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DOE-VFP; Surface Engineered Multifunctional Zeolite Composite for Photodegradation of Per- and Polyfluoroalkyl substances (PFAS) in Aqueous Medium

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ABSTRACT

Per- and Polyfluoroalkyl substances (PFAS) are widely used compounds proven to bioaccumulate and result in detrimental health effects. On October 18, 2021 the United States Environmental Pollution Agency (EPA) released a strategic roadmap to address PFAS that includes the investment in effective research that accelerates cleanup. Existing water treatment technologies for PFAS removal are based on adsorptive removal, are commonly single-use and result in pollutant-laden waste, leading to costly disposal processes. Here we proposed the development of a zeolite-TiO_2 composite for removal and degradation of PFAS. The composite is advantageous as it can be easily integrated into water treatment facilities, is multifunctional, and minimizes waste through regeneration.

We studied the adsorptive capacity of zeolites 13X, 3A, 4A and 5A for an anionic PFAS surrogate, methyl orange (MO). Zeolite 3A showed the highest adsorptive capacity, followed by 4A, 5A, and 13X when incubated with 15 ppm MO for 3 hours. Depositing Au-nanospheres on the zeolites surface reduced MO adsorption for all zeolites. We also investigated the photodegradation capacity of TiO_2, Fe_2O_3, Au-TiO_2, and Au-Fe_2O_3, ranking their performance as $TiO_2 > Fe_2O_3 >$ Au-$TiO_2 >$ Au-Fe_2O_3 under 254 nm light in a 10 ppm MO solution.

Our results highlight the favorable adsorption of small pore size zeolites for PFAS surrogates and the potential of TiO_2 as a photocatalyst for PFAS degradation. We can further study and integrate the composite's components at our home institution. Other notable achievements of our VFP team includes the submittion of two funding proposals, two poster presentations and one invited talk thus showcasing our progress.

INTRODUCTION

BACKGROUND AND RESEARCH OBJECTIVES

Per- and polyfluoroalkyl substances (PFAS) refers to a group of over 6,500 anthropogenic compounds broadly used in commercial and industrial applications.[1] On October 18, 2021 the United States Environmental Pollution Agency (EPA) released a strategic roadmap to address PFAS that includes the investment in effective research that accelerates cleanup. Existing water treatment technologies for PFAS removal are based on adsorptive removal using granular activated carbon (GAC) or ion-exchange resins. However, these technologies are commonly single-use and result in pollutant-laden waste, leading to costly disposal processes.[2], [3] To tackle these limitations, we proposed a PFAS removal and degradation strategy using a zeolite-TiO_2 composite as our VFP project for the summer (Figure 1). The composite is advantageous in that it can easily be integrated into water treatment facilities, is multifunctional and can be regenerated therefore minimizing waste.

