



Monolithic ceramic electrode for electrochemical deactivation of *Microcystis aeruginosa*



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ABSTRACT

Algae bloom is a major environmental problem that may occur in both freshwater and marine water, and thus it is important to develop effective manners for deactivating algae. In this study, we investigated the monolithic ceramic electrode (MCE) for electrochemical deactivation of *Microcystis aeruginosa*, a typical alga found in aquatic system. The results demonstrated that the MCE contained the mixed Magnéli-phases of Ti_4O_7 , Ti_5O_9 and Ti_9O_{17} , which could achieve efficient and stable deactivation of *M. aeruginosa* cells and removal of chlorophyll-*a*. The chlorophyll-*a* removal was shown to be positively correlated with the current density applied, reaching the maximum efficiency of 89.2% at reaction time of 120 min. The 8-day re-cultivation experiments showed the dependence of deactivation performance on total coulombs, and the coulombs in excess of 77.4 C could completely deprived the *M. aeruginosa* cells of propagation and proliferation. As shown from atomic force microscopy (AFM), scanning electron microscopy (SEM) and flow cytometric (FC) measurement, the algal cells underwent an irreversible damage of cell structure, isolation of intracellular components and dissolution of cytoplasm-like substances after being attacked by electrochemically produced oxidative species. The solution pH was observed to increase from 8.0 to 9.8 during 120-min electrolysis, which should be the consequence of leakage of cytoplasm containing a variety of small-molecule substances such as protein-, humus-, and sugar-like matters, indicated by 3D excitation-emission matrix (EEM) fluorescence spectra. This study provides a promising electrode material for effective electrochemical deactivation of algae in potential application of water purification.

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1. Introduction

Eutrophication is a major environmental concern, which can be accelerated by human activities associated with increased discharge of nitrogen and phosphorus elements into aquatic systems. The algae bloom can lead to grand challenges for drinking water sources, fisheries, recreational water bodies, and ballast water contamination [1]. For example, the algae prevent water body from reoxygenation and light penetration, and the algae in water treatment processes may lead to clogging or fouling of filters, membrane and devices, blooms of algal mats as well as disruption of floc settlement [2]. In addition, to avoid aquatic species invasion,

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the shipping ballast water has to be free of living algae before it can be discharged into new regions [3]. Some microalga like *Microcystis aeruginosa* (*M. aeruginosa*) can produce microcystins and cyanopeptolins that are highly toxic to aquatic ecosystem and human health [4,5]. Chlorine has long been widely used as an effective disinfectant for deactivation of algae. However, recent concerns on chlorine rise due to its activity to react with organic matters to form carcinogenic disinfection by-products (DBPs) like trichloro-methanes and chloroacetic acids [6,7]. A number of alternatives such as coagulation, flocculation, dissolved air flotation, filtration, and advanced oxidation process have been developed [8–10], but these approaches may have the problems of low efficiency, instability, and extensive energy consumption.

Electron offers an efficient, versatile, easy-to-operate and clean agent. Driven by the electrons, electrochemical advanced oxidation process can yield numerous kinds of oxidizing species like H_2O_2 , $\bullet OH$ or $\bullet O_2^-$ radicals, sulfate radicals, and active chlorine [11,12]. These intermediate components are highly active for oxidizing

organic pollutants and sterilizing bacteria or virus for disinfection purpose [13]. Recently, an increasing attention has been paid to deactivation of algae in water using electrochemical system with different types of anode materials. For example, Liang et al. [14] and Xu et al. [15] used Ti–RuO₂ anode for oxidation of *M. aeruginosa* via the generation of active oxidants during electrolysis, and they found the substantial dependence of inhibition on the anode materials, current density, and reaction time and mass transfer. Marcia et al. [16] achieved efficient electrochemical treatment of water containing *M. aeruginosa* in a fixed bed reactor with 3D conductive diamond serving as anodes under continuous operation. The removal of *M. aeruginosa* in water was accomplished by the mixture of electrogenerated oxidants, and the presence of algae could inhibit the production of toxic by-products. The boron-doped diamond (BDD) anode could also be efficient for deactivation of *Chlorella vulgaris* by continuous formation of active chlorine and other chloride oxidation products [17]. Recently, Long et al. [18] reported a significant enhanced removal of *M. aeruginosa* in electrochemical system with BDD anode by simple addition of 0.2 mmol L⁻¹ Fe²⁺ at pH-neutral conditions, and they obtained over 99.9% removal of *M. aeruginosa* in 60 min. However, there exists a dilemma for the selection of electrode material in terms of electrical conductivity, electrochemical activity, chemical stability, economic reliability and environmental availability. The BDD has been considered as the most promising candidate [19], but large surface area is necessary to match the capability of scale-up wastewater treatment, which adds the capital cost substantially (e. g. \$900 cm⁻² for BDD).

