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Effect of short exposure to electro-oxidation treatment on *Planktothrix rubescens*

Učinek kratke izpostavitve elektro-oksidaciji na *Planktothrix rubescens*

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Abstract: Cyanobacterial blooms in fresh water bodies have a serious negative impact on human, animal and environmental health. The impact of electro-oxidation of water containing *Planktothrix rubescens* in electrolytic cell equipped with diamond electrodes has been tested. The treatment had an immediate effect on cyanobacterial phycocyanin and chlorophyll fluorescence response and total cell biovolume. Cyanobacterial number reduced for 80 % 130 h after a single treatment of 500 mL of a water sample through electrolytic cell with a flow rate 1 L/min. Obtained results indicate a great potential of the method for in-lake cyanobacterial control.

Keywords: Electrolytic cell, boron doped diamond electrode, cyanobacterial bloom control, hydroxyl radicals

Izvleček: Pojav cianobakterijskega cveta v sladkih vodah negativno vpliva na zdravje ljudi, na živali in okolje. Z elektrolitsko celico, opremljeno z borom dopiranima diamantima elektrodama, smo povzročili elektrooksidacijo in testirali njen vpliv na *Planktotrix rubescens*. Tretiranje je imelo takojšen vpliv na fluorescenco klorofila, na fluorescenco cianobakterijskega fikocianina in na celotni biovolumen cianobakterijskih celic. Volumen vzorca je bil 500 ml, pretok skozi elektrolitsko celico pa je znašal 1l/min. 130 ur po tretiranju se je število cianobakterijskih celic zmanjšalo za 80 %. Rezultati kažejo na velik potencial te metode pri nadzoru cianobakterijske populacije.

Ključne besede: elektrolitska celica, z borom dopirana diamantna elektroda, cianobakterijski cvet, hidroksilni radikali

Introduction

Increased cyanobacterial concentrations and the resulting toxin formation have negative ecological, biogeochemical, health-related and economic impacts (Paerl et al. 2011). A toxic cyanobacterial species *Planktothrix rubescens* inhabits deep lakes and can bloom throughout the entire year (Sedmak et. al. 2008). A variety of conventional water treatments (chlorination, coagulation, filtration) have been developed to minimize the harmful effects of cyanobacterial bloom, which are based on the removal of the cyanobacterial biomass and do not completely remove microcystins from water (Falconer et al. 1989, Anderson et al., 2009, Pantelić et al. 2013).

Introduction of advanced oxidation technologies (ozonation, photochemical degradation, Fenton processes, sonolysis) has made total removal of cyanotoxins possible (de la Cruz et al. 2011, Barrington et al. 2013). The inactivation of cyanobacteria by electrochemical oxidation (ECO) in electrolytic cell equipped with high-performance electrodes represents a perspective alternative for water treatment with great potential, being economical, environmentally friendly and offering higher treatment efficiency (Zhank et al. 2009). Boron-doped diamond anode (BDDA) is known to have the highest potential of forming hydroxyl radicals ($^{\cdot}OH$) and exceptional chemical inertness and durability. Produced $^{\cdot}OH$ are powerful non-selective oxidizing agents, capable to react with organic matter. The aim of our work was to test the effect of the method for the reduction of *P. rubescens* biomass from natural water sample.

Materials and methods

The ECO treatment was performed in electrolytic cell, equipped with two 60 cm^2 large BDD electrodes (Condias, Germany), serving as anode and cathode, placed parallel 2 mm apart and forming 12 ml treatment chamber. The effect of the ECO was studied on *P. rubescens* taken from Lake Bled, Slovenia. The complete water sample (500 ml) with *P. rubescens* starting biovolume of 56 mm^3/L was pumped through the electrolytic cell at a constant flow rate of 1 L/min. The achieved ECO time on the electrodes was 0.72 s using 3 A current intensity. Submersible Sensors (Cyclops 7, Turner Designs, USA) were used for detecting the change in fluorescence of chlorophyll a (CHL) and phycocyanin (PC) after exposed stress in electrolytic cell. The effect of ECO was also monitored by determination of cyanobacterial biovolume (CEN EN 15204 2006) and the extraction of CHL (ISO 10260 2001) before and immediately after the treatment, and then every 24 hours for 5 days.

Results

Treating *P. rubescens* with BDD resulted in immediate effect in PC and CHL fluorescence (Fig. 1, results for CHL not shown). After a transient increase of the PC and CHL fluorescence, they both reduced up to 75 % in treated sample 130 h after the ECO compared to the control. Extraction of CHL supported these results, as its concentration dropped for 80 % (not shown). ECO also affected the cyanobacterial biovolume. It reduced for 21 % immediately after the treatment and for 80 % 130 h later.

