Sustainable Harmful Algal Bloom Mitigation by 3D Printed Photocatalytic Oxidation Devices (3D-PODs)

by Alan J. Kennedy, Andrew D. McQueen, Mark L. Ballentine, Brianna M. Fernando, Lauren R. May, Jonna A. Boyda, Christopher B. Williams, and Michael J. Bortner

PURPOSE: The impacts of Harmful Algal Blooms (HAB), often caused by cyanobacteria (Figure 1), on water resources are increasing. Innovative solutions for treatment of HABs and their associated toxins are needed to mitigate these impacts and decrease risks without introducing persistent legacy contaminants that cause collateral ecosystem impacts. This technical note (TN) identifies novel opportunities enabled by Additive Manufacturing (AM), or 3D printing, to produce high surface area advanced material composites to rapidly prototype sustainable environmental solutions for aquatic nuisance species control. This innovative research explores deployment of 3D-printable polymer composite structures containing nano-scale photocatalysts for targeted open water treatment of HABs that are customizable to the site-of-concern and also retrievable, reusable, and sustainable. The approach developed to control cyanobacteria HAB events has the potential to augment or replace broadcast, non-specific chemical controls that otherwise put non-target species and ecological resources at long-term risk. It can also augment existing UV-treatment HAB treatment control measures. The expected research outcome is a novel, effective, and sustainable HAB management tool for the US Army Corps of Engineers (USACE) and resource managers to deploy in their HAB rapid response programs. The research will provide a framework for scale-up into other manufacturing methods (e.g., injection molding) to produce the devices in bulk (quickly and efficiently). Research for this project title "Mitigation of Harmful Algal Bloom Toxins using 3D Printed Photocatalytic Materials (FY21-23)" was sponsored by the US Army Engineer Research Development Center's (ERDC) Aquatic Nuisance Species Research Program (ANSRP).

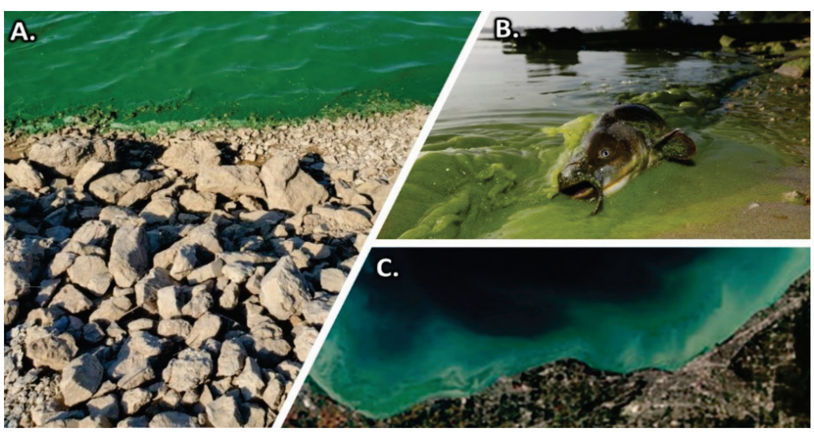

Figure 1. Harmful algal blooms, from (A) USACE Kansas City District; (B) Photo by Andy Morrison/The Blade via AP Photo; and (C) Herman et al. (2017).

BACKGROUND: USACE maintains and improves inland and intracoastal waterways, ports, and harbors throughout the United States. Threats from cyanobacteria (also known as blue-green algae) HABs to water resources, ecological receptors (e.g., biomass, hypoxia), and human health (e.g., toxin production) are increasing (Brooks et al. 2016; Berdalet et al. 2016; Grattan et al. 2016; ITRC 2020). Negative impacts include degraded water quality, increased turbidity, shading and decreased macrophyte production, anoxia, fish kills, noxious drinking water, impaired kidney/liver function, dermal irritation, reduced aesthetics, and lower recreational value (Pokrzywinski et al. 2021; Herman et al. 2017; ITRC 2020). Certain conditions (seasonality, sunlight, temperature, pH, conductivity, stratification, mixing) favor harmful blooms, including eutrophication with certain nitrogen:phosphorus ratios (Linkov et al. 2009; Pokrzywinski et al. 2021; Herman et al. 2017; ITRC 2020). The definition of a harmful bloom may be site- and stakeholder-specific (Pokrzywinski et al. 2021; USEPA 2019, 2015; WHO 2003). Cyanobacteria species can be planktonic or benthic, existing as single cells or as multi-cellular colonies, with some species diurnally migrating in the water column (Medrano et al. 2016; ITRC 2020). A commonly studied and problematic freshwater cyanobacterial species is *Microcystis aeruginosa* (Figure 2), which produces the cyanotoxin microcystin. The USACE needs a balanced approach to prevent and manage damage to resources, recreation, and operations due to HAB in an innovative, cost effective, and sustainable manner (Linkov et al. 2009; Pokrzywinski et al. 2021).