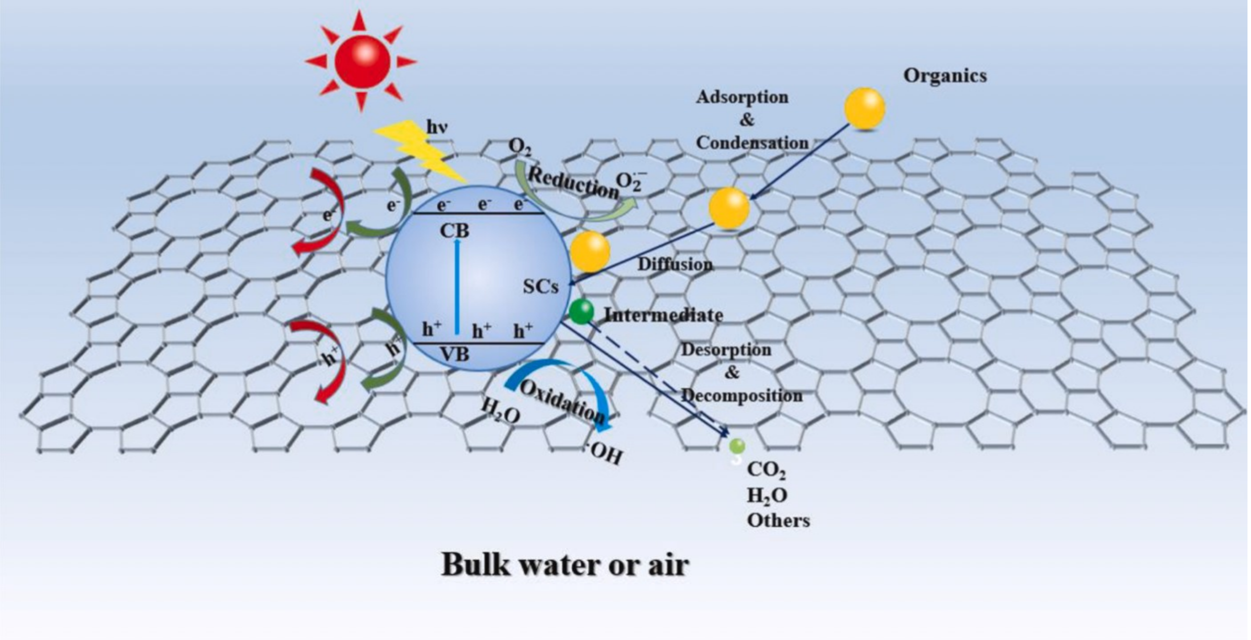


Figure 1: Schematic depiction of adsorption and photocatalystic degradation on the surface of zeolite-based composite. Adapted from G. Hu et al.[4]

Our proposed research objectives were to; (i) fabricate_a zeolitic membrane with different Si/Al ratios to tune hydrophobicity; (ii) incorporate TiO_2-based particles onto the membrane as photocatalysts using an in-situ precipitation sol-gel method; (ii) screen the composite for perfluorooctanoic acid (PFOA) adsorption in the 0.1-500 mg/L range. These research objectives were revised because of chemical reagent and instrumentation availability. The **main scientific goal** of this ongoing work remains the same, *to construct a zeolite-based composite with absorptivity and degradation capability for PFAS removal.* However, the **specific research objectives** for this summer internship were modified to include; (i) study the adsorptive capacity of commercial zeolites, (ii) design a method to deposit Au-nanospheres onto zeolite surfaces, (iii) explore the photocatalytic degradation performance of TiO_2 and Fe_2O_3, (iv) develop a protocol to expand photocatalytic performance to cover a broader solar spectrum range using Au-sensitized catalysts. Building on the established partnership, our team plans to further advance these objectives by continuing research activities at home institution in collaboration with SNRL throughout the year.

PROGRESS

SCIENTIFIC APPROACH, IMPACTS AND ACCOMPLISHMENTS

We approached the design of the composite by focusing on each component, the adsorbent and the photocatalyst. For these preliminary studies, anionic PFAS surrogate, methyl orange (MO) was used given the PFAS restrictions and regulations in place. MO has a strong absorbance signal at 465 nm when in pH 7 which enabled us to study adsorptive capacity and degradation performance using a straightforward UV-Vis method that can be performed at UPRM.

Undergraduate student, Alanna Nenadich, studied the adsorptive capacity (q) of four commercial zeolites; 13X, 3A, 4A and 5A. The highest adsorptive capacity was found for zeolite 3A (q = 1.94 µmol/g) followed by 4A (q = 1.32 µmol/g), 5A (q= 1.58 µmol/g) and lastly 13X (q= 1.23 µmol/g) when incubated in 15 ppm MO for 3-hour periods (figure 2). Depositing Au-nanospheres onto the zeolite's surfaces reduced the adsorptive capacity for all adsorbents. However, we believe Au-modified zeolites can be used as supports for UV-active photoactive catalysts to extent their degradation into the visible range of the solar spectrum. The photocatalytic component was studied by undergraduate student Michelle Cardona who explored the photodegradation capacity of TiO_2, Fe_2O_3, Au-TiO_2 and Au-Fe_2O_3. The photocatalytic degradation performance towards MO can be ranked as TiO_2, > Fe_2O_3 > Au-TiO_2 > Au-Fe_2O_3 when irradiated with 254 nm light for 2 hours (figure 3).

