DEPARTMENT OF ENVIRONMENTAL PROTECTION
Progress Report (Final Report)

Exhibit A

DEP Agreement No.:	INV12		
Grantee Name:	Florida Atlantic University (FAU)		
Grantee Address:	777 Glades Rd, Boca Raton, FL 33431		
Grantee's Grant Manager:	Muriel Industrious	**Telephone No.:**	954.236.1369
Reporting Period:	April 2021 – December 2022		
Project Number and Title:	Aqueous-Phase Phosphorus Removal: An Industrial Ecology Approach to Mitigate Algal Blooms (Project Number: INV12)		

Note 1: This report provides the Final Report for Project INV12. The activities were performed between April 2021 and December 2022.

Note 2: The Principal Investigator (PI) of this project is Dr. Masoud Jahandar Lashaki. The co-PIs are Dr. Daniel Meeroff and Dr. Peng Yi. The PI and co-PIs will be referred to as "Research Team" in this report.

Note 3: Ms. Muriel Industrious serves as the Grant Manager on behalf of FAU.

Note 4: Mr. Nick Daigle serves as the Grant Manager on behalf of Florida Department of Environmental Protection (FDEP). He will be referred to as "Grant Manager" in this report.

Students involved in Project INV12:

- Ali Ayub, MSc student; supervised by Dr. Jahandar Lashaki
- Sara Ahsan, MSc student; supervised by Dr. Jahandar Lashaki
- Ryan Thomas, MSc student; supervised by Dr. Jahandar Lashaki
- Mitchell Guirard, MSc student; supervised by Dr. Jahandar Lashaki
- Vithulan Suthakaran, MSc student; supervised by Dr. Meeroff
- Rishabh Rawal, MSc student; supervised by Dr. Meeroff
- Shahin Ahmed Sujon, MSc student; supervised by Dr. Yi
- Brandyn Nutter, PhD student; supervised by Dr. Jahandar Lashaki
- Amirjavad Ahmadian Hosseini, PhD student; supervised by Dr. Jahandar Lashaki
- Marina Kaisar, MSc student; supervised by Dr. Jahandar Lashaki

List of Tasks:

- Quality Assurance Project Plan (Task 1)
- Adsorbents Synthesis and Phosphate Removal Evaluation (Task 2)
- Optimization & Assessment (Task 3)
- Final Report (Task 4)

List of activities and deliverables for Task 1:

- The Research Team drafted a Quality Assurance Project Plan (QAPP). The first version of the QAPP was submitted to the Grant Manager on April 6, 2021.

- The FDEP Quality Assurance (QA) Team provided the Research Team with their comments and requested revisions on May 26, 2021.

- The Research Team revised the QAPP accordingly and submitted the modified version to FDEP on June 9, 2021.

- On June 21, 2021, the Grant Manager notified the PI that the QA Team found most revisions satisfactory; however, they still have multiple outstanding comments. To speed up the revision process, the PI requested a virtual meeting with the QA Team to discuss the comments. The PI virtually met with the Grant Manager and the QA Team on June 28, 2021, based on which a revised version of the QAPP, along with all required signatures, was submitted to the Grant Manager on June 30, 2021.

- The Grant Manager notified the PI on July 2, 2021, that the QAPP has been accepted and the Research Team can proceed with the experimental activities associated with Task 2.

- A revised QAPP was approved on October 5, 2021.

List of activities completed for Task 2:

- Literature review on activated carbon (AC) adsorbents and their use for gas-phase and aqueous-phase pollution treatment, particularly phosphate removal

- Literature review on AC synthesis, particularly using microwave heating

- Used the literature surveys to develop methods and to build setups

- Collected and cultivated cyanobacteria to harvest biomass

- Synthesized AC adsorbents using the biomass as precursor

- Evaluated the adsorptive properties of the adsorbents for aqueous-phase phosphate removal

- Improved the adsorptive properties of the adsorbents via surface modifications

- Explored the performance of eight performant adsorbents for phosphate removal in the presence of different concentrations

List of Task 2 deliverables:

- Summary of literature surveys conducted

- Summary of methods developed, and the experimental setups built

- Description of cyanobacteria collection, cultivation, and processing

- Summary of completed synthesis, screening, and evaluation activities

- Dates for the completed activities and interpretation of results

- Timestamped color photographs included in the body of the report

- On March 11, 2022, the Research Team submitted a draft report for Task 2 deliverables

- On April 11, 2022, the FDEP Grant Manager provided feedback on the report

- On April 19, 2022, the Research Team submitted a revised report to address FDEP comments

- On May 19, 2022, the FDEP Grant Manager officially approved Task 2 deliverables

List of activities completed for Task 3:

- Investigated the impact of adsorbent dosage on phosphorus removal performance of four performant adsorbent materials selected based on Task 2 results

- Identified a final candidate with best phosphorus removal performance, based on the above activity and the associated results

- Studied the impact of adsorption duration (i.e., contact time) on phosphorus removal performance of the final candidate

- Elucidated the impact of natural organic matter (i.e., COD) on phosphorus removal performance of the final candidate

- Evaluated the phosphorus removal performance of the final candidate in the presence of influent and effluent wastewater standard solutions

- Assessed the cyclic phosphorus removal performance of the final candidate

List of Task 3 deliverables:

- Summary of methods developed

- Summary of completed phosphorus removal performance evaluation activities

- Dates for the completed activities and interpretation of results

- Timestamped color photographs included in the body of the report

- QA/QC data

- The Draft Report for Task 3 Deliverables was submitted to the FDEP on October 31, 2022.

- On December 5, 2022, the FDEP Grant Manager officially approved Task 3 deliverables

List of Final Report content (Task 4):

- Information about the project

- Financial summary of the project

- Information about the project schedule

- Summary of Task 1 activities and deliverables

- Summary of Task 2 activities and deliverables, including photo documentation, discussion of results and the anticipated benefits, and monitoring activities such as QA/QC

- Summary of Task 3 activities and deliverables, including photo documentation, discussion of results and the anticipated benefits, and monitoring activities such as QA/QC

- The Draft Final Report was submitted to the FDEP on October 31, 2022

- On December 8, 2022, the FDEP Grant Manager provided feedback on the report

- The revised Final Report was submitted to the FDEP on December 15, 2022

This report is submitted in accordance with the reporting requirements of DEP Agreement No. INV12 and accurately reflects the activities associated with the project.

Signature of Grantee's Grant Manager Date

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1. Executive Summary

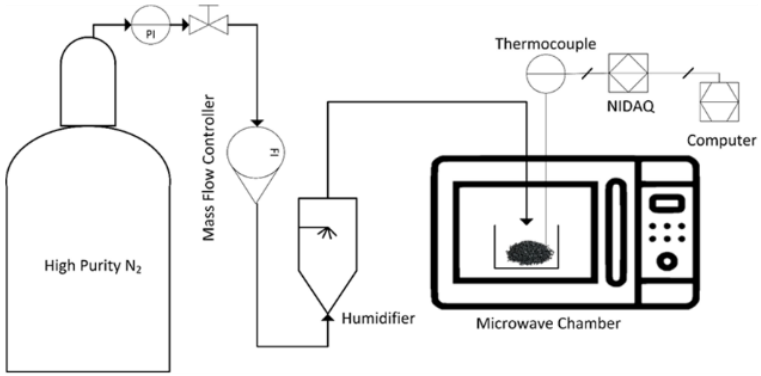
Algae are important contributors to marine life, food chain, and dissolved oxygen levels in surface waters.[1] However, high nutrient levels (e.g., nitrogen and phosphorus) and warm temperatures in surface waters, typically occurring in late summer or early fall, can enhance the overgrowth of certain algae types, forming foam- or scum-like masses known as Harmful Algae Blooms (HABs). When pushed to the shores by winds, waves, tides, and currents, the HABs release toxins such as cyanotoxins, brevetoxins, and hydrogen sulfide, causing a wide range of health issues in people, animals, and the ecosystem. Florida typically experiences HABs in saltwater, freshwater and brackish water bodies that may last up to five months. Apart from the environmental issues and adverse health impacts, Florida has suffered economically from HABs owing to the associated healthcare costs, the required clean-up activities, and losses in tourism revenues.[2] Consequently, further research is needed to mitigate the adverse environmental, societal, and economic impacts associated with HABs. This project aimed at mitigating HABs through an industrial ecology approach. Industrial ecology is a developing framework that attempts to reduce the environmental impacts of human activities via emulating the interconnections and interactions of natural ecosystems. Nature is a closed-loop system where all wastes produced are used as substrates for other organisms or processes. The overarching objective of this research project was to convert algae, which is of little value, into value-added adsorbent materials for the removal of aqueous-phase phosphate (Figure 1).

Cyanobacteria was collected from Lake Okeechobee followed by processing prior to activation using fast and energy-efficient microwave heating (i.e., synthesis duration of less than 10 minutes). The surface of the adsorbents was modified using different compounds, namely lanthanum chloride, magnesium chloride, magnesium oxide, and zinc chloride, to improve phosphate removal. The adsorbents, with and without modification, were evaluated for phosphate uptake to find the best-performing materials for further assessment. Multiple materials which were all modified with lanthanum chloride achieved near-complete phosphorus removal efficiency (99%+) over a wide range of concentrations (5, 10, and 20 mg/L). These best-performing adsorbents were evaluated in the presence of different adsorbent dosages and adsorption contact times to find optimum performance conditions. The best-performing material achieved near-complete phosphorus removal (99%+) at low adsorbent dosages (below 1 g/L) and short contact times (90%+ removal in less than 30 minutes). This final candidate was studied in the presence of

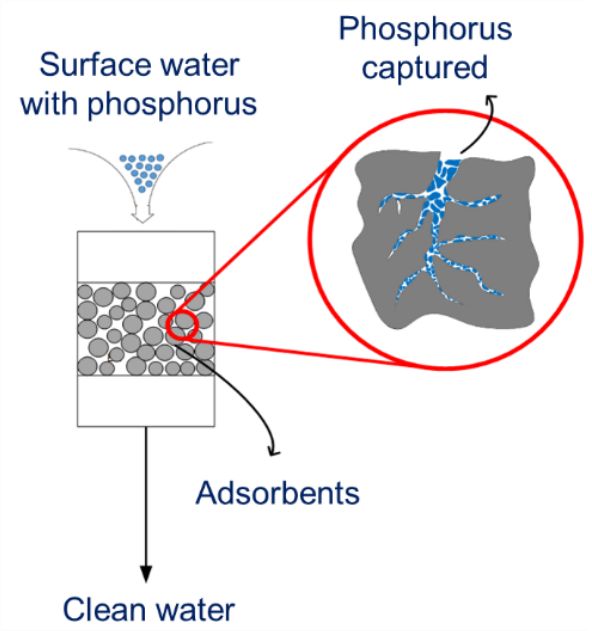
Natural Organic Matters (NOMs) to investigate its impact, or lack thereof, on phosphate removal. The results showed that phosphorus removal performance was not adversely affected in the presence of NOMs. The final adsorbent also underwent successive adsorption-desorption cycles to assess its long-term stability and performance. The results showed that the adsorbent could be regenerated for reuse and kept its performance over two successive cycles.

In summary, cyanobacteria biomass was upgraded to adsorbent materials for aqueous-phase phosphate removal. The project findings were encouraging and showed the immense potential of the proposed approach to battle HABs through nutrient removal, particularly adsorption of phosphorus from surface waters. Once implemented at large scale, the project results are expected to improve our socio-economic and environmental well-being, contributing to all sustainability pillars: society, environment, and economy. The outcomes not only enhance air and water quality and public health in communities across Florida, but also help develop a thriving recreation/tourism industry, fulfilling the goal of having a more prosperous and healthy society we all aspire to. This research project provided multifaceted training opportunities for 10 young scientists and engineers, which can prove invaluable in innovation-driven job markets. Moreover, commercializing this technology may create well-paying jobs in future. Based on the outcomes of this project, multiple follow-up studies are recommended: (i) scaling up the synthesis process to produce sizable amounts of the adsorbent materials without compromising their phosphorus adsorption performance, (ii) exploring the potential of the developed materials for combating either an actual HAB or for phosphorus abatement in general, (iii) examining the use of biomass from other commonly occurring algae for material synthesis, and (iv) studying the long-term regenerability of the adsorbent materials for successive cyclic use without major performance loss.

Cyanobacteria collection from Lake Okeechobee



Using fast, energy-efficient microwave heating at over 600 °C to convert cyanobacteria biomass to modified adsorbent materials



Using the adsorbent to remove phosphorus from surface waters

Figure 1: Project overview.

2. General Information About the Project

2.1 Project Location and Senior Team Members

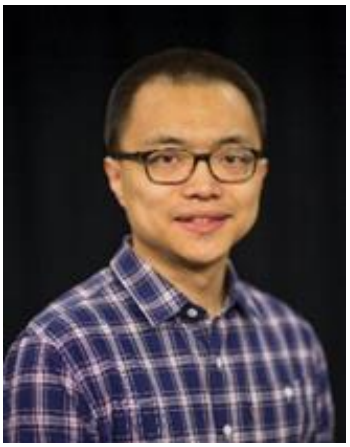
The project was performed in FAU campuses in Dania Beach and Boca Raton (Figure 2). The Dania Beach campus, also known as SeaTech campus, is located at 101 N Beach Rd, Dania Beach, FL 33004 (Latitude: 26.055038331781475; Longitude: -80.11327028274536). The campus is located in Broward County. The Boca Raton campus, also known as main campus, is located at 777 Glades Rd, FL 33431 (Latitude: 26.370606850171523; Longitude: -80.10434090894967). The campus is located in Palm Beach County.

Figure 2: FAU's SeaTech (Dania Beach; top) and Boca Raton (bottom) campuses.

Dr. Masoud Jahandar Lashaki served as the Principal Investigator (PI) of this Grant. He is an Assistant Professor in the Department of Civil, Environmental and Geomatics Engineering at Florida Atlantic University (FAU), and the Director of Air Emissions Characterization and Control Laboratory. He received his Ph.D. in Environmental Engineering from the University of Alberta (Edmonton, Canada) in 2015, where, in collaboration with Ford Motor Company, he developed novel materials, methods and computational models for air emissions control from the automobile manufacturing sector. From 2016 to 2018, he served as Natural Science and Engineering Research Council of Canada (NSERC) Postdoctoral Fellow at the University of Ottawa (Ottawa, Canada), where he developed tailor-made, hydrothermally stable materials for greenhouse gas mitigation. Prior to joining FAU, he served as a Research Engineer at Svante Inc. (formerly Inventys Inc.), a Canadian cleantech company, where he continued his research work on the development of CO_2 adsorbent materials with high stability and adsorption attributes. He attracted, as PI, Co-Investigator or Senior Personnel, several grants funded by the U.S. DOD, the U.S. EPA, the FDEP, Ford, Svante, NSERC, and Janke Foundation, totally over $2.5M. Dr. Jahandar Lashaki has co-authored over 25 journal articles in renowned venues, in addition to over 45 presentations at international conferences. His scholarly contributions have been recognized by over 30 institutional, national and international awards, totaling $165K.

Dr. Daniel Meeroff served as the first Co-PI of this Grant. He is Associate Chair and Professor in the Department of Civil, Environmental and Geomatics Engineering at FAU. Dr. Meeroff is also the Director of the Laboratories for Engineered Environmental Solutions. In 2014, Dr. Meeroff was awarded the Engineer's Council John J. Guarrera Engineering Educator of the Year for North America and was also elected the Distinguished Teacher of the Year for FAU by the students (FAU's highest teaching honor). In 2015, Dr. Meeroff was awarded the first ever Distinguished Research Mentor of the Year Award for FAU. Dr. Meeroff has received more than 50 research grants valued at over $14M supported by NSF, U.S. EPA, FEMA, Hinkley Center for Solid and

Hazardous Waste Management, FDEP, Florida Division of Emergency Management, and the Solid Waste Authority of Palm Beach County, among others. He has co-authored over 150 publications in peer-reviewed journals, professional periodicals, conference proceedings, book chapters, textbooks, and manuals. Dr. Meeroff's research interests include developing innovative treatment technologies that mimic natural systems, specifically by applying physical/chemical and microbiological processes in novel approaches. His specialties involve the application of advanced principles of chemistry and microbiology for solving environmental problems.



Dr. Peng Yi served as the second Co-PI of this Grant. He is an Assistant Professor in the Department of Civil, Environmental and Geomatics Engineering at FAU. He received his Ph.D. in Geography and Environmental Engineering from The Johns Hopkins University in 2013. His dissertation was on the fate and transport of carbonaceous nanoparticles. He also received postdoctoral training in Connecticut Agricultural Experiment Station in 2014 and studied the colloidal behaviors of biochar particles. Since joining FAU in 2015, he has published many papers on water treatment in high-impact-factor journals, such as *Environmental Science and Technology*, *Water Research*, *Chemical Engineering Journal*, *ACS ES&T Engineering*, *Separation and Purification Technology*, etc.

2.2 Project Timeline, Grant Award Amount, and Budget Summary

The project was originally scheduled as summarized in Table 1, with a total funding of $197,326.

Table 1. Original project timeline.

Task/ Deliverable No.	Task or Deliverable Title	Task Start Date	Task End Date
1a	Draft QAPP	7/1/2020	5/31/2022
1b	Final QAPP	7/1/2020	5/31/2022
2	Adsorbents Synthesis and Phosphate Removal Evaluation	7/1/2020	5/31/2022
3	Optimization & Assessment	7/1/2020	5/31/2022
4a	Draft Final Report	7/1/2020	5/31/2022
4b	Final Report	7/1/2020	5/31/2022

On May 9, 2022, the project timeline was amended as summarized in Table 2, providing a no-cost extension.

Table 2. Amended project timeline.

Task/ Deliverable No.	Task or Deliverable Title	Task Start Date	Task End Date
1a	Draft QAPP	7/1/2020	12/31/2022
1b	Final QAPP	7/1/2020	12/31/2022
2	Adsorbents Synthesis and Phosphate Removal Evaluation	7/1/2020	12/31/2022
3	Optimization & Assessment	7/1/2020	12/31/2022
4a	Draft Final Report	7/1/2020	10/31/2022
4b	Final Report	7/1/2020	12/31/2022

The project was originally budgeted as summarized in Table 3. There was no match or locally pledged contributions provided.

Table 3. Original project budget breakdown.

Task No.	Budget Category	Budget Amount
1	Not applicable	No cost
	Total for Task:	**$0**
2	Salaries	$73,935
	Fringe	$25,394
	Supplies	$7,500
	Contractual	$1,500
	Overhead/Indirect (24%)	$25,999
	Total for Task:	**$134,328**
3	Salaries	$36,076
	Fringe	$12,429
	Supplies	$2,000
	Contractual	$300
	Overhead/Indirect (24%)	$12,193
	Total for Task:	**$62,998**
4	Not applicable	No cost
	Total for Task:	**$0**
	Total:	**$197,326**

On May 9, 2022, and December 9, 2022, the project budget was amended as shown in Table 4.

Table 4. Amended project budget breakdown.

Task No.	Budget Category	Amended Budget Amount (05/09/2022)	Amended Budget Amount (12/09/2022)
1	Not applicable	No cost	No cost
	Total for Task:	**$0**	**$0**
2	Salaries	$73,912	$73,912
	Fringe	$5,956	$5,956
	Supplies	$3,492	$3,492
	Overhead/Indirect (24%)	$20,006	$20,006
	Total for Task:	**$103,366**	**$103,366**
3	Salaries	$63,865	$64,335
	Fringe	$4,101	$3,631
	Supplies	$6,008	$7,808
	Contractual	$1,800	$0
	Overhead/Indirect (24%)	$18,186	$18,186
	Total for Task:	**$93,960**	**$93,960**
4	Not applicable	No cost	No cost
	Total for Task:	**$0**	**$0**
	Total:	**$197,326**	**$197,326**

3. Quality Assurance Project Plan (Task 1; April-October 2021)

3.1 Organization's General Approach for Conducting Quality Research

The research mission of Florida Atlantic University is to expand and support the University's academic and research programs by (i) promoting the research, scholarly, creative and collaborative activities of faculty and students; (ii) enhancing the research infrastructure of the University to support the community in an ever-changing world; (iii) encouraging national and international partnerships for workforce development and commercialization of research endeavors; (iv) translating university discovery and innovations into viable business opportunities and economic development; and (v) engaging our communities in mutually beneficial research, education and outreach programs. FAU's College of ECS is committed to providing accessible and responsive programs of education and research recognized nationally for their high quality. The College intends to be the institution of choice for regional students, business, and industry. As a community of scholars, the College leads by example and with vision, inspiration, integrity, and a shared sense of purpose. Through its programs, the College (i) educates those who will contribute to the advancement of technical knowledge and who will be leaders in their profession; (ii) conducts basic and applied research in engineering, computer science and related interdisciplinary areas; and (iii) provides service to the engineering and computer science professions, to the State of Florida, to the nation, and to the community at large.

3.2 Project and Quality Objectives

The overarching objective of this research is to convert algae to adsorbents for removal of aqueous-phase phosphate. Algae will be converted to activated carbon adsorbents using rapid energy-efficient microwave heating. The surface of the adsorbents will be modified using different additives to improve phosphate removal. The adsorbents, with and without modification, will be evaluated for phosphate uptake to determine the best-performing materials for further assessment. The selected adsorbents will be evaluated in the presence of different phosphate concentrations, adsorbent dosages, and contact times to determine optimum performance conditions. Final adsorbent candidates will be also studied in the presence of humic acids, to mimic exposure to Natural Organic Material (NOM), to investigate its effects if any on phosphate removal. One final adsorbent will undergo successive adsorption-desorption cycles to assess its long-term stability and performance in the presence of natural surface water samples. Project costs will be optimized via synergistic collaboration among the team members. Materials synthesis and testing costs will

be minimized by using (i) algae as a low-cost precursor, (ii) energy-efficient microwave heating, and (iii) inexpensive reagents for adsorbent modification and regeneration. The project improves our socio-economic and environmental well-being, contributing to all sustainability pillars: society, environment, and economy. Algae will be upgraded to adsorbents for phosphate removal, contributing to the mitigation of future algal blooms. The outcomes not only enhance air and water quality and public health in communities across Florida, but also help develop a thriving recreation/tourism industry, fulfilling the goal of having a more prosperous and healthy society we all aspire to.

3.3 Assessing the Success of the Project

To ensure successful completion of the project, Key Performance Metrics, including productivity and research quality, scope of work, and project costs will be monitored, as follows:

Productivity and Research Quality: The PI and Co-PIs will hold weekly meetings with their research teams for briefing on accomplishments during the previous week, sharing information, discussing progress, overcoming any setbacks, and brainstorming on how to tackle challenges.

Scope of Work: While the scope of the project has been clearly established via extensive communications with the team members, unavoidable changes will be discussed promptly and dealt with to keep the project on time and on budget. In case of any changes to the Scope of Work, the QAPP will be updated accordingly. Timely progress on scope of work will be ensured through close interaction with the team members. Monthly meetings among the whole team will summarize accomplishments and progress on project schedule and will outline tasks to be accomplished in the upcoming month. This is also an opportunity to review challenges and identify arising opportunities.

Project Cost: Measuring how costs are managed is critical to the project's success. Costs will be closely monitored via comparing the total effort to the budgeted effort, assessing the utilization of resources, and assuring low defects throughout the project.

3.4 Scope and Application of Sampling/Analytical Methods for Collecting Primary Data

The following procedures will be used to collect primary data. A detailed copy of all the procedures will be available on a shared computer in the PI's and Co-PIs' labs for the team members to follow. In all cases, the activity will be completed in duplicates to ensure reproducibility. The research team has many years of experience in operating and maintaining the research instruments used in this project. For in-house instruments, the PI and Co-PIs will perform the required calibrations and

standard tests based on manufacturer's guidelines. For external instruments, the PI will check the QC procedures with the corresponding research facility prior to initiating any contracts. All records relevant to such calibrations and standard tests will be maintained and will be provided to the FDEP for auditing, upon request.

Algae Collection: Samples of freshwater cyanobacteria (algae) will be obtained from direct collection from the field or from a third party. Prior to any algae collection activity, written permission will be obtained from the Department Grant Manager. Field samples of algae from surface water will be collected following the FDEP SOP FS 7000 (General Biological Community Sampling) and FS 2100 Surface Water Sampling procedures using a standard surface grab sample (FS 2000) within the first 0.3 m of the water column directly into amber glass bottles or plastic sample bags without chemical preservation. Samples will be kept on ice without exposure to light until returned to the lab. Under no circumstances will sargassum be collected. During algae collection, information such as the coordinates of the location, weather, visual observations, etc. will be documented. No other measurements will be taken during algae collection. This includes (i) not measuring water quality parameters (e.g., dissolved oxygen, pH), (ii) not collecting field samples other than the algae, and (iii) not measuring nutrients or any other physical or chemical parameters in the surface water. Alternatively, if we collaborate with an external contractor for algae collection, the same field information will be sought from the company, and we will ask them to follow the same procedures.

Algae Growth: Once in the lab, the collected algae will be filtered and washed with deionized (DI) water (three times) followed by inoculation in 20-liter flasks, as described elsewhere.[3] Deionized water will be produced in our lab using an existing system (MP-3A; Mega-Pure System). An initial algae density of 10 g/l will be used. Algae "food" in the amount of 500 ml will be added to each flask once at the beginning of inoculation. The "food" consists of $Ca(NO_3)_2.4H_2O$ (50 mg); KNO_3 (100 mg); $NaNO_3$ (50 mg); Na_2SO_4 (40 mg); $MgCl_2.6H_2O$ (50 mg); KH_2PO_4 (100 mg); and H_3BO_3 (20 mg) added to one liter of deionized water. The "food" will be prepared in our lab after purchasing the chemicals. All preparation information, namely chemical name, supplier name, purity, purchase date, lot numbers, expiration dates, and preparation dates will be documented. The flasks will be continuously aerated with 0.5 L/min of air. After three days, the algae will be harvested through filtration.

Activated Carbon Synthesis Procedure: The collected algae will be washed with copious amounts of water followed by drying at elevated temperature in the presence of air. If needed, the algae will be treated with hydrochloric acid solutions to remove ash, metals and minerals, followed by filtration, rinsing with copious amounts of water, drying as described above, and then ground and sieved.[4,5] The processed algae powder will be activated in a microwave oven using different activation durations, and the activation medium will be continuously purged with humidified gas.[6] . At the end of activation period, the temperature of the activated algae will be measured using a thermocouple. When needed, different surface modifications will be performed for improving aqueous-phase phosphate removal by activated carbons, including the use of $ZnCl_2$ and MgO as activation agent[7] and impregnation of $MgCl_2$, $LaCl_3$, or other metal oxides into the adsorbent structure.[8,9] The specified adsorbent modifications will be conducted as described elsewhere.[7,8,9] In all cases, the materials will be archived in sealed vials until use.

Assessing the Thermal Stability of Activated Carbons: Using a Thermogravimetric Analyzer (TGA 550, TA Instruments) available in the PI's lab, all activated carbons will be analyzed in terms of thermal stability through a procedure described in the PI's previous studies.[10,11,12,13] Activated carbon samples will be heated from 25 °C to 800 °C at 1 °C/min in a N_2 flow rate greater than 50 standard cubic centimeters per minute (SCCM).

Analyzing the Structural Properties of Activated Carbons: Using a surface area and porosity analyzer available in the PI's lab (ASAP 2020 Plus MP, Micromeritics) and following the procedure reported in his previous research articles,[10,11,12,13] all synthesized activated carbon samples will be characterized in terms of structural properties using N_2 adsorption at −196 °C. This instrument measures the volume of N_2 adsorbed (v) as a function of relative pressure (P/P_0). Prior to analysis, samples will be degassed for five hours at 120 °C to remove moisture. Specific surface area will be calculated by the Brunauer-Emmette-Teller (BET) method[14] using relative pressures ranging from 0.01 to 0.07 to avoid overestimation due to quasi-capillary condensation in micropores.[15] The two consistency criteria will be considered to ensure the validity and accuracy of the BET surface area calculations.[16] Total pore volume will be recorded at $P/P_0 = 0.975$. Quenched Solid Density Functional Theory (QSDFT) method[17] will be used to obtain Pore Size Distribution (PSD) and the V-t method[18] will be used to obtain micropore volume.

Evaluating Phosphate Uptake: Adsorption experiments will be conducted using pre-determined adsorbate concentrations (e.g. 5 to 100 mg P/L) and adsorbent dosages (e.g. 0.2 to 5.0 g/L).

