Destruction of Cyanobacterial Toxins in Water with Germicidal UV-254 nm-based Homogeneous and Solar-based Heterogeneous Advanced Oxidation Processes

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PI: Dionysios D. Dionysiou, Ph.D., Professor

Environmental Engineering and Science Program,

University of Cincinnati, Cincinnati, OH 45221-0012

Email: dionysios.d.dionysiou@uc.edu

Fax: +1-513-556-2599; Tel: +1-513-556-0724

1. A completion report

The project focused on the destruction of the cyanobacterial toxins by advanced oxidation technologies (AOTs), using both homogeneous and heterogeneous systems. The increasing occurrence of cyanobacterial blooms in surface water resources has become intense around the world. The blooms could not only produce many odor or taste issues, but also result in cases of livestock deaths or human health disorders [1]. Toxic freshwater cyanobacteria such as *Microcystis* could produce cyclic hepatotoxins called microcystins (MCs). They are found to be persistent in aquatic systems [2]. Chronic exposure due to the presence of MCs in drinking water is thought to be a contributing factor in primary liver cancer [3]. Their effect is accumulative and the cancer risk could increase by exposure to even very low levels of the toxins [4]. Cylindrospermopsin (CYN) is a tricyclic guanidine alkaloid and protein synthesis-inhibitor. This toxin is believed to be responsible for a major human poisoning in the "Palm Island mystery disease". CYN is a hepatotoxin, and beside liver damage, it causes damages to the kidneys, spleen, intestine, thymus, and heart in vertebrates [8-12]. During this period of the project (March 1, 2009 through November 30, 2010), various research activities were conducted to evaluated the degradation of cyanobacterial toxins, such as microcystins and cylindrospermopsin, by solar-based heterogeneous and germicidal UV-254 nm-based homogeneous advanced oxidation processes.

Part I. Destruction of Cyanobacterial Toxins in Water with Solar-based Heterogeneous Process.

1. Research Objectives

Solar-driven photocatalytic systems, such as titanium dioxide (TiO_2), were explored for the destruction of cyanotoxins in water. TiO_2 photocatalyst has been considered a key material in the destruction of recalcitrant organic pollutants in water and air as well as for killing pathogenic microorganisms. Recent studies have dealt with the modification of this material towards visible light sensitization via doping of TiO_2. A successful approach is the use of non-metal elements, such as C, F, N, S and P, to activate the catalyst under visible light due to either band gap narrowing or the creation of mid gap levels in the TiO_2 lattice. The objective was to investigate sol-gel based approaches to developed TiO_2 films with enhanced structural and optical properties towards the improvement of photocatalytic activity of TiO_2 under visible light irradiation. This is one of the few studies that deal with the synthesis of these nanostructured visible light activated TiO_2 photocatalyst using surfactant templating strategies in sol-gel methods. The results and

findings obtained in this study are promising, considering: (i) versatile applications of this method, (ii) immobilization of TiO_2 for more engineered approach and application, and (iii) controllability of the physicochemical properties of TiO_2 at the nano-level for sustainable applications.

2. Methodology and Findings

In one of the studies, we report on the synthesis, characterization and environmental application of immobilized nitrogen and fluorine co-doped TiO_2 (NF-TiO_2) photocatalyst. A fluorosurfactant-based sol-gel approach was employed to enhance the physicochemical properties and photocatalytic activity of NF-TiO_2 under visible and UV light for the degradation of the hepatotoxin microcystin-LR (MC-LR). The films were characterized by XRD, ESEM, TEM, AFM, EPR, micro-Raman, XPS, UV-vis spectroscopy and porosimeter analysis. The results revealed that by modifying the molar ratio of the fluorosurfactant, we could effectively control the physicochemical properties and obtain films with high BET surface area and porosity, small crystallite size and narrow pore size distribution. UV-vis spectroscopy showed an increase in the absorption capacity of NF-TiO_2 in the visible light range compared to reference films. The existence of interstitial nitrogen and substitutional fluorine in the TiO_2 lattice was determined by XPS. Comparative EPR measurements between the co-doped and reference samples identified distinct N spin species in NF-TiO_2, with a high sensitivity to visible light irradiation. The abundance of these paramagnetic centers verifies the formation of localized intra-gap states in TiO_2 and implies synergistic effects between fluorine and nitrogen dopants. Micro-Raman spectroscopy showed the growth of small amounts of brookite concomitantly with the major anatase TiO_2 phase, which could promote the system's photocatalytic activity through the formation of anatase/brookite heterojunctions. Analysis of the lower frequency E_g anatase Raman mode indicated the occurrence of size effects reflecting phonon confinement in the anatase nanocrystallites as well as deviations from stoichiometry due to structural defects in the co-doped sample. NF-TiO_2 films effectively degraded MC-LR under visible and UV light compared to reference film. Similar MC-LR degradation rates under visible light after three cycles revealed high mechanical stability and no irreversible changes of the film during photocatalysis. This process has the potential of providing environmentally benign routes for drinking water treatment with solar powered photocatalytic systems.