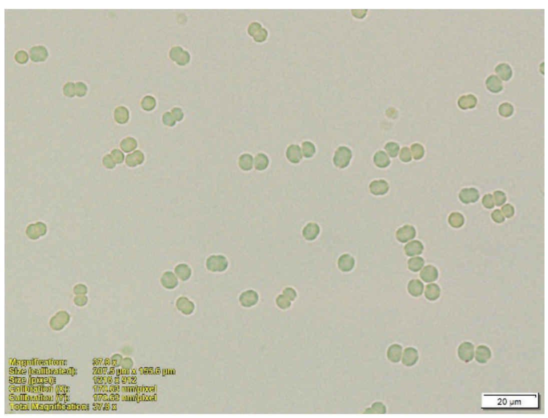

Figure 2. Optical microscopy image of *Microcystis aeruginosa*. Photo by Brianna Fernando, ERDC Environmental Laboratory.

Currently, available field-deployable HAB chemical management strategies consist of registered copper- and peroxide-based products (Millward et al. 2007; Lynn et al. 2007; Pokrzywinski et al. 2021; Herman et al. 2017; ITRC 2020). While copper products have demonstrated effectiveness, copper is toxic to fish, zooplankton, and mollusk species (Closson and Paul 2014; Bishop et al. 2014; Kennedy et al. 2006; Kennedy et al. 2013; Johnson et al. 2008). Peroxide-based algaecides are also toxic to non-target species (Gaikowski et al. 1999; Geer et al. 2016; Reichwaldt et al. 2012), but may dissipate in the environment (Matthijs et al. 2012; Geer et al. 2017). Similarly, application of other oxidants (i.e., chlorine and potassium permanganate) are discussed in Herman et al. (2017), Kinley et al. (2020), and ITRC (2020). Many chemical control options are short-term strategies that may kill target HAB species immediately but, with undesirable side effects including toxin release from the lysed cells (Kenefick et al. 1993) and unintended impacts on non-target species. Some alternatives to algaecides include nutrient reduction intervention using aluminum sulfate and non-chemical controls such as horizontal flushing/scouring, mechanical mixing, floating covers (e.g., shade balls), physical cavitation, and bio-controls may also be applied with varying degrees of success (Pokrzywinski et al. 2021; Herman et al. 2017; ITRC 2020). There is recent interest in identifying alternative effective chemical control solutions that increase long-term sustainability and decrease unintended impacts (e.g., residuals in the environment).

Photocatalytic materials such as nano-scale titanium dioxide (TiO_2) in the presence of ultra-violet (UV) light can degrade certain chemical classes, including polycyclic aromatic hydrocarbons (Yang et al. 2017; Zhang et al. 2008; McQueen et al. 2021) and perfluorinated compounds (Cho 2011; Gomez-Ruiz et al. 2018; Wang and Zhang 2011). A relatable application to infrastructure includes use of photocatalytic TiO_2 for self-decontaminating cement for air pollutants (Diamond et al. 2017). Strong evidence supports that reactive oxygen species (ROS) released from TiO_2 during exposure to solar radiation (UV light) provides a viable, reusable, and sustainable treatment technology for HAB (Miller et al. 2012; Fan et al. 2020) and the released algal toxins (Hu et al. 2017; Zhang et al. 2020; Wang et al. 2017; Song et al. 2018). Low collateral damage to non-target species is expected since non-photo irradiated TiO_2 nanoparticles have relatively lower hazard to non-target aquatic life (Diamond et al. 2017; Kennedy et al. 2017) since TiO_2 releases localized free radicals only when exposed to UV-sunlight and those radicals have a half-life of less than 1 sec (Kikuchi et al. 1997). However, the technology requires further development to realize feasible field deployment.