Different concentrations of phosphorus will be prepared and verified at FAU using the EPA-approved ascorbic acid method, EPA 365.3 (also Standard Methods 4500-P E).[19] This procedure has a method detection limit of 0.02 mg/L as P. Phosphorus will be added to the reaction chamber using a commercially available standard reference material. The mixture will be shaken continuously in a mechanical shaker at room temperature under ambient light conditions. After the specified time interval (e.g. 0-24 hours), the mixture will be filtered, and phosphate concentration will be measured using the same EPA-approved ascorbic acid method. In this method, total phosphorus is digested using acid, persulfate, and heat to convert organic and condensed inorganic phosphates (meta-, pyro- or other polyphosphates) to reactive orthophosphate, which reacts with molybdate and antimony ions in an acidic solution to form an antimony-phosphomolybdate complex. The complex is reduced by ascorbic acid to phosphomolybdenum blue. The absorbance is proportional to the concentration of phosphate. A standard curve will be plotted for this purpose using the absorbance of several phosphate standard solutions measured by a UV-vis spectrophotometer at 880 nm. QA/QC will include a blank, standard reference material control check, and a matrix spike sample for every ten (10) samples analyzed. Published limits for control checks are on the order of +/- 0.1 mg/L as P. If needed, we will send out samples to a NELAC-certified lab to validate our in-house procedure. For corrective actions, refer to "QA/QC Procedures".

Measuring the Chemical Oxygen Demand (COD): Measurements of COD will be conducted at FAU to determine the concentration of humic acids in the sample. EPA Method # 410.4 (Detection of Chemical Oxygen Demand by Colorimetry) uses the dichromate reaction digestion method with colorimetric measurement to estimate the amount of organic matter in water. It is a measurement of the oxygen equivalent of the materials present in the water that are subject to oxidation by a strong chemical oxidant, in this case dichromate is used. Samples, blanks, and standards in sealed tubes are heated in an oven or block digester in the presence of dichromate at 150 °C. After two hours, the tubes are removed from the digester, cooled, and measured spectrophotometrically at 600 nm. When a sample is digested, the dichromate ion oxidizes COD material in the sample. Digestion consists of the reaction of oxidizable organic compounds, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic ion (Cr^{3+}). Both chromium species are colored and absorb in the visible region of the spectrum. The chromic ion absorbs strongly in the 600-nm region, where the dichromate has nearly zero absorption. The most common interferent in this analysis is chloride

ion (and other halogen ions). Chloride reacts with silver ion to precipitate silver chloride, and thus inhibits the catalytic activity of silver. In addition, chlorides are quantitatively oxidized by dichromate and represent a positive interference. The maximum amount of chloride is on the order of 2000 mg/L. The suggested value is 1000 mg/L in diluted samples. Total dissolved solids will be measured with a calibrated YSI Professional Plus multiparameter meter to ensure that samples meet the interference criterion. Samples outside of the range will be diluted using deionized water. Once every ten (10) samples and at least once per batch, a positive calibration control check sample will be analyzed. The method detection limit is 0.7 mg/L as O_2. Published limits for control checks are on the order of +/- 0.5 mg/L as O_2. If needed, we will send out samples to a NELAC-certified lab to validate our in-house procedure. For corrective actions, refer to "QA/QC Procedures".

Data Documentation: The importance of data documentation in scientific and engineering research is recognized and supported by the PIs. All PIs' laboratories are networked with FAU's secured data center, which provides secure access to all data as well as an additional external backup drive that can be used in the event of an emergency. Data will be stored in both the PI's working laptops and the cloud desktop of FAU which has assigned up to four terabytes capacity to each faculty member. The backup of the data will be happening on daily basis considering that such archiving and backup is common practice at FAU. Security of the data will be ensured by providing limited access to the data storage (e.g. drive) to only those faculty members, researchers and students who have permission from the PIs or a relevant FAU IT staff. The research team will also collaborate with the FAU library towards long-term data curation and preservation. The FAU library is committed to providing long-term access to the digital work it contains and adheres to digital preservation best practices to ensure data accessibility and usability in perpetuity. Data retention will be at least five years after the conclusion of the award or after public release, whichever comes later. To ensure ongoing and long-term security of the data generated by this project, a complete copy of materials will be generated and stored independently on primary and backup sources for the PIs. On completion of the project, the PIs will identify which project materials are of probable long-term interest for archiving and preservation.

QA/QC Procedures: Sample handling and custody requirements will be monitored after each sample is collected and during the transfer of the samples to the laboratories. The blank samples (i.e., DI water) containing no phosphorus or COD will be used every time when phosphorus concentration or COD needs to be measured for experimental samples. Additional quality control

procedures are described in the individual analyte SOPs, field sampling protocols, and data management procedures, described above. For phosphorus and COD measurements, the method blank must be below the reporting limit, and the calibration curve verification (CCV) sample must be within 10% of the expected value. If this criterion is not achieved, the affected samples will have the analysis repeated, and if the criterion is not met after repeating the analysis, the data will be flagged. The FAU Laboratories for Engineered Environmental Solutions, which is managed by Dr. Meeroff, is equipped with the required instrumentation, techniques, and qualified staff to perform the analyses described in this QAPP. Laboratory SOPs related to sample handling chain-of-custody, field logs, instrumentation, and analytical methods have been developed and adhere to FD 1000.

Regeneration of Adsorbents: For cyclic experiments, the phosphate uptake of spent adsorbent will be recovered via washing with deionized water and 0.01 molar NaOH (three times each), followed by a rinse with ethanol. After drying at 60 °C overnight, the regenerated adsorbent will be reused for the subsequent phosphate removal cycle. Further details about this procedure can be found elsewhere.[3]

3.5 Secondary Data

When needed, the structural properties of activated carbons will be analyzed using Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-Ray Spectroscopy (EDS). The analysis will be conducted at Florida Center for Analytical Electron Microscopy, housed in Florida International University (FIU). The pertinent analytical procedures will be developed in collaboration with the staff at the corresponding research facility and will be added to the QAPP as an appendix.

3.6 Planning Review Technical Audits

The FAU team will complete an initial review of the Grant QA Plan relative to the completed field and laboratory activities to determine if data quality objectives are being met, identify any improvements to be made to project activities, and refine the sampling and/or analytical design or schedule, if applicable. The initial review will be completed after the second completed sampling and analysis event, but no later than the fourth. In the context of this project, sampling event refers to algae collection while analysis event refers to characterizing the thermal stability and structural properties of activated carbons as well as phosphate uptake and COD measurements. Whereas we expect only one sampling event, the analysis events happen much more frequently throughout the

project. The FAU team will conduct ongoing planning review technical audits annually thereafter for the remainder of the Grant, if applicable to the duration of the Grant. For both initial and ongoing planning review technical audits, a summary of the review, including any corrective action plans or amendments to the Grant QA Plan, will be sent to the DEP Grant Manager within one month of the review. A copy of all submitted documents will be maintained with the permanent project records. The initial and ongoing planning review technical audits will include statements about data usability relative to the Grant data quality objectives and any data quality indicators that may be specified in the Grant, its exhibits, the QA Plan, or the QA Requirements. This usability determination will consider all applicable data quality acceptance and usability criteria for quality control and environmental sample results for the Grant, as specified in the procedures, test methods, QA Plan, other Grant exhibits, or the QA Requirements.

3.7 Expected Data and the Associated Format

The types of data generated from this project include: (i) Algae collection and growth procedures that will be recorded in sampling forms and lab books. (ii) Activated carbon synthesis procedures that will be recorded by the PI's group members in lab books. (iii) Nitrogen physisorption measurements on the activated carbons to calculate specific surface area, pore volume and pore size distribution, which will be measured in the PI's lab and data will be stored in an Excel spreadsheet. (iv) Thermal stability measurements on the activated carbons that will be measured in the PI's lab and data will be stored as Excel spreadsheet. (v) Structural properties of the activated carbons characterized at FIU, which will be stored as JPG files. (vi) Phosphate uptake measurements that will be collected in the Co-PIs' labs and stored in an Excel spreadsheet. (vii) COD measurements that will be collected in the Co-PIs' labs and stored in an Excel spreadsheet (viii) Activated carbon regeneration procedures that will be recorded by the PI's group members in lab books. For nitrogen physisorption and thermal stability measurements, the Excel spreadsheets are created by the software associated with the instrument and will be stored as read-only files. For phosphate and COD measurements, the Excel spreadsheets will be created by the research team member in charge of the activity, and the data entry will be QA/QC'ed to ensure accuracy. In all cases, the Excel spreadsheets are only accessible and/or editable by the PI, the co-PIs, and the student(s) in charge of data collection. For the data recorded in lab books, nothing will be obliterated or erased, and only strikethrough will be used, when needed.

3.8 Reporting, Documentation and Records Retention

Reporting, documentation, and records retention will follow the provisions specified in FDEP's "Exhibit D_Standard_QA_Requirements_Grants" document that was shared with the FAU team. All field and laboratory data and records, supporting information, and any other documentation and reports associated with work performed for this Grant will be retained for a minimum of five years after the generation (or completion) of the records applicable to the Grant. All records, data, and information that are associated with work performed under this Grant will be organized so that any information can be quickly and easily retrieved for inspection, copying or distribution. Upon request by the Department Grant Manager or as required by the Grant, copies of all records, data, and information that are associated with work performed under this Grant will be submitted to the Department Grant Manager.

3.9 Data Dissemination

The sharing of research results will be consistent with institutional policies governing intellectual property, copyright, and the dissemination of research products. Data will be made accessible to public immediately after publication in peer-reviewed scientific journals. Submission for publication will be timely and will be only made to authoritative journals. Data dissemination will also happen through poster/oral presentations at national and/or international conferences held in the U.S. After publication, all the published data will be made available to anyone interested. The PI/Co-PIs will upload all the published data on their research websites. While the team cannot ensure that all the raw data will be downloadable directly for external visitors, they are willing to send the raw data to the interested persons upon request. Once the data are approved for sharing, and any data use agreements are signed and in place, the data will be transferred. FAU College of ECS Information Technology Group will be asked to establish a File Transfer Protocol site for an easy and fast access to the stored data.

3.10 Lab Safety

Lab safety is of utmost importance. This project involves the use of hazardous chemicals. All student team members will complete relevant trainings required by FAU's Office of Environmental Health and Safety (EHS), including (i) Laboratory Safety, (ii) Fire Safety and Prevention, (iii) Portable Fire Extinguisher Training, (iv) Hazard Communication: An Employee's Right to Understand, (v) Hazardous Material Handling and Storage, and (vi) Bloodborne Pathogen Awareness. The PI and Co-PIs have passed all the trainings listed above and will walk the team

members every step of the way to ensure a safe and healthy research environment. Apart from trainings, the PI and CO-PIs have worked with FAU's EHS to take additional measures for lab safety, including (i) compiling and/or collecting Chemical Hygiene Plan, Standard Operating Procedure and Chemical Safety Data Sheet and keeping copies in a physical binder and on the desktop of a common lab computer, (ii) posting "Emergency Contact Form" in multiple places in the lab, (iii) establishing a satellite accumulation area for hazardous and non-hazardous wastes, and (iv) creating a chemical inventory.

4. Adsorbents Synthesis and Phosphate Removal Evaluation (Task 2; May 2021 to March 2022)

4.1 Literature Review (May-December 2021)

4.1.1 Introduction

Activated carbon (AC) is a common material used in the treatment of water, wastewater and air due to its adsorption ability, cost efficiency, and thermal and chemical stability.[20,21] It has been observed that aqueous and gaseous pollutants have a propensity to adsorb to the porous surfaces of AC due to the high surface area of the material which can range from 500–1500 m^2/g.[22] The adsorption capacities of different forms of AC differ due to their varying properties such as pore volume, pore size, and chemical functional groups, etc.[23] There are many different forms of AC such as biochar, activated carbon fibers (ACF), and carbon nanotubes (CNT).[24] The typical processes in which organic compounds will adsorb to carbonaceous material is through the hydrophobic effect, pi bonds, hydrogen bonds, van der Waals interactions, covalent interactions and electrostatic interactions. Using pyrolysis and activation at elevated temperatures, AC is generally produced from woody biomass, agricultural wastes, and/or coal.[25] Physical and/or chemical activations are commonly used to prepare AC. Whereas physical activation is done at high temperatures (up to 1000°C) and in the absence of an activation agent, chemical activation benefits from the presence of an activation agent and is typically competed at relatively lower temperatures (450–900°C).[26] Owing to its fast heating, high energy efficiency, and selective heating, microwave heating is widely used for environmental applications. Carbonaceous materials have high dielectric loss; hence, they can be heated quickly in microwave. To that end, microwave heating is a great candidate for synthesizing AC.[26]

4.1.2 Activation Parameters

Numerous biomass precursors were examined as relevant candidates for microwave-assisted activation of carbon, which are shown in Table 5. The most successful yields of AC resulted from microwaves ranging in power from 600-700 watts and reaching a temperature of approximately 600-1000°C. Common heating durations were in the range of less than 10 minutes, however, there were exceptions in the case of one-step activation requiring longer duration activation times on the order of 30 minutes. Based on this information, microwave heating durations of 3, 5, 7, and 9

minutes will be used in this research. Typical activation agents used were potassium hydroxide (KOH), zinc chloride ($ZnCl_2$), and potassium carbonate (K_2CO_3).[25,26,27,28,29,30,31,32,33]

Table 5. Activation Parameters for Different Carbon Precursors.

Precursor	**Activation Agent**	**Agent to Precursor Ratio**	**Power (Watts)**	**Duration (min)**	**Temperature (°C)**	**Reference**
Cotton stalk	KOH	0.6	680	10	-	25
Orange peel	K_2CO_3	1.25	600	6	700	25
Jackfruit peel	NaOH	-	600	7	-	27
Peanut shell	H_2SO_4	-	700	20	800	25
Coconut shells	NaOH	3	< 3000	5-7	900	28
Wood sawdust	K_2CO_3	1.26	600	6	700	25
Bamboo	H_3PO_4	1	200	2	600	25
Sewage sludge	ZnCl2	-	800	103	600	25
Tea waste	H_3PO_4	3	900	0.5	1000	29
Palm Oil shell	Varies	-	1200	15	-	30
Coconut husk	KOH	1.25	600	6-8	700	31
Microalgae waste	KOH	0.5 and 1	-	30	750	32
Sugarcane bagasse	KOH	1.25	600	5	700	33

4.1.3 Structural Properties

The structural properties of activated carbon will differ between varying organic precursors. After activation, the carbon particles will have nanoporous slits throughout. This factor determines the surface area, pore volume, and pore size. Table 6 displays the structural properties of the ACs listed in Table 5.

Table 6. Structural Properties of Different ACs.

Precursor	**Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Pore Size (nm)**	**Reference**
Cotton stalk	157-795	0.083–0.63	2.4–3.2	25
Orange peel	213-1352	0.09–0.57	1.8–2.3	25
Jackfruit peel	1286	0.764	2.375	27
Peanut shell	54-395	0.210	2.56–3.54	25
Coconut shells	901-2825	0.59–1.49	2.5–2.75	28
Wood sawdust	1496	0.39–0.864	2.3	25
Bamboo	320-1409	0.18-0.67	1.9	25
Sewage sludge	124-389	0.1–0.24	1.2–3.7	25
Tea waste	1157	0.5	-	29
Palm Oil shell	1253	0.83	2.65	30
Coconut husk	1356	0.38	2-4.5	31
Microalgae waste, agar meal	1121-2118	1.14	< 0.7	32
Sugarcane bagasse	1620	0.979	2.4	33

4.1.4 Gas-Phase Adsorption

AC is a non-polar adsorbent and thus is selective toward non-polar, hydrophobic compounds.[24] In order to enhance the adsorption of polar and/or hydrophilic compounds by AC, a number of modification techniques have been studied and implemented such as heating, pyrolysis, acid or base treatment, microwave heating , ozonation, plasma treatment, and impregnation.[23,24] However, the functional groups that specific forms of AC will develop depend heavily on the carbon precursor, activation technique, and modification agent.[5] Commonly used modification agents for VOC removal are KOH, sodium hydroxide (NaOH), and K_2CO_3.[23,34] Once activated, the carbon is often used for adsorption of acetone, toluene, benzene, and other hydrocarbons.[34] Different physical forms of ACs, including Powdered Activated Carbon (PAC), Granular Activated Carbon (GAC), Activated Carbon Fibers (ACF), Carbon Molecular Sieves (CMS), and Carbon Nano Tubes (CNTs), have been investigated for pollutant control from gas streams. Photos of these carbon types can be seen in Figure 3 through Figure 7.[35,36,37,38,39]

Figure 3: Powdered Activated Carbon (PAC).

Figure 4: Granular Activated Carbon (GAC).

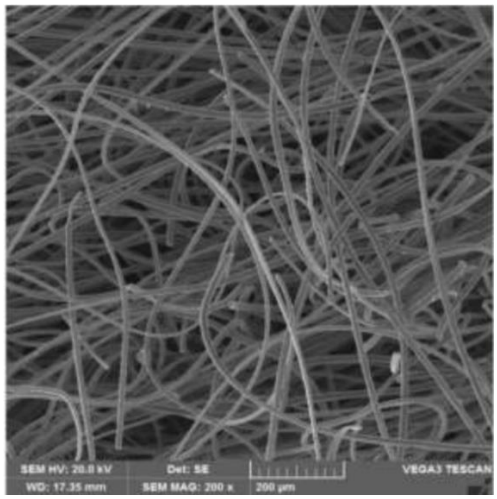


Figure 5: Activated Carbon Fibers (ACF).

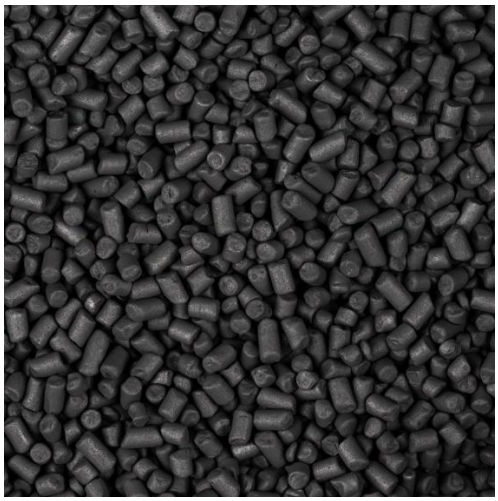


Figure 6: Carbon Molecular Sieve (CMS).

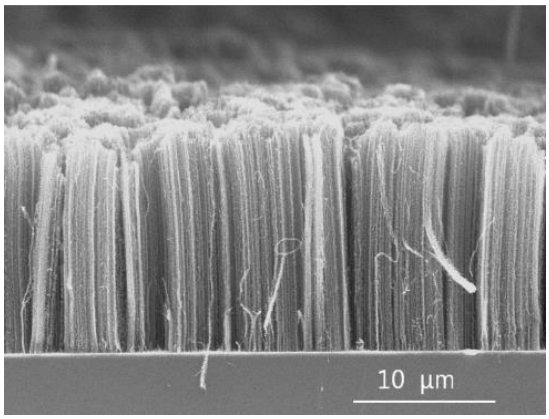


Figure 7: Carbon Nanotubes (CNT)

Table 7 summarizes the activation methods and structural properties of various precursors used for gaseous applications.

Table 7. Summary of ACs synthesized for gaseous applications.

Precursor	**Activation Method**	**Activation Agent**	**Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Reference**
grass cuttings horse manure beer waste bio sludge	hydrothermal carbonization	CO_2	841 749 622 489	0.379 0.816 0.317 0.387	40
teak saw dust	slow pyrolysis	steam	439-1150	-	41
peanut hulls	unknown	steam $ZnCl_2$ KOH H_3PO_4	97-253	0.053-0.223	42
corncobs	slow pyrolysis	steam and H_3PO_4	607-960	0.296-0.629	43
white pine wood powders	microwave heating	$ZnCl_2$	1048-1549	0.12-0.70	44
oil palm stone	microwave heating	CO_2	412.5	-	45

Table 8 summarizes the adsorption performance of ACs used for gaseous applications, particularly Volatile Organic Compounds (VOC).

Table 8. Adsorption capacities of different ACs for VOCs.

Precursor	Physical Form	BET Surface Area (m^2/g)	Adsorption Temperature (°C)	VOC Type and Concentration (mg/l)	Uptake (mg/g)	Reference
Coal	Commercial GAC	807	30	Acetonitrile, 43	10	46
Coal	Commercial GAC	807	30	Acetonitrile, 2700	76	
PAN	Commercial ACF	832	30	Acetonitrile, 43	12	
PAN	Commercial ACF	832	30	Acetonitrile, 2700	56	
Pitch	Commercial ACF	1518	30	Acetonitrile, 43	15	
Pitch	Commercial ACF	1518	30	Acetonitrile, 2700	80	
Bio sludge	GAC	757	30	Acetonitrile, 2700	41	
Coal	Commercial GAC	807	30	Chloroform, 90	146	
Coal	Commercial GAC	807	30	Chloroform, 7800	284	
PAN	Commercial ACF	832	30	Chloroform, 90	174	
PAN	Commercial ACF	832	30	Chloroform, 7800	235	
Pitch	Commercial ACF	1518	30	Chloroform, 90	128	
Pitch	Commercial ACF	1518	30	Chloroform, 7800	600	
Bio sludge	GAC	757	30	Chloroform, 7800	244	
Coconut	GAC	1511	25	Toluene, 500	392	47
Novoloid	ACF	1472	25	Toluene, 500	505	47

4.1.5 Aqueous-Phase Adsorption

ACs have shown success in removing organic pollutants from water due to their ability to remove and control synthetic and naturally occurring organic chemicals.[48] ACs can be used for aqueous-phase treatment and removal of contaminants, including herbicides, VOCs, and heavy metals.[49] The primary sources of metal contamination in the water supply come from industrial reject (mining, metal plating, car manufacturing, painting) and agricultural practices. Heavy metals are considered hazardous with the most toxic being chromium, lead, mercury, nickel, and cadmium according to the World Health Organization. Activated carbon can be effective at removing metals depending on the chemistry of the metal ion complex, pH of the solution, porosity, surface area, and the size of the adsorbing species.[50] The removal efficiencies of organic and inorganic contaminants from the aqueous phase depend largely on pore volume. Owing to their low economic value, high abundance, and low ash content, agricultural wastes have been considered a potential precursor for producing ACs used for water and wastewater treatment. Table 9 details the activation of several wastes and their effectiveness at aqueous-phase contaminant removal. Woody precursors can be converted into AC by both physical and chemical activation. Developed materials are highly effective at removing heavy metals such as chromium from the aqueous phase producing better results than commercially prepared AC. A summary of the activation of several woody precursors and their applications are presented in Table 10 and Table 11.

Table 9. Aqueous-phase application of AC derived from agricultural waste.

Precursor	Target Contaminant	Observation(s)	Reference
Olive Seed	Dye (methylene blue)	The AC obtained through chemical activation using KOH removed the dye with comparable capacities to commercial AC.	51
Rice Husk	Dye (malachite green)	AC treated with H_3PO_4 using carbonization temperature of 500°C showed adsorption capacities comparable to commercial AC.	52
	Dye (acid yellow, acid blue)	Showed low capacity for dye.	53
	Humic Acid	Uptake was directly related to amount of phosphoric acid used at 500°C.	54
Almond Shell	VOCs	The best AC had large surface area.	55
Sugar Cane	Dye (Acid blue 80)	AC prepared from precursor with high ash content presented high surface area (614-1433 m^2g^{-1}) and well-developed microporous texture. Chemical carbonization and gasification were effective at low temperature.	56
	Melanoidin (brown polymer)	When prepared by steam, adsorption capacity was comparable to commercial AC.	57
Olive Cake	Herbicides	Better performance compared to commercial ACs with the ability to absorb herbicides.	58
Coirpith	Heavy metals	Showed great potential for removal of toxic metals from industrial wastewater.	59

Table 10. Summary of activation using woody precursors.

Precursor	**Activation Agent**	**Observations**	**Reference**
Cedar wood and its shavings	CO_2 and H_2O_2	H_2O_2 positively influences the pore development.	60
Cedar wood	CO_2 and H_2SO_4	Dehydration of raw material with H_2SO_4 improved porous texture and adsorption capacity.	61
Teak saw dust	Steam	AC with a surface area of 1150 $m^2\ g^{-1}$ and pore volume of 0.43 $cm^3\ g^{-1}$ was obtained.	62
Pinewood saw dust	CO_2 with metal oxide impregnation	AC was found to be suitable support for metal oxide catalyst. Adequate porous texture could be induced by proceeding to the impregnation step before CO_2 activation.	63

Table 11. Application of AC Prepared from Woody Precursors

Precursor	**Target Contaminant**	**Observation(s)**	**References**
Eucalypt sawdust	Phenol	Phenol was adsorbed faster on PAC. Higher dosage of AC in the granule form increased adsorption rate and maximum uptake	64
Fir Wood	Dyes, phenols	Surface areas from 1371 to 2821 m^2g^{-1} and pore volumes from 0.81 to 1.73 cm^3g^{-1}. High adsorption capacities were obtained. CO_2 gasification time influenced dye adsorption.	65
	Chromium (VI)	Adsorption of Cr (VI) was highest at pH = 3 and increased with temperature. The KOH-AC showed higher adsorption capacity than the commercial carbon.	66
Mahogany saw dust	Acid dyes	AC showed an adsorption capacity of 138.8 mg g^{-1} and potential to replace commercial carbon for dye removal.	67
Pinus wood	Organics	AC showed similar organic removal efficiency than electron beam process, if adequate irradiation dose was delivered to the organic pollutant.	68

Figure 8 shows the adsorption capacities of ACs derived from different sources for the removal of organic and inorganic pollutants from wastewater.

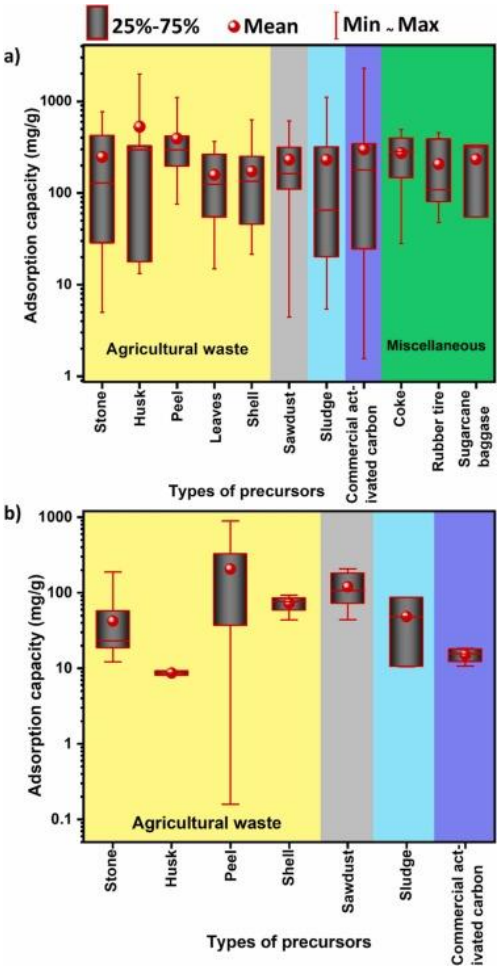


Figure 8: Variation in adsorption capacities of different precursors for removal of (a) organic and (b) inorganic contaminants from wastewater.[50] *Different precursors, namely agricultural waste, sawdust, sludge, commercial activated carbon, and miscellaneous, are highlighted with different colors.*

4.1.6 Phosphorus Adsorption

Elevated levels of phosphorus (P) concentrations released into the environment have become a global issue threatening aquatic ecosystems.[69] This process is referred to as eutrophication in which excess nutrients such as nitrogen and phosphorus are discharged into a body of water. High concentrations of P results from anthropogenic activities such as fertilizer runoff from agricultural practices, leaking septic systems, and discharge from sewage treatment plants.[70] A common environmental issue associated with the increase of nutrients in water is algal blooms. Algal blooms are defined as a rapid growth of algae that covers the surface of waters. This contributes to decreased levels of dissolved oxygen (DO), increased water temperatures, and the production of algae toxins harmful to human and animal health.[71] As algal blooms become more prevalent, research is needed to determine a solution to reduce eutrophication.

In natural aquatic systems, phosphorus is found in the form of organic and inorganic phosphate (PO_4^{3-}).[72] For many years, the removal of phosphorus has been completed through both chemical and biological processes. The chemical treatment process involves adding metal salts to the water to create a reaction with the soluble phosphate to form precipitates.[73] The precipitated P can then be either removed through gravity settling or filtration.[72] Some metal salts used for chemical treatment consist of ferric chloride, ferrous sulfate, ferrous chloride, and ferric sulfate. The limitation of chemical treatment falls short in that this method requires large amounts of chemicals to precipitate P and has the potential to add additional contaminants to the water.[72] Due to this, new phosphorus treatment methods have been an ongoing research topic.