The evaluation of NF-TiO_2 photocatalyst for the degradation of MC-LR under visible light in the presence of different water quality parameters (i.e., natural organic matter, pH, alkalinity and dissolved oxygen) was also investigated. It was found that the degradation

rate of MC-LR was higher under acidic conditions than in alkaline pH due to electrostatic interaction between the positively charge nanoparticle and the negatively charge cyanotoxin. The addition of carbonate to concentrations of 50, 100 and 150 mg $CaCO_3$/L at pH 7.0 reduced the degradation of MC-LR with the highest reduction at a concentration of 150 mg $CaCO_3$/L. The increase of carbonate ions can scavenge the radicals species formed during visible light irradiation of NF-TiO_2. In the case of natural organic matter (i.e., fulvic acid and humic acid), the inhibitive effect of fulvic acid, both at 5 and 10 mg/L, was larger than that of the humic acid at neutral pH due to the higher degree of aromaticity of the fulvic acid. Even though there was inhibition in the presence of natural organic matter, degradation of MC-LR was observed at all pH tested with a highest degradation at acidic conditions. In the absence of oxygen (N_2 purged), a reduction on the degradation rate of MC-LR was observed while under oxygen saturated conditions (O_2 purged); an enhancement on MC-LR rates was obtained. Real water samples from Lake Erie and Florida (St. John's River) were spiked with MC-LR but no degradation was observed after 5 hrs of visible light irradiation with NF-TiO_2. The water quality parameters suggest that the alkaline pH of the water, along with the high alkalinity and TOC values, strongly inhibits the performance of NF-TiO_2 under the conditions tested. A manuscript on the results is published in *Water Research* and a conference proceeding is accepted for *the 20th IOA World Congress – 6th IUVA World Congress*, May 23-27, 2011, Paris, France (Note appendix A and B for publication details).

Part II. Destruction of Cyanobacterial Toxins in Water with Germicidal UV-254 nm-based Homogeneous Process.

1. Research Objectives

Hydrogen peroxide, under the irradiation of UV, produces the generation of nonselective and powerful hydroxyl radicals. The combined UV/H_2O_2 has some advantages compared to other advanced oxidation processes, e.g., it does not have phase transfer problems and it is a green technology that neither UV nor H_2O_2 produces harmful residues [5, 6]. In US EPA's disinfection guidance manual (2006), the 22, 22, and 186 mJ/cm^2 UV doses are required for a 4-log inactivation of *Cryptosporidium*, *Giardia* and Virus (*Adenovirus*) respectively [7]. It is thus an advantage if the required UV dose for the destruction of certain amount of microcystin is within the disinfection UV dose. In this part of project, we aim at (i) studying the degradation of MC-LR by UV-254 nm/H_2O_2, (ii) evaluating the effects of UV dose on the degradation, (iii) investigating the effect of selected important

water quality parameters, and (iv) using real water samples as background solutions to investigate the behavior of the toxins.