TECHNOLOGY DESCRIPTION: This research evaluates the efficacy of TiO_2 particles (Figure 3) on cyanobacteria and HAB management. It also aims to optimize deployability of retrievable and reusable photocatalytic TiO_2 structures that sustainably treat HAB and their toxins in closed photocatalysis water treatment systems and in open natural water bodies. Results of this research could overcome an identified technical barrier to treating HAB in water discharges; specifically, there is currently no viable and scalable method to keep TiO_2 nanoparticles immobilized in the zone of UV-light penetration into water in close proximity to the HAB (Hu et al. 2017; Kinley et al. 2018). Environmental fate and transport research conducted at ERDC's Environmental Laboratory (ERDC-EL) indicates TiO_2 nanoparticles rapidly agglomerate and settle in the aquatic environment (Kennedy et al. 2017). Thus, agglomerated (and settled) TiO_2 nanoparticles will not provide optimal exposed surface area or remain in the photoactive zone of the water column. A technology is needed for UV-treatment systems (e.g., inline treatment, deployable UV-drones) to ensure the TiO_2 photocatalysts remain within the treatment system and in the zone of UV-light penetration.

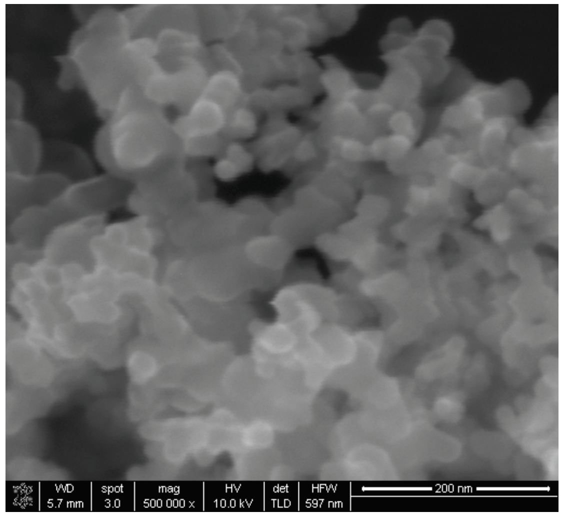

Figure 3. TiO_2 nanoparticles used in this research. Scanning electron microscopy image by Kyle Klaus, ERDC-Geotechnical Structures Laboratory.

Embedding TiO_2 in a binder that does not impact its photocatalytic effectiveness is the proposed solution. Recent developments in low cost and user friendly 3D printing (Campbell et al. 2011; Kalsoom et al. 2016; Canessa et al. 2013), including fused filament fabrication (FFF) material extrusion (Figure 4), have provided momentum for novel environmental applications (Kennedy et al. 2021; Thakkar et al. 2016; Martín de Vidales et al. 2019; Friedmann et al. 2019; Kalsoom et al. 2018; Hu and Jiang 2017; Skorski et al. 2016; Jo et al. 2017; Yusoff Nurul Husna et al. 2021) directly applicable to immobilizing photocatalysts into 3D printable polymer composites (Sangiorgi et al. 2019; McQueen et al. 2021). This promising research is inherently scalable provided availability of portable, low cost 3D printers or traditional polymer mass production processing methods (e.g., injection molding).

Our research objective is immobilizing photocatalytic TiO_2 nanoparticles in 3D printed polymer binder feedstocks to position TiO_2 in the water column and harness direct sunlight (or increase kinetics of existing UV-treatment systems) to release ROS and treat released cyanotoxins – then investigate treatment effectiveness initially in controlled laboratory mesocosms. Joo et al. (2020) and Kim et al. (2018) indicate the ability to treat algae with polymer spheres provides justification for further applied research; their research adhered TiO_2 to the outside of the spheres (produced after conventional manufacturing), which requires multiple steps and may result in a limited effective lifetime if the material degrades and the particles are released.

