S Cyprus University of Technology

Faculty of Geotechnical Sciences and Environmental Management

Doctoral Dissertation

RESTORATION OF SURFACE WATERS CONTAMINATED WITH CYANOBACTERIA HARMFUL BLOOMS (CYANO-HABs) THROUGH NOVEL CHEMICAL OXIDATION PROCESSES

Eleni C. Keliri

Limassol, December 2022

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…Dedicated to her loving memory…

ABSTRACT

Cyanobacteria (blue-green algae) are phototrophic microorganism that represent an essential component of the food web in all aquatic ecosystems. However, the effects of climate change and anthropogenic activities have intensely increased the load of nutrients in surface waters around the globe, making cyanobacterial harmful blooming (cyano-HABs) more persistent and prevalent, adding further pressure on the already scarce fresh water supply. Their overgrowth is causing undesirable odor, color, and taste to the water, as well as toxicity since certain strains of cyanobacteria are producing secondary metabolites, called cyanotoxins which are lethal to both humans and animals. Currently an array of methods has been applied to mitigate the negative effects of cyano-HABs, that differ in cost, efficiency, and environmental impact. Those can be categorized as physical, chemical, and biological treatment methods based on their application type. Chemical methods are the most applied ones for being efficient, cost effective, and having long-lasting treatment results. The most recently developed method is the use of liquid hydrogen peroxide (H_2O_2) in affected surface waterbodies which is by far the least hazardous chemical, among the treatment options, used for *in-situ* treatment. However, studies have shown that its efficiency varies based on the species type and density as well as on matrix composition. In cases of high contamination, the use of higher doses of H_2O_2 than the recommended > 5 mg L^{-1} dose, are required. which negatively impact zooplankton and other non-targeted species. In this doctoral thesis, peroxide releasing compounds were utilized to test their potency to mitigate cyano-HABs as novel treatment alternatives to the high doses of liquid hydrogen peroxide. More specifically, the following oxidants were utilized: magnesium peroxide (MgO_2) granules, calcium peroxide (CaO_2) granules and powder, CaO_2 granules enclosed in fabrics (GEF), and peroxymonosulfate (PMS). Calcium peroxide granules enclosed in textile materials and single low doses of peroxymonosulfates outperformed liquid H_2O_2 treatment in terms of efficiency, required dose, and environmental friendliness.

Treatment with liquid H_2O_2 in concentrations 1 to 5 mg L^{-1} had no effect on the phycocyanin fluorescence (Ft) and quantum yield of PSII (Fv/Fm) indicating an ineffective treatment for the dense (1 million cells $mL^{-1} \pm 20\%$) and naturally occurred *Merismopedia* sp. bloom, while 1 g L^{-1} CaO_2 granules succeeded in treating the bloom. In another study, metallic peroxide granules tested for their H_2O_2 releasing capacity in

filtered St. George Lake matrix, where they released significantly higher H_2O_2 concentration and therefore had better mitigation efficiency than MgO_2 granules. CaO_2 granules releasing capacity was also tested in three different matrixes: MQ-water, River Water and Dam water. Release kinetics results showed that matrix composition influences the H_2O_2 release by granules. In extra-pure water (milli-Q) the release of H_2O_2 was limited in comparison with its release in surface waters of CaO_2 granules. For instance, dam water which was the least contaminated water, resulted in higher and continuous H_2O_2 yield of around 6 mg L^{-1} for 1 g L^{-1} CaO_2 granules applied, whereas an equal CaO_2 dose in river water with elevated physicochemical characteristics released around 5 mg L^{-1} H_2O_2, and in lake water was around 3 mg L^{-1}. Similar release experiments were performed in surface water spiked with humics, and BG-11 medium of different concetrations. Results have shown that humics can activate CaO_2 granules through an interfacial mechanism causing the simultaneous generation of hydroxyl and hydroxyalkyl radicals. Additionally, application of CaO_2 granules and liquid H_2O_2 in BG-11 matrices of different dilutions showed lower H_2O_2 availability than what expected, indicating that the presence of micronutrients and trace elements into the water can consume and/ or interact with the available H_2O_2.

A toxicity study on invertebrate species of CaO_2 granules revealed the undesirable effects on *Echinogammarus veneris* when applied in doses higher than 1 g L^{-1}. Treatment of cultivated cultures with CaO_2 granules, showed that doses higher than 0.2 and 1.0 g L^{-1} CaO_2 granules were efficient to treat *Microcystis* sp. and *Aphanizomenon* sp. in Kouris Dam matrix, respectively. Finally, treatment experiments of cyano-HABs contaminated water with PMS outperformed equal doses of liquid H_2O_2. Instant oxidant quantification during treatment also showed that PMS has a residual effect while H_2O_2 is rapidly being consumed or decomposed, supporting further the competence of PMS compared with H_2O_2 as a novel treatment method. Treatment experiments indicated that slow H_2O_2 releasing CaO_2 granules, and PMS could be alternative solutions to liquid hydrogen peroxide, when applied in appropriate doses, but further investigation is needed before their field applications to ensure safety of the aquatic ecosystem.

Keywords: cyanobacteria, oxidant, restoration, surface water, treatment