2. Methodology and Findings. Photochemical Degradation of MC-LR: Fundamental Studies.

Studies have been carried out in a laboratory scale collimated beam system with low pressure germicidal lamps (254 nm) in the presence of hydrogen peroxide. Chemical actinometry methods and radiometer method were used to determine the UV-254 nm fluence. It was found that a 93.9% removal of MC-LR with an initial concentration of 1 mg/L was achieved with a UV dose of 80 mJ/cm^2 and an initial H_2O_2 concentration of 30 mg/L. The degradation of MC-LR increased with an increase in the UV dose, following a UV-dose-based pseudo-first-order kinetics. Reaction solutions with different pH values were prepared in phosphate buffer. It was suggested that the impact of pH was mild when it was neutral or slightly basic, which means, in natural waters, the required background pH condition could not be as limiting effect as compared to some other technologies, such as the Fenton reagent. The oxidant, hydrogen peroxide, played an important role in the process. At low concentrations, there was a linear relationship between the pseudo-first-order reaction rate constant with the concentration of H_2O_2. After it reached a "threshold" concentration, its scavenger effects became more obvious. The results show that the % removal rate decrease with increase in initial concentration of MC-LR but the initial degradation rate was increasing as the initial MC-LR concentration increased. Alkalinity affected significantly the degradation rates of MC-LR, especially with carbonate alkalinity. Fortunately the pH in real waters is generally neutral in which the alkalinity is mainly bicarbonate alkalinity. When samples with natural organic matter (NOM) and real water samples spiked with MC-LR were used to compared and verify the results, it was clearly shown that the degradation of MC-LR decreased significantly. The impact factors could be the presence of NOM and alkalinity. A manuscript on the results is submitted to *Water Research* (Note appendix C for publication details).

3. Methodology and Findings. Photochemical Degradation of Cylindrospermopsin and the Mixtures of Microcystins.

In the same system, the degradation of the mixtures of microcystins was also investigated by UV/H_2O_2. We found the degradation of the cyanotoxins studied were all a function of UV fluence in both UV direct photolysis system and UV/ H_2O_2 advanced oxidation system, following UV fluence-based pseudo-first-order reaction kinetics, no matter when it was individual cyanotoxin or the toxin mixtures. The addition of H_2O_2 increased

significantly the destruction of the microcystins. The observed behavior of different microcystins towards UV/H_2O_2 was similar. It was also found that the removal of total microcystins decreased when the initial pH values increased and MC-LR was more vulnerable to the change of pH values than MC-RR. CYN is another category of cyanotoxins. UV-254 nm irradiation had nearly no effect on the degradation of CYN with the UV fluence used here. It seemed to be influenced much more than microcystins by the presence of alkalinity and natural organic matters when tap water was used as background matrix, reducing the removal at 80 mJ/cm^2 of UV fluence from 83.7% to 11.2%. A conference proceeding on this result was accepted by *the 20th IOA World Congress – 6th IUVA World Congress*, May 23-27, 2011, Paris, France (Note appendix D for publication details).

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2. Publication citations

I. Journal Articles

(1) Pelaez, Miguel, Polycarpos Falaras, Kevin E. O'Shea, Armah A. de la Cruz and Dionysios D. Dionysiou, 2011, Effects of Water Parameters on the Degradation of Microcystin-LR under Visible Light-activated TiO_2 Photocatalyst, *Water Research* doi:10.1016/j.watres.2011.04.036.

(2) He, Xuexiang, Miguel Pelaez, Judy A. Westrick, Kevin E. O'Shea, Anastasia Hiskia, Theodoros Triantis, Triantafyllos Kaloudis, Mihaela I. Stefan, Armah A. de la Cruz and Dionysios D. Dionysiou. Efficient Removal of Microcystin-LR by UVC/H_2O_2 in Synthetic and Natural Water Samples, *Submitted to Water Research, May 2011*.

II. Proceedings

(1) Pelaez, Miguel, Polycarpos Falaras, Erick R. Bandala, Patrick Dunlop, Anthony Byrne, Armah A. de la Cruz and Dionysios D. Dionysiou, TiO_2-based Enhanced Photocatalytic Degradation and Disinfection of Water Under Solar Light Irradiation, *Conference proceeding at the 20th IOA World Congress – 6th IUVA World Congress*, May 23-27, 2011, Paris, France.