Current research on eutrophication involves developing inexpensive adsorbents for the uptake of phosphate from aqueous solutions. Adsorbents are porous solid materials that are able to withhold solute molecules from a liquid or gas solution.[74] This process is referred to as adsorption in which the molecules of an adsorbate bind to the surface of a specific material.[75] Carbon adsorbents have provided promising results for phosphorus removal due to their surface properties and high phosphorus adsorption capacity.[76] Examples of adsorbents commonly tested consist of zeolites, clay minerals, activated carbon, and biochar. Among these adsorbents, carbonaceous adsorbents in the form of PAC and biochar have shown a significant uptake of phosphorus due to their high porosity and surface area.[76] Specifically, PAC can have a surface area ranging from 500 to 1500 m^2/g.[77] This suggests that high surface areas increase adsorption sites resulting in a greater uptake of the adsorbate adsorbed.[72]

A 2016 study presented the importance of surface area in adsorption by comparing the phosphate adsorption of PAC in comparison to GAC.[69] PAC has a small particle size between 10 to 100 μm whereas GAC has a larger particle size and smaller external surface.[78] Theoretically, this indicates that PAC should have a higher phosphate adsorption capacity. Results from this study supported this claim when it was found that in three hours, at a phosphate concentration of 5 mg/L and an adsorbent dosage of 1 g/L, PAC and GAC had a phosphate removal efficiency of 51.62% and 40.29% respectively. Under the same conditions when the phosphate concentration was increased to 20 mg/L, the phosphate adsorption for both PAC and GAC were < 50% and < 20% respectively. A greater than 80% removal rate of phosphate was only achieved for both adsorbents when the phosphate concentration was lowered to 1 mg/L. This study showcased that ACs alone without additives are not sufficient to adsorb phosphorus at high concentrations (> 20 mg P/L) in water.

In phosphorus adsorption research, the goal is to achieve > 90% removal of phosphorus using a small adsorbent dosage. To attain this high percent removal, modification agents have been studied in which different modification agents are added to ACs to increase their phosphorus adsorption capacity. Modification agents bind to the surface of carbon adsorbents adding active sites to the adsorbent.[79] Active sites are locations on the surface of an adsorbent that aid in the adsorption of an adsorbate.[79] Common modification agents used for phosphorus adsorption are metal ions such as magnesium (Mg), aluminum (Al), iron (Fe), calcium (Ca), and lanthanum (La). As summarized in Table 12, a phosphorus adsorption capacity greater than 90% can be achieved when modification agents are utilized. Lanthanum chloride ($LaCl_3$) serves as the most viable modification agent based on a comprehensive review article.[72] In stormwater and wastewater, the phosphorus concentration is typically around 2 mg P/L.[71] However, in this specific study a high P concentration of 100 mg P/L was utilized to showcase extreme conditions. Specifically, at an adsorbent dosage of 1 g/L and a P concentration of 100 mg P/L, 56.8% of P was adsorbed. This indicates that at a P concentration of 2 mg P/L a greater that 99% removal of phosphorus can be achieved. In addition to $LaCl_3$, other modification agents which present promising P adsorption results consist of $MgCl_2$, MgO, and $ZnCl_2$. Based on this information, $LaCl_3$, $MgCl_2$, MgO, and $ZnCl_2$ will be used as modification agents in this research. Also, phosphorus concentrations of 5, 10, and 20 mg/l will be used for screening experiments, providing us with an opportunity to compare our results with the literature.

Table 12. Phosphorus adsorption capacity of different ACs.

Adsorbent	Adsorbent Dosage (g/L)	Solution Concentration (mg/L)	Adsorption Performance	Contact Time (h)	Reference
PAC	1	5 (PO_4^{3-})	51.62%	3	69
GAC	1	5 (PO_4^{3-})	40.29%	3	69
PAC: Zero-valent iron nanoparticles (nZVI)	2	50 (P)	69%	24	70
	8	50 (P)	99.5%	24	70
Biochar: Mg-Al	2	10 (P)	95%	4	71
Teak leaf-based activated carbon: $ZnCl_2$	1	100 (PO_4^{3-})	95%	4	80
$La(OH)_3$:Ni	1	10 (P)	8.4 mg P/g	5	81
$La(OH)_3$:Ni	1	5 (P)	3.88 mg P/g	5	81
Biochar: La	2	300 (PO_4^{3-})	46.37 mg PO_4^{3-}/g	24	82
Biochar: $ZnCl_2$	2	20 (P)	9.39 mg P/g	24	72
Biochar: MgO	2	20 (P)	8.42 mg P/g	24	72
Biochar: $MgCl_2$	10	84 (P)	7.5 mg P/g	12	72
Biochar: Mg-Al	1	1000 (PO_4^{3-})	626 mg PO_4^{3-}/g	24	72
Biochar: $LaCl_3$	1	100 (P)	56.82 mg P/g	12	72
Biochar: $FeCl_3$	20	20 (PO_4^{3-})	0.963 mg PO_4^{3-}/g	24	72

4.2 Building Microwave Setup (July-September 2021)

Based on the literature review, an experimental setup was designed and assembled for microwave heating, as shown in the schematic diagram in Figure 9. The setup consists of a kitchen microwave oven (Black and Decker, model: EM720CB7; output power: 700 W; Figure 10) for activation of precursors. The microwave enclosure should be continuously purged during operation with humid nitrogen, for which a hole was drilled on the top surface of the chamber (Figure 11). A glass funnel was used as a purge tube inside the microwave to ensure dispersion of nitrogen throughout the sample (Figure 12). High-purity (99.999%) nitrogen was supplied by gas cylinders purchased from NexAir. The cylinders were connected to gas regulators to control pressure (Figure 13). A gas flowmeter (manufactured by MasterFlex) with a span of 0-65 units, equivalent to 0-1 liter/min or 0-15.8 gal/hour, was used to control the gas flow rate (Figure 14). The gas was humidified by passing it through a gas bubbler (i.e., humidifier) manufactured by ChemGlass (Figure 15). The humid nitrogen was then directed into the microwave enclosure through the hole described above. To measure sample temperature after microwave heating, an 18-inch, k-type thermocouple manufactured by Omega was used (Figure 16). The thermocouple was connected to a data acquisition chassis made by National Instruments (Figure 17). To measure temperatures, microwave heating was stopped, followed by inserting the thermocouple into the core of the algae sample and reading the resulting temperature from the computer screen using LabVIEW software (Figure 18). The temperature was also recorded using an infrared thermometer (Figure 19).

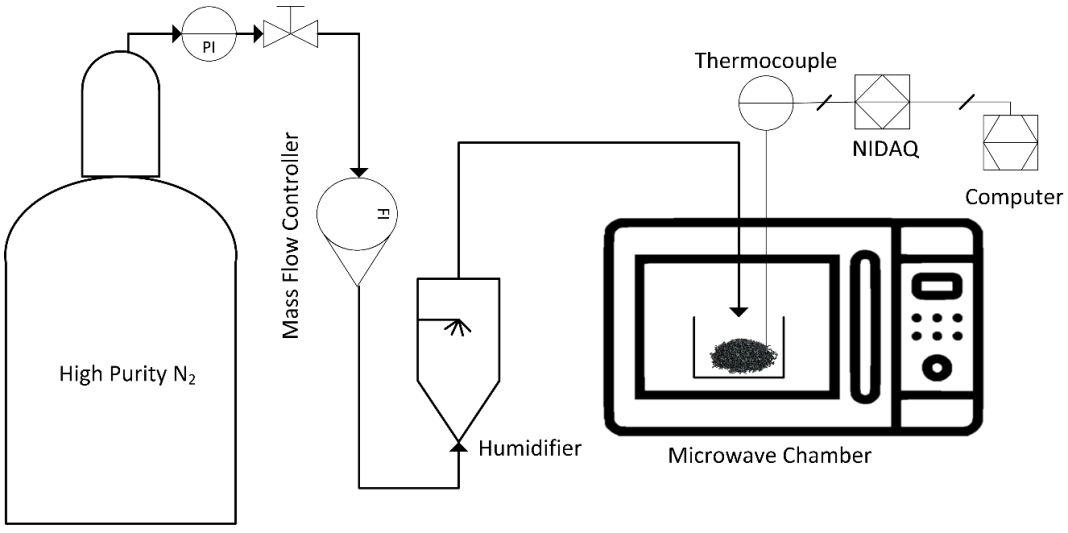


Figure 9: Schematic diagram of the experimental setup for microwave heating.

Specifications

Model:	EM720CB7
Rated Voltage:	120V~60Hz
Rated Input Power(Microwave):	1050W
Rated Output Power(Microwave):	700W
Oven Capacity:	0.7 Cu.ft
Turntable Diameter:	10 inch
External Dimensions:	17.3 X13 X 10.2 inch (440X330X259mm)
Net Weight:	Approx.21.6 Lbs (9.82 kg)

Figure 10: The specifications of the microwave oven.

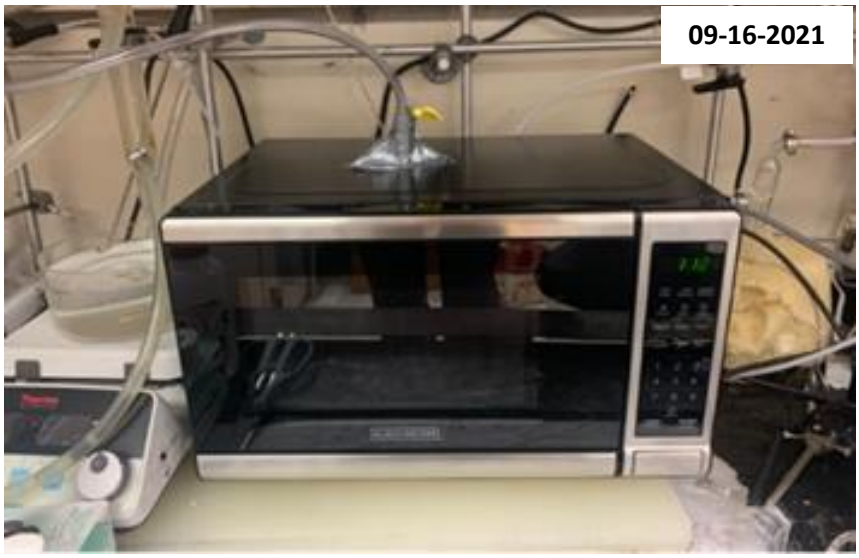


Figure 11: The connections on the microwave oven.

Figure 12: Inside of the microwave oven.

Figure 13: Gas cylinders with regulators.

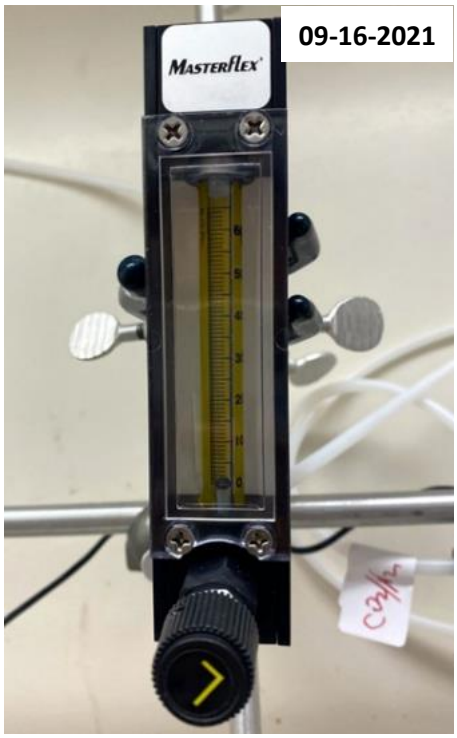


Figure 14: Gas flowmeter.

Figure 15: Gas bubbler.

Figure 16: K-type thermocouple

Figure 17: Data acquisition chassis made by National Instruments.

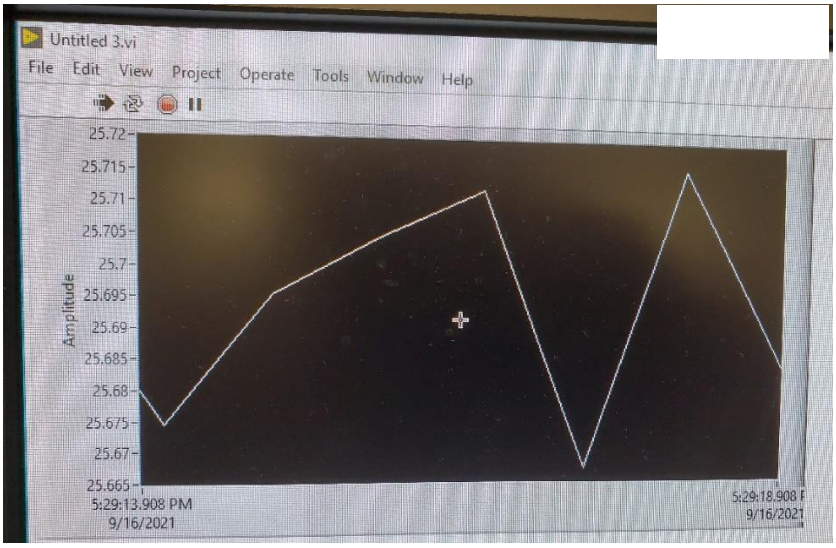


Figure 18: Temperature signal collected by LabVIEW software.

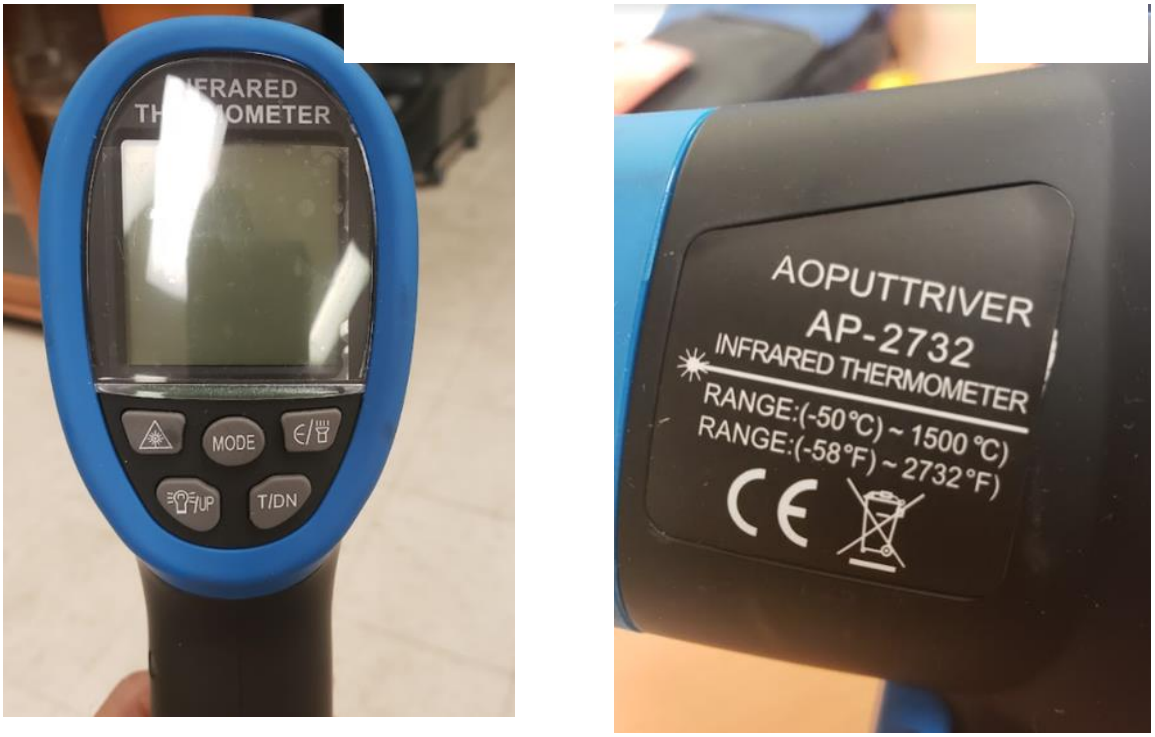


Figure 19: Infrared thermometer.

4.3 Processing of Commercial AC (July-September 2021)

4.3.1 Grinding and Sieving

Necessary experimental methods were first developed and refined using a commercial activated carbon (Alfa Aesar; Figure 20). The adsorbent pellets were placed in a grinder (Figure 21). The grinder was then sealed and run in intervals of approximately 20 seconds. This was repeated 2-3 times until very fine particles remained. The resulting powder was then placed in a No. 100 mesh sieve and the fine particles that passed through the sieve were collected on a tray below as shown in Figure 22. The sieve was agitated and held just above the tray until no further particles passed through the sieve. Once no additional particles were passing through the sieve, the sample was collected in a container and the mass was recorded. The grinder and sieve specifications are shown in Table 13.

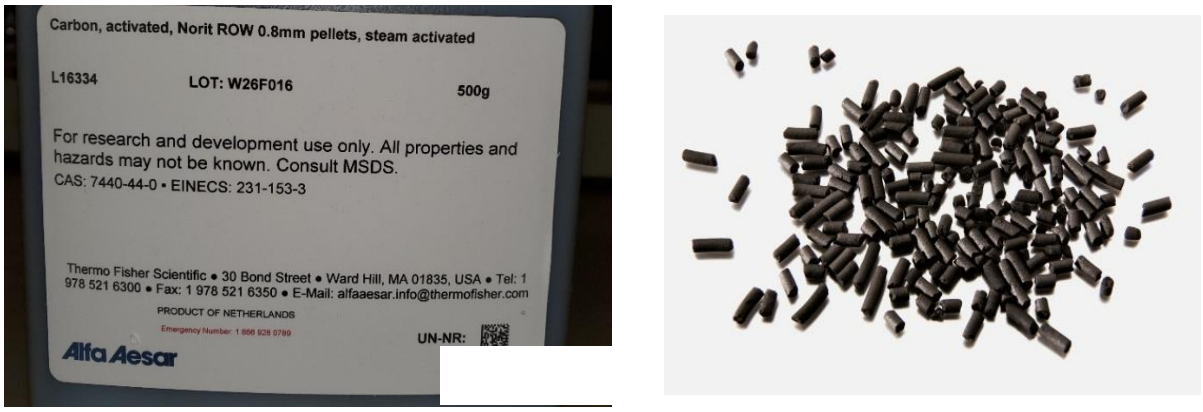


Figure 20: Commercial activated carbon. Top row: (left) material container, and (right) adsorbent pellets in their original form.

Figure 21: Grinder used to process AC.

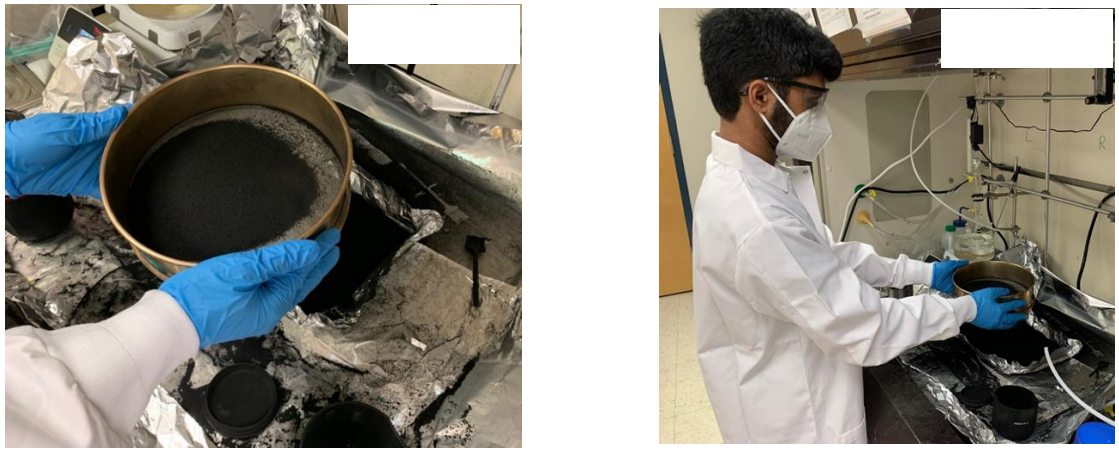
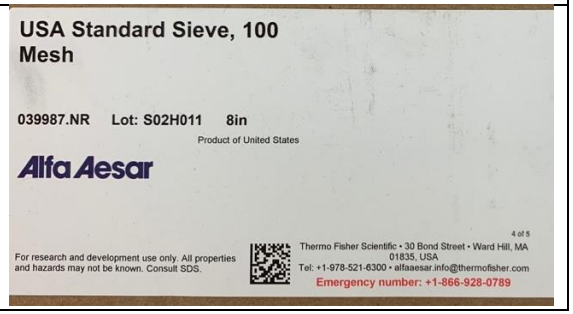


Figure 22: Left: Ground AC on sieve No. 100. Right: Student researcher sieving the carbon.

Table 13: Grinding/Sieving Tools Information.

Item Name	Brand	Model	Lot Number	Purchase Date	Picture
Electric Grinder	Watifisa	M150B	N/A	August 23, 2021	
USA Standard Sieve, 100 Mesh	Alfa Aesar	N/A	S02H011	August 20, 2021	

4.3.2 Microwave Heating

Using the microwave setup, the sieved carbon was heated. The sample reached temperatures of 1139 and 1310°F after one and two minutes, respectively, followed by leveling off at about 1500°F (Figure 23).

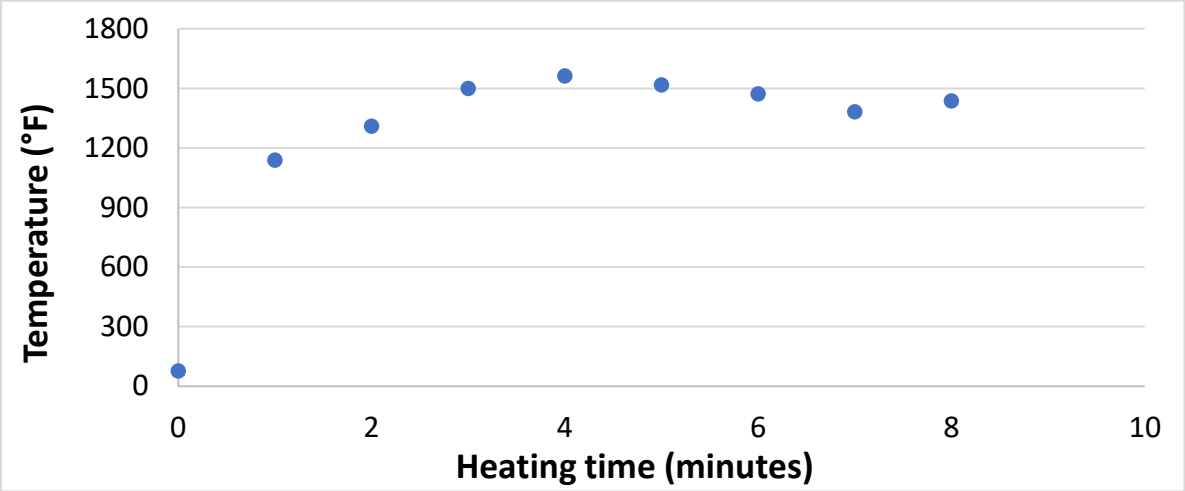


Figure 23: Temperature profile for mesh 100 commercially available activated carbon as a function of microwave heating duration.

4.3.3 Thermal Analysis

Minerals such as inorganic materials and metals might cause sparks during microwave heating. To assess the presence of minerals, the sieved carbon was studied using a Thermogravimetric Analyzer (TGA) available in the PI's lab (Figure 24). This is a research grade TGA featuring a sensitive vertical thermo-balance with an auto-switching dual range microbalance (0-200 mg, and 0-1000 mg sample weight range). This TGA utilizes a horizontal gas purge system that produces excellent baseline flatness and sensitivity over the temperature range from ambient to 1000°C (1832°F). The instrument is equipped with a Blending Gas Delivery Module (BGDM) that provides additional gas handling and control capabilities. There are two gas inlet ports on the TGA and the BGDM accepts up to two inlet gases and provides purge gas control to the furnace of the TGA. The BGDM used in conjunction with the TGA allows for automated switching between the gas ports, as well as software-controlled blending of binary mixtures of gases. The BGDM is compatible with the following gases: N_2, Ar, He, Air, O_2, CO_2, and forming gas (4% H_2 in 96% N_2). This accessory helps study the thermal and oxidation stability of many materials in a controlled atmosphere.

Figure 24: Top left: TGA instrument. Top right: Blending Gas Delivery Module. Bottom: High-purity and custom-made gas cylinders connected to gas regulators.

The sieved commercial activated carbon was studied using TGA to evaluate its thermal stability and minerals content. The sample was heated from 25 to 800°C (77 to 1472°F) at a heating rate of 1°C/min (1.8°F/min) in the presence of 100 standard cm^3/min of nitrogen, to remove all volatile

species. Once reaching the target temperature, the purge gas was switched to air for 30 minutes to burn the carbonaceous residue. Any material remaining at the end of the experiment was categorized as minerals (i.e., ash), which typically contains inorganic materials and metals. As shown in Figure 25, the volatile content of the commercial activated carbon was 10 wt.%, and its ash content was 4.5 wt.%. The latter observation necessitates additional treatment to remove the ash from the sieved carbon prior to microwave heating. Pictures of the TGA sample holder before and after testing are provided in Figure 26.

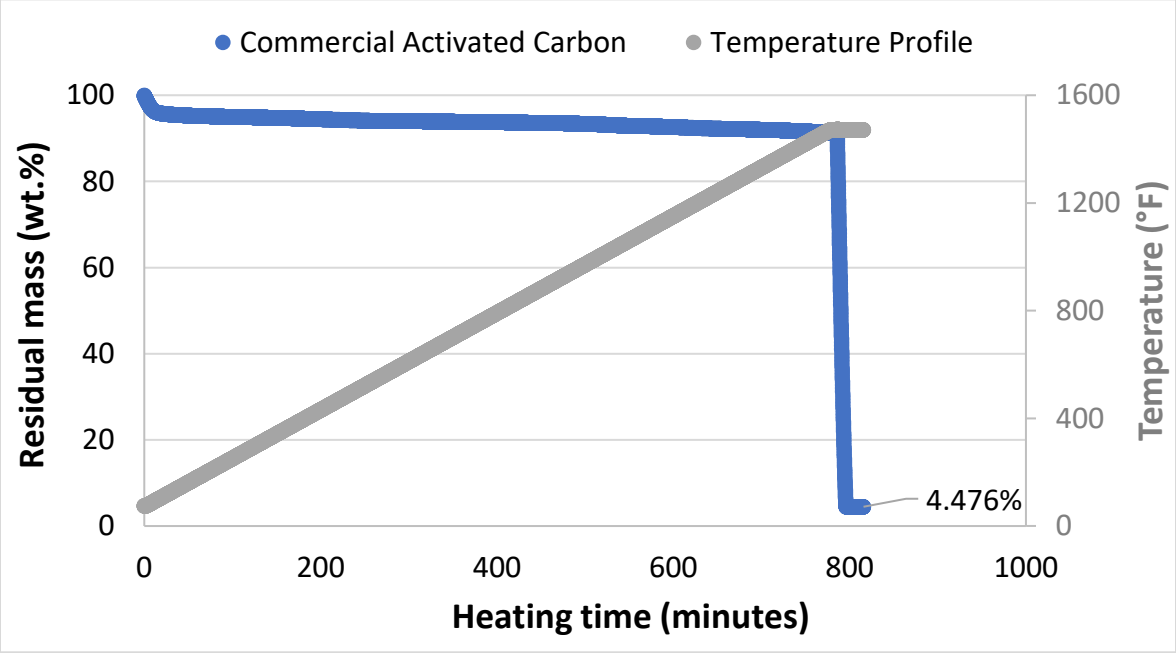


Figure 25: Temperature profile and mass loss data during TGA analysis of sieved carbon.

Figure 26: TGA sample holders before and after testing. Left: Commercial activated carbon before heating. Right: Residual ash from commercial activated carbon after heating.

4.3.4 Acid Treatment for Ash Removal

Acid treatment was completed on the commercial activated carbon (Figure 27). Ten grams of the material was treated with 1-molar hydrochloric acid (HCl), which was prepared using 37% HCl diluted with deionized water. The resulting mixture was stirred continuously for one hour at room temperature. After one hour, the treated activated carbon was filtered with a Buchner funnel and rinsed with copious amounts of deionized water until reaching neutral pH. The recovered activated carbon was dried in an oven at 120°C for 24 hours.

