JOURNAL OF ENVIRONMENTAL SCIENCES XX (2016) XXX–XXX

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

Electrochemical inactivation of cyanobacteria and microcystin degradation using a boron-doped diamond anode — A potential tool for cyanobacterial bloom control

Andrej Meglič[1], Anja Pecman[2], Tinkara Rozina[3], Domen Leštan[2], Bojan Sedmak[4,*]

1. Arhel Ltd., Pustovrhova c. 63, SI-1000 Ljubljana, Slovenia. E-mail: andrej.meglic.info@gmail.com
2. Centre for Soil and Environmental Sciences, Biotechnical Faculty, University of Ljubljana, Jamnikarjeva 101, SI-1000 Ljubljana, Slovenia
3. Envit Ltd., Vojkova c. 63, SI-1000 Ljubljana, Slovenia
4. Department of Genetic Toxicology and Cancer Biology, National Institute of Biology, Večna pot 111, SI-1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:
Received 15 June 2015
Revised 21 October 2015
Accepted 19 February 2016
Available online xxxx

Keywords:
Cyanobacterial bloom control
Boron-doped diamond anode
Electro-oxidation
Microcystin degradation
Protein phosphatase-1 inhibition
Water remediation

ABSTRACT

Cyanobacterial blooms are global phenomena that can occur in calm and nutrient-rich (eutrophic) fresh and marine waters. Human exposure to cyanobacteria and their biologically active products is possible during water sports and various water activities, or by ingestion of contaminated water. Although the vast majority of harmful cyanobacterial products are confined to the interior of the cells, these are eventually released into the surrounding water following natural or artificially induced cell death. Electrochemical oxidation has been used here to damage cyanobacteria to halt their proliferation, and for microcystin degradation under *in-vitro* conditions. Partially spent Jaworski growth medium with no addition of supporting electrolytes was used. Electrochemical treatment resulted in the cyanobacterial loss of cell-buoyancy regulation, cell proliferation arrest, and eventual cell death. Microcystin degradation was studied separately in two basic modes of treatment: batch-wise flow, and constant flow, for electrolytic-cell exposure. Batch-wise exposure simulates treatment under environmental conditions, while constant flow is more appropriate for the study of boron-doped diamond electrode efficacy under laboratory conditions. The effectiveness of microcystin degradation was established using high-performance liquid chromatography–photodiode array detector analysis, while the biological activities of the products were estimated using a colorimetric protein phosphatase-1 inhibition assay. The results indicate potential for the application of electro-oxidation methods for the control of bloom events by taking advantage of specific intrinsic ecological characteristics of bloom-forming cyanobacteria. The applicability of the use of boron-doped diamond electrodes in remediation of water exposed to cyanobacteria bloom events is discussed.

* *Corresponding author*. E-mail: bojan.sedmak@nib.si (Bojan Sedmak).

http://dx.doi.org/10.1016/j.jes.2016.02.016
1001-0742 © 2016 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

A variety of techniques has been developed to minimize the harmful effects of cyanobacterial blooms that are based on the removal (Falconer et al., 1989) and/or destruction of the cyanobacterial community and their toxic products (Fan et al., 2013; Rodriguez et al., 2007). Frequently used conventional methods include filtration, flocculation, coagulation and sedimentation, although these are only efficient for the removal of cyanobacteria, and not for cyanotoxin degradation, and therefore disposal of the residual material is necessary (Lawton and Robertson, 1999). In natural environments, competitive adsorption with suspended and dissolved natural organic substances can significantly reduce the effectiveness of the adsorption of selected cyanotoxins, and therefore impede their removal (Donati et al., 1994; Tran and Drogui, 2013).

Various advanced oxidation processes have already been used for cyanotoxin degradation (Sharma et al., 2012; Zong et al., 2013). Among the electrochemical processes, the application of boron doped diamond (BDD) electrodes is one of the most promising. Oxidation of organics and oxygen evolution take place on BDD electrodes mediated by hydroxyl radicals (•OH) that are generated from the discharge of water (Simond et al., 1997). The •OH is a powerful non-selective oxidizing agent that can react with organic matter, with the production of dehydrogenated or hydroxylated by-products that can then undergo total mineralization. Moreover, •OH is responsible for the generation of reactive oxygen species (ROS), such as O_3 and H_2O_2, which can also then react with organic matter (Pérez et al., 2010). Boron-doped diamond electrodes have technologically important characteristics, with a wide potential window and corrosion stability in aqueous media (Panizza and Cerisola, 2005).