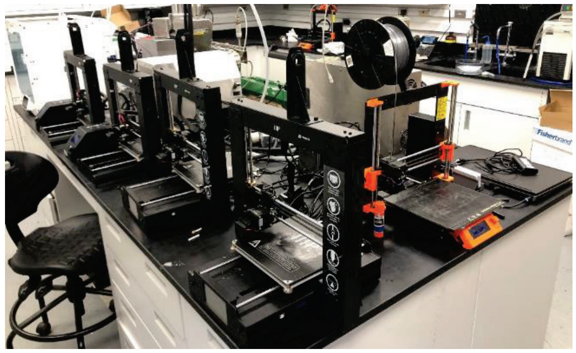

Figure 4. An additive manufacturing laboratory at ERDC-EL including fused filament fabrication printers and extruders. Photo by Alan Kennedy.

We, the principal investigators, are transitioning lessons learned from previous polymer-composite environmental applications research (Kennedy et al. 2021; Kennedy et al. 2021; McQueen et al. 2021) to develop customizable, deployable, retrievable, and reusable 3D printed structures specifically designed for HAB control. For environmental applications using polymer 3D printing, selection of environmentally compatible polymers is paramount to avoid adverse impacts and microplastic contamination (Sutliff et al. 2020; Browne 2015; Browne et al. 2011; Geyer et al. 2017). This effort offers two innovations to previous approaches: (1) integration of TiO_2 into the biopolymer polylactic acid (PLA) instead of polymers such as polystyrene which are problematic microplastics in the environment (Geyer et al. 2017; Browne 2015); and (2) optimizing and customizing the TiO_2 integration into the deployable and retrievable polymer structures through compounding and 3D printing (Figure 5). 3D printing is exploited as a low cost, rapid prototyping research tool to create and iteratively improve customizable, field deployable, retrievable, and reusable devices for treating HAB that can be deployed to the field for on-site, on-demand production. Previous (non-HAB) work has shown efficacy for compounding and 3D printing TiO_2 in polymers and provided evidence that the photocatalyst is reusable (Mendez-Arriaga et al. 2019; Jo et al. 2017; McQueen et al. 2021). While weak layer-by-layer adhesion and inherent porosity within parts produced by material extrusion 3D printing are known disadvantages for structural applications due to anisotropic mechanical properties (Verbeetenet al. 2020), such characteristics present an advantage for environmental applications due to the creation of greater surface area structures allowing increased water contact, adsorptive activity (Kennedy et al. 2021), and theoretically free radical release.

Figure 5. Compounding of photocatalytic TiO_2 into the 3D printable polymer polylactic acid (PLA). Step 1: pure polymer pellets fed into the extruder; step 2: pellets melted and compounded with TiO_2; step 3: composite filament is cooled; step 4: filament is spooled; step 5: TiO_2 polymer composite filament is 3D printed into structures for HAB treatment efficacy testing. Photographs by A. Kennedy.

The commonly studied cyanobacteria *Microcystis aeruginosa* was cultured in-house at ERDC-EL (Figure 6) and tested in the absence and presence of simulated natural sunlight (including UV) with various treatments and comparative controls: (1) cyanobacteria only; (2) cyanobacteria + 3D printed PLA; and (3) cyanobacteria + 3D printed PLA- TiO_2 composite. Treatments featured cyanobacteria suspended in a surface water-relevant matrix approximating a field-relevant HAB. The custom PLA-TiO_2 composite filaments (Figure 5, step 4) were 3D printed into high surface area geometries such as screens (Figure 5, step 5), lattices (Figure 7), and spheres (Figure 8) for HAB treatment efficacy testing. Cell counts were assessed before and after treatment and results were standardized to baseline cell population growth. The laboratory trials generated during the first year of this research (FY21) are promising, indicating the 3D printed structures continue releasing ROS to treat the surrounding water, eradicating >90% of *Microcystis* toxin.

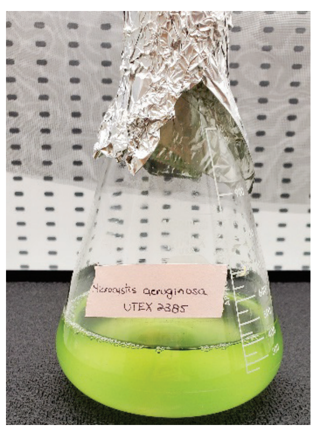

Figure 6. In-house culture of *Microcystis aeruginosa* (UTEX 2385). Photo by Brianna Fernando.

