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Characteristic changes in algal organic matter derived from *Microcystis aeruginosa* in microbial fuel cells

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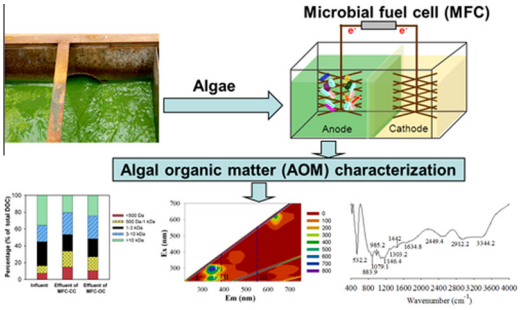
HIGHLIGHTS

- Algal organic matter (AOM) was degraded in microbial fuel cells (MFCs).
- AOM degradation was more completely by MFC than by fermentation.
- Changes in AOM compositions and structures during MFC treatment were characterized.
- Several different methods are used in AOM characterization.

GRAPHICAL ABSTRACT



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ABSTRACT

The objective of this study was to investigate behavior of algal organic matter (AOM) during bioelectrochemical oxidation in microbial fuel cell in terms of compositions and structures. Study revealed that the AOM derived from blue-green algae *Microcystis aeruginosa* could be degraded more completely (82% COD removal) in microbial fuel cells (MFCs) than by anaerobic fermentation (24% COD removal) in a control reactor without closed-circuit electrode and electricity was produced simultaneously. A variety of techniques were used to characterize the changes in AOM compositions and structures during bioelectrochemical oxidation. The presence of syntrophic interactions between electrochemical active bacteria and fermentative bacteria to degrade large molecular organics into small molecular substances, which could be oxidized by electrode but not by fermentation. The dominant tryptophan protein-like substances, humic acid-like substances and Chlorophyll *a* in AOM were highly degraded during MFC treatment.

1. Introduction

Algae, being rich in lipid, protein and carbohydrate, is considered as a promising biomass energy due to its high growth rates, round year production, high bio-fuel yields, small occupied space, and other benefits (e.g. CO_2 capture, wastewater nutrients removal) (Mata et al., 2010; Scott et al., 2010). To date, algal biomass has been mainly used to produce bio-fuels (e.g. bio-diesel and bio-ethanol), methane, and hydrogen via various physical, chemical and biological methods (Chisti, 2007; Hirano et al., 1998; John et al., 2011; Nath and Das, 2004; Singh and Gu, 2010).

Microbial fuel cells (MFCs) can directly generate electricity by oxidizing organic compounds with the help of bacterial electrochemical reactions (Logan et al., 2006). Many new technologies have recently emerged by integrating MFC with algae for renewable energy production and wastewater treatment. First, algae

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biomass including living cell, dry mass, algae residue produced from other water/wastewater treatment processes can be directly used as fuels in MFCs for current production (Kondaveeti et al., 2014; Velasquez-Orta et al., 2009; Wang et al., 2012b). In this way, pretreatment procedures (e.g. alkaline, heat, and microwave) are normally necessary to dissolve algae cell walls for improvement of performance (Gadhamshetty et al., 2013; Xiao and He, 2014). Second, algae as phototrophic microorganisms can also be used to supply MFC cathode with oxygen for electron reduction as well as to reduce CO_2 and produce valuable biomass simultaneously (Wang et al., 2010; Xiao and He, 2014). Third, MFC can be integrated with an algal bioreactor with division of labor for removal of organics (in MFC) and nutrients (in the algal reactor) from wastewaters as well as bio-energy (electricity and biomass) production (Xiao et al., 2012).

In these algae/MFC systems, algae play a role of fuel or functional microorganism to facilitate the reactions in process. In any case, effluents would be produced and finally enter environment. It is necessary to evaluate their environmental risks before being discharged. Because algae biomass has complex chemical compositions and cell itself can generate extensive amount of algal organic matter (AOM), algal toxins, taste and odor compounds with its metabolic excretion, decay and autolysis (Henderson et al., 2010; Her et al., 2004). If these compounds can't be degraded completely by MFC, they will deteriorate effluents to result in water body pollution or affect the performance of subsequent treatment processes. For example, harmful disinfection byproducts (DBPs) will be produced after the effluent containing AOMs through tertiary treatment (e.g. disinfection), and the DBPs toxicity are closely related to the compositions and structures of AOM. Characterization of AOM is necessary to evaluate the risk of effluent discharge. Bioelectricity production from blue-green algae coupled algal toxins (MC-RR and MC-LR) removal was achieved in a single chamber tubular MFC (Yuan et al., 2011). The genotoxic agents in the polluted lake water were almost completely removed in a single-chamber air–cathode MFC (He et al., 2013). Our previous studies showed that precursors of disinfection byproduct (trihalomethane) were effectively reduced in a two-chamber MFC (Wang et al., 2012a). However, few studies so far have systematically researched on changes in AOM during MFC treatment in terms of composition, molecular weight, structures and so on. Hur et al. (2014) have used acidifying dry algae (green algae, *Scenedesmus obliquus*) powder as MFC substrate to reveal that AOM compositions would sequentially change with order of proteins, acidic functional group, polysaccharides and amino.

