Enhancing photocatalytic degradation of the cyanotoxins microcystin-LR and nodularin with the addition of sulfate-radical generating oxidants

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Abstract This study dealt with enhancing the photocatalytic oxidation (PCO) of the hepatotoxic cyanotoxins microcystin-LR (MC-LR) and nodularin (NOD) via the addition of the sulfate-radical producing oxidants persulfate (PS) and peroxymonosulfate (PMS). Initially, the optimum experimental conditions were established. The average photon flux at λ=365 nm of the UVA lamp used was determined with ferrioxalate actinometry at 0.59 ± 0.05 W. Oxidant addition showed enhanced PCO rates for both toxins. In the case of MC-LR it reduced the electrical energy of the system by ~14% and ~50%, for PS and PMS, respectively. Quenching studies with methanol and tetra-butyl alcohol asserted the role of sulfate radicals during treatment. Toxicity studies based on the inhibition of the PP1 enzyme showed reduction of toxicity in the treated samples.

Keywords: microcystins, nodularins, persulfate, peroxymonosulfate, TiO_2 photocatalysis

1. Introduction

Cyanobacteria (blue-green algae) are phototrophic microorganisms and represent an essential component of the food web in all aquatic ecosystems. However, certain strains of cyanobacteria have the ability to produce bioactive secondary metabolites (also known as cyanotoxins) that have detrimental effects on mammalian health. Eutrophication of surface waters can lead to the formation of cyanobacteria harmful algal blooms (Cyano-HABs) that directly affect water quality by producing undesirable color, taste, odor and by releasing harmful cyanotoxins into the water. Human activities (i.e., sewer runoffs, overuse of fertilizers) and global warming have resulted in an increasing prevalence and persistence of Cyano-HABs globally [Carmichael 1994; Antoniou 2013]. Cyano-HABs are affecting surface water resources and have forced restrictions on water availability for millions of people worldwide. Specifically, the incidences in Lake Taihu in China, (2007) and Lake Erie in USA (2014) alone have affected water availability for more than 2 million people combined.

Cyanotoxins are categorized based their chemical structure and their impact on mammalian health. Cyclic polypeptides consisting usually of hepta- and pepta- amino acids can cause hepatotoxicity. Two very characteristic examples of these groups are microcystin-LR (MC-LR) and nodularin (NOD), respectively. Studies have shown that under bloom conditions, it is highly probable that more than one class of toxins will require treatment [Diehnelt 2006].

Conventional methods (coagulation, flocculation, rapid sand filtration) can remove cyanobacterial cells efficiently but have limited ability to remove cyanotoxins [Antoniou 2005]. On the other hand, pilot scale studies have shown that the application of mechanical force on the cyanobacterial cells during treatment can cause them to lyse and increase the soluble fraction of the cyanotoxins [Schmidt 2002]. Therefore, current research efforts are focusing on establishing appropriate treatment strategies to deal the side effects of persistent blooms. Herein, photocatalytic advanced oxidation processes (AOPs) based the activation of oxidants, catalysts, and their combination were tested for the removal of MC-LR and NOD. Photocatalytic oxidation (PCO) with titanium dioxide (TiO_2) under UVA radiation is considered a "green technology" with high efficiencies for water purification and detoxification. To enhance PCO degradation most studies use hydrogen peroxide (H_2O_2) because it does not leave any harmful residuals. This study chose to use sulfate radical generating oxidants persulfate ($S_2O_8^{2-}$, PS), peroxymonosulfate (HSO_5^-, PMS) instead, since sulfate radicals have higher redox potential for electron abstraction than hydroxyl radicals and can cause selective oxidation.

To the best of our knowledge, this is the first study investigating the coupling of TiO_2/UVA with these oxidants for the removal of cyanotoxins.

2. Materials and Methods

Reagent grade cyanotoxins were obtained from Enzo Life Sciences (Lausen, Switzerland). Analysis was performed using reversed-phase HPLC with photodiode array detection [Lawton 1994]. Analysis of samples for the detection of transformation products was performed using Acquity UPLC system with photodiode array (ACQUITY

UPLC PDA) equipped with Tandem Quadruple Time of Flight (Xevo QToF) in series (Waters, Elstree, UK). The PCO experimental set up consisted of a UVA lamp at a set distance of 20 cm, a continously stirred 30 mL brosilicated glass reactor vessel, and a cooling fan to keep the solution temperature below T=35 ^{o}C. During PCO the treated solution (V=10 mL) was also aerated. The toxicity removal of the treated samples was measured based on the inhibition of the protein phosphatases enzymes (PP1).