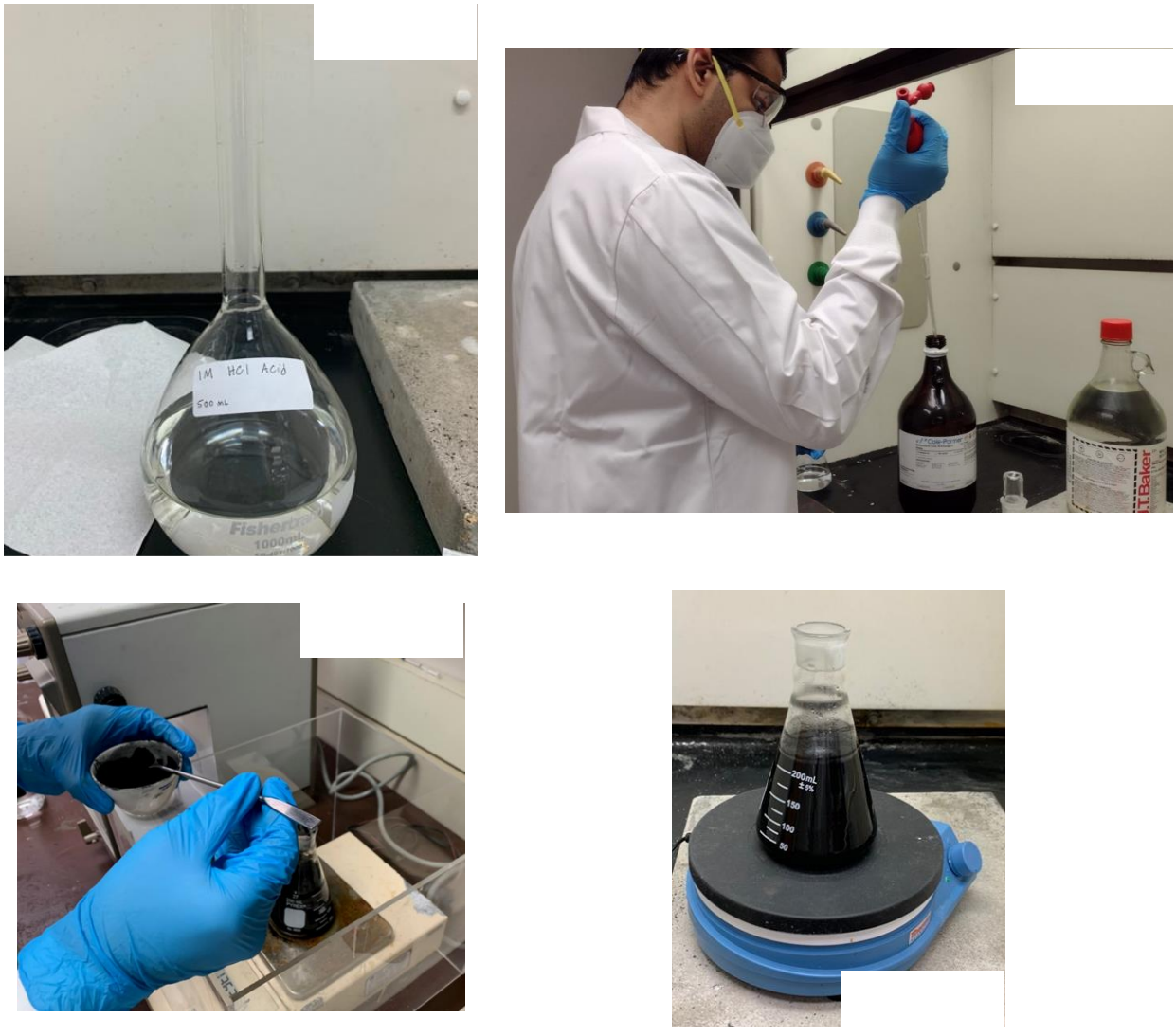


Figure 27: Acid treatment procedures. Top row: (left) HCl solution, and (right) student researcher preparing acid solutions. Bottom row: (left) student researcher transferring the activated carbon to acid solution, and (right) stirring the acid solution and activated carbon.

4.3.5 Thermal Analysis of Acid-Treated Samples

The acid-treated sample was tested by TGA. As shown in Figure 28, treatment with HCl was successful in removing 80% of the ash. The developed technique was later used for ash removal from cyanobacteria biomass (see the next Section).

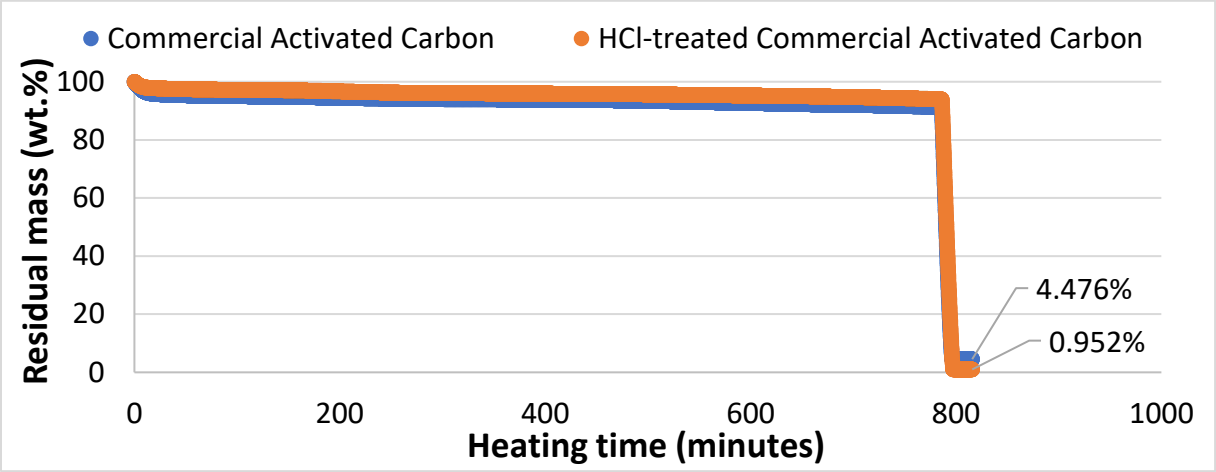


Figure 28: TGA analysis of commercial activated carbon after treatment with HCl.

4.4 Phosphorus Measurements Methods (July-September 2021)

4.4.1 Calibration Curve

A phosphate standard solution of 100 mg/L as $PO_4^{3-}$was obtained from Hach. The phosphorous (P) concentration of this stock solution was calculated to be 32.62 mg P/L. Analysis of phosphorus was conducted using the Phosphorus (Reactive) TNT Reagent Set, Low Range from Hach (Method 8048, Product #: 2742545; Figure 29). This procedure is approved by the USEPA and is equivalent to Standard Method 4500-P-E. A detailed description of this method is enclosed as a separate attachment. The detection range is from 0.06 to 5.00 mg/L of PO_4^{3-} (0.02 to 1.6 mg P/L). Hereafter, all concentrations and measurements are reported in mg/L of P. For calibration, seven concentrations were selected (0 mg P/L, 0.02 mg P/L, 0.05 mg P/L, 0.10 mg P/L, 0.25 mg P/L, 0.5 mg P/L, 1 mg P/L, and 1.5 mg P/L). Following this method, the calculated amount of stock solution and deionized water was micropipetted into the Reactive Phosphorus Test 'N Tube Vial (total volume = 5 mL). The cap was then put back on the vial and inverted to mix the sample. After this, the vial was wiped clean with a kimtech wipe and inserted into the spectrophotometer (DR 5000, Hach) to zero out the device (Figure 30). After this, one PhosVer 3 Phosphate Powder Pillow packet was added to the vial. The vial was then shaken for a minimum of 20 seconds and a timer for two minutes was set to let the reaction where ascorbic acid reduces the mixed phosphate/molybdate complex results in a molybdenum blue color (Figure 31). Once the timer expires, the vial was wiped clean and inserted into the spectrophotometer and measured at a wavelength of 880 nm to read the absorbance (Figure 32). The collected data from the calibration curve samples was then plotted on Microsoft Excel where the absorbance is on the Y-axis, and the phosphorus concentration is on the X-axis. The graph plotted produced the equation $y = 0.5784x + 0.0035$ and an R^2 equal to 0.9995 (Figure 33).

Figure 29: Reactive Phosphorus Test 'N Tube Vial with no sample added.

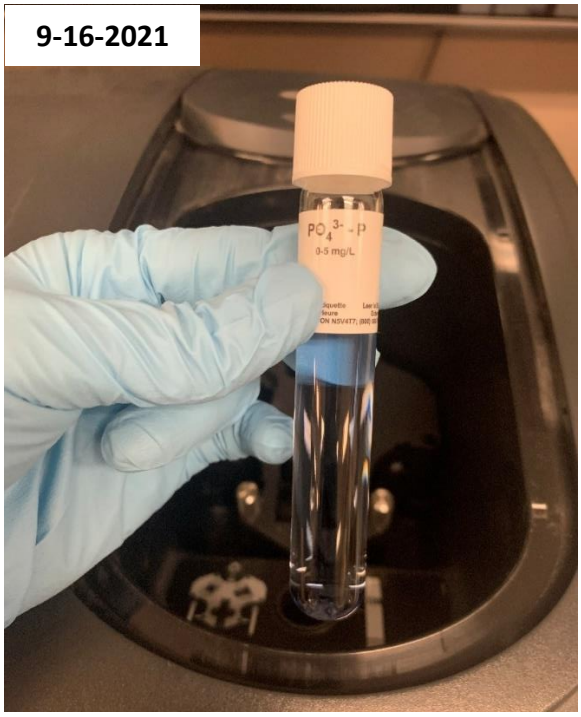


Figure 30: Spectrophotometer being zeroed out with just the Reactive Phosphorus Test 'N Tube Vial and 5 mL of sample.

Figure 31: Reactive Phosphorus Test 'N Tube Vial after the sample and PhosVer 3 Phosphate Powder Pillow packet has been added to the test tube.

Figure 32: Reactive Phosphorus Test 'N Tube Vial being read in the spectrophotometer after adding the sample and the PhosVer 3 Phosphate Powder Pillow packet to the test tube.

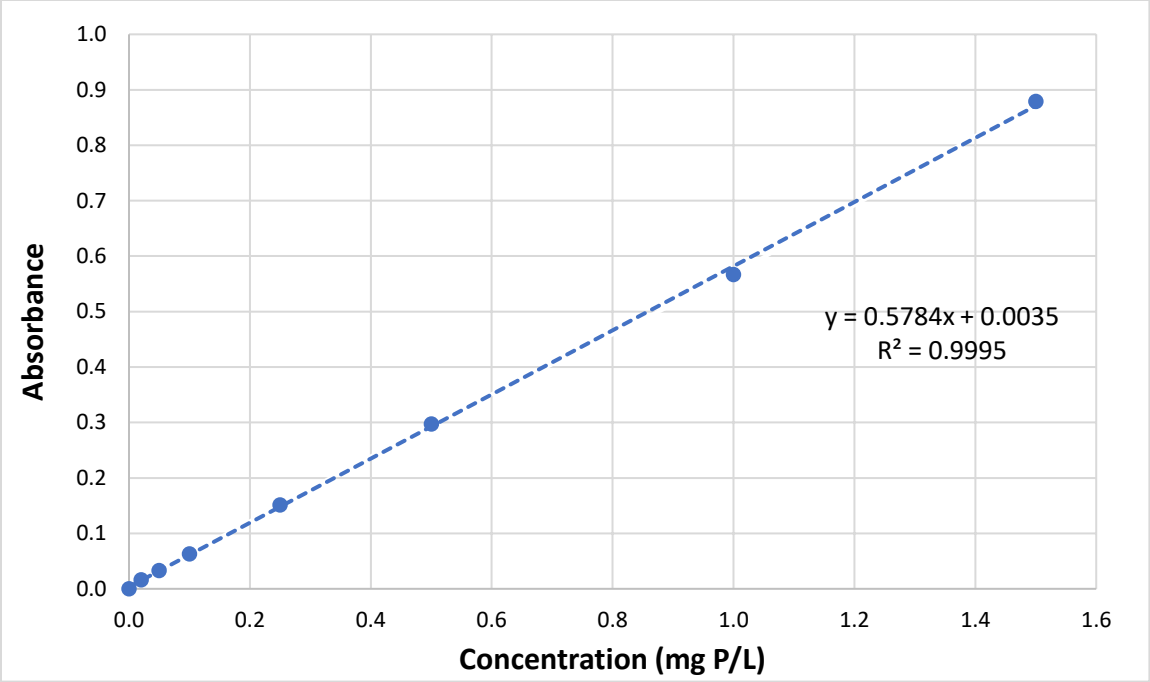


Figure 33: Calibration curve.

4.4.2 Methods for Phosphorus Adsorption Experiments

Depending on the desired concentration, the stock solution was diluted to concentrations of 5 mg P/L, 10 mg P/L, and 20 mg P/L. Phosphorus analysis was conducted as described in the previous section. Prior to running the adsorption tests, aliquots of the 5 mg P/L, 10 mg P/L, and 20 mg P/L solutions were diluted to 1 mg P/L and read in the spectrophotometer to verify that the correct concentrations were developed (Figure 34). Once the concentrations were verified, 100 mL of the designated P concentration was transferred to a beaker. Then, 0.1 gram of adsorbent was weighed on an analytical scale and added to the beaker (Figure 35). Unless otherwise stated, the adsorbent dosage was 1 g/L, and the solutions were mixed for 24 hours with a magnetic stirrer (Figure 36). After 24 hours, the solutions were drawn with a syringe, and the adsorbent was filtered with a 0.7 µm syringe filter to obtain the final P concentration (Figure 37). QA/QC, including blank check and calibration curve verification, were completed in accordance with the QAPP.

Figure 34: Absorbance being measured in the DR 5000 spectrophotometer.

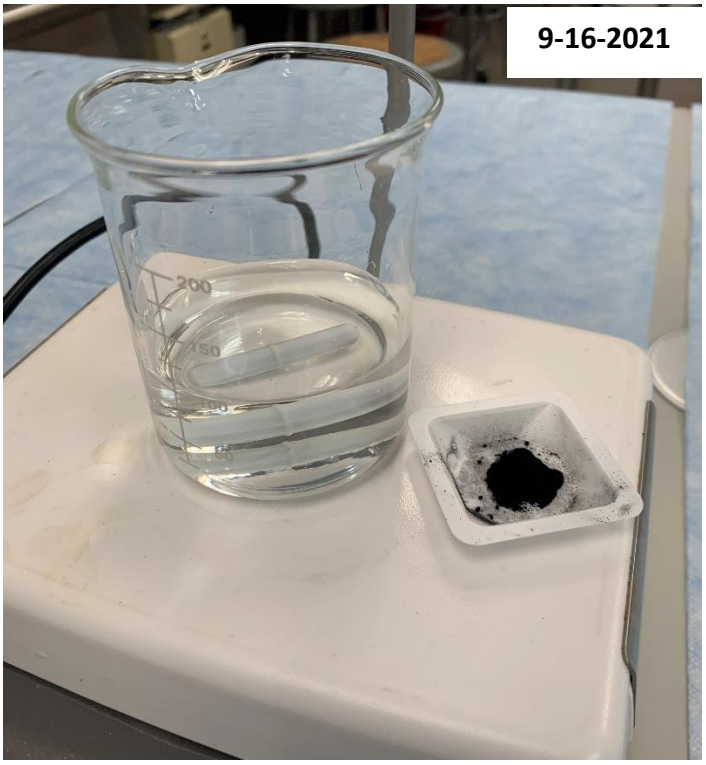


Figure 35: 100 mL of solution with 0.1 g of adsorbent.

Figure 36: Vortex forming during the mixing of adsorbent and solution.

Figure 37: Syringe and syringe filter used to filter the adsorbent from the solution.

4.5 Cyanobacteria Collection, Cultivation, Processing, and Testing (October-December 2021)

4.5.1 Collection

On October 6, 2021, based on communication with the FDEP, Ryan Thomas and Mitch Guirard traveled to the Pahokee Marina on Lake Okeechobee (190 N Lake Ave. Pahokee, FL 33476; Figure 38 and Figure 39) to collect cyanobacteria (herein referred to as algae).

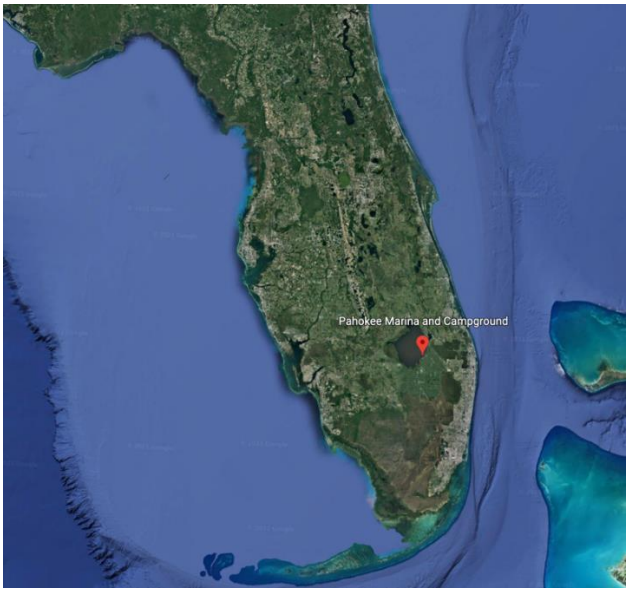


Figure 38: Location of Pahokee Marina within Florida.

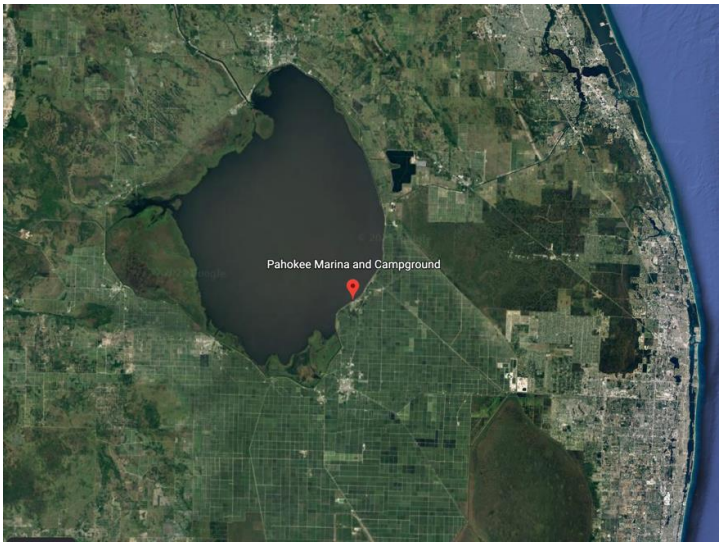


Figure 39: Location of Pahokee Marina.

The weather was partly cloudy and 31 degrees Celsius with a relative humidity of 64%. A description of the marina and weather conditions can be seen in Figure 40. It should be noted that there were signs warning of the presence of Blue Green Algae at the marina. These signs can be seen in Figure 41.

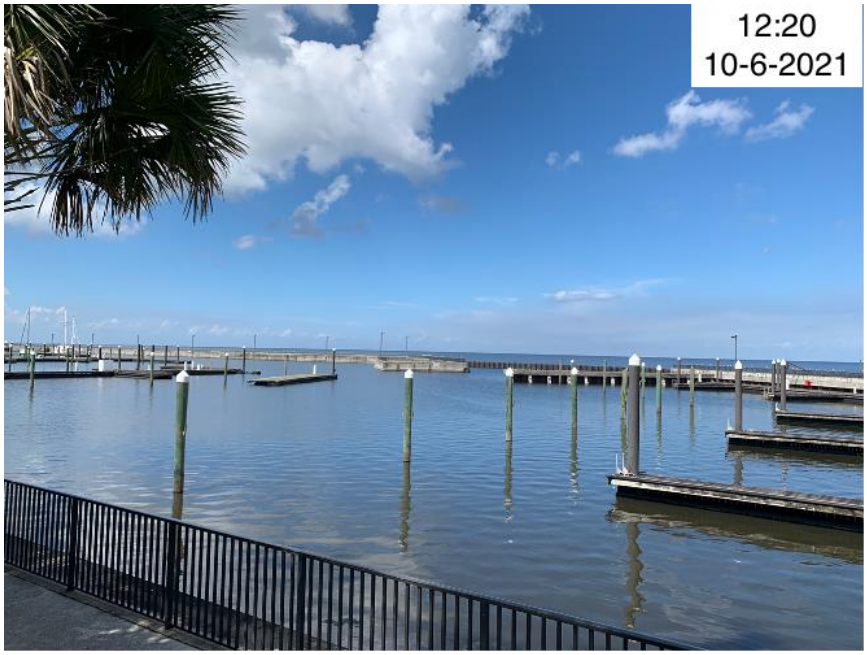


Figure 40: Pahokee Marina.

Figure 41: Blue Green Algae warning sign.

All the locations outlined by the FDEP were then assessed for the presence of the Blue Green Algae. The sites of interest were labeled PM1 through PM5. The location of these sites at the marina can be seen in Figure 42. The collection was conducted in accordance with the QAPP.

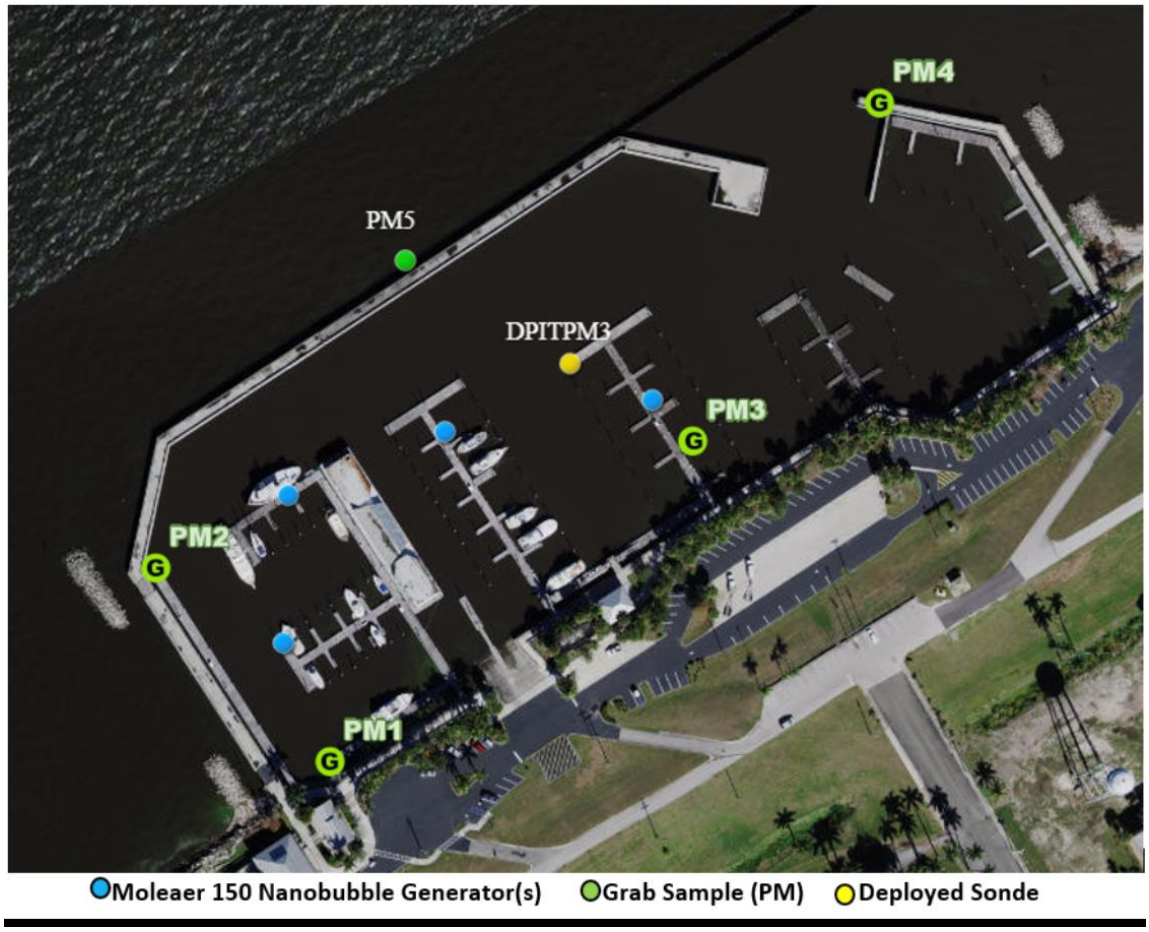


Figure 42: Blue Green Algae sampling location sites provided by the FDEP.

The first samples taken were from PM2. The location and algae can be seen in Figure 43 through Figure 47. Once removed from the water, the algae was put into the amber glass collection jar. The amber jar was immediately labeled and put on ice after collection as seen in Figure 48. The associated field log is shown in Figure 49.

Figure 43: Northwest facing walking path on dock to get to site PM2.

Figure 44: Northwest direction path toward site PM2.

Figure 45: Site PM2 looking Northwest.

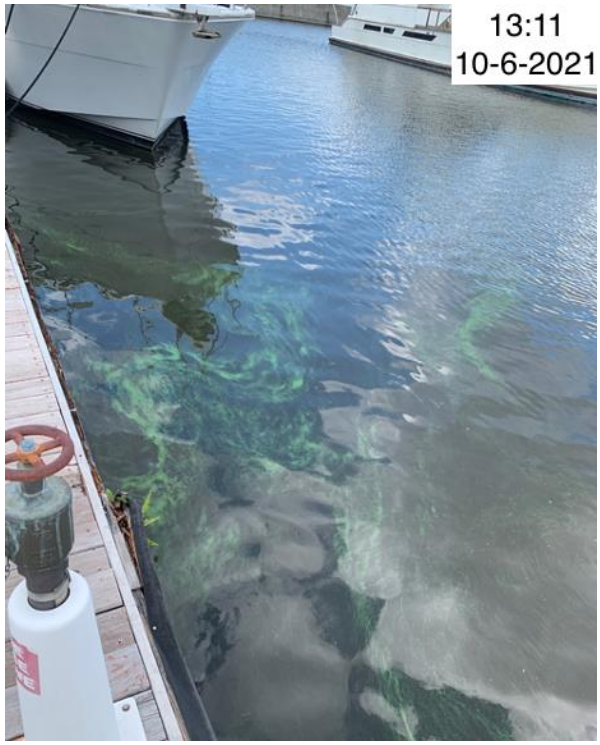


Figure 46: Blue Green Algae at site PM2.

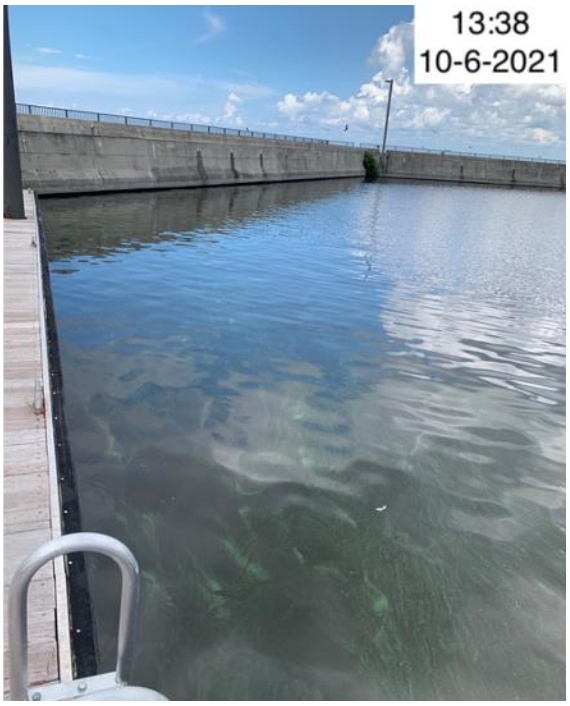


Figure 47: Blue Green Algae at the end of site PM2.

Figure 48: Algae jars on ice.

Florida Atlantic University
Department of Civil Engineering

Field Log

Project Name: FLDEP Cyanobacteria collection	Site ID Code: *yymmddsr*	Sample ☒	Dup ☐
Site Name: Pahokee Marina	Latitude (xx° xx.xxx'): 26.8252906	Longitude (xx° xx.xxx'): -80.6688805	
Sampled By (print name/affiliation): Ryan Thomas, Mitch Guirard	Sample Date (mm/dd/yy): 10/06/21	Sample Time (hh:mm): 13:00 - 14:15	

TIDAL CONDITIONS (ebb, flood, slack; high, med, low)						RAINFALL RECORDS (in.)			CURRENT DIRECTION		CURRENT STRENGTH		
Ebb ☐	Flood ☐	Slack ☐	High ☐	Med ☐	Low ☐	Prev. 24 hrs	Prev. 3 days	Prev. week	In ☐	Out ☐	Strong ☐	Moderate ☐	Weak ☐

GENERAL CONDITIONS				TEMPERATURES		CLIMATE CONDITIONS				
Weather 89966				Air Temp. (°C) 00020	Water Temp. (°C) 00010	Avg Wind	Max Wind	Rel. Hum. ♦%	Heat Stress ♦%‡°F	Dewpoint ♦°F
1. Clear ☐	2. Partly Cloudy ☒	3. Cloudy ☐	4. Rainy ☐	31°c		5 mph		64%		

SAMPLE INFORMATION										
Sample ID *yymmddsr-p*: PM-2			Secchi Depth (m) 00078		Sample Depth (m) 00068		Total Depth (m) 00064		COMMENTS, which document anything that could affect sample (i.e. unusual circumstances; boat traffic, sea birds overhead, pets, evidence of litter, winds, etc.)	
Rep. No. STORET CODE	SC (mS/cm) 00094	Conductivity (mS/cm) 47004	TDS (mg/L) 47004	Salinity (ppt) 00480	DO (%) 00301	DO (mg/L) 00299	pH (x.xx) 00400	ORP (mV) 00090		
1										
2										
3										

Version 2007

Designed by: D.E. Meeroff, Ph.D.

Figure 49: Field log for PM2.

The next site location that algae was collected was PM3. This site had significantly less algae than PM2. Site PM3 can be seen in Figure 50 through Figure 52.

Figure 50: Northwestern path to site PM3.

Figure 51: Site PM3 looking Northwest.

Figure 52: Blue Green Algae at site PM3.