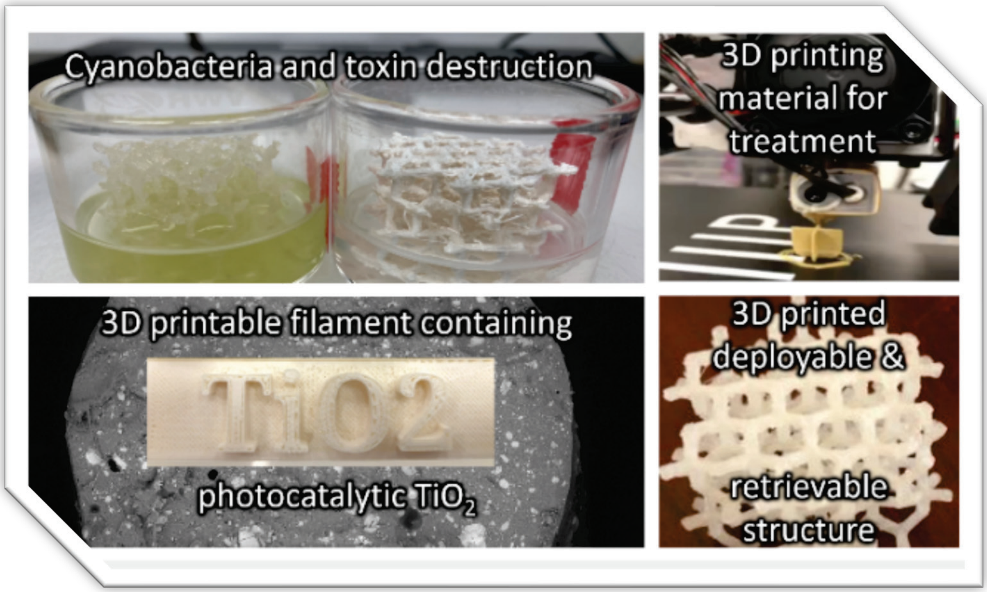

Figure 7. 3D printed photocatalyst composites for HAB mitigation. Graphic by A. Kennedy.

PATH FORWARD: Future work will include: (1) print parameter and design optimization to maximize TiO_2 concentration at the surface of the structure; (2) determining the kinetics (i.e., necessary treatment duration) of the novel treatment structures under known UV-light intensity exposures; (3) mesocosm demonstration of the developed customizable, deployable, retrievable, and reusable devices to treat HAB and degrade the released microtoxin; and (4) developing a research and development roadmap of the technology's maturation, including mass production and field deployment scalability. One concept for field deployable structures includes interlinked lattices providing a flexible, deployable floating structure readily retrieved following treatment (Figure 8). The resulting successful printable photocatalytic composite materials and printed and deployable structures will be available for transition to USACE Districts. A defined plan and roadmap for technology production scale up and field deployability will be publicly disseminated.

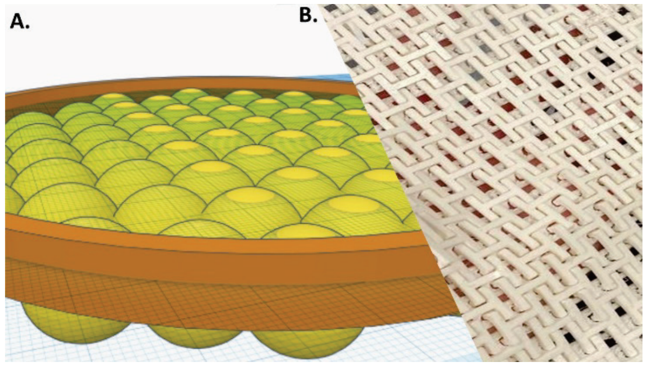

Figure 8. Panel A provides a cartoon representation of subsurface floating photocatalytic spheres for HAB treatment produced by polymer compounding and 3D printing (Photograph/graphic by Alan Kennedy). Panel B shows a 3D printed flexible, high surface area structure that can float at the surface of water or applied to existing waterborne infrastructure (Photograph/ graphic by Mark Ballentine).

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