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Electrochemical inactivation of *Microcystis aeruginosa* using BDD electrodes: Kinetic modeling of microcystins release and degradation

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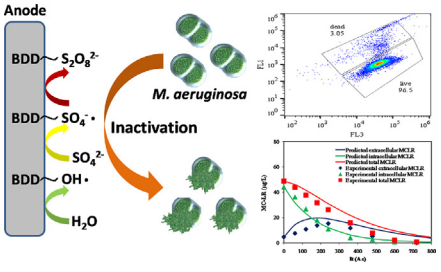
HIGHLIGHTS

- Electrochemical inactivation of *M. aeruginosa* by BDD electrodes was proposed.
- Flow cytometry and confocal laser scanning microscopy were used.
- A kinetic model was developed to predict the MCLR concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

Electrochemical inactivation of cyanobacteria using boron-doped diamond (BDD) electrode were comprehensively investigated in this study. The pulse amplitude modulated (PAM) fluorometry, flow cytometry, and confocal laser scanning microscopy (CLSM) were used to characterize the photosynthetic capacity and cell integrity of *Microcystis aeruginosa*. Persulfate is in-situ generated and activated during the process and responsible for the inactivation of *M. aeruginosa*. The inactivation efficiency increases along with the increase of applied currents. Additionally, a kinetic model based on a sequence of two consecutive irreversible first-order processes was developed to simulate the release and degradation of microcystins (MCLR). The model was able to successfully predict the concentration of extracellular, intracellular and total MCLR under different applied currents and extended exposure time.

1. Introduction

Cyanobacterial blooms frequently occur worldwide in lakes and reservoirs due to the serious problem of eutrophication [1–3]. Specific cyanobacterial speices (e.g., *Microcystis aeruginosa*) can release algal organic matters (AOM) including microcystins, endotoxins and odor & taste compounds into water during cells growth and lysis, and pose a great challenge to conventional water purification processes [4–6]. In drinking water treatment plants (DWTPs), floatation achieved good reputation in removing algal cells, especially in Australia. And coagulation is considered as a key barrier for removal of cyanobacteria and their associated metabolites under most circumstances [7]. However, excessive dosages of coagulants are required due to the negatively charged cells and

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surface-adsorbed organic matters, and thus increase the economic cost and sludge production [8,9]. Furthermore, released AOM entering downstream drinking water treatment processes may contribute to the formation of disinfection by-products (DBPs) during chlor(am)ination [10,11]. Pre-oxidation, especially with permanganate [12–14], chlorine [15–18], ozone [14], ferrate [19], and chlorine oxide [20], is deemed effective in inactivating *M. aeruginosa* and promoting the coagulation of cyanobacterial cells and their organic matters.

However, the conventional oxidants also have several drawbacks, such as formation of halogenated DBPs, increasing of water colority, inconvenience of storing and transporting [17,21]. Therefore, advanced treatment technologies are required to removal cyanobacterial cells from water. Electrochemical oxidation processes (EOPs) have shown an outstanding ability for the treatment of polluted waters [22–24]. During the EOPs, a variety of oxidants (e.g., chlorine, hydrogen peroxide, persulfate, ozone and ferrate) can be generated depending on the electrolytes and electrodes [24]. EOPs have drawn considerable research attention due to its simplicity and robustness in operation and would become a promising technology in the future owing to the rapid development of electric power from wind and solar sources. Recently, Bruguera-Casamada et al. have reported that electrochemical oxidation with a boron-doped diamond (BDD) anode was very effective for Gram-negative and Gram-positive bacteria in low conductivity sulfate medium [25]. In previous studies, EOPs have been applied to treat algae-laden water in laboratory by many researchers as potential alternatives [26–28]. In general, BDD electrodes and Ti/RuO_2 electrodes were used in NaCl electrolytes to produce active chlorine via reactions (1)–(3). However, the presence of chloride ions could promote the formation of chlorinated byproducts, such as chlorate, perchlorate, trihalomethanes and haloacetic acids, which may be even more toxic [29,30]. Besides, nitrate and phosphate electrolytes are also not good choices since N and P may lead to water eutrophication. To avoid secondary pollution, sulfate medium is used as supporting electrolytes in this study due to its low cost, high efficiency, easy access, and lack of formation of halogenated DBPs. Possible reactions occurred in sulfate electrolytes are listed as Eqs. (4)–(7) [31–33].