Small amounts of algae were collected at site PM3 and was placed in a jar on ice. The associated field log is shown in Figure 53.

Florida Atlantic University
Department of Civil Engineering

Field Log

Project Name: FLDEP Cyanobacteria collection	Site ID Code: *yymmddsr*	Sample ☒	Dup ☐
Site Name: Pahokee Marina	Latitude (xx° xx.xxx'): 26.8256894	Longitude (xx° xx.xxx'): -80.6671481	
Sampled By (print name/affiliation): Ryan Thomas, Mitch Guirard	Sample Date (mm/dd/yy): 10/06/21	Sample Time (hh:mm): 14:27 - 14:45	

TIDAL CONDITIONS (ebb, flood, slack; high, med, low)						RAINFALL RECORDS (in.)			CURRENT DIRECTION		CURRENT STRENGTH		
Ebb ☐	Flood ☐	Slack ☐	High ☐	Med ☐	Low ☐	Prev. 24 hrs	Prev. 3 days	Prev. week	In ☐	Out ☐	Strong ☐	Moderate ☐	Weak ☐

GENERAL CONDITIONS				TEMPERATURES		CLIMATE CONDITIONS				
Weather 89966				Air Temp. (°C) 00020	Water Temp. (°C) 00010	Avg Wind	Max Wind	Rel. Hum. ♦%	Heat Stress ♦%‡°F	Dewpoint ♦°F
1. Clear ☐	2. Partly Cloudy ☒	3. Cloudy ☐	4. Rainy ☐	31 °C		5 mph		64%		

SAMPLE INFORMATION

Sample ID *yymmddsr-p*: PM-3

Rep. No. STORET CODE	SC (mS/cm) 00094	Conductivity (mS/cm) 47004	TDS (mg/L) 47004	Salinity (ppt) 00480	DO (%) 00301	DO (mg/L) 00299	pH (x.xx) 00400	ORP (mV) 00090
1								
2								
3								

Secchi Depth (m) 00078 | Sample Depth (m) 00068 | Total Depth (m) 00064

COMMENTS, which document anything that could affect sample (i.e. unusual circumstances; boat traffic, sea birds overhead, pets, evidence of litter, winds, etc.)

Version 2007 — Designed by: D.F. Meeroff, Ph.D.

Figure 53: Field log for PM3.

Site PM4 was then surveyed and was determined to be unsafe to proceed toward. There was yellow caution tape blocking off that section of the dock. The entrance to site PM 4 can be seen in Figure 54.

Figure 54: Site PM4 entrance looking Northwest.

The next site observed was PM1. No algae was collected from this site because none was found throughout the area. The area of site PM1 can be seen in Figure 55 through Figure 58.

Figure 55: Path to site PM1 looking Southwest.

Figure 56: Path toward PM1 looking Southwest.

Figure 57: Water at Site PM1.

Figure 58: Water at site PM1.

Site PM5 was then assessed and had no algae viable for collection. The conditions of site PM5 can be seen in Figure 59 through Figure 62.

Figure 59: Northwestern path toward site PM5.

Figure 60: Path toward site PM5 looking Northeast.

Figure 61: Water at site PM 5, lake side.

Figure 62: Water at site PM5, marina side.

4.5.2 Cultivation and Filtration

The collected Blue Green Algae was cultivated in the lab using the method described in the QAPP. The chemicals listed in Table 14 were used to prepare "algae food" according to the recipe described in the QAPP. A 1-liter volumetric flask was used to mix the chemicals followed by the addition of deionized water to the 1-liter mark. The contents are to be mixed thoroughly to ensure proper dissolution (Figure 63).

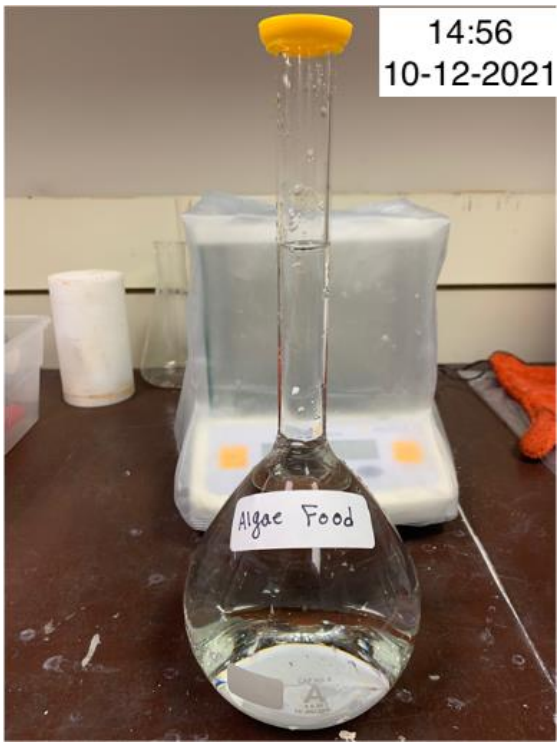
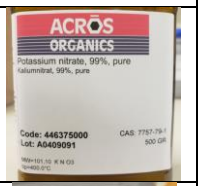
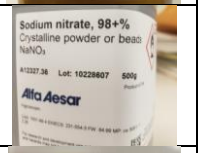
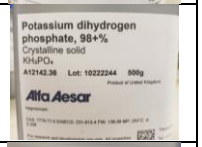
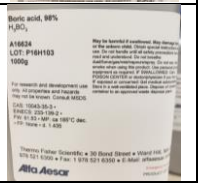


Figure 63: 1-Liter of Prepared Algae Food

Table 14. List of chemicals used to prepare "algae food".

Chemical	Chemical	Supplier Name	Purity	Lot #	Purchase	Expiration	Picture
Potassium Nitrate	KNO_3	Acros Organics	99%	A0409091	September 30, 2021	N/A	
Sodium Nitrate	$NaNO_3$	Alfa Aesar	98+%	10228607	September 30, 2021	N/A	
Calcium Nitrate Tetrahydrate	$CaNO_3 \cdot 4H_2O$	Acros Organics	99+%	A0419864	September 30, 2021	N/A	
Sodium Sulfate, Anhydrous	Na_2SO_4	Alfa Aesar	99%	10235582	September 30, 2021	N/A	
Magnesium Chloride Hexahydrate	$MgCl_2 \cdot 6H_2O$	Acros Organics	99+%	B0151506A	September 30, 2021	N/A	
Potassium Dihydrogen Phosphate	KH_2PO_4	Alfa Aesar	98+%	10222244	September 30, 2021	N/A	
Boric Acid	H_3BO_3	Alfa Aesar	98%	P16H103	September 30, 2021	N/A	

The collected cyanobacteria was added to each of the two 5-gallon jugs containing water and algae food (Figure 64). Aerators were fed into each jug and secured to support algae growth. The aerators were equipped with a splitter for proper distribution.

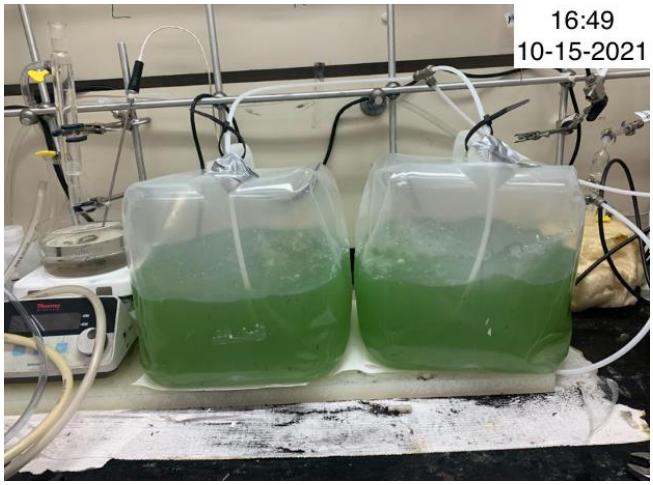


Figure 64: Five-gallon jugs used to cultivate cyanobacteria.

To collect cyanobacteria, gravity filtration was used to separate the biomass from the solution (Figure 65). Once filtered, the biomass was cultivated again, as described above. A total of three cultivation rounds were performed to collect enough biomass for processing and use.

Figure 65: Cyanobacteria filtration.

4.5.3 Biomass Treatment and Analysis

Once enough cyanobacteria biomass was collected, the filtered biomass was dried in an oven and stored in jars until processing (Figure 66).

Figure 66: Dried cyanobacteria biomass.

The dried biomass was analyzed using TGA, as described previously. The ash content of the biomass was determined to be 9.167 wt.% (Figure 67). To remove the ash, treatment with HCl was conducted, as detailed earlier and shown in Figure 68. HCl-treated biomass was recovered by gravity filtration (Figure 69 and Figure 70), dried in oven (Figure 71), and stored in jars (Figure 72). The HCl-treated biomass was analyzed by TGA and showed 88% ash removal (Figure 67).

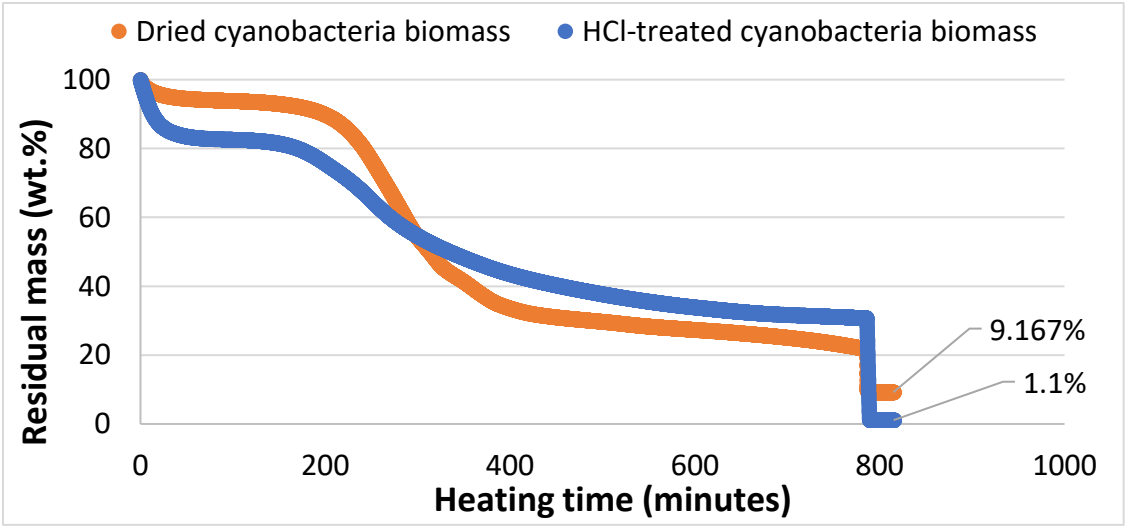


Figure 67: TGA analysis of cyanobacteria biomass before and after HCl treatment.

Figure 68: Biomass and HCl solution stirring.

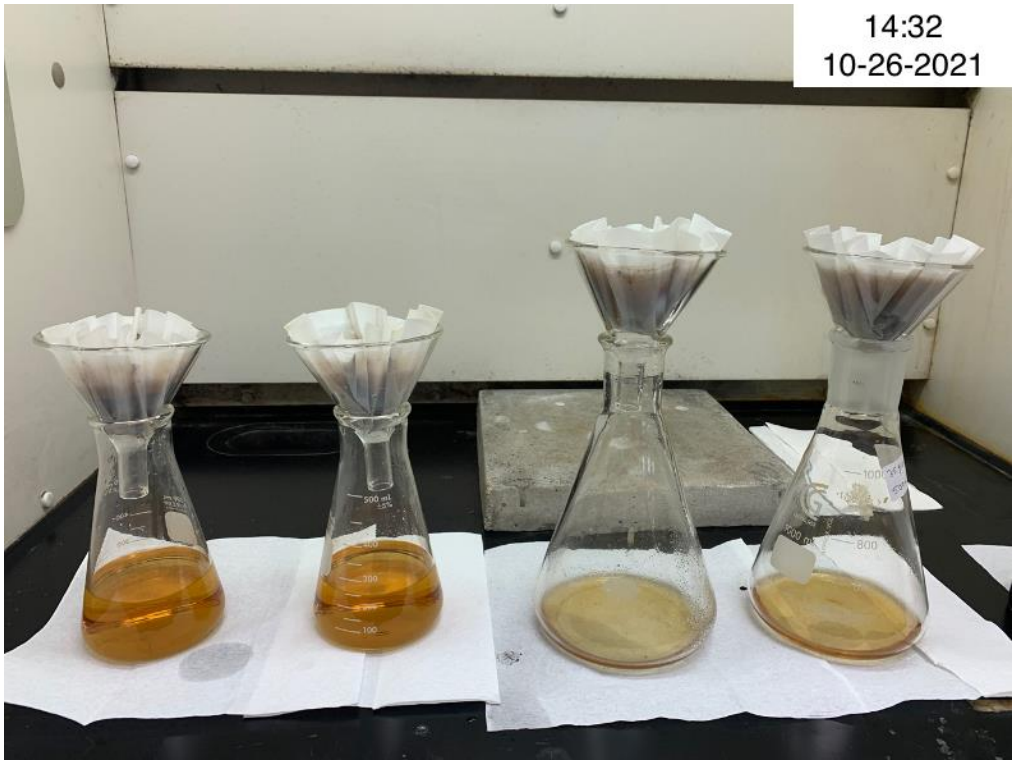


Figure 69: Gravity filtration of HCl-treated biomass.

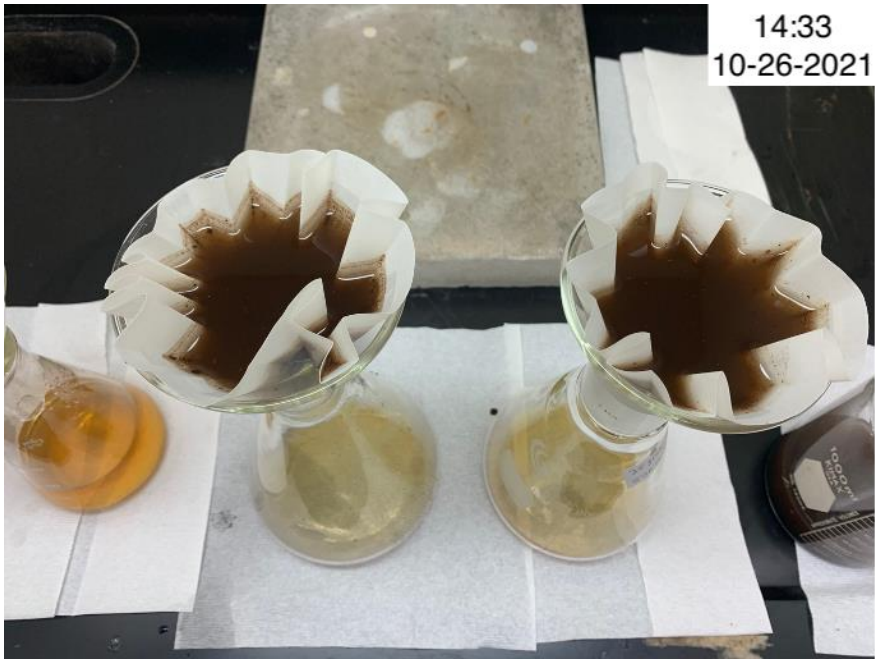


Figure 70: Gravity filtration of HCl-treated biomass.

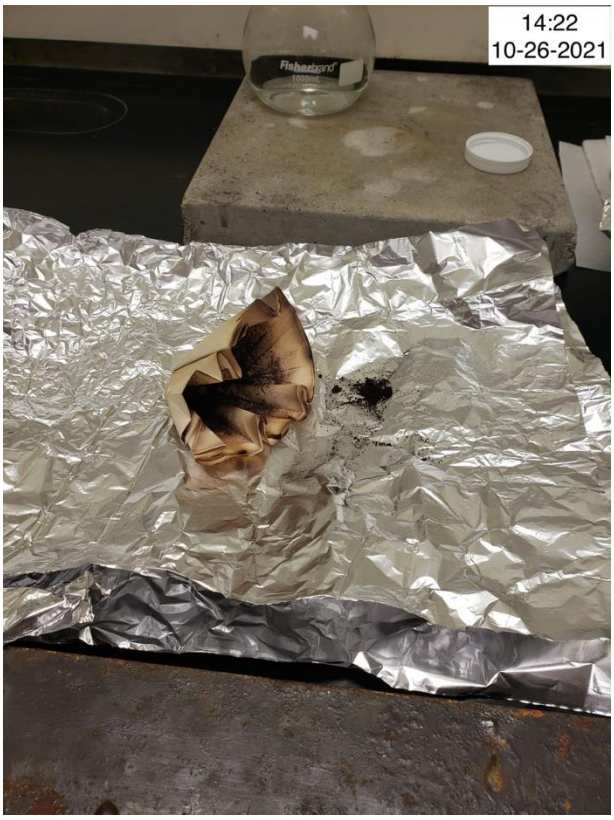


Figure 71: Dried HCl-treated biomass.

Figure 72: Dried HCl-treated biomass stored in jars.

4.5.4 Grinding and Sieving of the HCl-treated Biomass

The HCl-treated biomass was ground and sieved like the commercial AC (Figure 73).

Figure 73: HCl-treated biomass prior to grinding.

The sample was then sieved to mesh-100 and stored in jars, as can be seen in Figure 74 through Figure 76. This sample was labelled as “FLDEP1”.

Figure 74: Ground biomass inside mesh-100 sieve.

Figure 75: Sieving the biomass.

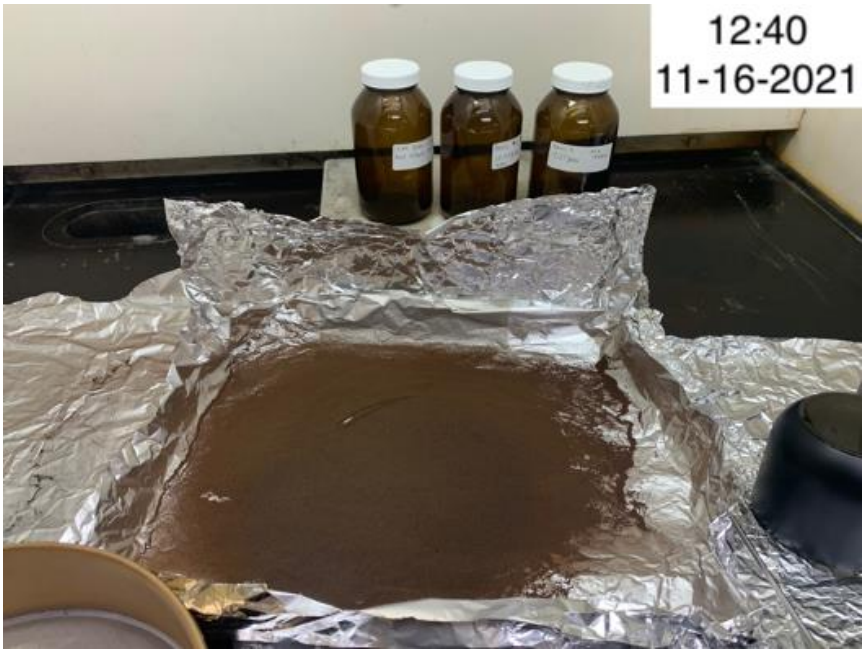


Figure 76: Sieved biomass + storage in jars.

4.5.5 Phosphorus Adsorption by Algae

The processed algae was tested for phosphorus removal in the presence of 5 mg P/L. However, no removal was observed, indicating the need for thermal and/or chemical modification.

4.6 Microwave-Assisted Modification of AC (November-December 2021)

Before testing on algae, the necessary methods for microwave-assisted modification/activation were developed and refined for sieved commercial AC. This also helped us in determining the best modification agents (MA) for use in algae-based adsorbents. Different modification agents, namely zinc chloride ($ZnCl_2$), magnesium chloride ($MgCl_2$), lanthanum chloride heptahydrate ($LaCl_3.7H_2O$), and magnesium oxide (MgO) were used. From here on, lanthanum chloride heptahydrate will be referred to as $LaCl_3$. More information about the MAs can be found in Table 15. Initially, sieved AC was used as precursor (P). This sample was labelled as "FLDEP2".

Different MA to P mass ratios of 0.5, 1.0, 1.5, and 2.0 were used to determine the suitable amount of MA to be used for modification. The calculation of MA:P was straightforward for all MAs except $LaCl_3$. Due to the $LaCl_3$ having seven molecules of water attached to it, its mass ratios need to be adjusted to compensate. Therefore, to get a proper mass of $LaCl_3$, its mass should be divided by 0.66. This number was calculated by dividing the molecular weight of $LaCl_3$ (245.26 g/mol) to the molecular weight of $LaCl_3.7H_2O$ (371.37 g/mol). For example, for "FLDEP5" with MA:P ratio of 1.0, five grams of precursor was mixed with 7.57 grams of $LaCl_3.7H_2O$.

Using "FLDEP2" as precursor and three minutes of microwave heating, 16 samples were made, as listed in Table 16. For easier comparison, a second sample ID protocol was developed, as shown in parentheses in Table 16. For "FLDEP3" through "FLDEP19", the samples were labelled as AC-X-Y, where "AC" shows that the precursor was mesh-100 commercial AC. "X" represents the MA type and can be Z for $ZnCl_2$, MC for $MgCl_2$, MO for MgO, or L for $LaCl_3$. "Y" corresponds to the MA:P ratios used (0.5, 1, 1.5, or 2). One more sample was made by heating the precursor for three minutes in the absence of any MA. This sample was labelled as "FLDEP20". The sample was also labelled as AC-NM, where "AC" shows that the precursor was mesh-100 commercial AC, and "NM" stands for no modification. Comparing the phosphorus removal performance of this sample with "FLDEP2" will assist in isolating the impact of MA and microwave heating on adsorption performance.

Table 15. List of modification agents.

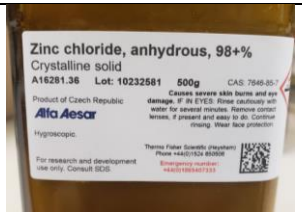
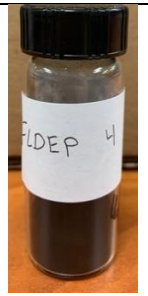
Chemical	Formula	Supplier	Lot Number	Purity	Purchase	Expiration	Picture
Lanthanum Chloride Heptahydrate	$LaCl_3.7H_2O$	Alfa Aesar	10235332	99%	October 27, 2021	N/A	
Magnesium Chloride	$MgCl_2$	Acros Organics	A0427244	100%	October 27, 2021	N/A	
Zinc Chloride, Anhydrous	$ZnCl_2$	Alfa Aesar	10232581	98+%	October 27, 2021	N/A	
Magnesium Oxide	MgO	Acros Organics	A0417470	98%	October 27, 2021	N/A	

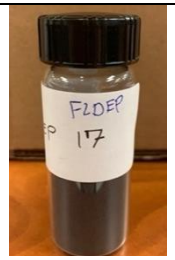
Table 16. List of synthesized samples using "FLDEP2" as precursor. Microwave heating duration of three minutes for all samples. *

Sample ID	Date Created	MA	MA:P Mass Ratio	Mass of P (g)	Mass of MA (g)	Final Temperature (°C)	Picture of Sample
FLDEP3 (AC-Z-1)	12/2/21	$ZnCl_2$	1.0	5.0	5.0	500	
FLDEP4 (AC-MC-1)	12/2/21	$MgCl_2$	1.0	5.0	5.0	500	
FLDEP5 (AC-L-1)	12/2/21	$LaCl_3$	1.0	5.0	7.57	575	

Sample ID	Date Created	MA	MA:P Mass Ratio	Mass of P (g)	Mass of MA (g)	Final Temperature (°C)	Picture of Sample
FLDEP6 (AC-Z-0.5)	12/8/21	$ZnCl_2$	0.5	5.0	2.5	546	
FLDEP7 (AC-MC-0.5)	12/8/21	$MgCl_2$	0.5	5.0	2.5	573	
FLDEP9 (AC-Z-1.5)	12/8/21	$ZnCl_2$	1.5	5.0	7.5	537	

Sample ID	Date Created	MA	MA:P Mass Ratio	Mass of P (g)	Mass of MA (g)	Final Temperature (°C)	Picture of Sample
FLDEP10 (AC-MC-1.5)	12/8/21	$MgCl_2$	1.5	5.0	7.5	470	
FLDEP11 (AC-L-1.5)	12/8/21	$LaCl_3$	1.5	5.0	11.36	640	
FLDEP12 (AC-L-0.5)	12/16/21	$LaCl_3$	0.5	5.0	3.79	555	

Sample ID	Date Created	MA	MA:P Mass Ratio	Mass of P (g)	Mass of MA (g)	Final Temperature (°C)	Picture of Sample
FLDEP13 (AC-L-2)	12/16/21	$LaCl_3$	2.0	5.0	15.15	622	
FLDEP14 (AC-MC-2)	12/16/21	$MgCl_2$	2.0	5.0	10.0	496	
FLDEP15 (AC-Z-2)	12/16/21	$ZnCl_2$	2.0	5.0	10.0	538	

Sample ID	Date Created	MA	MA:P Mass Ratio	Mass of P (g)	Mass of MA (g)	Final Temperature (°C)	Picture of Sample
FLDEP16 (AC-MO-0.5)	12/17/21	MgO	0.5	5.0	2.5	638	
FLDEP17 (AC-MO-1)	12/17/21	MgO	1.0	5.0	5.0	614	
FLDEP18 (AC-MO-1.5)	12/17/21	MgO	1.5	5.0	7.5	693	

Sample ID	Date Created	MA	MA:P Mass Ratio	Mass of P (g)	Mass of MA (g)	Final Temperature (°C)	Picture of Sample
FLDEP19 (AC-MO-2)	12/17/21	MgO	2.0	5.0	10.0	613	
FLDEP20 (AC-NM)	12/21/21	N/A	N/A	5.0	N/A	620	

* FLDEP8 was synthesized using the same conditions as FLDEP12. However, the material got contaminated during the synthesis, so it was not used further.

The microwave setup described earlier was used for sample synthesis. A ceramic dish was used to measure the required mass of the precursor (Figure 77).

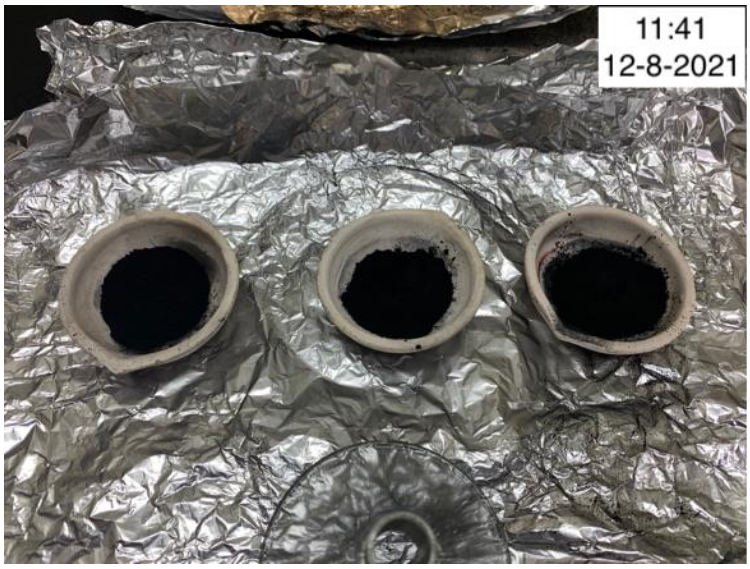


Figure 77: Precursor weighed prior to synthesis.

In a small beaker, the required mass of the MA was mixed with 20 mL of deionized water (Figure 78).

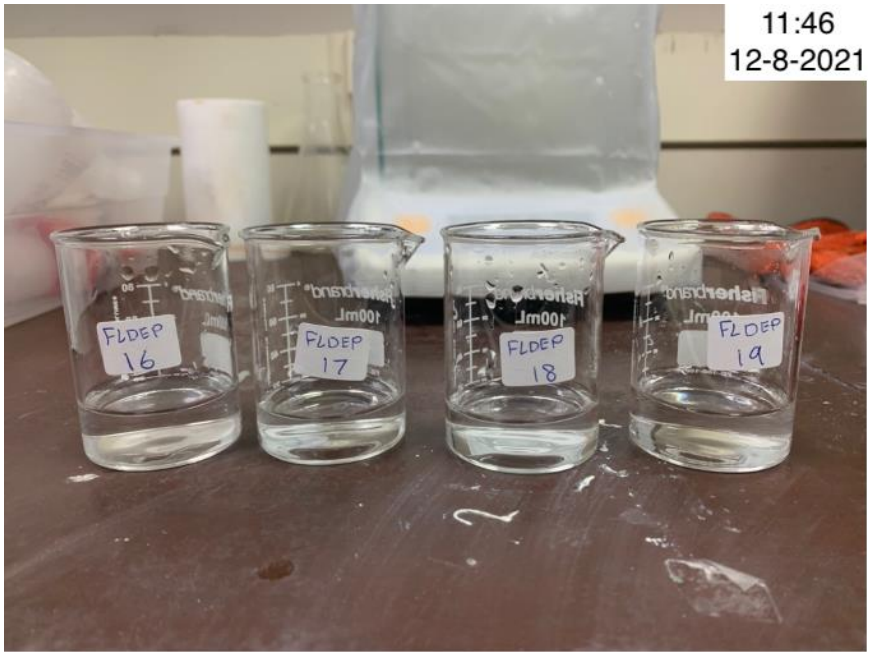


Figure 78: MAs mixed with 20 mL of deionized Water.