Titanium suboxides have a crystal structure of oxygen deficiency for every *n*th layer, resulting in the shear planes where 2D chains of octahedra become face sharing to accommodate the deficiency in oxygen [20]. This unique structure leads to a combination of outstanding electrical conductivity approaching to that of metals at room temperature and great corrosion resistance close to that of ceramic materials [21,22]. For example, the most common component of Ti₄O₇ (*n* = 4, under trade name Ebonex[®], Atraverda Ltd, U.K.) exhibits a great conductivity of ~1050 S cm⁻¹, which is even higher than that of graphitic carbon (~727 S cm⁻¹) [22]. These properties make Ti₄O₇ suitable for many electrochemical applications, such as cathodic oxygen reduction [23], water splitting [24], as well as pollutant removal [25–29].

The Magnéli-phase titanium suboxides have been shown effective for electro-oxidation of many types of pollutants [30–33]. In our previous study, we developed macroporous monolithic Magnéli-phase titanium suboxides, an electrode material having good conductivity, excellent stability, and high oxygen evolution potential [26]. In particular, the macroporous structure is preferred because it can provide larger electrochemically active surface area. Besides, the protons produced from water oxidation can maintain a much lower local pH in the porous apertures than in bulk solution, which is favorable for increasing the activity of •OH radicals and formation of active chlorine. With the unique structure and properties, the macroporous monolithic titanium suboxides could be used as anode material for not only efficient treating industrial dyeing and finishing wastewater, but also enriching electrochemically active microorganisms in bioelectrochemical systems [34]. The titanium suboxides are able to electrochemically produce loosely adsorbed •OH radicals in the potential region of water discharge, which will be highly desirable for destructing the cell structure and algae deactivation.

In this study, the macroporous monolithic titanium suboxides (*i. e.* monolithic ceramic electrode; MCE) are investigated for electrochemically oxidative deactivation of target *M. aeruginosa*, a most frequently found alga in aquatic environment. First, we characterized the morphology, crystalline structure, and corresponding

electrochemical properties of MCE. Second, the material was examined for electrochemical removal of algal cells, chlorophyll-*a*, and the stability. Third, the re-cultivation of algae was tested to evaluate the effectiveness of electrochemical deactivation. Last, the mechanisms for destruction of algae cell were discussed.

2. Materials and methods

2.1. Preparation of monolithic ceramic electrode

The Magnéli-phase MCE, produced from high-temperature reduction of rutile TiO₂ by H₂ was supplied by Ti-Dynamics Co. Ltd. (China). In brief, rutile TiO₂ powders were mixed with water and isopropanol (1:1, v/v) to decrease the capillary force of powders, followed by drying and addition of a 5% (w/w) polyethylene oxide binder. The mixture was compressed at 20 MPa to form a plate shape. The plate blocks were sintered in air at a temperature of 1050 °C for 24 h, and then transferred into a furnace for reduction at H₂ atmosphere at 1050 °C for 4 h in the presence of carbon as porosity-producing agent. The white TiO₂ powders were gradually changed to dark blue suboxides as the oxygen vacancies were generated. The suboxides mixed with a certain amount of binders were hot-pressed into a monolithic ceramic electrode bulk.

2.2. Microalgae and culture

The algae *M. aeruginosa* used in this study were purchased from Biological Resource Center, Institute of Microbiology, Chinese Academy of Sciences (IMCAS-BRC) and the medium culture was BG-11 [14]. The culture was inoculated with 15–20% pure *M. aeruginosa* in sterilized flasks and was cultivated under illumination for 14 days until the cyanobacteria were within logarithm growth phase. The light was continuously supplied by incandescent lamp upon automated 14 h/10 h light/dark cycle at room temperature (25 ± 1 °C). The algae in late exponential growth stage were selected as the target for electrolysis experiments.

2.3. Electrolysis experiments

The electrolysis experiments were conducted in a 125 mL cubic Plexiglas reactor with the dimensions of 5 cm × 5 cm × 5 cm. The apparatus was equipped with MCE anode (effective area of 17.2 cm²) and a stain steel (SS) cathode, placed in an opposite position with electrodes distance of 5 cm. The culture media were used as the electrolyte to perform batch-mode deactivation experiments by using DC power supply (current density of 1–10 mA cm⁻²) at reaction time of 0–120 min. The silicone gaskets were used to seal the reactor to avoid water leakage and the agitation was implemented to enhance mass transfer. The reactor was designed to minimize the influence of water reduction during sample collection. All the experiments were carried out at room temperature (25 ± 1 °C) and 1.0 atm pressure.

2.4. Analyses and calculations

The crystalline structure of as-prepared MCE material was identified by using X-ray diffraction (XRD) based on X-ray diffractometer (Bruke D8 Adv., Germany) using CuK α radiation ($\lambda = 0.15406$ nm) at a power of 40 keV × 30 mA. The morphology of MCE and algal cells were observed by using field emission scanning electron microscope (Guanta 200F, FEI, U.S.). The high-resolution transition electron microscopy (HRTEM) was performed on F-30ST (Tecnai, FEI). The electrochemical properties of MCE were performed using PARSTAT (CHI750D, Chenhua Co. Ltd.) electrochemical system at room temperature (25 °C). Cyclic

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