Oxidative stress can provoke irreversible cell damage to cyanobacteria (Ding et al., 2012). This can be induced by various techniques, such as exposure to UV radiation, application of oxygen peroxide, and advanced oxidation procedures. These agents can act on cyanobacteria to have dual effects that are manifested through their direct external impact on the cells, and through their eliciting of intracellular ROS overproduction (Ding et al., 2012, 2013; Li et al., 2015). Both of these effects can also lead to residual inactivation of the cyanobacteria (Li et al., 2015). Such irreversible inactivation of cyanobacteria has been described as apoptosis and apoptotic-like programmed cell death. These subpopulations of cells cannot recover, as has been demonstrated by their complete loss of autofluorescence and detection of DNA unfolding and dissolution using nucleotide staining and other immunostaining methods.

Under calm-water conditions during bloom events, specific physiological characteristics separate cyanobacteria from other planktonic species: their buoyancy regulation and nitrogen fixation, according to nutrient and light availability during water stratification. It is relatively simple to locate the position of large aggregations of cyanobacteria using fluorescence sensors that allow directed targeting during sanitation measures. Here, we present laboratory experiments that are based on electrochemical degradation of cyanobacteria and their products as a potential tool in the control of cyanobacterial blooms. This method has the additional advantage that it provides simultaneous destruction of the cyanobacteria and their toxins.

1. Experimental

The electrochemical treatment was carried out in a single-compartment electrolytic cell made of Plexiglas. The experimental set-up is schematically shown in Fig. 1. The electrode set consisted of one anode and one cathode placed parallel to each other with 1.96 mm between them. The BDD plate (Condias, Germany) had a surface area of 8 cm^2 and served as the anode (BDDA), with a same-sized stainless steel plate as the cathode. The volume of the cell was 1.6 mL. The BDDA plate had a niobium base that was coated with a conductive polycrystalline diamond layer, whereby the conductivity of the BDDA was regulated by the addition of boron. The surface of the BDDA was cleaned before each run, using ethanol, Milli-Q water, and Jaworski growth medium in succession. The current density was adjusted to 10 mA/cm^2 using a laboratory direct-current power supply in constant-current mode (GPS-4303, Gwinstek, China).

The experimental set-up consisted of three groups: (1) Batch-wise flow-through exposures of the cyanobacterial cells in suspension (Fig. 1a); (2) Batch-wise flow-through exposures of a microcystin solution (Fig. 1a); (3) Constant flow-through exposures of microcystin solutions (Fig. 1b).

A peristaltic pump (Dynamax RP-1, Rainin, USA) was used to circulate the suspension/solution through the electrolytic cell, with a constant flow rate of 10 mL/min. The electro-oxidation time was 9.5 sec per passage through the electrolytic cell. This thus defined the batch-wise flow-through as electro-oxidation of 9.5 sec per passage (*e.g.*, 10 passages: electro-oxidation, 95 sec), and the constant flow-through as electro-oxidation of 9.5 sec per 1 min operation time (*e.g.*, 10 min operation time: electro-oxidation, 95 sec).

1.1. *Batch-wise flow-through exposure of cyanobacterial cells in suspension*

1.1.1. *Cyanobacterial strains and cultivation*

The *Microcystis aeruginosa* axenic microcystin-producing unicellular PCC7806 strain from the Pasteur Institute (Paris, France), and the NIES-843 strain from the National Institute of Environmental Studies (Japan) were grown and maintained under sterile conditions in 100-mL flasks with 50 mL Jaworski (PCC7806) or BG11 (NIES-843) medium, while exposed to daylight. The cell counts were determined using a haemocytometer (Blaubrand, Germany). Relatively high concentrations of cells were used (about 5.0×10^6 cells/mL) to effectively monitor numerous responses at the cell and the cell-population levels, including cell proliferation. The cyanobacterial cells were inspected under an inverted fluorescence microscope, photomicrographs were taken, and the cells were measured on each sampling day. At least 100 randomly selected cells were discriminated on the basis of their autofluorescence and measured.

The influence of the electrochemical treatment on cell proliferation was studied on the PCC7806 strain using batch-wise

Please cite this article as: Meglič, A., et al., Electrochemical inactivation of cyanobacteria and microcystin degradation using a boron-doped diamond anode — A potential tool for..., J. Environ. Sci. (2016), http://dx.doi.org/10.1016/j.jes.2016.02.016