The solution was then added to the ceramic dish containing the precursor and carefully mixed until the precursor was in full contact with the solution. The sample was then placed in oven for one hour to evaporate the water present (Figure 79).

Figure 79: Mixture of MA and precursor in oven.

After cooling down the dish to room temperature, it was placed in the microwave chamber under humid nitrogen purge for 15 minutes (Figure 80). The purge keeps air out of the chamber, preventing the sample from catching fire at elevated temperatures.

Figure 80: Ceramic dish containing MA and precursor placed in microwave prior to heating.

A heating duration of three minutes was applied based on the literature review. The samples were kept under careful observation during heating (Figure 81). At the end of the heating, the temperature of the sample was recorded. All samples were very hot (typically 500-700°C) and glowing by this time (Figure 82).

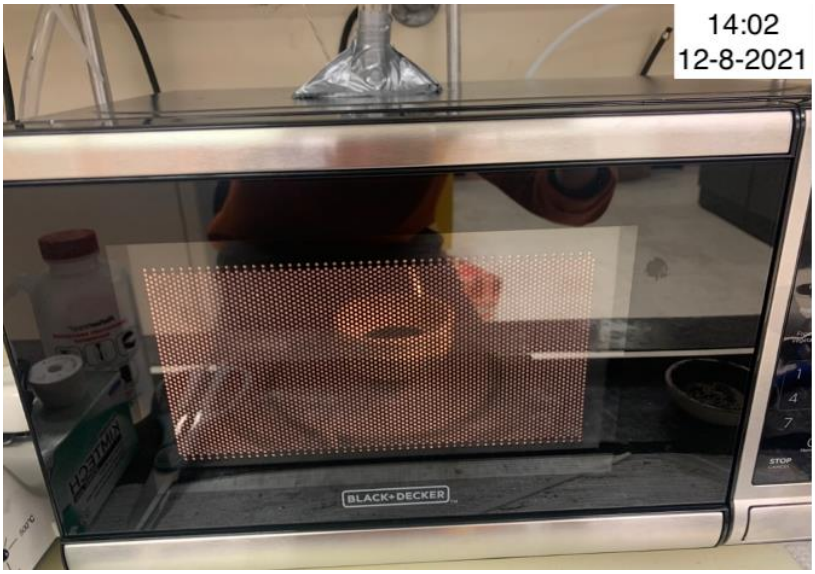


Figure 81: Sample during heating.

Figure 82: Hot sample right after microwave heating.

The dish was allowed to cool to room temperature. An Erlenmeyer flask was prepared with a filter paper and the solution was poured through slowly (Figure 83).

Figure 83: Filtering and rinsing the modified samples.

The samples were rinsed with copious amounts of deionized water to ensure removal of any residual MA. The filtered samples were then placed in oven for drying (Figure 84).

Figure 84: Rinsed Samples Placed in Oven to Dry

The samples were allowed to dry overnight and were collected the next day. The samples were weighed and stored in vials (Figure 85).

Figure 85: Storage of modified samples.

4.7 Phosphorus Adsorption by AC-Based Samples (September 2021-March 2022)

All samples from the previous section were assessed in terms of aqueous-phase phosphorus removal (Table 17). The following conditions were used in all cases:

- Concentration of 5 mg P/L
- Contact time of 24 hours
- Adsorbent dosage of 1 g/L

The commercial AC ("FLDEP2") showed an average removal efficiency of 41.2%, which is in line with previous investigations on GAC and PAC (Table 12). Heating the same sample for three minutes in the absence of MA ("FLDEP20") resulted in lower average removal efficiency of 13.8%, possibly due to destruction of its porous structure. Treating the commercial AC ("FLDEP2") with different MAs resulted in mixed findings. Samples modified with $MgCl_2$ ("FLDEP4", "FLDEP7", "FLDEP10", and "FLDEP14") and MgO ("FLDEP16", "FLDEP17", "FLDEP18", and "FLDEP19") experienced lower removal efficiencies than "FLDEP2", possibly due to combination of pore blockage and destruction of porous structure. In contrast, most samples modified with $LaCl_3$ ("FLDEP5", "FLDEP11", "FLDEP12", and "FLDEP13") and $ZnCl_2$ ("FLDEP3", "FLDEP6", "FLDEP9", and "FLDEP15") experienced higher removal efficiencies than "FLDEP2". Based on these findings, $LaCl_3$ (MA:P ratios of 1 and 1.5) and $ZnCl_2$ (MA:P ratio of 2) were chosen for modification of algae-based samples (see next section). QA/QC, including blank check and calibration curve verification, were completed in accordance with the QAPP, which all passed the criteria.

Table 17. Summary of phosphorus adsorption experiments by AC-based samples.

Sample ID	Trial No.	Initial Conc. (mg P/L)	Final Conc. (mg P/L)	Dilution Factor	Method Detection Limit (mg P/L)	Percent Removal (%)	Flags
FLDEP2 (AC)	1	4.75	2.20	5	0.10	53.7	-
	2	4.74	2.83	5	0.10	40.3	-
	3	4.73	2.74	5	0.10	42.1	-
FLDEP3 (AC-Z-1)	1	4.75	1.77	5	0.10	62.7	-
	2	4.76	1.79	5	0.10	62.4	-
FLDEP4 (AC-MC-1)	1	4.76	4.75	5	0.10	0.2	-
	2	4.75	4.80	5	0.10	0.0	-
FLDEP5 (AC-L-1)	1	4.75	<0.10	5	0.10	>97.9	U
	2	4.75	<0.02	1	0.02	>99.6	U
	3	4.73	0.05	1	0.02	98.9	-
FLDEP6 (AC-Z-0.5)	1	4.72	3.07	5	0.10	34.9	-
	2	4.75	4.42	5	0.10	7.0	-
	3	4.74	3.34	5	0.10	29.6	-
FLDEP7 (AC-MC-0.5)	1	4.73	4.43	5	0.10	6.4	-
	2	4.75	4.50	5	0.10	5.3	-
FLDEP9 (AC-Z-1.5)	1	4.73	2.17	5	0.10	54.2	-
	2	4.75	2.10	5	0.10	55.8	-
FLDEP10 (AC-MC-1.5)	1	4.74	4.41	5	0.10	7.0	-
	2	4.75	4.34	5	0.10	8.6	-
FLDEP11 (AC-L-1.5)	1	4.77	<0.10	5	0.10	>97.9	U
	2	4.75	<0.02	1	0.02	>99.6	U
	3	4.72	<0.02	1	0.02	>99.6	U

Sample ID	Trial No.	Initial Conc. (mg P/L)	Final Conc. (mg P/L)	Dilution Factor	Method Detection Limit (mg P/L)	Percent Removal (%)	Flags
FLDEP12 (AC-L-0.5)	1	4.75	<0.10	5	0.10	>97.9	U
	2	4.68	<0.02	1	0.02	>99.6	U
	3	4.68	<0.02	1	0.02	>99.6	U
FLDEP13 (AC-L-2)	1	4.75	<0.10	5	0.10	>97.9	U
	2	4.77	<0.02	1	0.02	>99.6	U
	3	4.77	<0.02	1	0.02	>99.6	U
FLDEP14 (AC-MC-2)	1	4.75	3.92	5	0.10	17.5	-
	2	4.77	4.13	5	0.10	13.4	-
FLDEP15 (AC-Z-2)	1	4.75	0.17	5	0.10	96.4	-
	2	4.74	0.18	5	0.10	96.2	-
	3	4.77	0.18	1	0.02	96.2	-
	4	4.77	0.14	1	0.02	97.2	-
FLDEP16 (AC-MO-0.5)	1	4.75	4.22	5	0.10	11.2	-
	2	4.72	4.34	5	0.10	8.0	-
FLDEP17 (AC-MO-1)	1	4.75	4.55	5	0.10	4.2	-
	2	4.72	4.20	5	0.10	10.9	-
FLDEP18 (AC-MO-1.5)	1	4.78	4.67	5	0.10	2.2	-
	2	4.68	4.34	5	0.10	7.3	-
FLDEP19 (AC-MO-2)	1	4.78	4.24	5	0.10	11.2	-
	2	4.71	4.20	5	0.10	10.8	-
FLDEP20 (AC-NM)	1	4.70	3.99	5	0.10	15.1	-
	2	4.74	4.15	5	0.10	12.5	-

U = Indicates analyzed for but below laboratory detection limit

4.8 Microwave-Assisted Modification of Cyanobacteria Biomass (January 2022)

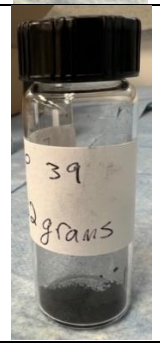
Based on phosphorus removal results from the previous section, $LaCl_3$ and $ZnCl_2$ were chosen and used for modification of the algae precursor. A total of 16 samples were made using the following conditions:

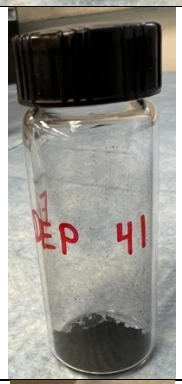
- Microwave heating of the algae precursor (no MA) for 3, 5, 7 and 9 minutes
- $LaCl_3$ to algae ratio of 1.0 using microwave heating durations of 3, 5, 7 and 9 minutes
- $LaCl_3$ to algae ratio of 1.5 using microwave heating durations of 3, 5, 7 and 9 minutes
- $ZnCl_2$ to algae ratio of 2.0 using microwave heating durations of 3, 5, 7 and 9 minutes

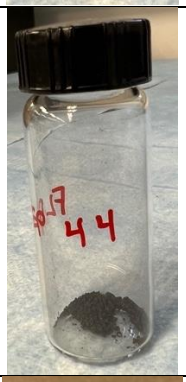
A summary of synthesized samples is shown in Table 18. The synthesis procedure was similar to the AC-based samples, except (i) a lower mass of algae precursor ("FLDEP1"; 2.0 grams) was used, and the MA mass was adjusted accordingly. (ii) A lower volume of deionized water (8 ml) was used to mix the MA and P. At the end of microwave heating, sample temperatures as high as 770°C were recorded.

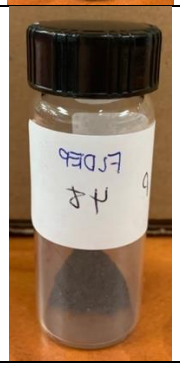
All algae-based samples were assessed using TGA, as described before. The results are shown in Figure 86 through Figure 89. For easier comparison, the plots were made using the sample IDs shown in parentheses in Table 18. For "FLDEP37" through "FLDEP40", the samples were labelled as A-NM-X, where "A" shows that the precursor was algae, "NM" stands for no modification, and "X" corresponds to the microwave heating duration used (3, 5, 7, or 9 minutes). For "FLDEP41" through "FLDEP52", the samples were labelled as A-B-C-D, where "A" shows that the precursor was algae, "B" could be L ($LaCl_3$) or Z ($ZnCl_2$), "C" could be 1, 1.5, or 2 depending on MA:P ratio, and "D" corresponds to the microwave heating duration used (3, 5, 7, or 9 minutes). Based on TGA results, a longer microwave heating duration in combination with a higher MA:P ratio generally resulted in higher ash content, suggesting better incorporation of the modification agents ($LaCl_3$ or $ZnCl_2$) into the synthesized samples. QA/QC, including blank check and calibration curve verification, were completed in accordance with the QAPP, which all passed the criteria.

Table 18. List of synthesized samples using "FLDEP1" as precursor.

Sample ID	Date	MA	MA:P Mass Ratio	Mass of P (g)	Mass of MA (g)	Heating Time (min)	Final Temperature (°C)	Picture of Sample
FLDEP37 (A-NM-3)	1/13/22	N/A	N/A	2.0	N/A	3	614	
FLDEP38 (A-NM-5)	1/13/22	N/A	N/A	2.0	N/A	5	475	
FLDEP39 (A-NM-7)	1/13/22	N/A	N/A	2.0	N/A	7	628	

Sample ID	Date	MA	MA:P Mass Ratio	Mass of P (g)	Mass of MA (g)	Heating Time (min)	Final Temperature (°C)	Picture of Sample
FLDEP40 (A-NM-9)	1/13/22	N/A	N/A	2.0	N/A	9	485	
FLDEP41 (A-L-1-3)	1/14/22	$LaCl_3$	1.0	2.0	3.03	3	688	
FLDEP42 (A-L-1-5)	1/14/22	$LaCl_3$	1.0	2.0	3.03	5	705	

Sample ID	Date	MA	MA:P Mass Ratio	Mass of P (g)	Mass of MA (g)	Heating Time (min)	Final Temperature (°C)	Picture of Sample
FLDEP43 (A-L-1-7)	1/14/22	$LaCl_3$	1.0	2.0	3.03	7	711	
FLDEP44 (A-L-1-9)	1/14/22	$LaCl_3$	1.0	2.0	3.03	9	711	
FLDEP45 (A-L-1.5-3)	1/19/22	$LaCl_3$	1.5	2.0	4.55	3	770	

Sample ID	Date	MA	MA:P Mass Ratio	Mass of P (g)	Mass of MA (g)	Heating Time (min)	Final Temperature (°C)	Picture of Sample
FLDEP46 (A-L-1.5-5)	1/19/22	$LaCl_3$	1.5	2.0	4.55	5	720	
FLDEP47 (A-L-1.5-7)	1/19/22	$LaCl_3$	1.5	2.0	4.55	7	746	
FLDEP48 (A-L-1.5-9)	1/19/22	$LaCl_3$	1.5	2.0	4.55	9	721	

Sample ID	Date	MA	MA:P Mass Ratio	Mass of P (g)	Mass of MA (g)	Heating Time (min)	Final Temperature (°C)	Picture of Sample
FLDEP49 (A-Z-2-3)	1/20/22	$ZnCl_2$	2.0	2.0	4.0	3	585	
FLDEP50 (A-Z-2-5)	1/20/22	$ZnCl_2$	2.0	2.0	4.0	5	698	
FLDEP51 (A-Z-2-7)	1/20/22	$ZnCl_2$	2.0	2.0	4.0	7	703	

Sample ID	Date	MA	MA:P Mass Ratio	Mass of P (g)	Mass of MA (g)	Heating Time (min)	Final Temperature (°C)	Picture of Sample
FLDEP52 (A-Z-2-9)	1/20/22	$ZnCl_2$	2.0	2.0	4.0	9	682	

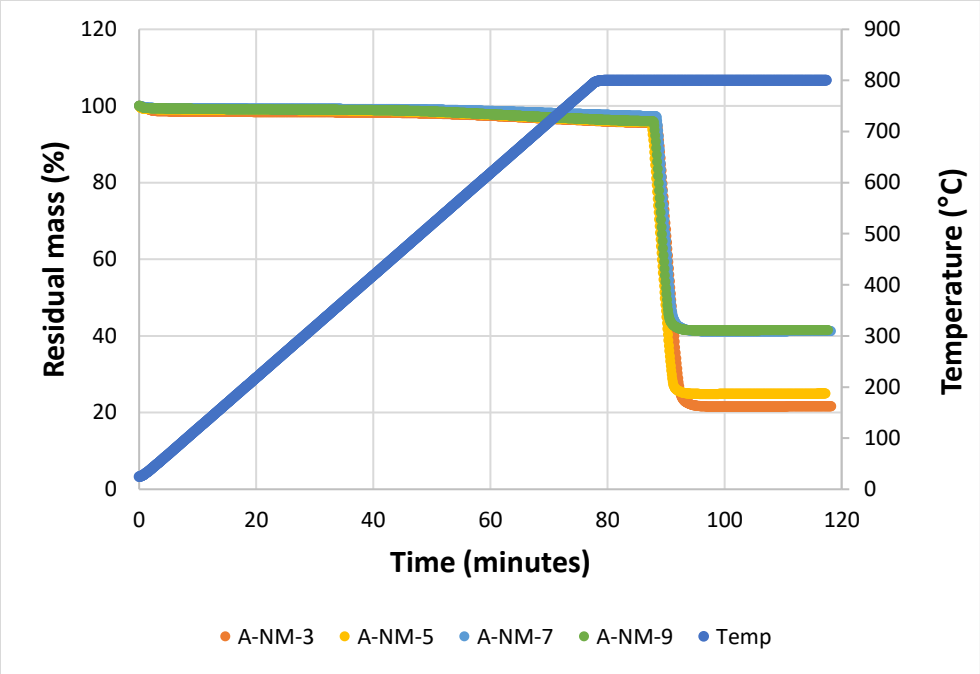


Figure 86: TGA results for algae-based samples heated with no MA.

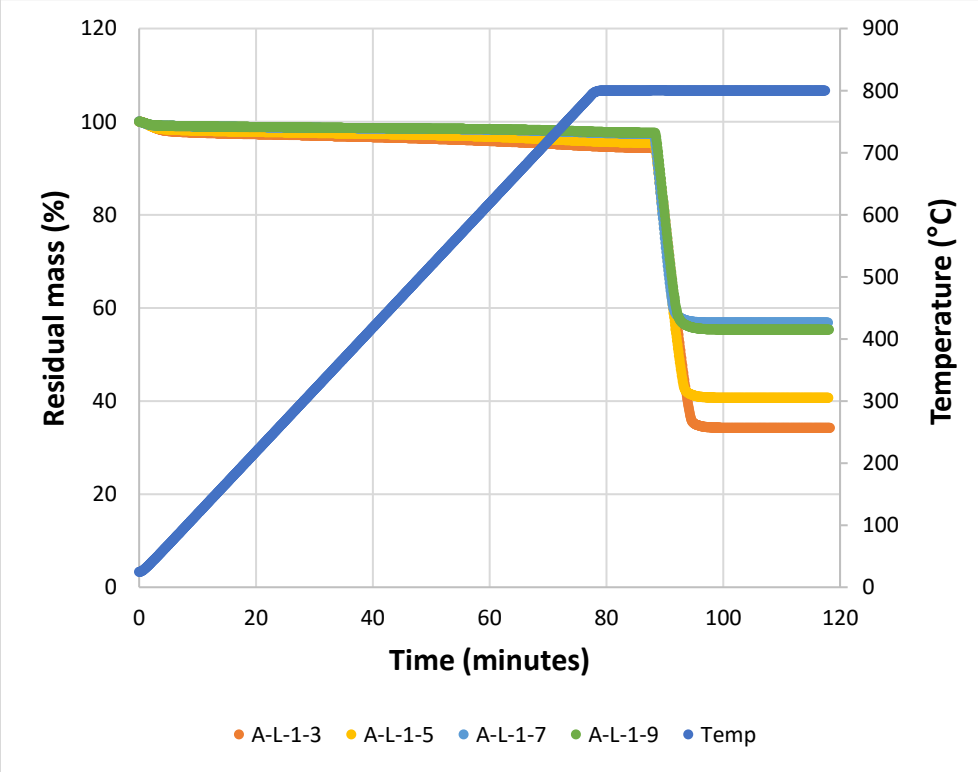


Figure 87: TGA results for algae-based samples heated in the presence of $LaCl_3$ with MA:P mass ratio of 1.0.

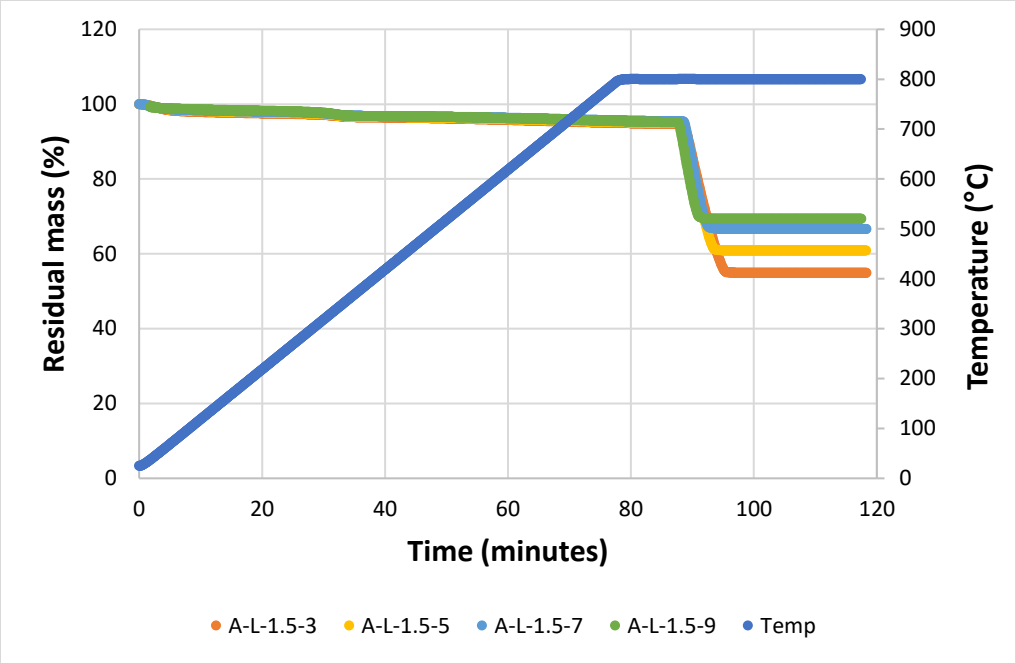


Figure 88: TGA results for algae-based samples heated in the presence of $LaCl_3$ with MA:P mass ratio of 1.5.

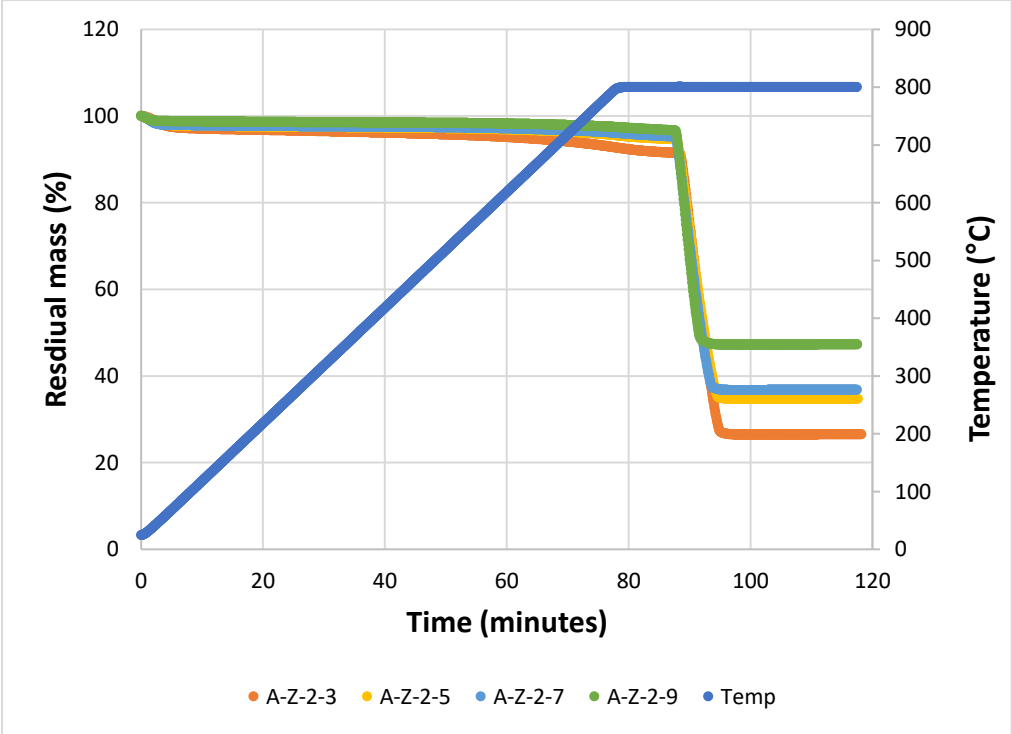


Figure 89: TGA results for algae-based samples heated in the presence of $ZnCl_2$ with MA:P mass ratio of 2.0.

4.9 Phosphorus Adsorption by Algae-Based Samples (January-March 2022)

All samples from the previous section plus the algae precursor ("FLDEP1") were assessed in terms of aqueous-phase phosphorus removal (Table 19). The following conditions were used in all cases:

- Concentration of 5 mg P/L
- Contact time of 24 hours
- Adsorbent dosage of 1 g/L

The algae precursor ("FLDEP1") and the samples made by heating the algae precursor in the absence of any MA ("FLDEP37" through "FLDEP40") did not show any phosphorus removal. Samples modified with $ZnCl_2$ ("FLDEP49" through "FLDEP52") experienced an improvement in removal efficiency relative to non-modified samples ("FLDEP37" through "FLDEP40"). However, the removal efficiencies were generally low and never exceeded 30%. In contrast, samples modified with $LaCl_3$ ("FLDEP41" through "FLDEP48") consistently showed near-complete phosphorus removal. Therefore, these eight samples were shortlisted for additional investigations in the presence of different phosphorus concentrations of 5, 10, and 20 mg P/L. The excellent performance of our $LaCl_3$-modified adsorbent samples is consistent with previous studies listed elsewhere.[72] QA/QC, including blank check and calibration curve verification, were completed in accordance with the QAPP, which all passed the criteria.

Table 19. Summary of phosphorus adsorption experiments by algae-based samples.

Sample ID	Trial No.	Initial Conc. (mg P/L)	Final Conc. (mg P/L)	Dilution Factor	Method Detection Limit (mg P/L)	Percent Removal (%)	Flags
FLDEP1 (Algae)	1	4.78	5.07	5	0.10	0.0	-
	2	4.79	4.98	5	0.10	0.0	-
FLDEP37 (A-NM-3)	1	4.78	5.00	5	0.10	0.0	-
	2	4.71	5.02	5	0.10	0.0	-
FLDEP38 (A-NM-5)	1	4.78	5.10	5	0.10	0.0	-
	2	4.71	5.09	5	0.10	0.0	-
FLDEP39 (A-NM-7)	1	4.78	4.99	5	0.10	0.0	-
	2	4.71	4.99	5	0.10	0.0	-
FLDEP40 (A-NM-9)	1	4.78	4.94	5	0.10	0.0	-
	2	4.79	5.07	5	0.10	0.0	-
FLDEP41 (A-L-1-3)	1	4.70	<0.10	5	0.10	>97.9	U
	2	4.79	0.04	1	0.02	99.2	-
	3	4.79	<0.02	1	0.02	>99.6	U
FLDEP42 (A-L-1-5)	1	4.70	<0.10	5	0.10	>97.9	U
	2	4.79	<0.02	1	0.02	>99.6	U
	3	4.79	<0.02	1	0.02	>99.6	U
FLDEP43 (A-L-1-7)	1	4.70	<0.10	5	0.10	>97.9	U
	2	4.71	<0.02	1	0.02	>99.6	U
	3	4.79	<0.02	1	0.02	>99.6	U
FLDEP44 (A-L-1-9)	1	4.70	<0.10	5	0.10	>97.9	U
	2	4.71	<0.02	1	0.02	>99.6	U
	3	4.72	<0.02	1	0.02	>99.6	U

Sample ID	Trial No.	Initial Conc. (mg P/L)	Final Conc. (mg P/L)	Dilution Factor	Method Detection Limit (mg P/L)	Percent Removal (%)	Flags
FLDEP45 (A-L-1.5-3)	1	4.73	<0.10	5	0.10	>97.9	U
	2	4.71	<0.02	1	0.02	>99.6	U
	3	4.71	<0.02	1	0.02	>99.6	U
FLDEP46 (A-L-1.5-5)	1	4.73	<0.10	5	0.10	>97.9	U
	2	4.71	<0.02	1	0.02	>99.6	U
	3	4.71	<0.02	1	0.02	>99.6	U
FLDEP47 (A-L-1.5-7)	1	4.73	<0.10	5	0.10	>97.9	U
	2	4.71	<0.02	1	0.02	>99.6	U
	3	4.71	<0.02	1	0.02	>99.6	U
FLDEP48 (A-L-1.5-9)	1	4.73	<0.10	5	0.10	>97.9	U
	2	4.71	<0.02	1	0.02	>99.6	U
	3	4.71	<0.02	1	0.02	>99.6	U
FLDEP49 (A-Z-2-3)	1	4.73	3.69	5	0.10	22.0	-
	2	4.76	3.66	5	0.10	23.1	-
FLDEP50 (A-Z-2-5)	1	4.73	4.88	5	0.10	0.0	-
	2	4.76	4.02	5	0.10	15.5	-
	3	4.71	4.21	5	0.10	10.6	-
FLDEP51 (A-Z-2-7)	1	4.76	3.56	5	0.10	25.2	-
	2	4.74	3.38	5	0.10	28.7	-
FLDEP 52 (A-Z-2-9)	1	4.76	4.53	5	0.10	4.8	-
	2	4.76	3.44	5	0.10	27.7	-
	3	4.63	3.20	5	0.10	30.9	-

U = Indicates analyzed for but below laboratory detection limit

4.10 Phosphorus Adsorption with Different Concentrations (January-March 2022)

The eight shortlisted samples from the previous section ("FLDEP41" through "FLDEP48") were assessed in terms of aqueous-phase phosphorus removal in the presence of different concentrations (Table 20). The following conditions were used in all cases:

- Concentrations of 5, 10, and 20 mg P/L
- Contact time of 24 hours
- Adsorbent dosage of 1 g/L

For "FLDEP41" through "FLDEP44", near-complete phosphorus removal was observed in the presence of 5 and 10 mg P/L. However, the removal efficiencies dropped when tested in the presence of 20 mg P/L. In contrast, for "FLDEP45" through "FLDEP48", near-complete phosphorus removal was observed at all concentrations, owing to their higher lanthanum loading relative to the former group (compare Figure 87 and Figure 88). Therefore, these four samples were shortlisted for future investigations (i.e., Task 3). QA/QC, including blank check and calibration curve verification, were completed in accordance with the QAPP, which all passed the criteria.