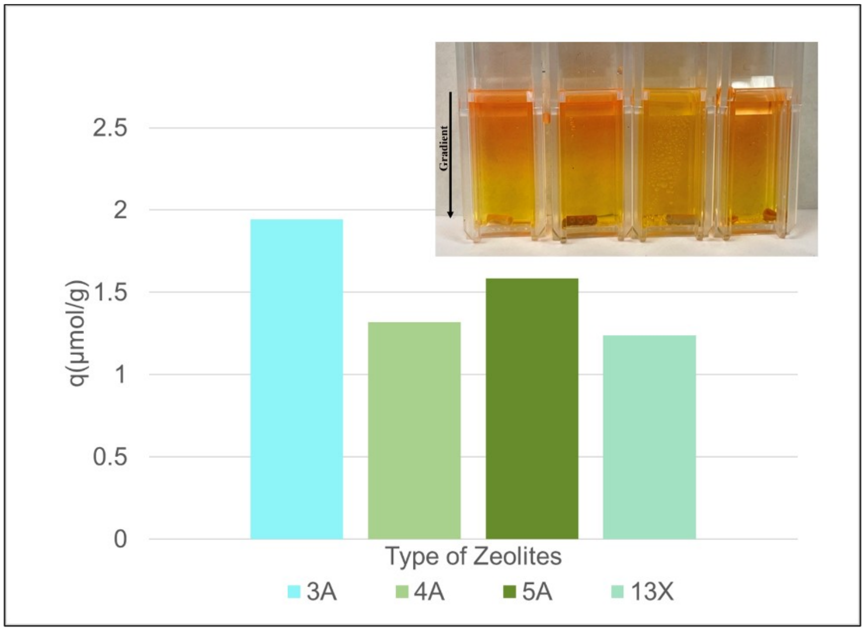


Figure 2: Adsorption capacity of unmodified zeolites 3A, 4A, 5A and 13x in 15 ppm methyl orange, an anionic PFAS surrogate, solution after three-hour incubation. Insert shows unmodified zeolites after incubation. A color gradient for methyl orange, resulting from increasing pH alkalinity, is observed due to alkaline nature of commercial zeolites.