This study aimed at examining the changes in the characteristics of AOM derived from *M. aeruginosa.* during MFCs operation, and further exploring the biodegradability of AOM in MFCs. In addition, results were compared with those in MFC operated in open circuit condition, which has not been investigated in previous studies. Several characterization methods including ultrafiltration, fluorescence EEM spectroscopy, FT-IR spectroscopy and UV–visible absorbance were used.

2. Methods

2.1. Preparation of AOM solution

M. aeruginosa (blue-green algae, Collection No. HB909) were obtained from the Culture Collection of Algae at the Institute of Hydrobiology, Chinese Academy of Sciences, and were grown using BG11 media in an air-conditioned light incubator at 30 ± 1 °C (GZX-250, Taisite Instruments Inc., China). Algae were extracted on day 33, corresponding to the growth phase of stationary. The algae cells in BG11 medium were broken by ultrasound (3.5 W/mL) using a sonicator (Sonics Vibracell VCX-130 PB, 130 W, 20 kHz) for 20 min at 4 °C. The solution was collected and filtered through a filter with a pore diameter of 0.45 μm to remove the residual solids. The filtrate was AOM solution including extracellular organic matter (EOM) and intracellular organic matter (IOM) with dissolved organic carbon (DOC) of 141 ± 33 mg/L and chemical oxygen demand (COD) of 525 ± 11 mg/L.

2.2. MFC construction and operation

H-type double chambers MFC were constructed as previously described (Wang et al., 2012a,b). Both the anode and cathode chambers were cuboid (7 cm length × 4.5 cm width × 7 cm height) with a working volume of 200 mL. They were separated by a cation exchange membrane (CEM) (CMI-7000, Membrane International Inc., USA) with an effective area of 30.25 cm^2. Anode and cathode were ammonia gas treated graphite brushes (4 cm diameter × 4 cm length; fiber: T700–12 K, Toray Industries Co., Ltd.). The distance between anode and cathode was 5 cm. An Ag/AgCl reference electrode (+0.2 V versus standard hydrogen electrode) was used to measure the electrode potentials. Two electrodes were connected to an external resistor (1 kΩ) with copper wire.

The MFC anode was inoculated with polluted water obtained from a heavily eutrophic lake. The mixed solution of 50 mL polluted water and 150 mL AOM solution containing 50 mM nutrient phosphate buffer (Na_2HPO_4 4.58 g/L, $NaH_2PO4{\cdot}H_2O$ 2.45 g/L, KCl 0.13 g/L, and NH_4Cl 0.31 g/L) was filled into anode chamber for start-up. The cathode chamber was filled with same 50 mM phosphate buffered solution and was continuously aerated at 100 mL/min to provide dissolved oxygen as the electron acceptor for the cathode. Once a voltage of >100 mV was obtained, the inoculum was omitted and replaced by AOM solution. The AOM solution was replaced when the voltage decreased to <50 mV in each batch cycle. When a reproducible maximum voltage was obtained for at five batch cycles, the anode was considered fully enriched with electrochemically active bacteria (EAB).

A MFC with electrochemically active anode but operated at open circuit (MFC-OC) was served as a control for studying the effect of other bacteria, except for electrochemically active bacteria, on the biodegradation of AOM in MFC. All tests were conducted in fed-batch mode over more than three batch cycles at room temperature (21 ± 2 °C).

2.3. Analysis methods

2.3.1. Chemical analysis

Dissolved organic carbon (DOC) was measured with a TOC/TN analyzer (TOC-VCPH/TNM-1, Shimadzu, Japan). Chemical oxygen demand (COD) was measured following standard methods. UV_{254} was measured by an ultraviolet–visible spectrophotometer (UV-2550, Shimadzu, Japan). Specific ultraviolet absorbance (SUVA) was calculated as (UV_{254}/DOC) × 100. Measurements were made in triplicate.

2.3.2. Electrochemical analysis

Voltage (mV) across a external resistor (1 kΩ) was automatically recorded using a data acquisition system (2700, Keithley Instruments Inc., USA) connected to a computer. The open circuit voltage (OCV) (without a circuit load) was obtained by removing the external load. Voltage was converted to volumetric power density P (W/m^3) via the equation $P = UI/V_a$, where U is the voltage (V), I is the current (A), and V_a is the net liquid volume (m^3) in the anode chamber. The maximum power density was determined by varying the external resistance (50 Ω–100 kΩ).