Table 20. Summary of phosphorus adsorption experiments by algae-based samples in the presence of different concentrations.

Sample ID	Trial No.	Initial Conc. (mg P/L)	Final Conc. (mg P/L)	Dilution Factor	Method Detection Limit (mg P/L)	Percent Removal (%)	Flags
FLDEP41 (A-L-1-3)	1	4.70	<0.10	5	0.10	>97.9	U
	2	4.79	0.04	1	0.02	99.2	-
	3	4.79	<0.02	1	0.02	>99.6	U
	1	9.3	<0.20	10	0.20	>97.8	U
	2	9.5	<0.02	1	0.02	>99.8	U
	3	9.5	<0.02	1	0.02	>99.8	U
	1	19.0	8.49	20	0.40	55.3	-
	2	19.0	8.90	20	0.40	53.2	-
FLDEP42 (A-L-1-5)	1	4.70	<0.10	5	0.10	>97.9	U
	2	4.79	<0.02	1	0.02	>99.6	U
	3	4.79	<0.02	1	0.02	>99.6	U
	1	9.3	<0.20	10	0.20	>97.8	U
	2	9.5	<0.02	1	0.02	>99.8	U
	3	9.5	<0.02	1	0.02	>99.8	U
	1	19.0	7.87	20	0.40	58.6	-
	2	19.0	8.07	20	0.40	57.5	-

Sample ID	Trial No.	Initial Conc. (mg P/L)	Final Conc. (mg P/L)	Dilution Factor	Method Detection Limit (mg P/L)	Percent Removal (%)	Flags
FLDEP43 (A-L-1-7)	1	4.70	<0.10	5	0.10	>97.9	U
	2	4.71	<0.02	1	0.02	>99.6	U
	3	4.79	<0.02	1	0.02	>99.6	U
	1	9.3	<0.20	10	0.20	>97.8	U
	2	9.5	<0.02	1	0.02	>99.8	U
	3	9.5	<0.02	1	0.02	>99.8	U
	1	19.0	7.31	20	0.40	61.5	-
	2	19.2	5.07	20	0.40	73.6	-
	3	18.7	4.79	20	0.40	74.4	-
FLDEP44 (A-L-1-9)	1	4.70	<0.10	5	0.10	>97.9	U
	2	4.71	<0.02	1	0.02	>99.6	U
	3	4.72	<0.02	1	0.02	>99.6	U
	1	9.3	<0.20	10	0.20	>97.8	U
	2	9.5	<0.02	1	0.02	>99.8	U
	3	9.5	<0.02	1	0.02	>99.8	U
	1	19.0	10.81	20	0.40	43.1	-
	2	19.2	3.79	20	0.40	80.3	-
	3	18.7	4.24	20	0.40	77.3	-

Sample ID	Trial No.	Initial Conc. (mg P/L)	Final Conc. (mg P/L)	Dilution Factor	Method Detection Limit (mg P/L)	Percent Removal (%)	Flags
FLDEP45 (A-L-1.5-3)	1	4.73	<0.10	5	0.10	>97.9	U
	2	4.71	<0.02	1	0.02	>99.6	U
	3	4.71	<0.02	1	0.02	>99.6	U
	1	9.3	<0.20	10	0.20	>97.8	U
	2	9.5	<0.02	1	0.02	>99.8	U
	3	9.5	<0.02	1	0.02	>99.8	U
	1	19.0	<0.40	20	0.40	>97.9	U
	2	19.0	1.28	1	0.02	93.3	-
	3	19.2	<0.02	1	0.02	>99.9	U
	4	18.7	<0.02	1	0.02	>99.9	U
FLDEP46 (A-L-1.5-5)	1	4.73	<0.10	5	0.10	>97.9	U
	2	4.71	<0.02	1	0.02	>99.6	U
	3	4.71	<0.02	1	0.02	>99.6	U
	1	9.2	<0.20	10	0.20	>97.8	U
	2	9.5	<0.02	1	0.02	>99.8	U
	3	9.5	<0.02	1	0.02	>99.8	U
	1	18.5	<0.40	20	0.40	>97.8	U
	2	19.0	<0.02	1	0.02	>99.9	U
	3	18.7	<0.02	1	0.02	>99.9	U

Sample ID	Trial No.	Initial Conc. (mg P/L)	Final Conc. (mg P/L)	Dilution Factor	Method Detection Limit (mg P/L)	Percent Removal (%)	Flags
FLDEP47 (A-L-1.5-7)	1	4.73	<0.10	5	0.10	>97.9	U
	2	4.71	<0.02	1	0.02	>99.6	U
	3	4.71	<0.02	1	0.02	>99.6	U
	1	9.2	<0.20	10	0.20	>97.8	U
	2	9.5	<0.02	1	0.02	>99.8	U
	1	18.5	<0.40	20	0.40	>97.8	U
	2	19.0	<0.02	1	0.02	>99.9	U
	3	18.7	<0.02	1	0.02	>99.9	U
FLDEP48 (A-L-1.5-9)	1	4.73	<0.10	5	0.10	>97.9	U
	2	4.71	<0.02	1	0.02	>99.6	U
	3	4.71	<0.02	1	0.02	>99.6	U
	1	9.2	<0.20	10	0.20	>97.8	U
	2	9.5	<0.02	1	0.02	>99.8	U
	1	18.5	<0.40	20	0.40	>97.8	U
	2	19.0	<0.02	1	0.02	>99.9	U
	3	18.7	<0.02	1	0.02	>99.9	U

U = Indicates analyzed for but below laboratory detection limit

4.11 QA/QC

4.11.1 Blank

All blank samples were below laboratory method detection limit (Table 21).

Table 21. QA/QC data for blank samples (no dilution used).

Trial No.	Sample	Absorbance	Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Flags
1	DI Water	0.004	<0.02	0.02	U
2	DI Water	0.004	<0.02	0.02	U
3	DI Water	0.003	<0.02	0.02	U
4	DI Water	0.004	<0.02	0.02	U
5	DI Water	0.004	<0.02	0.02	U
6	DI Water	0.004	<0.02	0.02	U
7	DI Water	0.003	<0.02	0.02	U
8	DI Water	0.004	<0.02	0.02	U
9	DI Water	0.003	<0.02	0.02	U
10	DI Water	0.004	<0.02	0.02	U
11	DI Water	0.004	<0.02	0.02	U
12	DI Water	0.004	<0.02	0.02	U
13	DI Water	0.003	<0.02	0.02	U
14	DI Water	0.004	<0.02	0.02	U

U: Blank sample below laboratory method detection limit.

4.11.2 Calibration Curve Verification

All calibration verifications met calibration acceptance criteria (less than 10% error and within ± 0.1 mg P/L; Table 22).

Table 22. QA/QC data for calibration curve verification (no dilution used).

Trial No.	Conc. (mg P/L)	Absorbance	Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Percent Error (%)	Flags
1	0.5	0.271	0.46	0.02	8	-
2	0.5	0.278	0.47	0.02	6	-
3	0.5	0.273	0.47	0.02	6	-
4	0.5	0.270	0.46	0.02	8	-
5	0.5	0.268	0.46	0.02	8	-
6	0.5	0.275	0.47	0.02	6	-
7	0.5	0.270	0.46	0.02	8	-
8	0.5	0.273	0.47	0.02	6	-
9	0.5	0.275	0.47	0.02	6	-
10	0.5	0.269	0.46	0.02	8	-
11	0.5	0.268	0.46	0.02	8	-
12	0.5	0.280	0.48	0.02	4	-
13	0.5	0.282	0.48	0.02	4	-
14	0.5	0.276	0.47	0.02	6	-

4.11.3 Matrix Spike Verification

All matrix spike verifications met calibration acceptance criteria (less than 10% error and within ± 0.1 mg P/L; Table 23).

Table 23. QA/QC data for matrix spike verification (no dilution used).

Trial No.	Conc. (mg P/L)	Absorbance	Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Percent Error (%)	Flags
1	1	0.573	0.98	0.02	2	-
2	1	0.571	0.98	0.02	2	-
3	1	0.570	0.98	0.02	2	-
4	1	0.572	0.98	0.02	2	-
5	1	0.573	0.98	0.02	2	-
6	1	0.573	0.98	0.02	2	-
7	1	0.570	0.98	0.02	2	-
8	1	0.573	0.98	0.02	2	-
9	1	0.573	0.98	0.02	2	-
10	1	0.570	0.98	0.02	2	-
11	1	0.571	0.98	0.02	2	-
12	1	0.570	0.98	0.02	2	-
13	1	0.570	0.98	0.02	2	-
14	1	0.570	0.98	0.02	2	-

5. Optimization & Assessment (Task 3; March-October 2022)

5.1 Impact of Adsorbent Dosage and Adsorption Duration (Task 3.1; March-June 2022)

5.1.1 Adsorbent Dosage

For assessing the impact of adsorbent dosage, the materials listed in Table 24 were tested, which were chosen based on Task 2 findings. In addition to baseline dosage of 1 g/L, values of 0.2, 0.4, 0.6, and 0.8 g/L were used. To obtain these adsorbent dosages, 0.02, 0.04, 0.06, 0.08, and 0.1 grams of the corresponding sample were added to 100 mL of the solution containing 5 mg P/L. While all four materials achieved near-complete phosphorus removal for adsorbent dosages of 0.4-1.0 g/L, only one adsorbent (i.e., FLDEP45) achieved near-complete removal at adsorbent dosage of 0.2 g/L (Table 25). This material was synthesized using lanthanum chloride to precursor mass ratio of 1.5 with three minutes of microwave heating. This material was chosen as the final candidate for all subsequent investigations. QA/QC, including blank check (Table 27), calibration curve verification (Table 28), and matrix spike verification (Table 29) were completed in accordance with the QAPP, which all passed the criteria.

Table 24. List of samples studied for the impact of adsorbent dosage (all synthesized using cyanobacteria biomass as precursor; P).

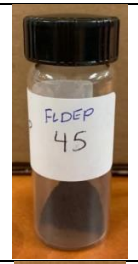
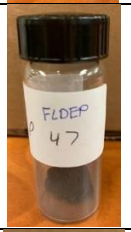
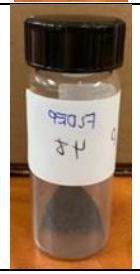
Sample ID	Modification Agent (MA)	MA:P Mass Ratio	Mass of P (g)	Mass of MA (g)	Heating Time (min)	Final Temperature (°C)	Picture of Sample
FLDEP45 (A-L-1.5-3)	$LaCl_3$	1.5	2.0	4.55	3	770	
FLDEP46 (A-L-1.5-5)	$LaCl_3$	1.5	2.0	4.55	5	720	
FLDEP47 (A-L-1.5-7)	$LaCl_3$	1.5	2.0	4.55	7	746	
FLDEP48 (A-L-1.5-9)	$LaCl_3$	1.5	2.0	4.55	9	721	

Table 25. Summary of phosphorus adsorption experiments using different dosages of selected algae-based adsorbent materials. Nominal phosphorus concentration of 5 mg/L and adsorption duration of 24 hours were used in all cases.

Sample ID	Adsorbent Dosage (g/L)	Trial No.	Initial P Reading (mg P/L)	Final P Reading (mg P/L)	Dilution Factor	Method Detection Limit (mg P/L)	Percent Removal (%)	Flags
FLDEP45 (A-L-1.5-3)	1.0	1	4.73	<0.10	5	0.10	>97.9	U
		2	4.71	<0.02	1	0.02	>99.6	U
		3	4.71	<0.02	1	0.02	>99.6	U
	0.8	1	4.83	<0.02	1	0.02	>99.6	U
		2	4.83	<0.02	1	0.02	>99.6	U
	0.6	1	4.83	<0.02	1	0.02	>99.6	U
		2	4.83	<0.02	1	0.02	>99.6	U
	0.4	1	4.78	<0.02	1	0.02	>99.6	U
		2	4.78	<0.02	1	0.02	>99.6	U
	0.2	1	4.78	<0.02	1	0.02	>99.6	U
		2	4.78	<0.02	1	0.02	>99.6	U
		3	4.70	<0.02	1	0.02	>99.6	U
FLDEP46 (A-L-1.5-5)	1.0	1	4.73	<0.10	5	0.10	>97.9	U
		2	4.71	<0.02	1	0.02	>99.6	U
		3	4.71	<0.02	1	0.02	>99.6	U
	0.8	1	4.83	<0.02	1	0.02	>99.6	U
		2	4.83	<0.02	1	0.02	>99.6	U
	0.6	1	4.83	<0.02	1	0.02	>99.6	U
		2	4.83	<0.02	1	0.02	>99.6	U
	0.4	1	4.78	<0.02	1	0.02	>99.6	U
		2	4.78	<0.02	1	0.02	>99.6	U
	0.2	1	4.70	1.06	1	0.02	77.5	-
		2	4.70	1.01	1	0.02	78.6	-

Sample ID	Adsorbent Dosage (g/L)	Trial No.	Initial P Reading (mg P/L)	Final P Reading (mg P/L)	Dilution Factor	Method Detection Limit (mg P/L)	Percent Removal (%)	Flags
FLDEP47 (A-L-1.5-7)	1.0	1	4.73	<0.10	5	0.10	>97.9	U
		2	4.71	<0.02	1	0.02	>99.6	U
		3	4.71	<0.02	1	0.02	>99.6	U
	0.8	1	4.83	<0.02	1	0.02	>99.6	U
		2	4.83	<0.02	1	0.02	>99.6	U
	0.6	1	4.83	<0.02	1	0.02	>99.6	U
		2	4.83	<0.02	1	0.02	>99.6	U
	0.4	1	4.78	<0.02	1	0.02	>99.6	U
		2	4.78	<0.02	1	0.02	>99.6	U
	0.2	1	4.70	0.92	1	0.02	80.5	-
		2	4.70	1.01	1	0.02	78.5	-
FLDEP48 (A-L-1.5-9)	1.0	1	4.73	<0.10	5	0.10	>97.9	U
		2	4.71	<0.02	1	0.02	>99.6	U
		3	4.71	<0.02	1	0.02	>99.6	U
	0.8	1	4.83	<0.02	1	0.02	>99.6	U
		2	4.83	<0.02	1	0.02	>99.6	U
	0.6	1	4.83	<0.02	1	0.02	>99.6	U
		2	4.83	<0.02	1	0.02	>99.6	U
	0.4	1	4.78	<0.02	1	0.02	>99.6	U
		2	4.78	<0.02	1	0.02	>99.6	U
	0.2	1	4.70	1.85	5	0.1	60.5	-
		2	4.70	1.78	5	0.1	62.2	-

U = Indicates analyzed for but below laboratory detection limit.

5.1.2 Adsorption Duration

All previous measurements focused on equilibrium phosphorus removal performance of the adsorbents. In this section, kinetic experiments were performed to determine how fast the adsorption of phosphorus occurred. For evaluating the effect of adsorption duration, in addition to baseline of 24 hours, contact times of 2, 4, 6, 8, 10, 20, 30, 60, and 120 minutes were used. For these experiments, FLDEP45 was used as adsorbent (i.e., final candidate). For short contact durations (2 to 20 min), the final candidate achieved partial phosphorus removal of 34-98% (Table 26). For longer durations (30-1440 min), however, near-complete (i.e., > 99.6%) phosphorus removal was observed. QA/QC, including blank check (Table 27), calibration curve verification (Table 28), and matrix spike verification (Table 29) were completed in accordance with the QAPP, which all passed the criteria.

Table 26. Summary of phosphorus adsorption experiments using different contact times. Nominal phosphorus concentration of 5 mg/L, adsorbent dosage of 1 g/L, and final candidate adsorbent material (i.e., FLDEP45) were used in all cases.

Contact Time (min)	Trial No.	Initial P Reading (mg P/L)	Final P Reading (mg P/L)	Dilution Factor	Method Detection Limit (mg P/L)	Percent Removal	Flags
2	1	4.80	3.15	5	0.1	34.4	-
	2	4.80	2.95	5	0.1	38.5	-
4	1	4.80	2.52	5	0.1	47.5	-
	2	4.80	2.49	5	0.1	48.1	-
6	1	4.80	2.36	5	0.1	50.8	-
	2	4.80	2.30	5	0.1	52.1	-
8	1	4.80	2.04	5	0.1	57.5	-
	2	4.80	2.06	5	0.1	57.1	-
10	1	4.95	1.15	1	0.02	76.77	-
	2	4.95	1.01	1	0.02	79.60	-
	3	4.95	0.77	1	0.02	84.44	-
	4	4.84	0.98	1	0.02	79.68	-
20	1	4.95	0.09	1	0.02	98.2	-
	2	4.95	0.11	1	0.02	97.8	-
30	1	4.95	<0.02	1	0.02	>99.6%	U
	2	4.95	<0.02	1	0.02	>99.6%	U
60	1	4.84	<0.02	1	0.02	>99.6%	U
	2	4.84	<0.02	1	0.02	>99.6%	U
120	1	4.75	<0.02	1	0.02	>99.6%	U
	2	4.75	<0.02	1	0.02	>99.6%	U
1440	1	4.73	<0.10	5	0.10	>97.9	U
	2	4.71	<0.02	1	0.02	>99.6	U
	3	4.71	<0.02	1	0.02	>99.6	U

U = Indicates analyzed for but below laboratory detection limit

5.1.3 QA/QC: Blank

All blank samples were below laboratory method detection limit (Table 21).

Table 27. QA/QC data for blank samples (no dilution used).

Trial No.	Sample	Absorbance	Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Flags
1	DI Water	0.003	<0.02	0.02	U
2		0.003	<0.02	0.02	U
3		0.003	<0.02	0.02	U
4		0.004	<0.02	0.02	U
5		0.004	<0.02	0.02	U

U: Blank sample below laboratory method detection limit.

5.1.4 QA/QC: Calibration Curve Verification

Calibration verifications met acceptance criteria (< 10% error and within ± 0.1 mg P/L; Table 22).

Table 28. QA/QC data for calibration curve verification (no dilution used).

Trial No.	Nominal P Conc. (mg P/L)	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Percent Error	Flags
1	0.5	0.273	0.47	0.02	6	-
2		0.271	0.46	0.02	8	-
3		0.276	0.47	0.02	6	-
4		0.275	0.47	0.02	6	-
5		0.281	0.48	0.02	4	-

5.1.5 QA/QC: Matrix Spike Verification

Matrix spike verifications met acceptance criteria (< 10% error and within ± 0.1 mg P/L; Table 23).

Table 29. QA/QC data for matrix spike verification (no dilution used).

Trial No.	Nominal P Conc. (mg P/L)	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Percent Error	Flags
1	1.0	0.572	0.98	0.02	2	-
2		0.572	0.98	0.02	2	-
3		0.572	0.98	0.02	2	-
4		0.575	0.98	0.02	2	-
5		0.571	0.98	0.02	2	-

5.2 Impact of Natural Organic Matter on Phosphorus Removal (Task 3.2; July-September 2022)

5.2.1 COD Measurement Method

Using the final candidate (i.e., FLDEP45), the Research Team elucidated phosphorus removal in the presence of natural organic matter (Task 3.2). For chemical oxygen demand (COD) analysis, Hach Method 8000, particularly 3-150 mg/L COD (low range, LR; Item No. 2125815; Figure 90) and 20-1500 mg/L COD (high range, HR; Item No. 2125915; Figure 91) test vials were used. The LR and HR test vials have sensitivity of 3 and 23 mg/L COD, respectively, which correspond to the concentration change per 0.010 Abs change. These ranges are USEPA approved for wastewater analyses (Standard Method 5220 D). A detailed description of this method is enclosed as a separate attachment. The Research Team used Hach DRB200 Reactor (Figure 92) and Hach DR 5000 UV-Vis Laboratory Spectrophotometer (Figure 93) for COD analysis, including 430 COD LR and 435 COD HR programs for the corresponding test vials. For QA/QC, Hach COD Standard Solution, 800 mg/L (Item No. 2672629; Figure 94) was used. The standard solution was used without dilution for the HR test vial. For the LR test vial, however, the standard was diluted to 80 mg/L.

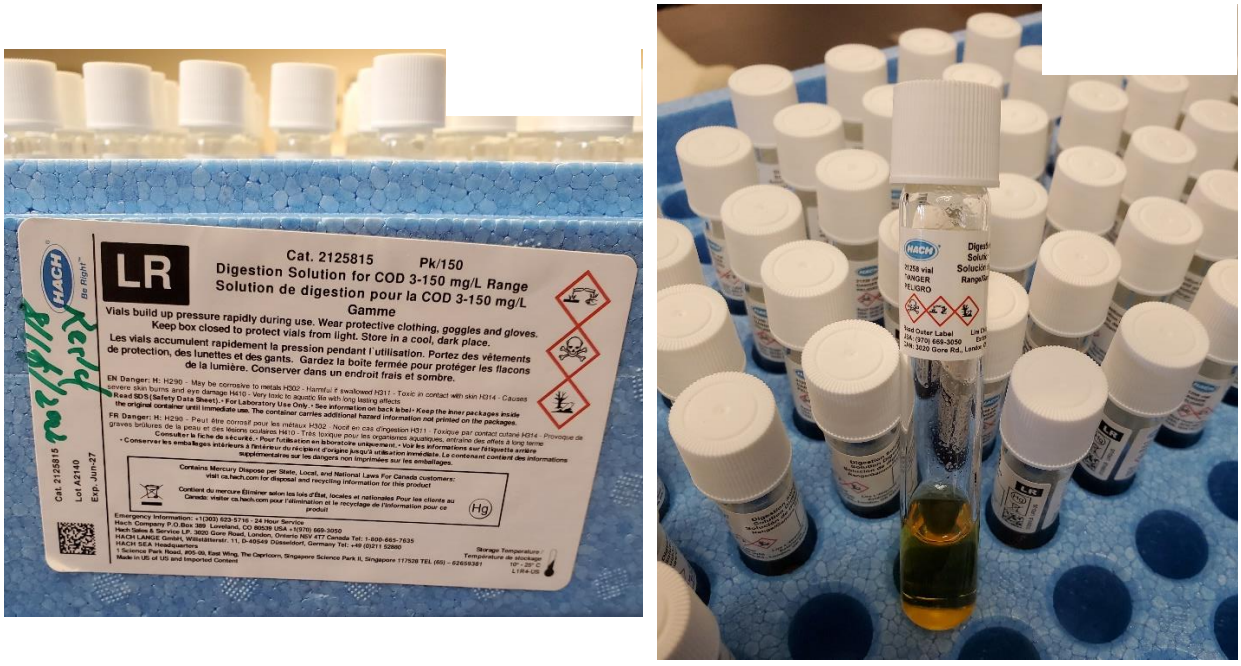


Figure 90: LR COD test vial.

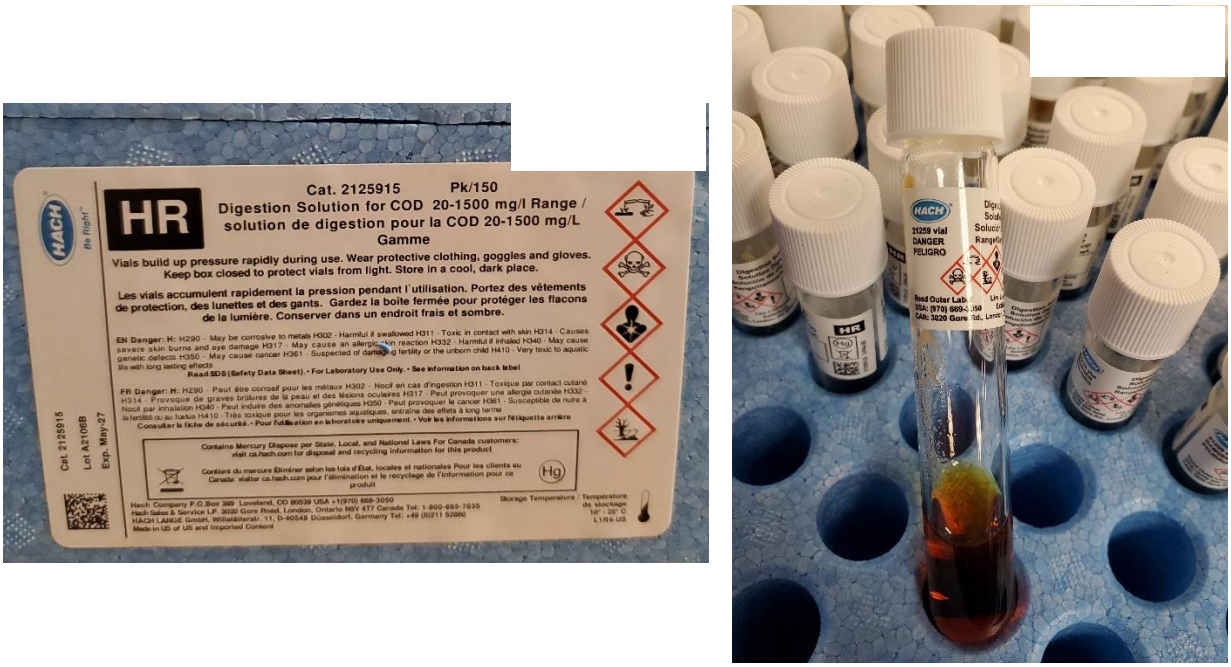


Figure 91: HR COD test vial.

Figure 92: Hach DRB 200 Reactor.

Figure 93: Hach DR 5000 UV-Vis Laboratory Spectrophotometer.

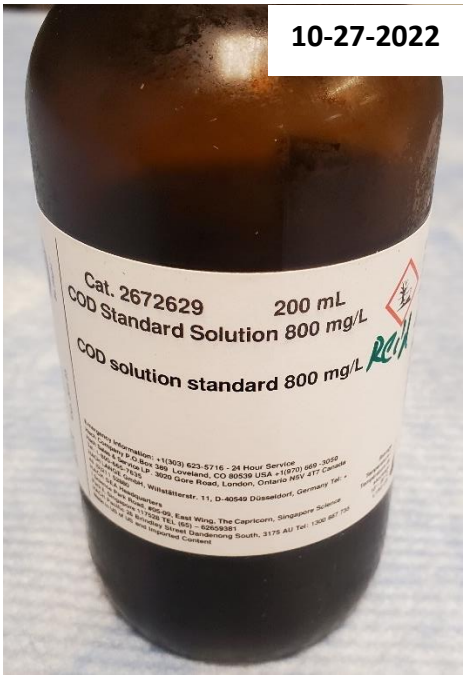


Figure 94: Hach COD Standard Solution, 800 mg/L.

5.2.2 Impact of Adsorbent on COD Reading

To find whether the adsorbent alone affects COD readings, experiments were conducted where 0.02, 0.04, 0.06, 0.08, or 0.1 gram of the final adsorbent (i.e., FLDEP45) was mixed with 100 mL DI water. After 24 hours of mixing, the mixtures were filtered with the syringe shown in Figure 37 to remove the adsorbent particles, followed by analyzing the filtrate for COD level in duplicates using the LR test vial, as described above (Figure 95 and Figure 96). Mixing the adsorbent with DI water, even at low dosages, caused a spike in COD readings (Table 30), likely due to ultrafine carbon particles escaping the filter. The QA/QC data is summarized in Table 31 and Table 32.

Figure 95: COD test vials being heated in Hach DRB 200 Reactor.