3. Results and Discussion

Initially, preliminary experiments were conducted to determine the best treatment conditions. It was decided to have an initial toxin concentration of ~5 mg/L, TiO_2 10 mg/L, and irradiation distance of reactor vessel from UVA lamp at 20 cm. The latter one was estimated to give an average photon flux at λ= 365 nm of 0.59 ± 0.05 W though ferrioxalate actinometry. Our data also indicated that the susceptibility of the two hepatotoxins towards PCO treatment did not significantly differ even at changing catalyst loadings. Though the molecular mass of MC-LR (heptapeptide) is ~170 amu higher than NOD (pentapeptide) both toxins contain similar functional groups which are highly susceptible to radical attack [Antoniou 2010; Liu 2005]. To be specific these groups are found in the ADDA chain and are the conjugated double carbon bonds and an aromatic ring.

To enhance degradation efficiency the oxidants persulfate and peroxymonosulfate were added at a concentration of 10 mg/L (equivalents of PS). The hepatotoxins where treated individually with each oxidant alone and in the presence of sulfate and hydroxyl radical quenchers to account for the percentage of degradation for each type of radical. Photolysis of the toxins with UVA radiation alone was proven inefficient to remove either of the cyanotoxins since their absorptivity at λ= 365 nm is negligible. When the two oxidants were added, MC-LR and NOD were completely removed the toxins at the end of treatment time (t=60min), however PS degradation occurred faster than PMS. This happens because the extinction co-efficient (ε) of PS at λ= 365 is twice as much as one of PMS. Nevertheless, the presence of both oxidants greatly enhanced the PCO degradation of the cyanotoxins with PS being more efficient than PMS for both toxins (Figure 1, shown the data for MC-LR). In order to compare the efficiency of each process the electrical energy per order E_{EO} was estimated [Bolton 2010]. 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 or air. The faster the degradation, the smaller the energy requirements of a treatment (Figure 1). Addition of PMS reduced the energy demands by 50% of MC-LR compared to conventional photocatalysis.

Finally, in order to prove that sulfate radicals also contributed in the removal of cyanotoxins quenching studies were performed. The presence of isopropyl alcohol that reacts with both types of radicals at molar ratio to the oxidant = [10000/1] caused greater reduction to the reaction rate compared to tetra-butyl alcohol at equivalent concentration that can only react with hydroxyl radicals. This serves as proof that even though the oxidants have low light adsorption at λ= 365 nm (ABS_{365} below 0.04 for 1.23 mM oxidant concentration), their activation was achieved and the generated sulfate radicals contributed to the degradation of the toxins. This is also evident from the initial transformation products detected that included hydroxylated products from hydroxyl addition and substitution of unsaturated carbon bonds.

Finally, the toxicity studies performed in the treated samples indicated that PCO degradation coupled with sulfate radicals generating oxidants resulted in loss of toxicity as confirmed by lack of PP1A inhibition.

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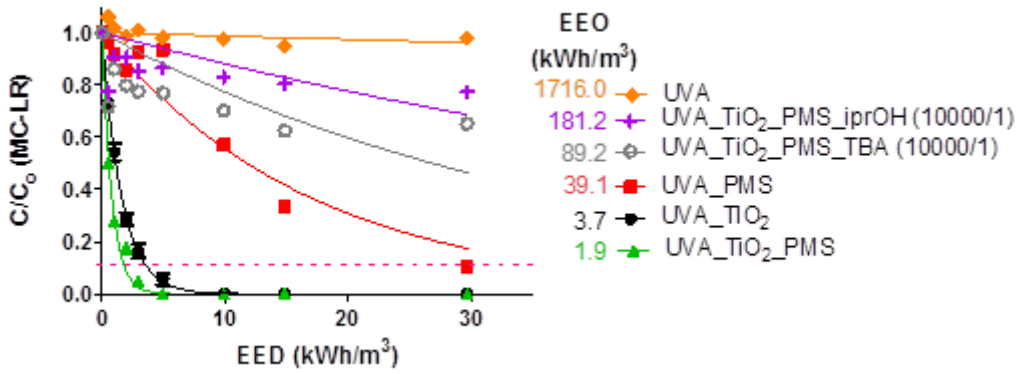

Figure 1: Estimated electrical energy per order for the removal of MC-LR with various treatment processes

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