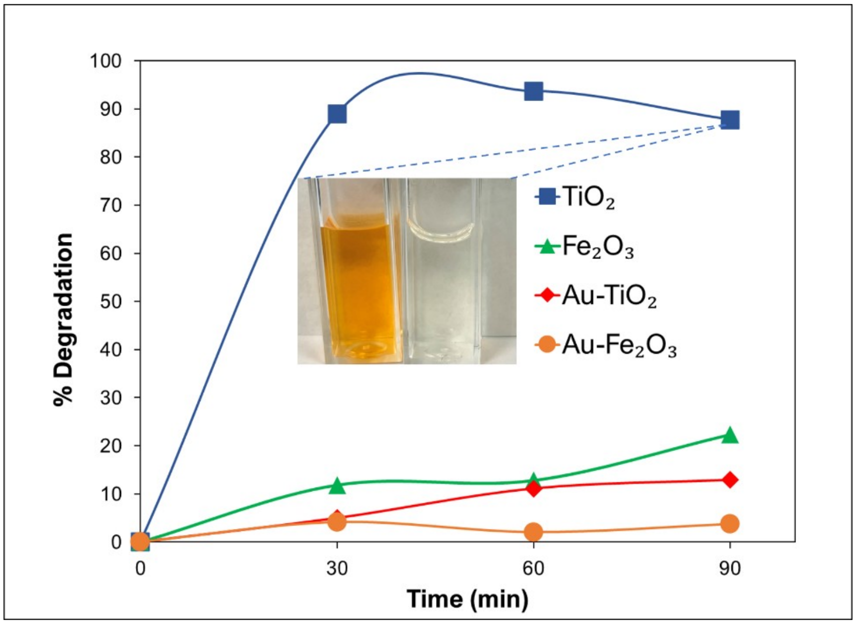
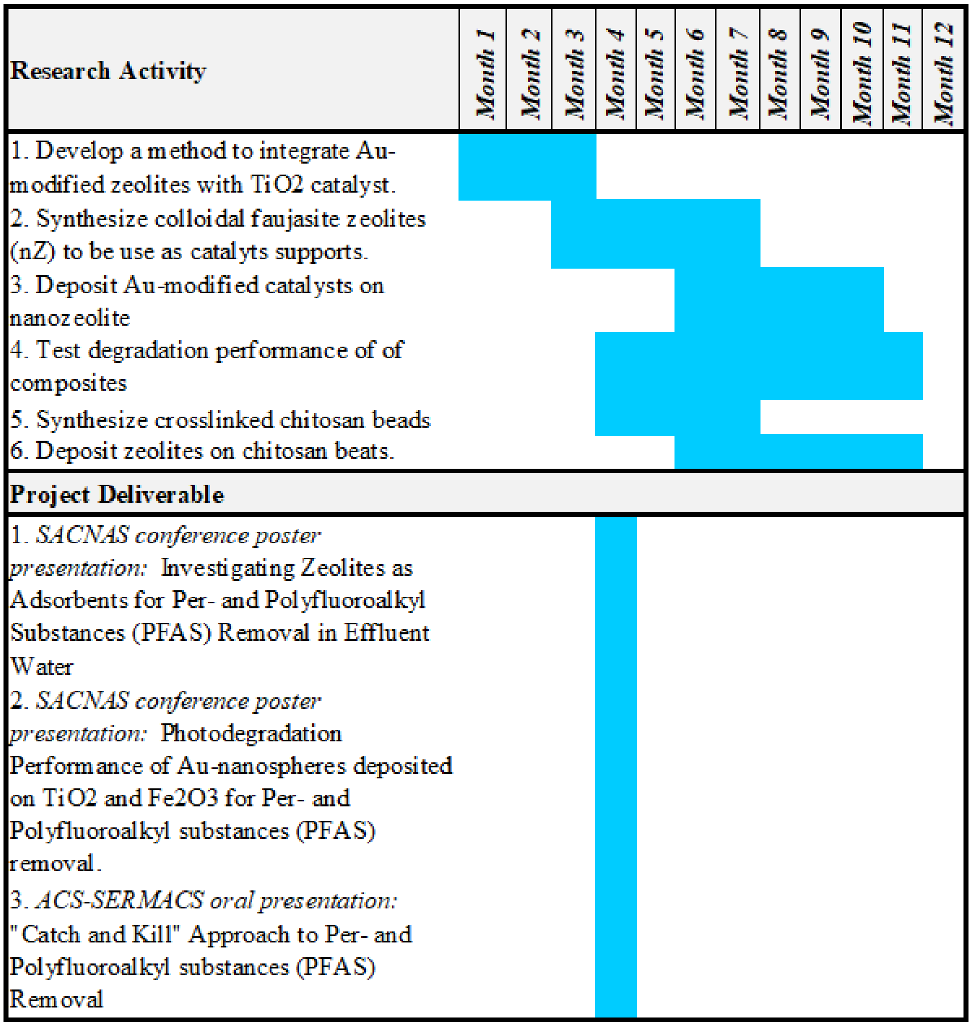


Figure 3: Photocatalytic degradation performance of TiO_2, Fe_2O_3, Au-TiO_2 and Au-Fe_2O_3. Insert shows the picture of the before and after photodegradation of 10 ppm methyl orange (MO) solution by TiO_2. The characteristic orange color of the 10 ppm MO solution disappears after 2 hours of 254 nm irradiation in presence of the catalysts.

Our results show that small pore size zeolites favor PFAS surrogate adsorption and that TiO_2 can act as a photocatalyst to promote PFAS degradation. We also developed a method for growing Au nanospheres onto zeolites and photocatalyst surfaces suitable for composite fabrication. More importantly, all chemistry methods developed during this internship can continue to be performed at our home institution. This accomplishment will enable us to further study the composite's components and later integrate them to achieve multifunctionality. In addition to experimental and technical accomplishments, our VFP team are submitted two external funding proposals submitted and resulted in one invited presentation and two student poster presentations.

