Development of Molecularly Imprinted Polymer Sensor for HAB Event Detections

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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 frequency of Harmful Algal Blooms (HABs) is rising, with potentially deleterious effects on drinking water supplies and recreational activities due to potent toxins generated during the bloom events. For successful mitigation of HABs, early detection of toxins is paramount; however, current techniques necessitate that samples be sent to laboratories for analysis by personnel with specialized equipment. To enable real-time field detection of toxins during a bloom event, the fabrication of a simple fluorometric sensor would be invaluable, allowing for a rapid response instead of waiting for laboratory test results.

Objective By synthesizing carbon-dot-embedded Molecularly Imprinted Polymer (MIP) silica particles, we aim to sense microcystin-LR (MCLR) using a fluorometric-based approach. We have developed several particles using unique amino acids, such as leucine and arginine, which are specific to MCLR. Additionally, the ADDA group is targeted using a 2-methoxy propyl benzene (adduct) synthesized in-house at ERDC, allowing us to detect total microcystin levels, not just MCLR itself.

Approach The project was refocused in FY22 to take a new approach utilizing more robust solution state synthetic MIP based particles. The previous electrochemical based studies were unsuccessful due to the heterogeneity found in electro polymerized MIP surfaces. At the end of FY22, Carbon Nano Dots (CNDs) were synthesized, as shown in Figure 2, and then CNDs were embedded during silica MIP particle synthesis and characterized via several surface-based techniques. These particles were dispersed in water and fluorescence studies performed. The Current quenching data has shown that arginine-based MIP particles are highly sensitive towards MCLR. Further studies are now being pursued to validate this unique method along with adduct based MIP particles.

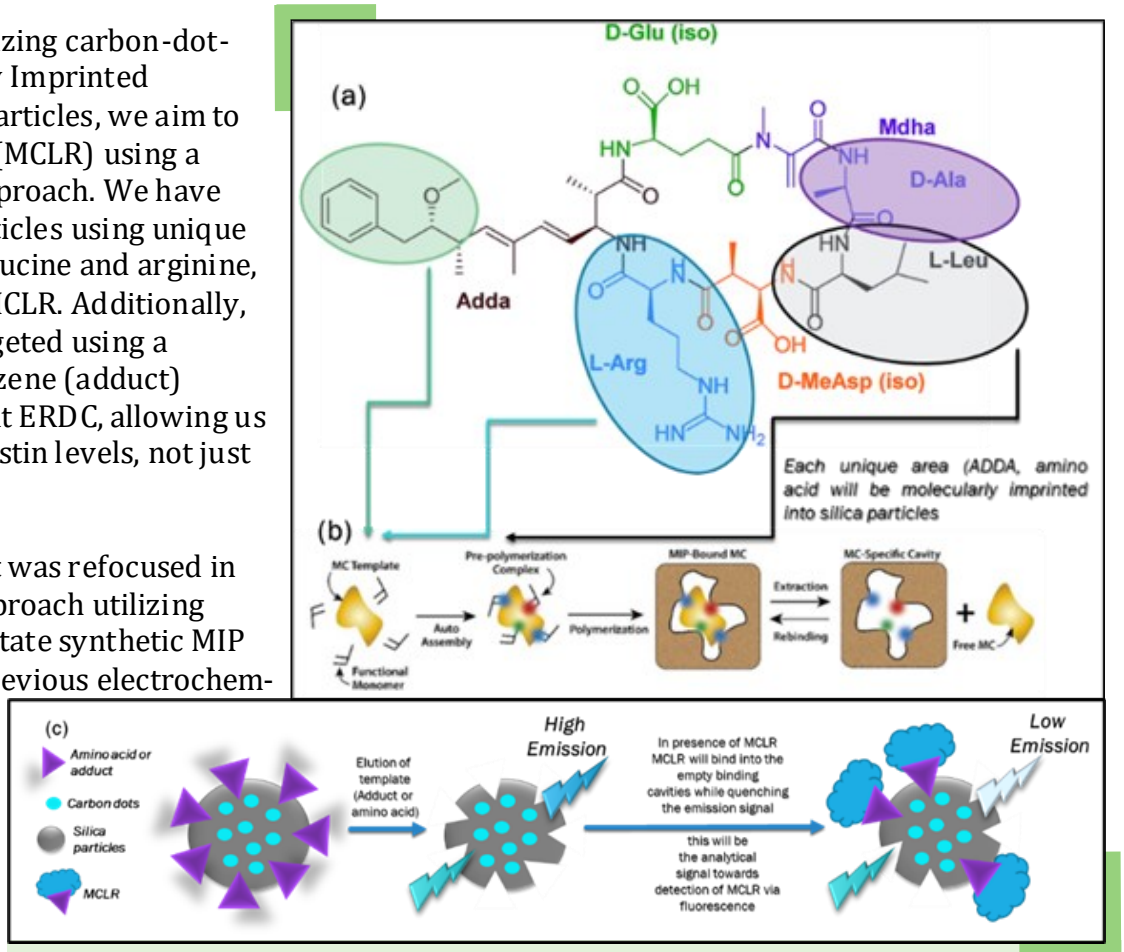

Figure 1: *(a) Molecular structure of microcystin-LR highlighted with areas of interest such as amino acids/ADDA adduct, (b) Scheme for molecularly imprinted polymer synthesis, and (c) Fluorescence-based approach for detection of MCLR with the utilization of carbon dots embedded silica MIP particles.*

