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

Lead: Alan J. Kennedy, ERDC, Alan.J.Kennedy@usace.army.mil

USACE Harmful Algal Bloom Research & Development Initiative

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

Problem

USACE maintains and improves inland and intra-coastal waterways, ports, and harbors. Threats from harmful algal blooms (HABs) to inland ecological resources and human health are increasing. Innovative solutions for HAB treatment (both cyanobacteria and thier toxins) are needed to mitigate blooms and decrease risks without introducing chemicals (e.g., copper algaecides, Tributyltin, and 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 the target for treatment; (2) develop standard protocol to make and 3D print devices (Figure 1 and Figure 2); (3) perform tests to optimize effectiveness and reduce impacts to nontarget organisms; and (4) demonstrate technology effectiveness in a USACE-relevant mesocosm or field scale.

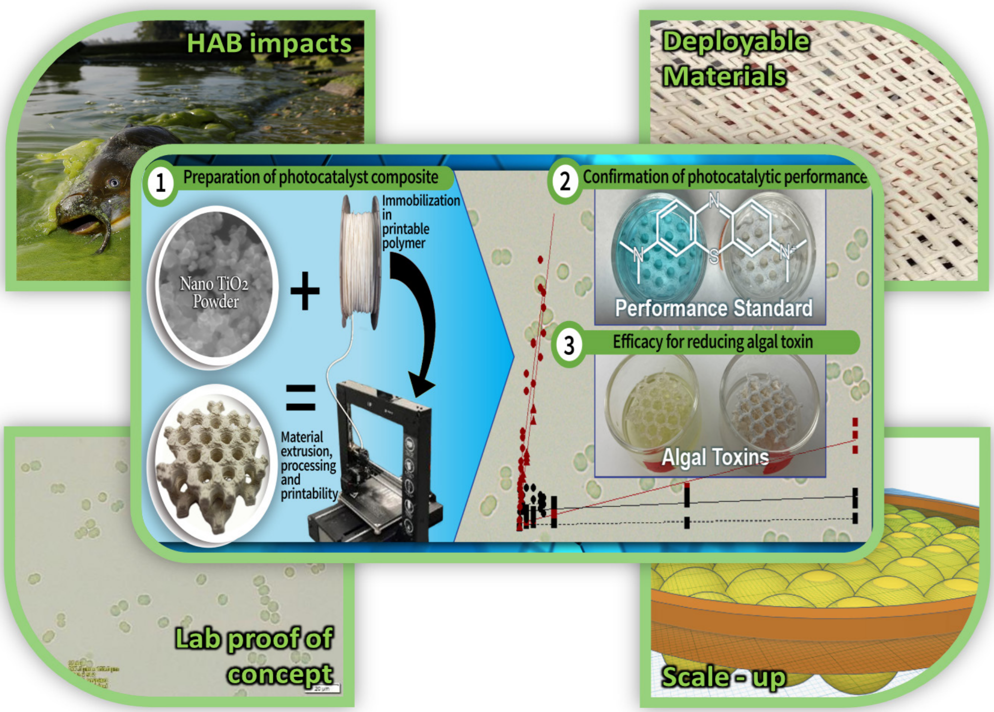

Figure 1. *Process for producing customizable, deployable, and retrievable material structures via 3D printing. https://doi.org/10.1016/j.cej.2022.140866*

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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 nontarget 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.

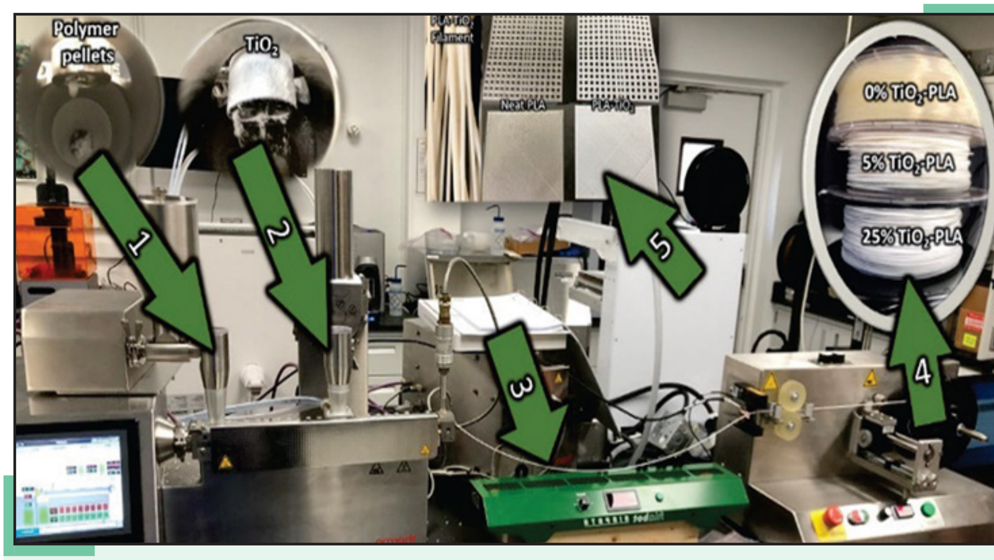

Figure 2. *Developed process to embed TiO_2 into filament that is 3D printable by inexpensive desktop printers. This process can be commercialized at a low cost. https://apps.dtic.mil/sti/citations/*