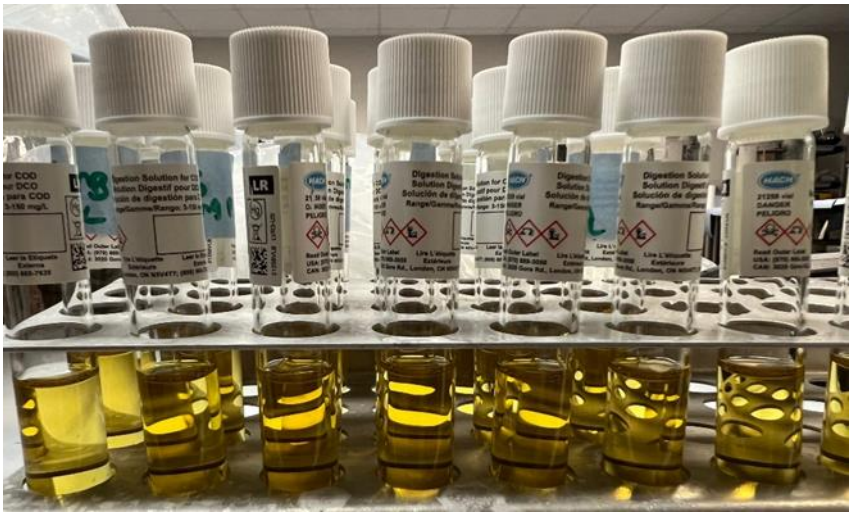


Figure 96: COD test vials placed in a tube rack to cool to room temperature prior to analysis using Hach DR 5000 UV-Vis Laboratory Spectrophotometer.

Table 30. Summary of results for the impact of adsorbent on COD readings.

Adsorbent Dosage (g/L)	Trial No.	COD Reading (mg/L)	Method Sensitivity (mg/L)	Flags
0.2	1	15	3	-
	2	21	3	-
0.4	1	20	3	-
	2	20	3	-
0.6	1	21	3	-
	2	15	3	-
0.8	1	18	3	-
	2	16	3	-
1.0	1	15	3	-
	2	17	3	-

Table 31. QA/QC data for blank sample.

Trial No.	Sample	COD Reading (mg/L)	Method Sensitivity (mg/L)	Flags
1	DI Water	0	3	U

U: Blank sample below laboratory method detection limit.

Table 32. QA/QC data for standard sample.

Trial No.	Sample	Nominal COD (mg/L	COD Reading (mg/L)	Method Sensitivity (mg/L)	Flags
1	Diluted COD standard	80	82	3	-

5.2.3 Preparation of Solutions with Different COD Levels

Chemical Oxygen Demand Quality Control Standard reference material supplied by Hach (COD of 617 mg/L; Item No. 2833510; Figure 97) was used to prepare solutions containing COD concentrations of 25, 37, 49, and 62 mg/L. Upon preparation, the actual COD levels were measured using the LR test vial described earlier. All COD readings were consistent with the anticipated values (Table 33). The QA/QC data is summarized in Table 34 and Table 35. These solutions were then used in some of the experiments described later in this document.

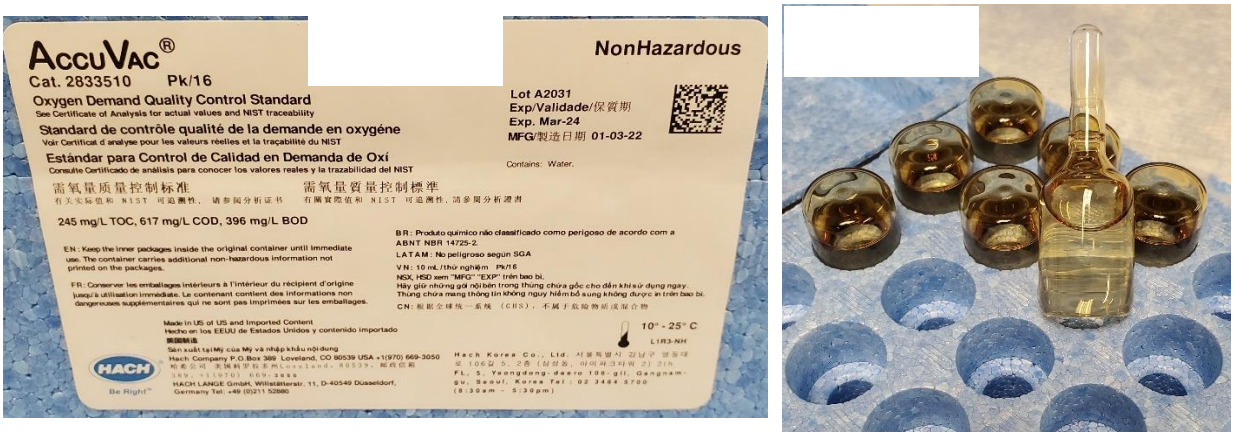


Figure 97: Hach Chemical Oxygen Demand Quality Control Standard.

Table 33. Summary of COD readings for solutions containing different nominal COD values.

Nominal COD Value (mg/L)	Trial No.	COD Reading (mg/L)	Method Sensitivity (mg/L)	Flags
25	1	29	3	-
	2	27	3	-
37	1	35	3	-
	2	34	3	-
49	1	54	3	-
	2	52	3	-
62	1	63	3	-
	2	65	3	-

Table 34. QA/QC data for blank sample.

Trial No.	Sample	COD Reading (mg/L)	Method Sensitivity (mg/L)	Flags
2	DI Water	0	3	U

U = Indicates analyzed for but below laboratory detection limit.

Table 35. QA/QC data for standard sample.

Trial No.	Sample	Nominal COD (mg/L	COD Reading (mg/L)	Method Sensitivity (mg/L)	Flags
2	Diluted COD standard	80	82	3	-

5.2.4 Impact of COD Level on Phosphorus Measurement

To determine if COD alone affects phosphorus readings, the four COD solutions prepared above were tested with phosphorus test kit, as described earlier. In all cases, adding a COD-containing solution to the phosphorus test kit resulted in a below-detection reading (Table 36). QA/QC, including blank check (Table 37), calibration curve verification (Table 38), and matrix spike verification (Table 39) were completed in accordance with the QAPP, which all passed the criteria.

Table 36. Summary of phosphorus concentration readings in the presence of COD.

Nominal COD Conc. (mg/L)	Trial No.	P Reading (mg P/L)	Method Detection Limit (mg P/L)	Flags
25	1	<0.02	0.02	U
	2	<0.02	0.02	U
37	1	<0.02	0.02	U
	2	<0.02	0.02	U
49	1	<0.02	0.02	U
	2	<0.02	0.02	U
62	1	<0.02	0.02	U
	2	<0.02	0.02	U

U = Indicates analyzed for but below laboratory detection limit.

Table 37. QA/QC data for blank samples (no dilution used).

Trial No.	Sample	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Flags
6	DI Water	0.004	<0.02	0.02	U

U = Indicates analyzed for but below laboratory detection limit.

Table 38. QA/QC data for calibration curve verification (no dilution used).

Trial No.	Nominal P Conc. (mg P/L)	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Percent Error	Flags
6	0.5	0.275	0.47	0.02	6	-

Table 39. QA/QC data for matrix spike verification (no dilution used).

Trial No.	Nominal P Conc. (mg P/L)	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Percent Error	Flags
6	1.0	0.575	0.99	0.02	1	-

5.2.5 Adsorbent Affinity for COD Removal

To determine the affinity of the final candidate for COD removal, the adsorbent was assessed in the presence of different COD concentrations developed earlier. In all cases, 0.1 gram of the final candidate was added to 100 mL of the COD-containing solutions, followed by 24 hours of mixing, after which the solution was filtered and analyzed for COD concentration in duplicates using LR COD test vial. As summarized in Table 40, the adsorbent showed no affinity for COD removal. In all cases, the final COD reading was notably higher than the initial value, most likely due to carbon particles escaping through the syringe filter, as described earlier. The QA/QC data is summarized in Table 41 and Table 42.

Table 40. Summary of COD removal performance of the final candidate.

Nominal COD Conc. (mg/L)	Trial No.	Initial COD Reading (mg/L)	Final COD Reading (mg/L)	Method Sensitivity (mg/L)	Flags
25	1	27	42	3	-
	2	27	44	3	-
37	1	35	54	3	-
	2	35	55	3	-
49	1	52	67	3	-
	2	52	67	3	-
62	1	63	77	3	-
	2	63	77	3	-

Table 41. QA/QC data for blank sample.

Trial No.	Sample	COD Reading (mg/L)	Method Sensitivity (mg/L)	Flags
3	DI Water	0	3	U

U = Indicates analyzed for but below laboratory detection limit

Table 42. QA/QC data for standard sample.

Trial No.	Sample	Nominal COD (mg/L	COD Reading (mg/L)	Method Sensitivity (mg/L)	Flags
3	Diluted COD standard	80	82	3	-

5.2.6 Phosphorus Removal in the Presence of COD

Phosphorus removal performance of the final candidate was assessed in the presence of different COD concentrations. The following solutions were utilized:

1) 25 mg/L COD + 5 mg P/L
2) 37 mg/L COD + 5 mg P/L
3) 49 mg/L COD + 5 mg P/L
4) 62 mg/L COD + 5 mg P/L

In all cases, 0.1 gram of the final candidate was added to 100 mL of the above solutions, followed by 24 hours of mixing, after which the solution was filtered and analyzed for COD and P concentrations in duplicates using the methods described earlier. As summarized in Table 43, the adsorbent showed no affinity for COD removal, while achieving near-complete phosphorus removal. In all cases, the final COD reading was notably higher than the initial value, most likely due to carbon particles escaping through the syringe filter, as described earlier. The QA/QC data for phosphorus measurements are summarized in Table 44, Table 45, and Table 46. The QA/QC data for COD measurements are summarized in Table 47 and Table 48.

Table 43. Summary of phosphorus removal performance of the final candidate in the presence of different COD levels. An initial nominal concentration of 5 mg P/L was used in all cases. The phosphorus method detection limit was 0.02 mg/L. The COD method sensitivity was 3 mg/L. None of the samples were diluted prior to the analyses, except for initial P analysis.

Nominal Initial COD (mg/L)	Trial No.	Initial COD Reading (mg/L)	Final COD Reading (mg/L)	Initial P Reading (mg P/L)	Final P Reading (mg P/L)	Percent Removal for P	Flags for P
25	1	27	42	4.75	<0.02	>99.6	U
	2	26	43	4.75	<0.02	>99.6	U
37	1	40	52	4.83	<0.02	>99.6	U
	2	39	52	4.85	<0.02	>99.6	U
49	1	52	65	4.71	<0.02	>99.6	U
	2	52	65	4.73	<0.02	>99.6	U
62	1	59	66	4.78	<0.02	>99.6	U
	2	59	66	4.74	<0.02	>99.6	U

U = Indicates analyzed for but below laboratory detection limit

Table 44. QA/QC data for blank samples (no dilution used).

Trial No.	Sample	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Flags
7	DI Water	0.004	<0.02	0.02	U

U = Indicates analyzed for but below laboratory detection limit.

Table 45. QA/QC data for calibration curve verification (no dilution used).

Trial No.	Nominal P Conc. (mg P/L)	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Percent Error	Flags
7	0.5	0.281	0.48	0.02	4	-

Table 46. QA/QC data for matrix spike verification (no dilution used).

Trial No.	Nominal P Conc. (mg P/L)	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Percent Error	Flags
7	1.0	0.571	0.98	0.02	2	-

Table 47. QA/QC data for blank sample.

Trial No.	Sample	COD Reading (mg/L)	Method Sensitivity (mg/L)	Flags
4	DI Water	0	3	U

U = Indicates analyzed for but below laboratory detection limit

Table 48. QA/QC data for standard sample.

Trial No.	Sample	Nominal COD (mg/L	COD Reading (mg/L)	Method Sensitivity (mg/L)	Flags
4	Diluted COD standard	80	82	3	-

5.2.7 Phosphorus Removal in the Presence of Natural Water Samples

The phosphate removal performance of the final candidate was studied in the presence of a Wastewater Influent Standard Solution supplied by Hach (Item No. 2833149), which contained Ammonia Nitrogen of 15 mg/L NH_3-N, Nitrate Nitrogen of 10 mg/L NO_3^--N, COD of 500 mg/L, Phosphate of 10 mg/L PO_4^{3-} (i.e., 3.26 mg P/L), Sulfate of 400 mg/L SO_4^{2-}, and TOC of 161 mg/L (Figure 98). Moreover, the phosphate removal performance of the final candidate was studied in the presence of a Wastewater Effluent Standard Solution supplied by Hach (Item No. 2833249), which contained Ammonia Nitrogen of 2 mg/L NH_3-N, Nitrate Nitrogen of 4 mg/L NO_3^--N, COD of 25 mg/L, Phosphate of 2 mg/L PO_4^{3-} (i.e., 0.66 mg P/L), Sulfate of 50 mg/L SO_4^{2-}, and TOC of 8 mg/L (Figure 98). In both cases, 0.1 gram of the final adsorbent was added to 100 mL of the above solutions, followed by 24 hours of mixing, after which the solutions were filtered and analyzed for COD and P concentrations in duplicates. For the wastewater influent standard solution, the HR COD test vial with method sensitivity of 23 mg/L was used. For the wastewater effluent standard solution, the LR COD test vial with method sensitivity of 3 mg/L was used. As shown in Table 49, for both solutions, the phosphate removal performance of the final candidate was not affected by the presence of the listed chemicals, achieving near-complete removal of phosphate. The QA/QC data for phosphorus measurements are shown in Table 50, Table 51, and Table 52. The QA/QC data for COD measurements are shown in Table 53 and Table 54.

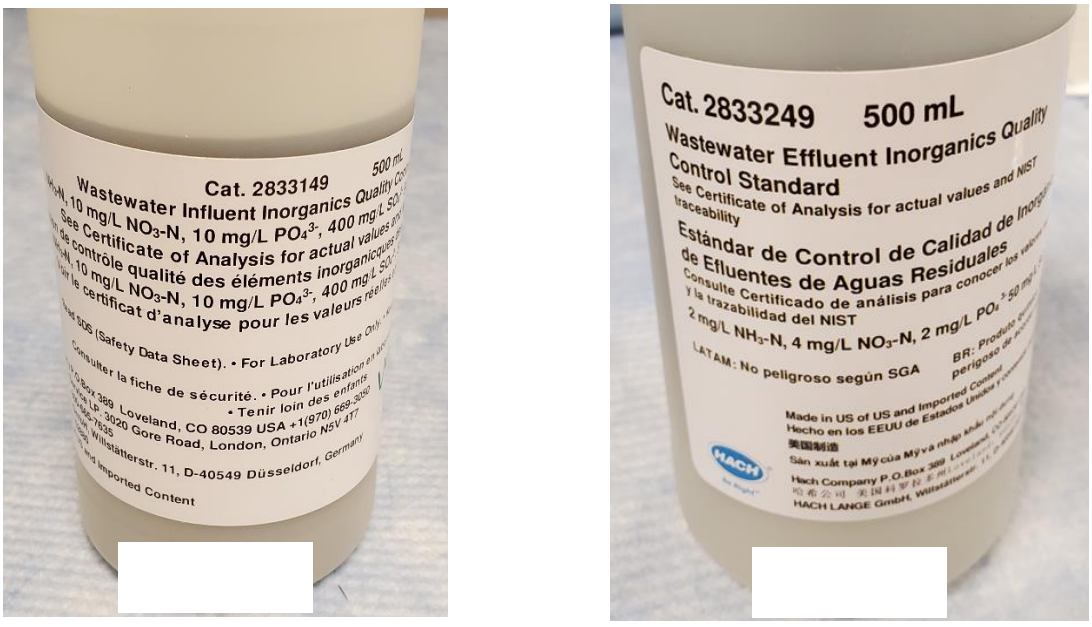


Figure 98: Wastewater influent (left) and effluent (right) standard solutions.

Table 49. Summary of phosphorus removal performance of the final candidate in the presence of wastewater influent and effluent standard solutions. The phosphorus method detection limit was 0.02 mg P/L for no dilution, and 0.06 mg P/L for dilution factor of 3. None of the samples were diluted prior to the analyses, except for initial P analysis in case of wastewater influent standard solution.

Nominal Initial COD (mg/L)	Trial No.	Initial COD Reading (mg/L)	Final COD Reading (mg/L)	Nominal Initial P Reading (mg P/L)	Initial P Reading (mg P/L)	Final P Reading (mg P/L)	Percent Removal for P	Flags for P
500	1	502	521	3.26	3.15	<0.02	>99.6	U
	2	500	524	3.26	3.15	<0.02	>99.6	U
25	1	24	37	0.66	0.61	<0.02	>99.6	U
	2	25	35	0.66	0.60	<0.02	>99.6	U

U = Indicates analyzed for but below laboratory detection limit

Table 50. QA/QC data for blank samples (no dilution used).

Trial No.	Sample	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Flags
8	DI Water	0.003	<0.02	0.02	U

U = Indicates analyzed for but below laboratory detection limit.

Table 51. QA/QC data for calibration curve verification (no dilution used).

Trial No.	Nominal P Conc. (mg P/L)	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Percent Error	Flags
8	0.5	0.275	0.47	0.02	6	-

Table 52. QA/QC data for matrix spike verification (no dilution used).

Trial No.	Nominal P Conc. (mg P/L)	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Percent Error	Flags
8	1.0	0.575	0.99	0.02	1	-

Table 53. QA/QC data for blank sample.

Trial No.	Sample	COD Reading (mg/L)	Method Sensitivity (mg/L)	Flags
5	DI Water	0	3	U

U = Indicates analyzed for but below laboratory detection limit

Table 54. QA/QC data for standard sample.

Trial No.	Sample	Nominal COD (mg/L	COD Reading (mg/L)	Method Sensitivity (mg/L)	Flags
5	COD standard	800	803	23	-

5.3 Cyclic Performance of the Final Candidate (Task 3.3; October 2022)

To elucidate the possibility of reusing the adsorbent material, the cyclic phosphate removal performance of the final candidate was studied in the presence of a solution containing 5 mg P/L (Figure 99). Also, the same experiment was conducted in the presence of the wastewater effluent standard solution described previously (Figure 99). In both cases, two successive cycles were conducted by adding 0.25 gram of the final adsorbent to 250 mL of the above solutions, followed by 24 hours of mixing, after which the solutions were filtered and analyzed for P concentrations in duplicates. After the adsorption step, both samples were filtered (Figure 100), then rinsed three times each with DI water, 0.01 M sodium hydroxide solution (Figure 101), and ethanol (Figure 101). The samples were then dried in oven at 60 °C (Figure 102), before performing the second cycle in a similar manner. As shown in Table 55, for 5 mg P/L, the first cycle showed a near-complete removal that dropped to nearly 90% in the second cycle, so the final candidate could be effectively used for multiple rounds of phosphorus removal. For the effluent solution, the phosphate removal performance of the final candidate was not adversely affected during cycling, achieving near-complete removal of phosphate both times. Future work may involve a higher number of consecutive cycles to obtain better insights about the lifetime of the adsorbent material. The QA/QC data for phosphorus measurements are shown in Table 56, Table 57, and Table 58.

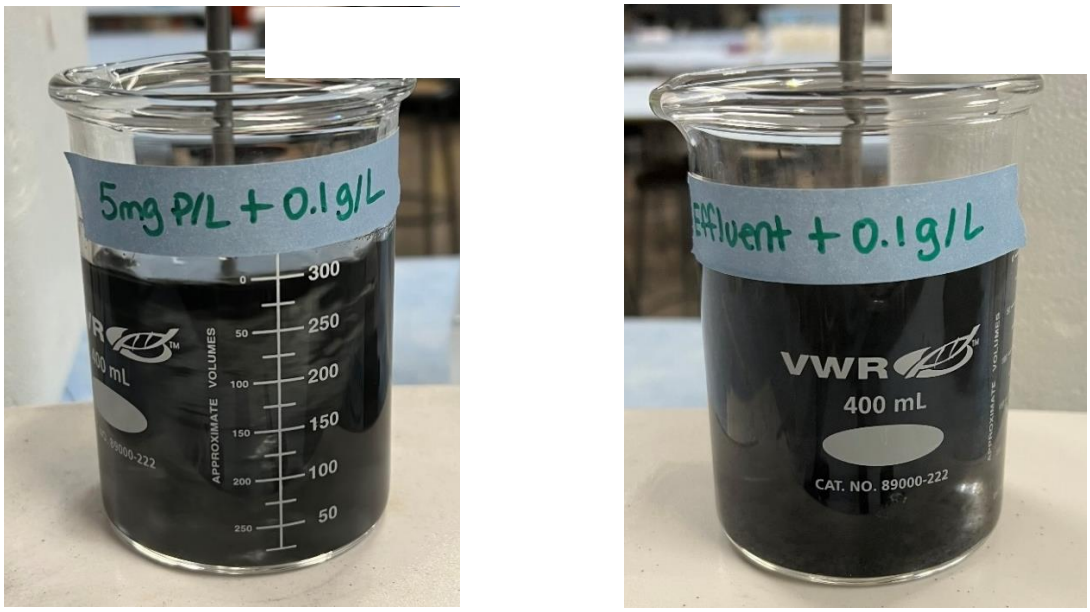


Figure 99: Cyclic experiments in progress.

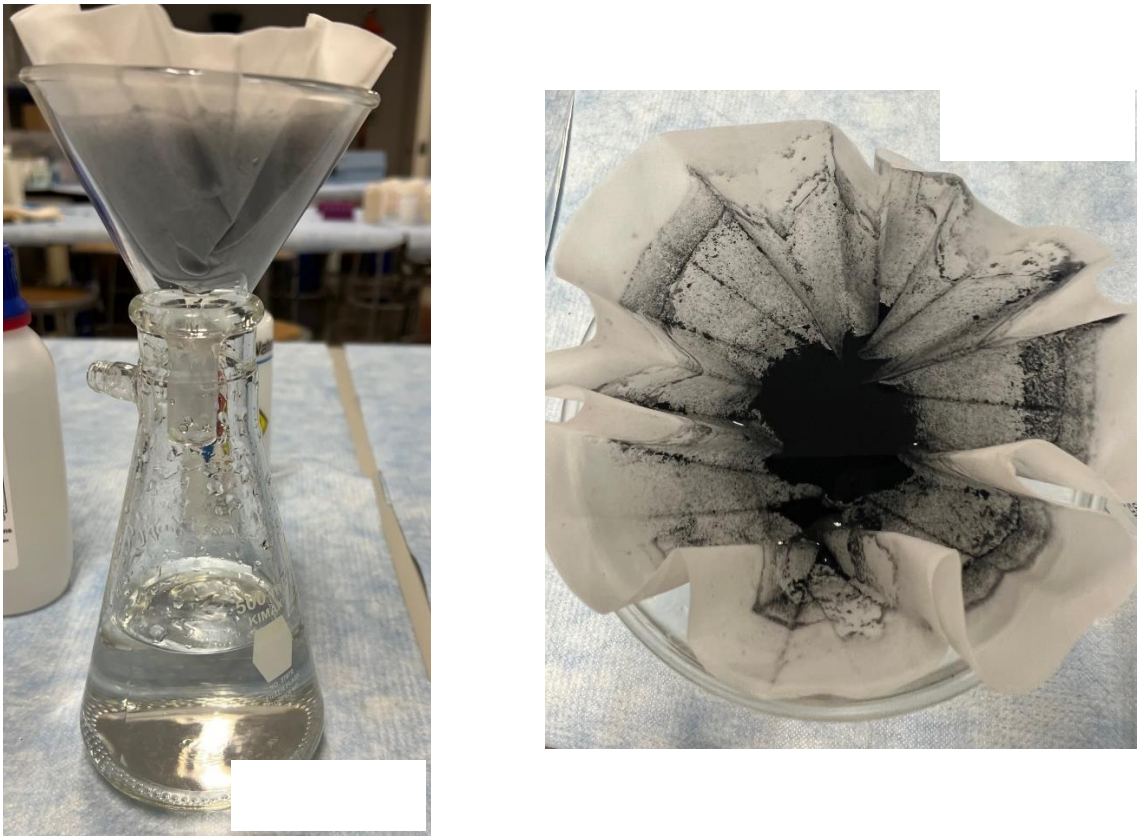


Figure 100: Adsorbent filtration and rinsing.

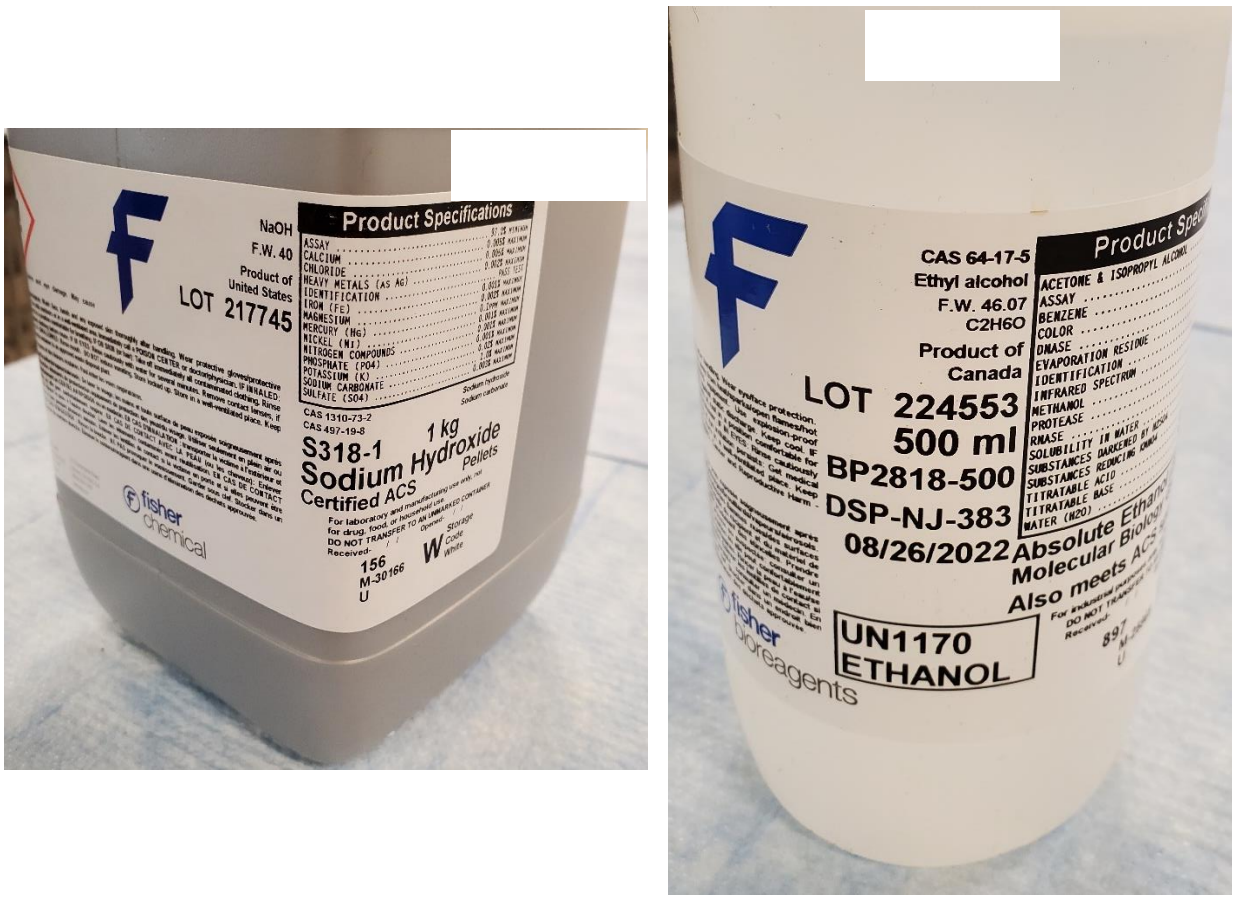


Figure 101: Sodium hydroxide (left) and ethanol (right) used for cyclic experiments.

Figure 102: Drying carbon samples in oven.

Table 55. Summary of cyclic phosphorus removal performance of the final candidate in the presence of different solutions. The phosphorus method detection limit was 0.02 mg P/L. None of the samples were diluted prior to the analyses, except for initial P analysis in case of first solution.

Solution	Cycle No.	Trial No.	Nominal Initial P Reading (mg P/L)	Initial P Reading (mg P/L)	Final P Reading (mg P/L)	Percent Removal	Flags
5 mg P/L	1	1	5	4.90	<0.02	>99.6	U
		2	5	4.90	<0.02	>99.6	U
	2	1	5	4.80	0.39	91.8	
		2	5	4.85	0.39	92.0	
Effluent Wastewater	1	1	0.66	0.61	<0.02	>99.6	U
		2	0.66	0.60	<0.02	>99.6	U
	2	1	0.66	0.61	<0.02	>99.6	U
		2	0.66	0.61	<0.02	>99.6	U

U = Indicates analyzed for but below laboratory detection limit

Table 56. QA/QC data for blank samples (no dilution used).

Trial No.	Sample	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Flags
9	DI Water	0.004	<0.02	0.02	U

U = Indicates analyzed for but below laboratory detection limit.

Table 57. QA/QC data for calibration curve verification (no dilution used).

Trial No.	Nominal P Conc. (mg P/L)	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Percent Error	Flags
9	0.5	0.268	0.46	0.02	8	-

Table 58. QA/QC data for matrix spike verification (no dilution used).

Trial No.	Nominal P Conc. (mg P/L)	Absorbance	P Conc. Reading (mg P/L)	Method Detection Limit (mg P/L)	Percent Error	Flags
9	1.0	0.570	0.98	0.02	2	-

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