Mitigation of Harmful Algal Bloom Toxins Using Deployable 3D Printed Photocatalytic Devices

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USACE Harmful Algal Bloom Research & Development Initiative

Delivering scalable freshwater HAB prevention, detection and management technologies through collaboration, partnership and cutting-edge science

Problem The USACE maintains and improves inland and intracoastal waterways, ports and harbors. Threats from Harmful Algal Blooms (HABs) to inland ecological resources and human health are increasing. Innovative solutions for HAB treatment (cyanobacteria and toxins) are needed to mitigate blooms and decrease risks without introducing chemicals (e.g., copper algaecides, Tributyltin, peroxides) that may have undesirable secondary effects.

Objective Development of an effective treatment strategy for HABs in open and closed water systems that is customizable, reusable and avoids chemical additives was our goal. Photocatalytic TiO_2 nanoparticles are effective in the lab for breaking down toxins under UV-light by activating short-lived free radicals. However, TiO_2 cannot be field-deployed as free particles because they settle out of the photoactive zone and disperse into the environment. Here we designed, developed and demonstrated 3D printable polymer composite containing TiO_2 photocatalyst as a sustainable HAB management technology.

Approach Our research approach involved four interrelated tasks: (1) determine TiO_2 effectiveness on HABs, with microcystin from *Microcystis aeruginosa* being our treatment target; (2) develop standard protocol to make and 3D print devices (Figure 1; Figure 2); (3) perform tests to optimize effectiveness and reduce impacts to non-target organisms; and (4) demonstrate technology effectiveness in a USACE-relevant mesocosm or field-scale.

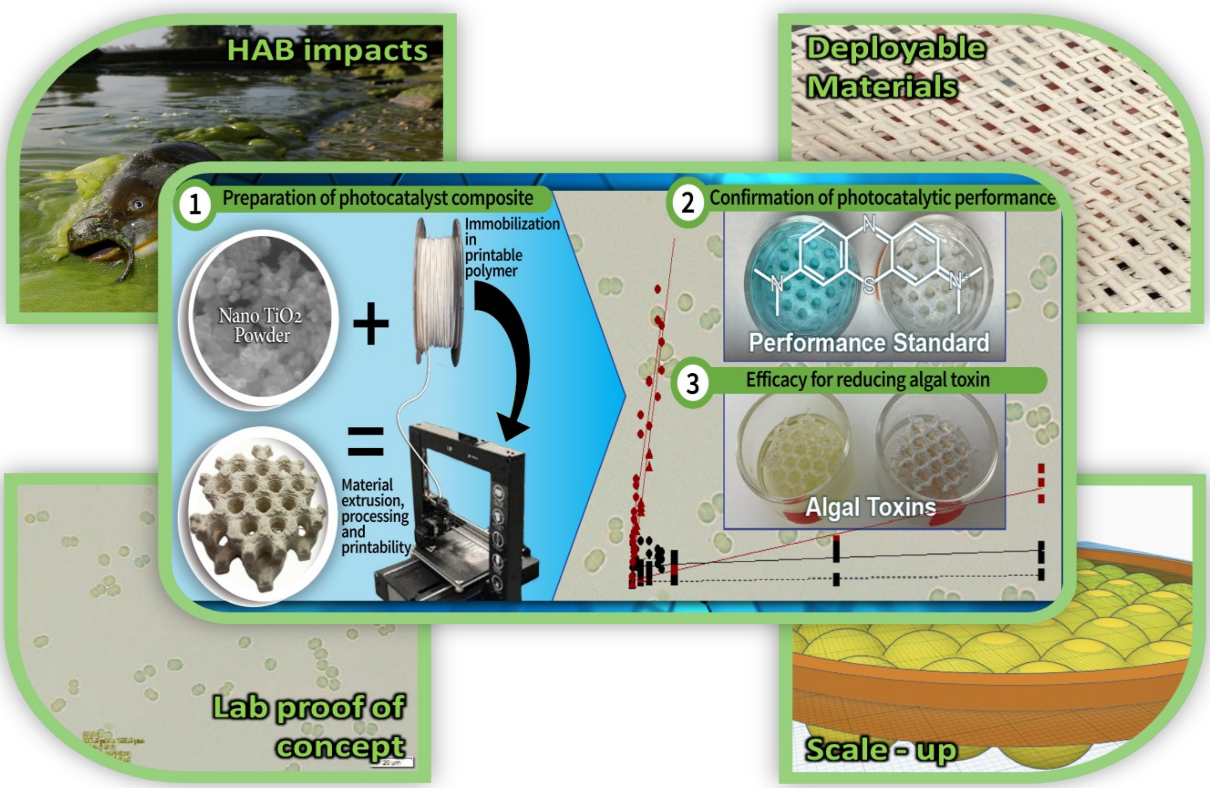

Figure 1: *Process for producing customizable deployable and retrievable material structures via 3D printing.*