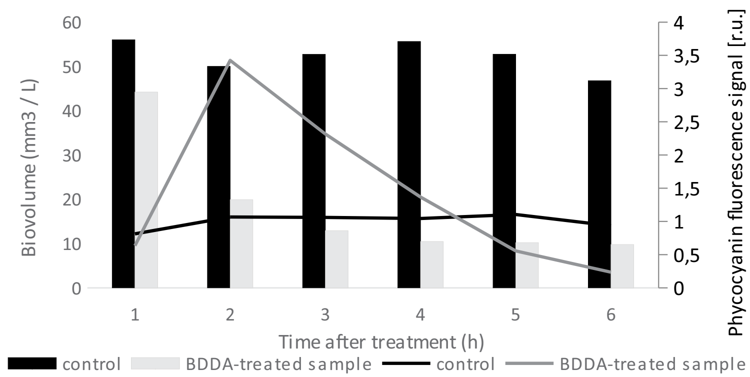

Figure 1: Phycocyanin fluorescence (line) and cyanobacterial biovolume (bar) in treated and control samples after the electro-oxidation treatment.

Slika 1: Fluorescenca fikocianina (črti) in biovolumen cianobakterij (stolpci) v kontrolnih in tretiranih vzorcih po elektro-oksidacijskem tretiranju.

Discussion

The three selected monitoring approaches enabled us to follow immediate and postponed effects of ECO treatment on *P. rubescens*. Besides an immediate biovolume reduction and therefore a die-off of a part of the population, a transient increase of fluorescence of PC and CHL immediately after the treatment was observed. This can be contributed to the stress response of the survived part of the cells, where the photosynthetic apparatus was damaged. After Zilinskas and Glick (1981), the increased fluorescence is the result of decoupling of PS II reaction centers from CHL, to which the energy from PC can no longer be transferred. The damages were detrimental; resulting in greatly reduced PC and CHL signals below the control level after 4 days (Fig. 1) and were in positive correlation with low concentration of extracted CHL and biovolume, showing on 80 % reduction of the *P. rubescens* population. Although the ECO time was very short, the immediate and postponed effects of ECO were observed even though $^{\cdot}$OH radicals are known to be short-lived (Pryor 1986). This indicates on gradual decrease of the cyanobacterial population, which is beneficial also from the point of cyanotoxins release. The use of BBD electrode has already proved to be effective also in extracellular cyanotoxins degradation and inactivation (Meglič et al. 2016). The effect of ECO using BDD electrodes on degradation of cyanotoxins in natural water samples is planned to be closely followed in our future experiments, as well as the effect of ECO on other biota for which larger scale experiments are planned.

Conclusions

Short-term exposure of natural water sample to ECO treatment applying BDD electrodes in laboratory environment caused a visible stress response of *P. rubescens*, resulting in an evident decrease in biovolume and concentration of CHL, indicating on efficiency of the novel method as an in-lake cyanobacterial control method. Measurement of the fluorescence of cyanobacterial pigments enabled the quantification and probably also the determination of their physiological state. Performance of simultaneous on-line fluorescence measurements immediately after the ECO treatment are therefore suggested in the case of further activities in natural environment to promptly react on increased density of cyanobacteria or their regrowth after the treatment and to keep the natural biodiversity balance.

Povzetek

Cvetenje cianobakterij v sladkovodnih telesih predstavlja resno težavo za zdravje ljudi in živali ter za okolje. Testirali smo vpliv okolju prijazne metode, elektro-oksidacije z diamantnimi elektrodami, na številčnost cianobakterij. Uporabili smo vodo iz Blejskega jezera, ki je vsebovala *P. rubescens*. Pri tretiranju smo 500 ml vzorca vode spustili skozi elektrolitsko celico z delovnim volumnom 12 ml in tokom 3 A. S pretokom 1 L/min smo dosegli elektrooksidacijski čas 0,72 s. Učinek tretiranja na fluorescenčni signal fikocianina in klorofila ter na skupni celični biovolumen je bil takojšen. Fluorescenca in koncentracija klorofila sta 130 ur po tretiranju upadli za 75 in 80 %, prav tako biovolumen cianobakterij. Rezultati kažejo, da ima uporabljena metoda velik potencial za izvajanje kontrole nad cianobakterijami v jezerih.

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