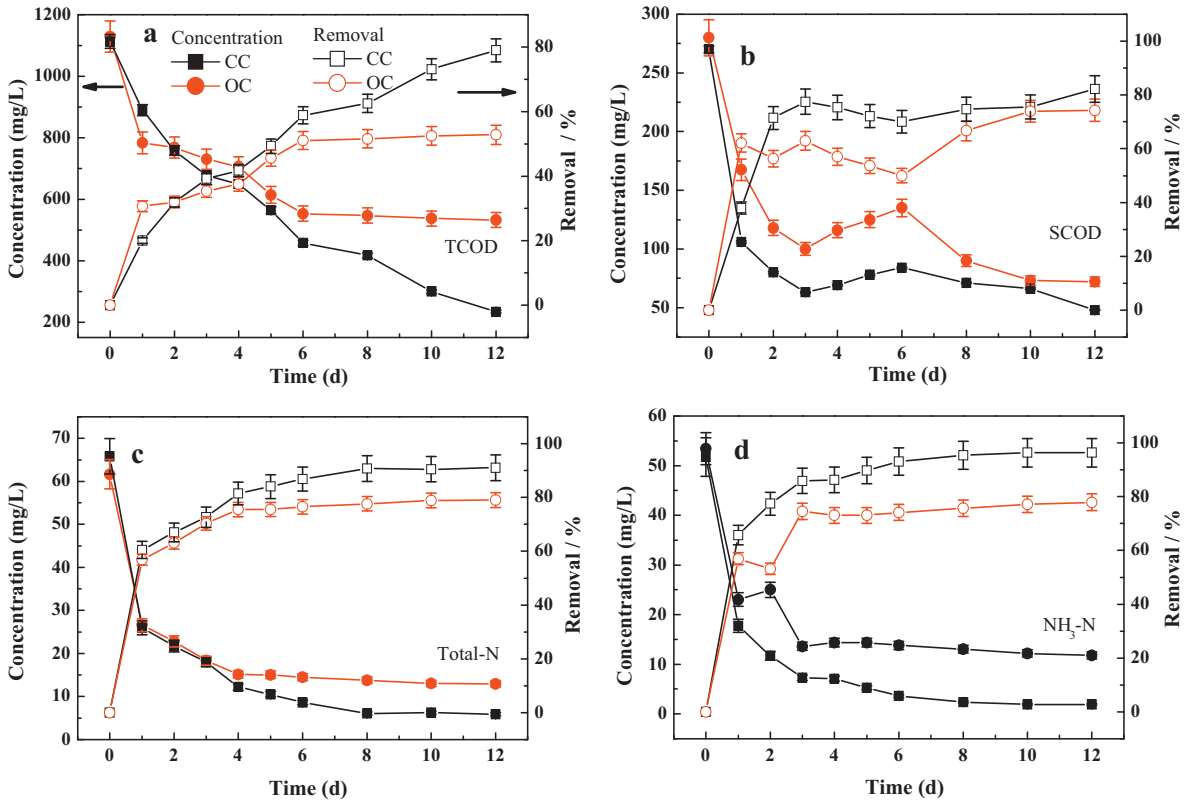

Fig. 2. TCOD (a), SCOD (b), total-N (c) and NH_3–N (d) concentration changes (solid symbols) and removal (open symbols) vs. time curves in MFCs at closed circuit (CC, square) and open circuit (OC, circle).

differences in power generation were perhaps due to the complexity of the substrates. MFCs fueled with a simple substrate such as glucose typically exhibit higher efficiencies than those fueled by more complex substrates due to the resistance of organic fractions to microbial degradation and the conversion of other organic fractions to degradation products without electrons being passed to the fuel cell [14]. The differences in power generation were also possibly resulted from the diversity in communities of anode biofilms enriched with different electron donors [15].