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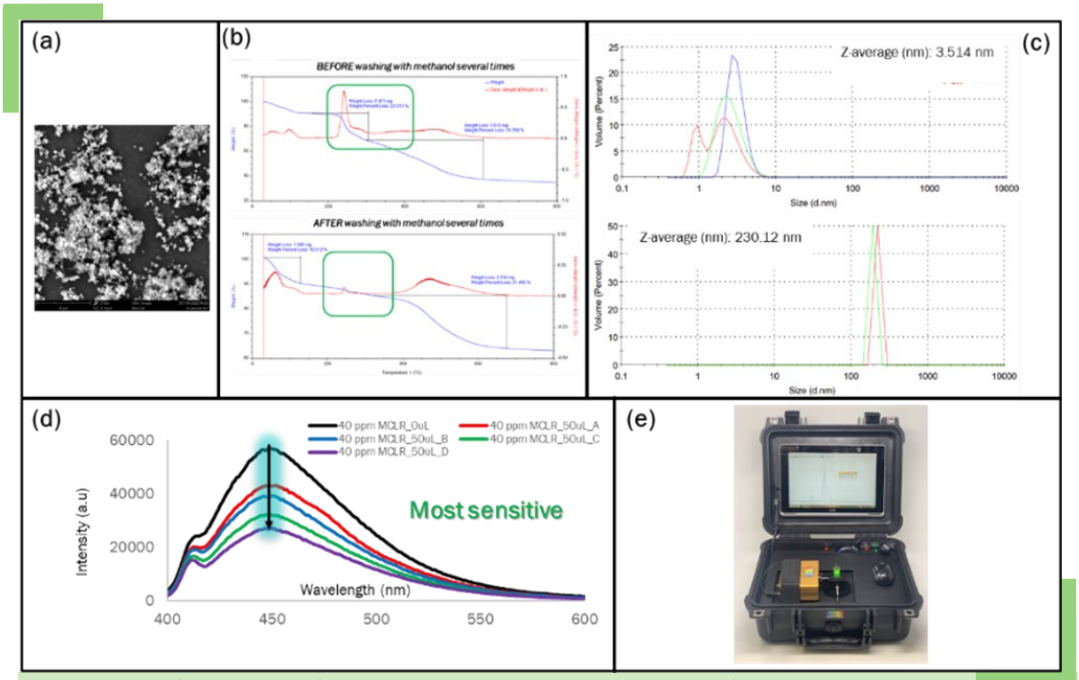

Figure 2: *(a) SEM image of synthesized silica MIP particles, (b) TGA data showcasing the successful template removal process, (c) particle size distributions for CNDs and MIP particles, (d) Fluorescence based quenching effect for arginine based MIP particles in the presence of 677 ppb MCLR (e) Portable fluorimeter system that will be used to transition this technology into field based applications.*

Major Milestones

Date	Milestone
FY21, Q1-Q4	Fabrication and Validation of MIP-Based Transducer
FY21, Q1-Q4	Publication: Review article published on MIP based detection for MCLR
FY21, Q1-Q4	Synthesis: Adduct synthesized to be used in electrochemical detection
FY21, Q1-Q4	Publication: Tech note published on synthesis of adduct compound
FY21, Q1-Q4	Selection of reporter Molecule: computational and NMR based binding studies were used to understand which monomer would work for eMIP based studies
FY21, Q1-Q4	Milestone: Found consistency in computational and NMR based binding data
FY22, Q1-Q4	Electro-polymerization of eMIP-based studies were unsuccessful à transition to MIP particle system with fluorescence-based detection
FY23, Q1	Fluorescent MIP synthesis and evaluation - current fluorescence results are promising, showing particles capable of binding to MCLR with quenching
FY23, Q2	Conference: ACS abstract spring 2023 (abstract submitted)
FY23, Q2	Draft and final report
Costs	**FY21:**$100K **FY22/FY23:**$152K **TOTAL:**$252K

Value to USACE Mission

The proposed sensor/cyanotoxin detection tool would allow for real-time field toxin detection during bloom events, thus enabling a rapid response, rapid communication with stakeholders, and therefore reduced risk of toxin exposure.

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