(2) He, Xuexiang, Armah A. de la Cruz and Dionysios D. Dionysiou, Destruction of cyanotoxins by UV/H_2O_2 advanced oxidation processes, *Conference proceeding at the 20th IOA World Congress – 6th IUVA World Congress*, May 23-27, 2011, Paris, France.

III. Presentations

(1) Pelaez, Miguel *, Armah A. de la Cruz and Dionysios D. Dionysiou, Nanostructured TiO_2 Nanoparticles and Films Activated under Visible Light for Water Purification. Oral Presentation at *the International Conference on Water, Environment and Health Sciences: The Challenges of the Climate Change, (ICWEHS)*, April 13-17, 2009, Cholula, Puebla, Mexico.

(2) Pelaez, Miguel *, Armah A. de la Cruz and Dionysios D. Dionysiou, Nitrogen and Fluorine co-doped TiO_2 Mesoporous Nanomaterials Activated under Visible Light Irradiation for Water Purification. Poster Presentation at *the International Conference on Particle Separations and Nanoparticles in Water*, June 3-5, 2009, Durham, North Carolina.

(3) Pelaez, Miguel *, Armah A. de la Cruz and Dionysios D. Dionysiou, Nanostructured Non-metal Doped TiO_2 for the Degradation of Microcystin-LR under Visible Light. Poster Presentation at *the 2nd International Conference from Nanoparticles and Nanomaterials to Nanodevices and Nanosystems (IC4N-2)*, June 28-July 3, 2009, Rhodes, Greece.

(4) Pelaez, Miguel, Polycarpos Falaras, Vlassis Likodimos, Athanassios G. Kontos, Kimberley Curell, Elias Stathatos and Dionysios D. Dionysiou*, Structural, Morphological and Optical Properties of Nanostructured NF-TiO_2 Films for the Photocatalytic Degradation of Emerging Micropollutants in Water under Visible and Solar Light. Oral Presentation at *the 239th American Chemical Society (ACS) National Meeting*, Division of Environmental Chemistry, March 21-25, 2010, San Francisco, California.

(5) Pelaez, Miguel *, Erick R. Bandala, Jordana Castillo, Patrick S.M. Dunlop, Anthony Byrne and Dionysios D. Dionysiou, Enhanced Photocatalytic Solar Disinfection (ENPHOSODIS) of *Escherichia coli* using Nitrogen and Fluorine co-doped Titanium Dioxide. Oral Presentation at the *239th American Chemical Society (ACS) National Meeting, Division of Environmental Chemistry*, March 21-25, 2010, San Francisco, California.

(6) He, Xuexiang, Miguel Pelaez* and Dionysios D. Dionysiou, Degradation of Microcystin-LR by UV/H_2O_2 Advanced Oxidation Process. Poster Presentation at *the 239th American Chemical Society (ACS) National Meeting*, Division of Environmental Chemistry, Session on General Posters, March 21-25, 2010, San Francisco, California.

(7) Pelaez, Miguel, Polycarpos Falaras, Vlassis Likodimos, Athanassios G. Kontos, Armah. A. de la Cruz and Dionysios D. Dionysiou*, Highly Efficient Nanocrystalline Visible light-activated TiO_2 films by Modified Sol-gel Methods for Sustainable "Green" Applications. Oral Presentation at *the 240th American Chemical Society (ACS) National Meeting, Division of Environmental Chemistry, Session on Heterogeneous Catalysis for Environmental and Sustainable Energy Applications*, August 22-26, 2010, Boston, Massachusetts.

(8) Pelaez, Miguel *, Erick R. Bandala, Jordana Castillo, Patrick S. M. Dunlop, Anthony Byrne and Dionysios D. Dionysiou, NF-co-doped TiO_2 for Visible/Solar Treatment and Disinfection of Water Including Applications in Developing

Countries. Poster Presentation at *the Water Energy in Changing Climates Conference*, Sept. 26-29, 2010, Pittsburgh, Pennsylvania.