3.2. Blue-green algae decomposition

MFC documented effective substrate degradation apart from power generation (Fig. 2). During MFC operation with diluted blue-green algae, TCOD decreased from 1113 to 234 mg TCOD/L in 12 days, representing a 78.9% of TCOD removal efficiency and a 73.24 mg TCOD/L-day of substrate degradation rate. They were obviously higher than those under open circuit conditions (52.8% of TCOD removal and 49.7 mg TCOD/L-day of degradation rate) (Fig. 2a) and also much higher than that under anaerobic reactors with only 15% of TCOD removal within 12 days (Fig. 3). As seen in Fig. 2b, the similar trend was also observed for SCOD. At the same time, the power generation from blue-green algae in MFCs coupled with high nitrogen removals (Fig. 2c and d). The concentration of total-N was decreased from 65.8 mg/L to 5.9 mg/L and the NH_3–N was decreased from 51.7 mg/L to 1.9 mg/L, showing an accelerated decomposition rate under closed circuit condition compared to open circuit condition. The removal efficiencies for total-N and NH_3–N were 91.0% and 96.8%, respectively. It has been already known that electrical energy could be produced from proteins which contain high level of nitrogen due to the presence of amino group in protein chains and even directly from ammonium as previous reported by Heilmann and Logan [16] and He et al. [17]. It was highly possible that the proteins or ammonium presented in blue-green algae had been contributed to the current generation, which led to a decrease in total-N and NH_3–N.

3.3. Microcystins removal

Blue-green algae blooms can have negative aesthetic and economic impacts, but the primary cause for concern is that they often produce potent hepatotoxins and neurotoxins which have been linked to severe illness and death in animals and humans. Microcystins, the cyclic heptapeptide toxins, are the naturally produced poisons stored in the cells of certain species of blue-green algae. These toxins are usually released into water when the cells rupture

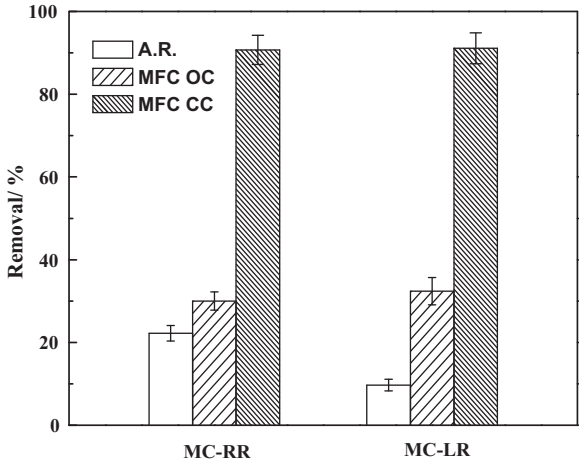

Fig. 3. Comparison of organic removal in MFCs at closed circuit (CC), open circuit (OC) and anaerobic reactors (A.R.) on the basis of MC-RR and MC-LR.

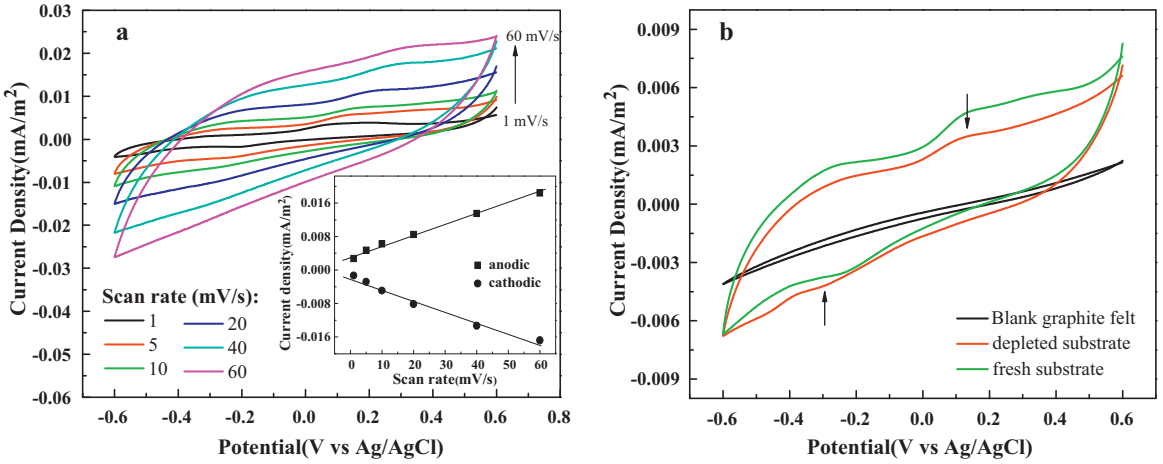

Fig. 4. CVs of anodic biofilm with substrate depletion at various scan rates: 1, 5, 10, 20, 40, and 60 mV/s (inset: anodic (square symbols) and cathodic (circle symbols) peak currents vs. scan rates) (a), and CVs of blank graphite felt and anodic biofilm at 5 mV/s (depleted and fresh substrate) (b).