$$2Cl^- - 2e^- \rightarrow Cl_{2(aq)} \quad (1)$$

$$Cl_{2(aq)} + H_2O \leftrightarrow HClO + Cl^- + H^+ \quad (2)$$

$$HClO \rightleftharpoons H^+ + ClO^- \; pK_{a1} = 7.5 \quad (3)$$

$$M + H_2O - e^- \rightarrow M(\cdot OH) + H^+ \quad (4)$$

$$2HSO_4^- - 2e^- \rightarrow S_2O_8^{2-} + 2H^+ \quad (5)$$

$$2SO_4^{2-} - 2e^- \rightarrow S_2O_8^{2-} \quad (6)$$

$$S_2O_8^{2-} \xrightarrow{BDD} \text{reactive species} \quad (7)$$

So far, various analytical techniques are developed to investigate the viability of algal cells, such as pulse amplitude modulation (PAM) fluorometry, flow cytometry and scanning electron microscopy (SEM) [34–36]. Advanced staining techniques coupled with optical microscopy, i.e., confocal laser scanning microscopy (CLSM), is a good method for detecting cell viability and membrane integrity as it does not require cell culturing [37]. CLSM has been widely used in microbial biofilms and activated sludge [38,39], but there is limited information regarding cyanobacterial cells [40]. Unlike flow cytometry, aiming to quantify the total fluorescence of all algal cells, CLSM can be applied to observe the change of fluorescence of a single cell.

The objective of this study were to: (1) compare inactivation efficiency of *M. aeruginosa* with different electrolytes and electrodes; (2) investigate variation of extracellular AOM components and changes of algae characteristics including cell morphology, cell integrity and surface properties; (3) develop a kinetic model to quantitatively describe MCLR release and degradation during EOPs.

2. Materials and methods

2.1. Materials and reagents

M. aeruginosa (FACHB-912) was obtained from the Institute of Hydrobiology, Chinese Academy of Sciences, and cultured in BG-11 media (no chloride ions, see SI Table S1) [41]. The cultures were incubated in 5-L conical flasks under a 12-h diurnal cycle. Glass microfiber filters (0.2 μm, GF/F) were purchased from Whatman (UK). Sodium sulfate, poly aluminium chloride (PAC) and all reagents used in BG11 media were supplied by Sinopharm Chemical Reagent Co. (China). BDD/Nb electrodes (2500 ppm boron, 25 × 50 × 1 mm, bipolar, 5 μm coating thickness) were purchased from NeoCoat® SA (Switzerland). Mixed metal oxide (MMO) electrodes (IrO_2-Ta_2O_5/Ti) and platinum (Pt) electrode were supplied by Shangxi Kaida (China). MCLR (>95%) isolated from *M. aeruginosa* was obtained from Alexis biochemicals (Switzerland). SYTOX green nucleic acid stain was provided by Invitrogen (USA).

2.2. Experimental procedures

Batch experiments were conducted open to the air and in a series of 200-mL borosilicate glass jars. The BDD (or MMO, Pt) anode and stainless steel cathode were set in parallel at a distance of 2.0 cm. The total submerged area of electrode was 10 cm^2 in the electrolytic cell and a direct current source was used to supply power. The experiments were performed with 1.0 ~ 4.0 × 10^6 mL^{-1} cells and 30 mM electrolyte (Na_2SO_4, $NaNO_3$, Na_2HPO_4). At each designed sampling time, 5 mL sample was harvested and quenched by excess $Na_2S_2O_3$, and then divided into two subsamples for MCLR analysis. The first subsample was immediately filtered through glass microfiber filters to remove residual cells for extracellular MCLR detection. The second subsample was subjected to three freeze/thaw cycles to analyze for the total MCLR. The intracellular MCLR was the difference between total MCLR and extracellular MCLR.

After 60 min reaction time, 5 mL samples were centrifuged at 5000*g* for 5 min, and the supernatant was filtered through 0.2 μm glass microfiber filters to conduct fluorescence analysis. The centrifuged cells were washed several times with 0.9% NaCl solution and then subjected to cell integrity tests. The residual solutions were further cultivated to measure the in vivo data of photosynthetic capacity and cells viability.

2.3. Analytical methods

2.3.1. Photosynthetic capacity

The pulse amplitude modulated (PAM) fluorometry can provide an effective method to determine the properties of photosynthetic systems based on the measurement of chlorophyll-*a* fluorescence. A PHYTO-PAM phytoplankton analyzer (Walz, Germany) was used to immediately analyze the photosynthetic capacity of algae cells (indicated by effective quantum yield, Φ) subsequent to harvesting from the culture according to the method described in our previous study [42].

2.3.2. Flow cytometry

Cell integrity during EOPs was determined using a flow cytometry (FC500, Beckman Coulter, USA) equipped with an argon laser emitting at a fixed wavelength of 488 nm for fluorescence measurement. Fluorescent filters and detectors were all standard with