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Results Lab results showed the photocatalytic performance of the 3D printed TiO_2 was equivalent to that of free TiO_2 (Figure 3) and provided multiple advantages: (1) reduced nanoparticle toxicity to non-target species; (2) retains reactive material in the water column for prolonged treatment; and (3) is retrievable and reusable. 3D printed TiO_2 also degraded microcystin and was 12 times faster than UV light alone (Figure 4). Photocatalyst interactions with the polymer locally reduces pH leading to enhanced microcystin adsorption to the photocatalyst and subsequent destruction. Further work will go toward faster treatment, technology scale up and road mapping, including preliminary field demonstration.

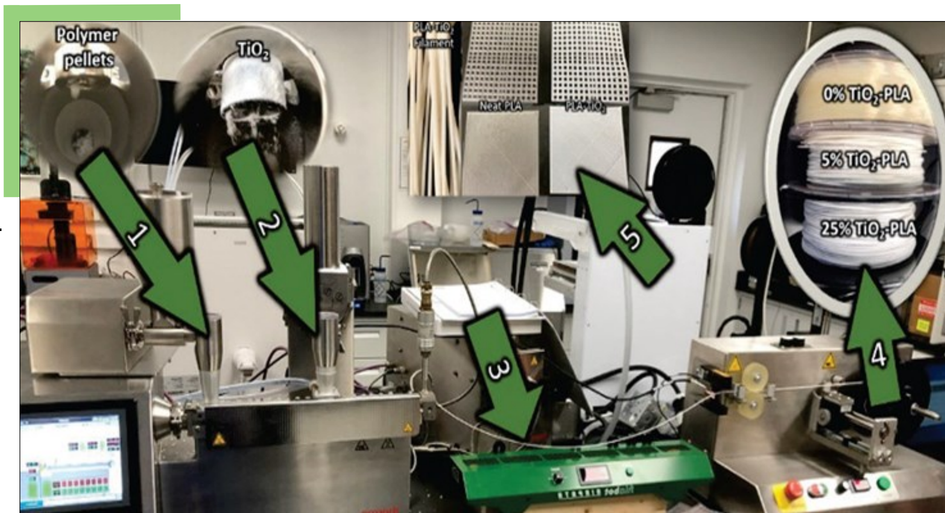

Figure 2: *Developed process to embed TiO_2 into filament that is 3D printable by inexpensive desktop printers. This process can be commercialized at low cost.*

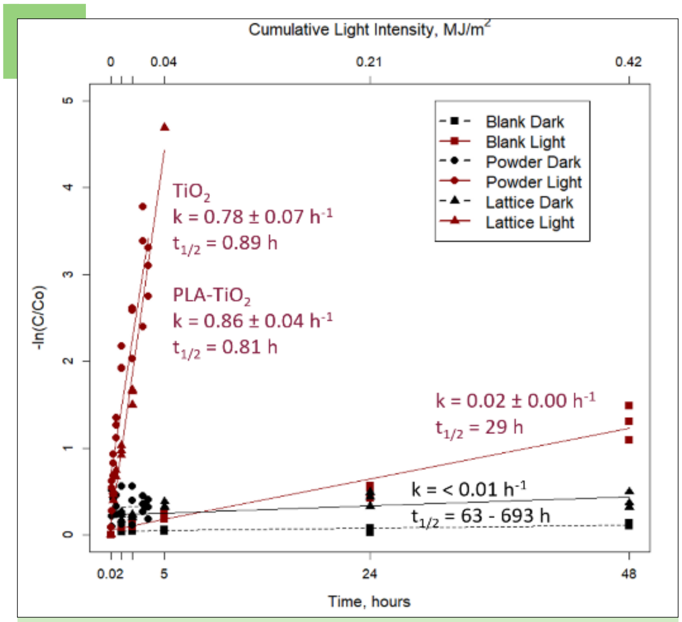

Figure 3: *Similar photocatalytic performance between free and 3D printed photocatalyst. These data demonstrate successful performance of 3D printed materials.*