FUTURE WORK

In the pursued of the main research objective, we have planned research activities that will focus on two strategies for composite design. One approach is to use higher surface area zeolites, known as colloidal zeolites, to increase the number of adsorption sites. A second approach seeks to construct a composite in which the main absorbent is chitosan beads. The corresponding research activities, and anticipated project deliverables, for both approaches can be found in the Gantt chart (table 1).



Research Activity	***Month 1***	***Month 2***	***Month 3***	***Month 4***	***Month 5***	***Month 6***	***Month 7***	***Month 8***	***Month 9***	***Month 10***	***Month 11***	***Month 12***
1. Develop a method to integrate Au-modified zeolites with TiO2 catalyst.	■	■	■									
2. Synthesize colloidal faujasite zeolites (nZ) to be use as catalyts supports.			■	■	■	■	■					
3. Deposit Au-modified catalysts on nanozeolite						■	■	■	■	■		
4. Test degradation performance of of composites				■	■	■	■	■	■	■	■	
5. Synthesize crosslinked chitosan beads				■	■	■	■					
6. Deposit zeolites on chitosan beats.						■	■	■	■	■	■	
Project Deliverable												
1. *SACNAS conference poster presentation:* Investigating Zeolites as Adsorbents for Per- and Polyfluoroalkyl Substances (PFAS) Removal in Effluent Water				■								
2. *SACNAS conference poster presentation:* Photodegradation Performance of Au-nanospheres deposited on TiO2 and Fe2O3 for Per- and Polyfluoroalkyl substances (PFAS) removal.				■								
3. *ACS-SERMACS oral presentation:* "Catch and Kill" Approach to Per- and Polyfluoroalkyl substances (PFAS) Removal				■								

Table 1: Gantt chart of planned research activities and anticipated project deliverables.

IMPACT ON LABORATORY OR NATIONAL MISSIONS

This research work focused on PFAS treatment directly impacts DOE's Soil and Groundwater program. Specifically, this work aligns with priority area 2 (PA2); *Effective and Sustainable Solutions for Plumes.*

CONCLUSIONS

The scientific approach to fabricate a material with the capacity of removing PFAS from water and degrading based on common water treatment absorbents enables cost-effective, deployable, and environmentally friendly technology. Our work as demonstrated the capacity of four commercially available zeolites to absorb methyl orange, a PFAS surrogate. Furthermore, we have found that such adsorptive capacity is reliant on pore size. Through our results we observed the viability of TiO_2 as a photodegradation catalyst for MO and the possibility of sensitizing it by growing Au nanospheres on its surface. Our findings pave the way for further experiments as preliminary proof of concept data was indeed collected during our VFP internship.

REFERENCES

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[5] J. Del Pilar Albadalejo *et al.*, “Ex Situ and In Situ Analyses of the Mechanism of Electrocatalytic Hydrogen Peroxide Production by CoxZn1–xO (0 < x < 0.018) Materials in Alkaline Media,” *ACS Appl. Energy Mater.*, vol. 5, no. 6, pp. 6597–6605, Jun. 2022, doi: 10.1021/acsaem.1c04030.

APPENDIX

I. PARTICIPANT TABLE

The participants of the Visiting Faculty Program, shown in Table 1, collaboratively worked towards advancing the proposed research goals. The faculty member provided assistance, mentorship, guidance, and training to ensure the progress of the research objectives. The host principal scientist supported the faculty member in these tasks and additionally organized weekly research progress meetings, handled administrative responsibilities such as ensuring student completion of required training, coordinated tours, and facilitated connections between students and other lab scientists. The host played a crucial role in ensuring compliance with DOE, SRNL, and safety regulations by submitting presentations, photos, and reports for external review and approval. Each research intern performed laboratory research activities and carried out data processing and analysis. Each student presented their progress on a weekly basis and successfully completed all necessary training for conducting their experiments.