or die and have caused several toxic incidents involving the death of people [18]. The major contributing factor to death of human was intravenous exposure to microcystin-RR (MC-RR), -LR (MC-LR), and -AR. Therefore, it is very important to investigate effective methods that can reduce the human's risk of microcystins exposure. However, many conventional water treatment technologies (e.g. coagulation, flocculation, sedimentation, and filtration) have been reported to be ineffective for removing them [19,20]. Within 12 days, MC-RR and MC-LR had 90.7% and 91.1% of removal efficiencies under closed circuit conditions in the MFCs, respectively, which are apparently higher than those under open circuit conditions (30.0% and 32.4%) and anaerobic reactors (22.2% and 9.7%) as shown in Fig. 3. These data indicated that MFC was a very effective technique for microcystins removal with a complete circuit. Under closed circuit conditions, electrons are collected by the anode and subsequently consumed by oxygen in an air-cathode MFC, which have been previously proved to be a more favorable pathway for the degradation of some contaminants than those using amended chemicals (i.e. nitrate and sulfate) as electron acceptors [21]. One previous study reported that microcystins could be more effectively biodegraded by indigenous microorganisms in the sediment coupling dissimilative nitrate reduction at anoxic conditions than that using oxygen as the electron acceptors at oxic conditions [22]. Probably for the same reason, the anode provided a more favorable electron pathway for the decomposition of microcystins under closed circuit conditions than that used oxygen as the electron acceptor under open circuit conditions. In addition, the obviously low microcystins removal obtained under an anaerobic condition without electron acceptor amendments further suggested the importance of a favored electron acceptor for the efficient biodegradation of microcystins. To better understand the biodegradation pathway and mechanism of microcystins, the dynamic behavior of microcystins biodegradation in MFCs is currently being studied.

3.4. Electrochemical behavior of anodic biofilm

Electrochemical behavior of MFC with blue-green algae was evaluated by using CVs. In the substrate depleted anodic solution, an oxidation peak was found at +0.14 V (vs. Ag/AgCl) in the forward scan and a reduction peak was found at −0.30 V (vs. Ag/AgCl) in the reverse scan (Fig. 4). By varying the scan rate, both anodic and cathodic peak currents were proportional to the scan rates, indicating a typical surface-controlled electrochemical process that represented the redox behavior of the electrochemical active bacteria in the anodic biofilm (Fig. 4a, inset). No clear redox couples were observed when a new carbon felt was used as the working electrode with the same anodic electrolyte (Fig. 4b). Accordingly, when the substrate depleted anodic solution was replaced by a fresh one in the MFC, the oxidation peak currents on CV had been increased, which demonstrated that the bio-oxidation of blue-green algae catalyzed by anodic biofilm was responsible for the current generation in this bioelectrochemical system.

4. Conclusion

In this study, blue-green algae were demonstrated to be effective energy sources for bioelectricity generation in a single-chamber tubular MFC. The maximum power density of 114 mW/m^2 was yielded at a blue-green algae concentration of 1113 mg COD/L. In addition to electricity generation, promising removal efficiencies of COD, total-N, and NH_3–N were obtained in the blue-green algae-fed MFC. Meanwhile, high removal efficiencies of microcystins (MC-RR and MC-LR) were also achieved. These results show that MFCs may offer the potential as a new technology to simultaneously produce bioelectricity from blue-green algae and remediate the blue-green algae contaminated environments.

Acknowledgements

This study was supported jointly by The 863 Program of China (2009AA05Z115), Guangdong Provincial Science–Technology Project (No. 2008A080800028 and 2009A080303005) and Guangdong education university–industry cooperation projects (2006D90704001).

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