(9) Pelaez, Miguel, Polycarpos Falaras*, Vlassis Likodimos, Athanassios G. Kontos, Armah A. de la Cruz and Dionysios D. Dionysiou, Synthesis and Characterization of N-F TiO_2 Nanomaterials for MC-LR Photodegradation. Poster Presentation at *the Autumn Event Joint Dissemination Workshop of the nano4water Cluster*, October 26, 2010, Aachen, Germany.

(10) Pelaez, Miguel *, Polycarpos Falaras, Vlassis Likodimos, Athanassios G. Kontos, Armah. A. de la Cruz and Dionysios D. Dionysiou, Synthesis and Performance of Highly Active Mixed-phase NF-TiO_2 Composite Photocatalysts for the Degradation of Microcystin-LR. Oral Presentation at *the 15th International Conference on TiO_2 Photocatalysis: Fundamentals and Applications*, November 15-18, 2010, San Diego, California.

(11) He, Xuexiang, Miguel Pelaez, Christopher D. Williams, Judy A. Westrick, Kevin E. O'Shea, Anastasia Hiskia, Theodoros Triantis, Armah A. de la Cruz and Dionysios D. Dionysiou*. Oral Presentation at *the 16th International Conference on Advanced Oxidation Technologies for Treatment of Water, Air and Soil (AOTs-16)*, November 15-18, 2010, San Diego, California.

(12) Pelaez, Miguel, Polycarpos Falaras, Vlassis Likodimos, Athanassios G. Kontos, Armah. A. de la Cruz and Dionysios D. Dionysiou*, Mesoporous Non-metal Doped TiO_2 for Visible Light-induced Photo-assisted Degradation of Microcystin-LR. Oral Presentation at *the Area of Materials & Nanotechnology, Symposium on Redox Processes on Nanoparticles, Nanomaterials, and Nanostructured Systems in the Environment, Pacifichem 2010*, December 15-20, 20010, Honolulu, Hawaii, USA.

(13) Pelaez, Miguel, Polycarpos Falaras, Vlassis Likodimos, Athanassios G. Kontos, Armah A. de la Cruz and Dionysios D. Dionysiou*, Novel NF-TiO_2-P25 Composite Photocatalyst for the Removal of Microcystins and Cylindrospermopsin under Visible and Solar Light. Oral Presentation at *the Division of Industrial and Engineering Chemistry, 9th Symposium on Nanotechnology and the Environment: Green Nanotechnology, 241st American Chemical Society (ACS) National Meeting & Exposition*, March 27-31, 2011, Anaheim, California.

(14) He, Xuexiang *, Armah A. de la Cruz and Dionysios D. Dionysiou, Destruction of Microcystins and Cylindrospermopsin in Various Water Samples by UV/H_2O_2 Process, Oral Presentation at *the 241st American Chemical Society (ACS) National Meeting, Division of Environmental Chemistry,* Mar 27-31, 2011, Anaheim, California.

3. Students supported by the project

(1) Miguel Pelaez

Ph.D. student, Environmental Engineering;

(2) Xuexiang He

Ph.D. student, Environmental Engineering.

4. Brief description of notable awards or achievements resulting from the project

(1) 2010 David Eye Scholarship to Miguel Pelaez. University of Cincinnati.
(2) 2010 Graduate Student Award in Environmental Chemistry, Division of Environmental Chemistry, American Chemical Society (to Miguel Pelaez).
(3) 2011 David Eye Scholarship to Xuexiang He. University of Cincinnati.

5. Appendix List.

Appendix A-published paper. Effects of Water Parameters on the Degradation of Microcystin-LR under Visible Light-activated TiO_2 Photocatalyst.

Appendix B-accepted proceeding. TiO_2-based Enhanced Photocatalytic Degradation and Disinfection of Water Under Solar Light Irradiation

Appendix C-submitted manuscript. Efficient Removal of Microcystin-LR by UV-C/H_2O_2 in Synthetic and Natural Water Samples.

Appendix D-accepted proceeding. Destruction of cyanotoxins by UV/H_2O_2 advanced oxidation processes.