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Electricity generation from dissolved organic matter in polluted lake water using a microbial fuel cell (MFC)

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ABSTRACT

A microbial fuel cell (MFC) was explored as a pretreatment method to remove dissolved organic matter (DOM) from polluted lake water and simultaneously generate electricity. After the MFC treatment, the total organic carbon concentration in the raw lake water was reduced by 50%, the physicochemical nature of DOMs was substantially altered. Protein-like substances in lake water were utilized as a major substrate for the MFC, while humic-like substances were refractory to the biodegradation. A further investigation into the bovine serum albumin utilization in an MFC confirms that the electricity generation was closely associated with the removal of protein-like substrates. Toxicity assessment by *Salmonella typhimurium* Sal94 indicates that the genotoxic agents in the polluted lake water were almost completely removed after the MFC treatment. This approach of coupling microbially-catalyzed electricity generation with DOM removal may offer a potential avenue for energy-efficient bioremediation of lake water.

1. Introduction

Water shortage and environmental pollution are raising global concern. In China, a considerable part of freshwater is from lake [1], but 55.8% of the lake waters fail to meet the standard of source water supply [2]. In most lakes, there is a high level of dissolved organic matter (DOM), which is refractory to biodegradation. The situation is further exacerbated by the frequently occurrence of algal bloom in recent years [3], which leads to exhausting of dissolved oxygen, increased death of aquatic lives, and thus raised level of the DOM. Generally, the algal biomass in lakes can be removed though salvage, but the organic substances and potential genotoxic agents produced by algal would persist in water.

Both physicochemical processes, such as chlorination, ozonation, membrane filtration, and biological processes have been adopted for treatment of polluted lake water [4–6]. Especially, an integrated application of different processes, such as the combination of ozonation and biofiltration, ozonation and membrane reactor, exhibited good performances [7,8]. Nevertheless, the overall treatment and energy efficiencies are yet to be improved to make these processes practically viable.

Microbial fuel cell (MFC), being widely recognized as a promising wastewater treatment technology, is capable of recovering electricity from organic pollutants to partially offset the treatment cost [9,10]. It has been demonstrated that MFC could effectively utilize not only degradable organics but also some biorefractory compounds such as p-nitrophenol as substrate [11,12]. Thus, it is expected that MFC might also facilitate removal of DOMs in polluted lake water by utilizing them for electricity generation or altering their genotoxicity, so that further purification of the water can be achieved in subsequent polishing steps. However, lake water is somewhat different from normal wastewaters. First, the organic content is very low even compared to low-strength wastewater like domestic wastewater. Secondly, the sources of organic matter in lake water are more diverse and complex. At last, the breakout of algae bloom would result in the production and accumulation of genotoxic substances in lake water. Therefore, it is still to be found out whether MFC can effectively utilize polluted lake water as substrate and how it would alter the composition of lake water.

Therefore, in this study the treatment of polluted lake water by a MFC was investigated with the following three objectives: (1) to explore the feasibility of abating pollution and altering DOM compositions of polluted lake water using a MFC; (2) to find out whether the potential genotoxic agents in the polluted lake water could be significantly reduced after the MFC treatment; and (3) to elucidate

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the mechanisms of DOM removal and genotoxicity reduction in such an MFC system.

2. Experimental

2.1. Reactor construction and operation

A single-chamber air-cathode MFC with the same configuration as described by Zang et al. [13] was used for the experiment. The cathode electrode was made of Pt-loaded carbon paper (2 cm × 2 cm, 2 mg/cm^2; GEFC Co., China). Activated carbon fiber, fabricated as described by Zhang et al. [14] was used as anode electrode. The bioanode was cultivated in another air-cathode MFC inoculated with anaerobic sludge, and acetate was used as substrate. A stable voltage output was obtained after 2-months cultivation, indicating that a consortium of electrochemically active microorganisms was enriched on the carbon fiber. Enrichment medium contained (in 1 l of 50 mM phosphate buffer, pH 7.0): NH_4Cl, 310 mg; KCl, 130 mg; $CaCl_2$, 10 mg; $MgCl_2{\cdot}6H_2O$, 20 mg; NaCl, 2 mg; $FeCl_2$, 5 mg; $CoCl_2{\cdot}2H_2O$, 1 mg; $MnCl_2{\cdot}4H_2O$, 1 mg; $AlCl_3$, 0.5 mg; $(NH_4)_6Mo_7O_{24}$, 3 mg; H_3BO_3, 1 mg; $NiCl_2{\cdot}6H_2O$, 0.1 mg; $CuSO_4{\cdot}5H_2O$, 1 mg; $ZnCl_2$, 1 mg, and CH_3COONa, 100 mg as substrate.

Water samples were collected from Chaohu Lake, the China's fifth largest freshwater lake. This lake is usually under severe contamination because of blue-green algae bloom. The water samples were filtered through gauzes to remove algal biomass and then centrifuged for 10 min at 6000 rpm and 4 °C. Aliquots of 400 ml supernatants were added into the MFC anode chamber, which was then purged with N_2 and sealed. A resistor of 1000 Ω was connected to the circuit. The MFC was operated under 28 °C and the voltage across the resistor was recorded continuously using an on-line data acquisition system. The anodic solution was sampled every 2 or 3 days for analysis.

