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Effective electrochemical inactivation of *Microcystis aeruginosa* and degradation of microcystins via a novel solid polymer electrolyte sandwich

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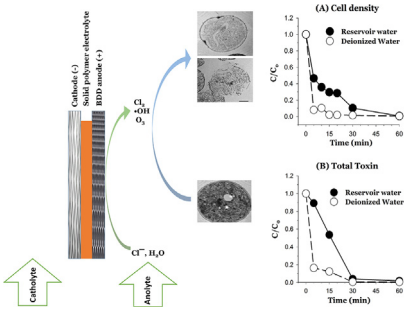
HIGHLIGHTS

- Toxic cyanobacteria and cyanotoxins were effectively removed by BDD electrode with SPE assembly.
- The treatment was conducted without chemicals addition or adjustment to electrical conductivity.
- The operational parameters and water matrices, including freshwater were investigated.
- Both electro-generated O_3 and Cl_2 species contributed to the treatment performance.
- The system is a promising method for water disinfection containing low EC and Cl^- with low cost.

GRAPHICAL ABSTRACT



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ABSTRACT

The treatment of toxic *Microcystis aeruginosa* (*M. aeruginosa)* by electrolysis using a boron-doped diamond (BDD) anode with a solid polymer electrolyte (SPE) was investigated. In order to examine the role of oxidizing agents, the electrolysis of *M. aeruginosa* was conducted in distilled deionised water (DIW) with and without sodium chloride aqueous electrolyte. Furthermore, to verify the system's ability for freshwater treatment without the addition of chemicals, we also tested filtered local reservoir water. *M. aeruginosa* cell inactivation and microcystins degradation occurred in the DIW system without a supporting aqueous electrolyte, but cell inactivation occurred at slightly slower rate compared to when 30 mg/L Cl^- was added. Even though these rates were even slower in the pre-filtered reservoir water, around 90% inactivation and toxin degradation was still observed after 30 min, and cells were not able to re-grow when subsequently exposed to optimum growth conditions. These results for the first time demonstrate the ability of the SPE system to efficiently treat contaminated freshwaters, even without the addition of chemicals or adjustment of electrical conductivity. Importantly, significant changes in cell morphology after electrolysis in different water matrices were observed. In the DIW with 30 mg/L Cl^- test based on the significant differences in oxidants concentrations in the presence and absence of *M. aeruginosa* suggest that there was a synergistic effect of *in situ* electro-generated ozone and chlorine species in cell inactivation, however, hydrogen peroxide did not seem to assist in the treatment performance. This study suggests that the electrochemical treatment of BDD with SPE, with and without supporting electrolyte is an effective method for the removal of both toxic cyanobacteria and cyanotoxins.

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1. Introduction

The potential risks associated with toxic cyanobacteria have raised growing environmental and public health concerns leading to an increasing effort into researching ways to bring about their removal from water, together with destruction of cyanotoxins [1,2]. A variety of toxins are synthesized by cyanobacteria and include hepatotoxins, neurotoxins, and cytotoxins which can cause a range of symptoms in humans from skin irritation to serious liver and nerve damage [3]. In addition, several cyanobacterial species have shown to synthesise and release 2-methylisoborneol (MIB) and geosmin; taste and odour (T & O) compounds, causing aesthetic problems in drinking water resources [1]. Direct ingestion of drinking water containing cyanotoxin is one of the most devastating routes of exposure [4], and therefore drinking water treatment should ensure the consumers' safety by removing both cell bound (intracellular) and dissolved (extracellular) cyanotoxins from water.

Drinking water treatment (DWT) combines a treatment train which can effectively remove cyanobacterial cells and cyanotoxins [2]. Notably, water disinfection and degradation of toxins and T&O compounds are commonly carried out by methods such as chlorination and ozonation within the DWTs. However, the efficiency of cell inactivation and toxin removal depends significantly on the type of chemical used, concentration, pH etc., and there has not been an individual chemical shown to remove all types of toxins efficiently [5,6]. Indeed, the removal efficiency within the same toxin variants has been reported to vary even under the same reaction conditions (e.g., microcystin-LR removal was higher than that of microcystin-RR by ozonation process) [7,8]. Therefore, the application of a particular disinfection method (e.g., ozonation) in treatment of water containing cyanobacteria/cyanotoxin should be chosen cautiously.

In recent years there has been increasing attention to the electrochemical oxidation process as a feasible alternative disinfection method to generate *in situ* a variety of oxidants that would achieve synergistic effects in the water disinfection process and toxin degradation [9]. Researchers have reported promising results from electrochemical treatments in relation to cyanobacterial cell inactivation [10–12], toxin removal [10,13–15] and also degradation of T&O compounds [16,17] using several electrode materials. Novel electrode materials, such as boron-doped diamond (BDD), are highly stabile and have generated a growing interest in the application of electrochemical processes in water disinfection [18]. Eventually during the electrolysis of water by BDD electrode, a cocktail of oxidizing agents is generated, including reactive oxygen species (ROS) such as ·OH, O_3 and H_2O_2 (Eqs. S1–S5), and active chlorine species (Eqs. S6–S9) [19–21], which are capable of removing a variety of cyanobacterial cells and cyanotoxins from water. However, the effectiveness of this process in water disinfection depends largely on system configuration, electrode material, electrolysis conditions and composition of the supporting electrolyte.

