EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

CYANOCOST – ES 1105 Action

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Cyanobacterial blooms and toxins in water resources: Occurrence, impacts and management.

Short Term Scientific Mission (STSM)

Treatment of cyanobacterial cell extracts with Advanced Oxidation Processes (AOPs): Kinetics and toxicity studies

Researcher

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She has a BSc in Chemistry (University of Cyprus, 2002) and a PhD on Water Quality (University of Cincinnati, 2010). Her work experience includes serving as a Guest Worker at the USEPA in Cincinnati and a postdoctoral fellow at DTU-Environment of the Technical University of Denmark. During her doctoral and postdoctoral tenures she utilized advanced oxidation technologies (AOTs) for the removal of emerging contaminants from water and wastewater. So far, she has authored 17 peer-review publications, 6 book chapters, and received 21 awards.

Host Organization

School of Pharmacy and Life Sciences, Robert Gordon University, Aberdeen, UK

Supervisor: Dr. Christine Edwards
Collaborators: Prof. Linda Lawton, Dr. Mahalakshmi Abhishek, Iosef Boraei, and Constantina M. Kyriakou



Objectives

The aim of this study was to compare the efficiency of light based Advanced Oxidation Processes (AOPs) on their efficiency to remove cyanotoxins from crude bloom/cell extracts since their treatment is closer to realistic treatment conditions. The study primarily focused on lysates of *Microcystis Aeruginosa* PCC7806 (producing mainly microcystin-LR), *Planktothrix Rubescens* (producing mainly desmethyl-microcystin-RR) and *Cylindrospermopsis Raciborskii* (producing cylindrospermopsin). The remaining cyanotoxin concentration following AOP treatment was quantified in an HPLC-PDA with methods developed by the CyanoSol Group. The study also aimed to identify and quantify the effects of the various pigments, that are found in each extract, on the removal efficiency of the cyanotoxins that each of the lysates contains. Finally, toxicity studies based on the inhibition of PP1 enzymes were performed.

Methodology

Preliminary experiments with MC-LR in Milli-Q water indicated that the best treatment conditions were toxin initial concentration ~5 mg/L, TiO_2 10 mg/L, and illumination with a UVA lamp at a distance of 20 cm. The average photon flux was determined with Ferrioxalate Actinometry at λ= 365 nm to be 35.58 ± 3.06 W. In addition, AOP treated samples were analyzed in a Waters HPLC-PDA (RT_{CYL} =6.9 min, RT_{dMCRR} =11,1 min, RT_{MCLR} = 14.5 min). The toxicity of the treated samples was measured based on the inhibition of the protein phosphatases enzymes (PP1) only for the lysates containing MC-LR and d-MC-RR. The treated samples also were measured with spectophotometer in 200-800 nm to follow the changes that the spectra of the lysates (containing the pigments phycocyanin and phycoerythrin) underwent. Data where processed based on the Bolton' s Equations for estimating Electrical Energy Demand (EED) and Electrical Energy per Order (E_{EO}). E_{EO} is a measure of the electrical energy (kWh) needed to reduce the concentration of a contaminant by one order of magnitude in 1 m^3 of contaminated water.

Results

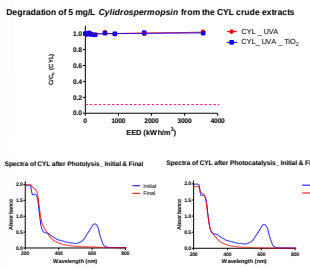
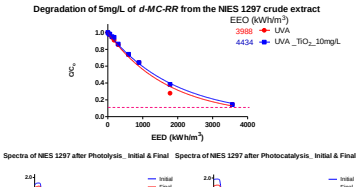


Fig. 1: Degradation of CYL with UVA and 10 mg/L TiO_2 /UVA.



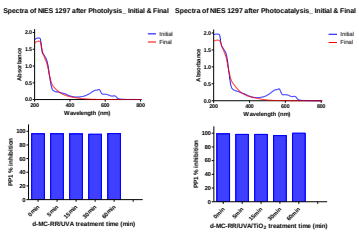
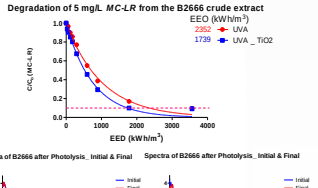


Fig. 2: Degradation of d-MC-RR with UVA and 10 mg/L TiO_2/ UVA.



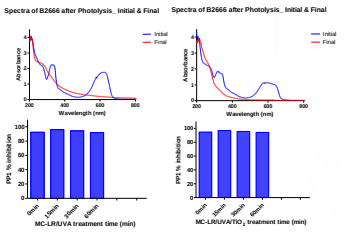


Fig. 3: Degradation of MC-LR with UVA and 10 mg/L TiO_2/ UVA.


Bolton Equations:

$$\log\left(\frac{C}{C_o}\right) = \frac{-EED}{E_{EO}} \Leftrightarrow C = C_o \cdot 10^{-\left(\frac{EED}{E_{EO}}\right)}$$

$$EED = \frac{Pt}{60V}\left(\frac{kW}{m^3} = \frac{W}{L}\right)$$

where: *EED* = electrical energy per order
P = total electrical power or flux entering the reactor (W)
t = treatment time (min)
V = volume of water treated (L)

James R. Bolton, *Ultraviolet Applications Handbook* Third Edition, Canada, Bolton Photosciences Inc., 2010.

Highlights

- The pigments acted as photosensitizers in the presence of UVA radiation and caused removal of cyanotoxins except for CYN.
- Susceptibility of the cyanotoxins towards PCO treatment vary significantly due to their structural differences. Though MC-LR and d-MC-RR belong to the same group of cyanotoxins, d-MC-RR was less susceptible to AOP treatment possibly because of shielding effects caused by the two arginine (R) groups in its structure.
- Catalyst addition (TiO_2) did not enhance toxin removal compared to photolysis possibly due to radical consumption by the matrix (pigments).
- Toxicity studies based on the inhibition of the PP1 enzyme showed no reduction of toxicity after 60 min of treatment because the remaining toxin concentration was still high enough to cause almost complete inhibition of the enzyme's activity (IC_{50}=7,4 μg/L).

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