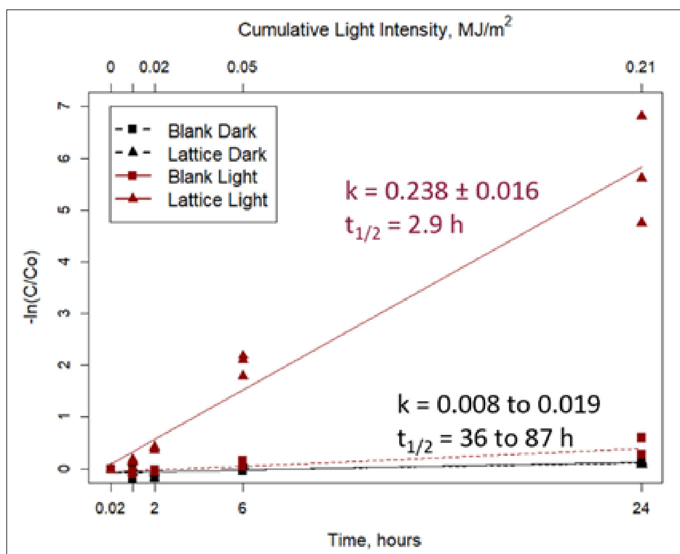

Figure 4: *3D printed photocatalytic materials destroys algal toxins (microcystin) within environmentally relevant timeframes and environmental conditions.*

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Major Milestones

Date	Milestone			
FY21, Q3	Photocatalyst effectiveness demonstration (Complete)			
FY21, Q3	Method to 3D print photocatalyst treatment (Complete)			
FY21, Q4	Technical Notes: Sustainable HAB mitigation by 3D Printed Photocatalytic Oxidation Devices (Published)			
FY22, Q1	Conference: Oral presentation at Society of Environ. Toxicol. & Chem. (SETAC); HABs session			
FY22, Q2	Conference: Oral presentation at American Chemical Society			
FY22, Q3	Material fabrication and proof of efficacy for microcystin reduction			
FY22, Q4	Journal Article: Degradation of MC toxin by 3D Printable Polymer Immobilized TiO_2 (in review Sept22)			
FY23, Q1	Conference: Oral presentation at 11th U.S. Symposium on Harmful Algae			
FY23, Q4	Demo and Technical Report: 3D printed, deployable/retrievable HABs control technology			
FY23, Q4	Prototypes and digital library available to USACE Districts for pilot use			
Costs	**FY21:**$256K	**FY22:**$197K	**FY23:**$232K	**TOTAL:**$685K

Partnership/Leveraging Opportunities

This effort has synergy with other Aquatic Nuisance Species Research Program sponsored projects including *Rapid Algae Flotation Techniques (RAFT)* (PI-Clinton Cender) and *Light-Based Mitigation Technology (LBMT)* (PI-Elizabeth Gao), with potential to float treat and UV treat HABs more effectively. A combination of the LBMT and 3D printed TiO_2 technologies is proposed to harness strengths of both for maximal HAB treatment effectiveness. A 3D printed flexible fabric mat could be used as a polishing step to reduce microcystin concentrations after LBMT inactivates the cells. The PIs have partners at USACE Jacksonville, Buffalo, Chicago, and Rock Island Districts.

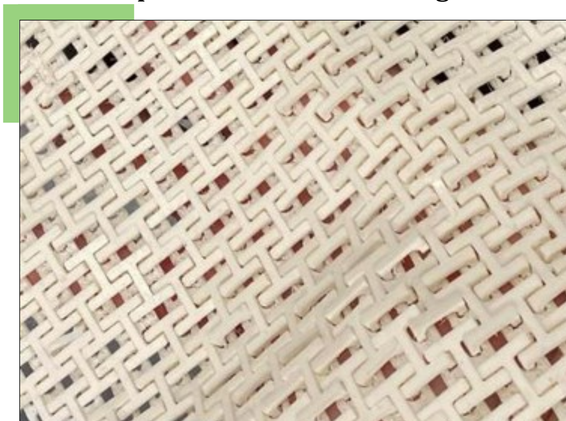

Figure 5: *Capability to 3D print flexible materials that can move with water.*

Value to USACE Mission

Optimization of deployable and retrievable technology available on-demand to combat HABs while avoiding legacy contamination (e.g., copper, peroxides, etc.). Provides USACE with a proactive, cost-effective and reusable HABs solution while maintaining a sustainable mission.