To get a better insight into the relationship between DOM decomposition and electricity generation, a model protein, bovine serum albumin (BSA), was also used as substrate for MFC. The reactor setup and operation were the same as above except for the use of BSA to replace acetate. Water samples were taken at the predetermined time intervals for analysis.

2.2. Chemical analysis

The concentration of total organic carbon (TOC) of water samples was measured with a TOC analyzer (VCPN, Shimadzu Co., Japan). The liquor samples were centrifuged at 12,000 rpm for 5 min, and the supernatant fluid was diluted to a range of 1–1000 mg/l with distilled water for TOC analysis. BSA concentration was determined using the modified Lowry methods with chicken egg albumin as the standard [15].

Three-dimensional excitation-emission matrix (EEM) fluorescence spectra of the water samples before and after the MFC treatment were measured using a luminescence spectrometry (LS-55, Perkin-Elmer Co., USA). The emission spectra from 250 to 700 nm at 0.5 nm increment repeatedly and the excitation wavelengths from 240 to 500 nm spaced by 10 nm intervals in the excitation domain were measured. Excitation and emission slits were both maintained at 10 nm, and the scanning speed was set at 1200 nm/min for all measurements. A 290 nm emission cutoff filter was used. The EEM fluorescence spectra data were processed and plotted using MatLab 7.0 (MathWorks Inc., USA).

The molecular weight (MW) distribution of water samples was measured using a gel permeation chromatography (GPC) (Waters 1515, Waters Co., USA) coupled with a UV absorbance detector. Deionized water was used as the eluent at a flow rate of 1.0 ml/min. Prior to the analysis, the samples were dialyzed with deionized water (2 h each time) for three times, and then filtrated through 0.45-mm acetate cellulose membranes.

Electrochemical measurements were conducted using an electrochemical workstation (CHI 660, Chenhua Instrument Co., China). The polarization curve was obtained using linear sweep voltammetry at a scan rate of 1 mV/s [11]. The current density and power density were normalized to the MFC volume of 400 ml.

2.3. Toxicity bioassay

Salmonella typhimurium Sal94 (*pRecA::LuxCDABE tolC^{C}Cm^{R}Amp^R*) strain was used to assay the environmental genotoxicity of the water samples [16]. Sal94 strain was cultured overnight in LB medium in a shaking incubator at 26 °C, with 30 μg/ml kanamycin added in order to maintain the plasmid. A 2000-fold dilution of the cell suspension was prepared using fresh LB without kanamycin. Water samples collected from the MFC were centrifuged at 12,000 rpm for 5 min. The supernatant of 100 μl was mixed and incubated with an equal volume of diluted bacterial solution in 2-ml Eppendorf tube at 26 °C. Sterile distilled water was used as the control. The emitted luminescence was monitored using a luminometer (GloMax 20/20, Promega, USA) for 5 s. Luminescence values are presented as arbitrary relative light units, or as the response ratio of luminescence of the induced sample to that of the blank control [17].

3. Results

3.1. DOM removal and electricity generation in the MFC

For the MFC system, the anode chamber was filled with the polluted lake water and operated under anaerobic conditions. No other external carbon sources were added. A gradual decline of TOC concentration from 62 mg/l to 30 mg/l was achieved in this system during the 45-days operation (Fig. 1). Meantime, a continuous generation of electricity was observed (Fig. 2A). The output voltage varied substantially over time. A relatively high voltage was obtained at the beginning, attributed to the presence of easily degradable components in the DOMs of lake water. With the fast depletion of such easily degradable contents, the voltage dropped rapidly. Then, the less-degradable organics were further utilized to sustain a continuous but slow-declining electricity generation. Similar profiles of voltage and TOC evolution over time were obtained in a repeated experiment, although at a much shorter time span

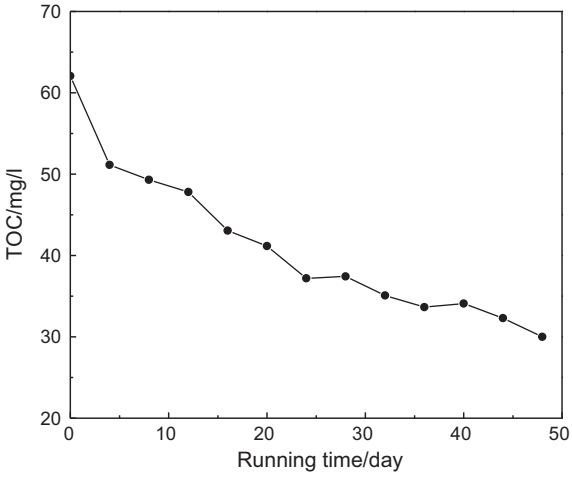

Fig. 1. TOC concentration profiles during the MFC treatment.