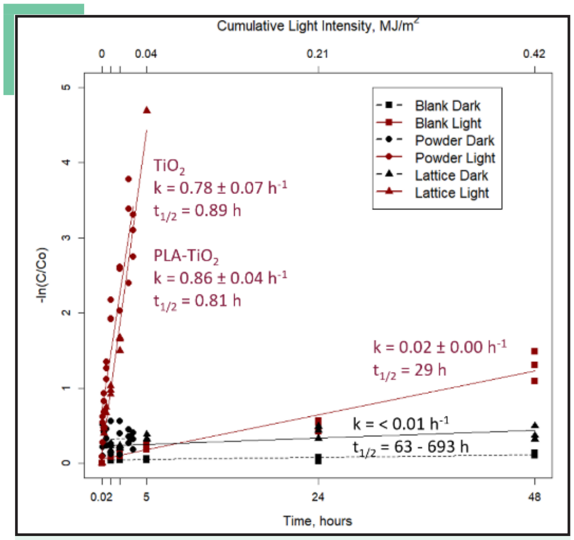

Figure 3: *Similar photocatalytic performance using methylene blue dye between free and 3D-printed photocatalyst. These data demonstrate successful performance of 3D-printed materials. https://doi.org/10.1016/j.cej.2022.140866.*

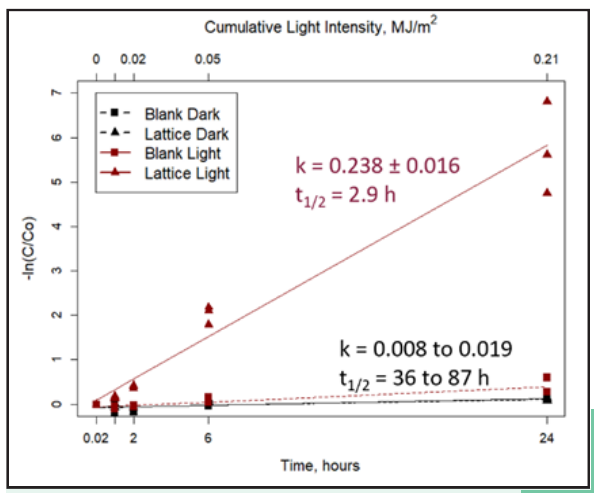

Figure 4: *3D-printed photocatalytic materials degrades algal toxins (microcystin) within environmentally relevant timeframes and environmental conditions. https://doi.org/10.1016/j.cej.2022.140866.*

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Major Milestones

Deliverable	Description
Publications	**Tech Note:** Kennedy et al. 2022. *Sustainable Harmful Algal Bloom Mitgation by 3D Printed Photocatalytic Oxidation Devices (3D-PODs).* ERDC/TN ANSRP-22-1. Vicksburg, MS: US Army Engineer Research and Development Center. https://apps.dtic.mil/sti/citations/AD1166826. **Journal Article:** Kennedy et al. 2023. “Degradation of Microcystin Algal Toxin by 3D Printable Polymer Immobilized Photocatalyic TiO_2.” *Chemical Engineering Journal* 455: 40866. https://doi.org/10.1016/j.cej.2022.140866. **Tech Report:** Kennedy et al. In prep. “Demo and Report: 3D printed, deployable/retrievable HABs control technology.” ERDC/EL TR.
Products	**Software:** Eventually, will have downloadables for printing and can place online **Patents:** In progress; met with patent attorney in March 2023
Tech Transfer	Prototypes and digital library available to USACE districts for pilot use

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) (PIs: Elizabeth Gao and Taylor Rycroft), 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.

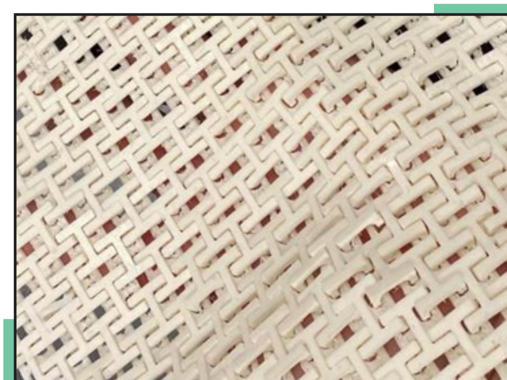

Figure 5: *Capability to 3D print flexible materials that can move with water.*

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.