NAME	INSTITUTION	ROLE
Joselyn Del Pilar Albaladejo, Ph.D	University of Puerto Rico, Mayaguez, P.R.	Assistant Professor Visiting Faculty
Simona H. Murph, Ph.D	Savannah River National Laboratory (SNRL), Aiken, SC	Principal Scientist SRNL VFP-Host
Alanna Nenadich	University of Puerto Rico, Mayaguez, P.R.	Undergraduate Research VFP Intern
Michelle Cardona	University of Puerto Rico, Mayaguez, P.R.	Undergraduate Research VFP Intern

II. SCIENTIFIC FACILITIES

The research activities took place at the Aiken County Government-Savannah River Research Campus, which serves as the home of the applied research center (ARC). This scientific facility provided the necessary laboratory space for conducting experiments. Moreover, the students utilized the Hitachi SU8200 scanning electron microscope, which is conveniently located at the ARC.

III. NOTABLE OUTCOMES

The following table shows the notable outcomes resulting from this program.

1. *Optimizing Functionality of Solid-state Materials for Sustainable Applications.* (**Invited talk**). DOE-EM-MSIPP Collaborative Workshop. June 28th
2. *Multifunctional Zeolite-Chitosan Composite for Degradation of Per- and Polyfluoroalkyl substances (PFAS) in Contaminated Water.* DOE-Collaborative Research **Proposal for External Funding**. Submitted on July 14th. Funding available $350,000· Award term: one year.
3. *Investigating Zeolites as Adsorbents for Per- and Polyfluoroalkyl Substances (PFAS) Removal in Effluent Water.* **SRNL Poster Presentation**. July 20th

4. *Photodegradation Performance of Au-nanospheres deposited on TiO_2 and Fe_2O_3 for Per- and Polyfluoroalkyl substances (PFAS) removal.* **SRNL Poster Presentation**. July 20th
5. *Surface Engineered Multifunctional Zeolite Composite for Photodegradation of Per- and Polyfluoroalkyl substances (PFAS) in Aqueous Medium*. **Research Report**. Visiting Faculty Program Deliverable *This report
6. Students toured the **Savannah River Nuclear Site (SRNS) Tank farm**. Tour led by David Newell. June 22nd.
7. *The Visiting Faculty Program: A student point of view lead by students Michelle Cardona and Alanna Nenadich.* (**Career talk**). DOE-EM-MSIPP Collaborative Workshop. June 28^{9h}
8. *Fighting forever chemicals with nanochemistry: Adsorption and Degradation Studies using PFAS surrogate.* (**Research talk**); *Michelle Cardona and Alanna Nenadich*. NNSA MSIPP intern and SRNL advisor visit. July 10th.
9. *Research Opportunity for Undergraduates Students in STEM (ROUSS) Scholarship. Funding provided by PR-LSAMP.* Submitted **research scholarship application** by *Alanna Nenadich*.
10. *Fighting "forever chemicals" with nanochemistry: our research experience at SNRL.* (**department seminar**); *Michelle Cardona and Alanna Nenadich*. UPRM-Chemistry Department. Fall 2023.

IV. RESEARCH VIBRANCY

Research Proposal for External Funding. As direct result of this appointment, and the established collaboration with Dr. Simona Murph, two external fund proposals were submitted. A RII Track-4 NSF proposal was submitted on April 4th and is currently pending review while a DOE-EM-MSIPP proposal was submitted on July 14th. Dr. Simona Murph is a Co-PI on both proposals.

Planned Returning Visit. Our current team intents to submit a VFP teacher track proposal to return in Winter 2024.

Joint Faculty Appointment at SRNL. The PI has spoken to the Director of Innovation and University Engagement office, Elizabeth Hoffman, in relation to the process associated to pursuing a joint appointment with SRNL.

Invited Lectures. The faculty member, Dr. Del Pilar, has invited Dr. Murph for a lecture to her QUIM3085: Environmental chemistry course. In addition, Dr. Adrian Gale, a VFP faculty member, has invited Dr. Del Pilar to give a talk at Benedict College during Winter 2024.

V. CONNECTION TO PROGRAMS AT HOME INSTITUTIONS

The newly established partnership between SRNL and UPRM, the largest HSI School of Engineering in the nation, will have a significant impact on training Hispanic scientists and engineers. Resulting from this VFP interaction, the PI will now help connect students to internship opportunities like Summer Undergraduate Laboratory Internship (SULI) and MSIPP.