From strictly engineering viewpoint, the electrical conductivity (EC) of the supporting electrolyte is strongly linked to the cost of the electrochemical process; where high voltage is found to those electrolytic mediums with low EC leading to a relatively high energy requirement. Such low EC containing waters may include freshwater resources, stormwater and a variety of industrial wastewaters such as food and pharmaceutical wastewater. For example, within 6 drinking water reservoirs in Victoria, Australia, the EC ranged from 45 to 215 μS/cm, from data recorded over five years (Table S1). So far, most published articles on the electrochemical inactivation of freshwater toxic cyanobacteria were conducted in synthetic waters where added electrolyte concentrations giving EC at least 2 times higher than those reported for freshwater matrices/types (e.g., Reservoir water, River water and etc.) [10,13]. To the best of our knowledge, published reports in optimizing the electrochemical process to treat freshwater cyanobacteria in their freshwater environments is limited [22]. Although the separation of ions in the added electrolyte from the treated water is possible [23], it is preferred to use a solid polymer electrolyte (SPE) in an anode/SPE/cathode sandwich assembly [24] in the electrochemical system instead of the addition of electrolyte in the aqueous solution. Recently, electrochemical treatment process that employ SPE and novel electrode materials such as BDD electrode has shown promising application to drive ozone production in the so-called the electrochemical ozone production process [25–28]. Interestingly, in this process, ozone is generated at high concentration in solutions with low electrical conductivity (EC) and operation under high-mixing [28,29]. The use of SPE in the electrochemical process seems to be a more suitable and 'greener' way to treat cyanobacteria in the freshwater characteristics that has low EC without the need for chemicals addition or ions separation from the treated water [30].

So far, there have been a small number of publications on the use of EOP for water and wastewater treatment; applications include synthetic dye degradation [29,31], Alcohol [24,32] and inactivation of bacteria such as *Escherichia coli* [33], and *Pseudomonas aeruginosa* [34]. These studies have shown outstanding performance in the removal of their perspective pollutants, however, to the best of our knowledge, the investigation of EOP for cyanobacterial inactivation or cyanotoxin removal has not yet been reported. Unlike *E. coli* and *P. aeruginosa* inactivation, the story is more complex when cyanobacteria are inactivated; upon lysis cyanobacterial cells release their intracellular toxins into the water and these must be eliminated as well.

This study was conducted to investigate the electrochemical ozone production process for *Microcystis aeruginosa* (*M. aeruginosa)* inactivation and toxin removal in simulated and real freshwater matrices using BDD anode. The cyanobacterium *M. aeruginosa* was selected for these studies because it is widely considered the most common toxic bloom-forming cyanobacterium in freshwater resources with the ability to release of a group of heptapeptide cyanotoxins known as microcystins [15,35]. The objectives of this work were to investigate (i) the influence of current density and flow rate on cell density and integrity (ii) the efficiency of the EOP process in cell inactivation in synthetic and natural freshwater matrices, (iii) understand the role of oxidizing agents, (iv) investigate the change in the profile of toxins during electrolysis, (v) examine the change of cell morphology before and after the treatment, and finally (vi) test the photosynthetic parameters and examine whether or not the treated cells could survive and re-grow following treatment. This paper presents the first that describes the inactivation and degradation of a cyanobacteria and its toxins in freshwaters using a SPE sandwich without chemical addition.

2. Materials and methods

2.1. Cyanobacterial culture

An Australian toxic strain of *M. aeruginosa* (CS558) was obtained from the Australian National Algae Culture Collection, CSIRO, Hobart, Australia [15,35]. The cyanobacteria were cultured in a batch mode at 25 °C using MLA as a culture medium [36]. The culture was exposed to a light intensity of 60 μmol photons $m^{-2} s^{-1}$ in a 12 h light/12 h dark cycle. The cells were collected from the culture for treatment in late exponential phase which was around the 9th and 14th day of growth (Fig. S1); cell-associated toxins are expected to reach a plateau at this stage [37].

2.2. Apparatus

The electrochemical system consisted of a sandwich of an anode, a cation exchange membrane (CEM) and a cathode bolted in 3 points using polycarbonate bolts and nails [25]. The cation exchange membrane (CEM) (Ultrex CMI-7000, Membranes International, U.S.A) thus acts as a solid polymer electrolyte (SPE). The functional group of this polymer is Sulphonic acid (Please see Table S2 for technical specifications) which is also the same as those commonly used Nafion® polymers