University at Buffalo
The State University of New York

Grant Information: Institution, Principal Investigator(s), Contact Information, Grant Number	SUNY at Buffalo **Project:** Model-Aided Design and Integration of Functionalized Hybrid Nanomaterials for Enhanced Bioremediation of Per- and Polyfluoroalkyl Substances (PFAS) **Project Leaders**: Diana S. Aga, Ian Bradley, Nirupam Aich (University of Nebraska-Lincoln), Carla A. Ng (University of Pittsburgh) **Funding Period:** 2021-2025
Technology	Catalytic graphene oxide-metal nanohybrids are being designed and synthesized to transform persistent PFAS to more biodegradable forms that are then fed into bioreactors containing microbial cultures to complete PFAS degradation. Computational models and high-resolution mass spectrometry techniques are being developed to understand, predict, and optimize the biodegradation process.
Innovation	**Materials:** (i) Redox-active reduced graphene oxide nano zerovalent iron (rGO–nZVI); and (ii) photocatalytic rGO-titanium dioxide (TiO2) or rGO-TiO2 and rGO- TiO2-nZVI. **Biological:** Selection of microbial communities and assessment of their potential to degrade structurally variable PFAS followed by identification of community structure, functional enzymes, and pathways. **Why is this technology/approach different than what is already in the market?** The model-aided approach for nano-enhanced PFAS biodegradation will allow predictive screening of materials to identify the most promising degradation pathways for a wide range of PFAS structures without producing toxic byproducts.
Contaminant and Media	**Contaminants:** PFOA, PFOS, GenX, 6:2 FTS, PFHxS, PFBS, PFBA, and other emerging PFAS **Media:** Surface water, wastewater, drinking water
Expansion Potential	**Looking Forward: What other contaminants/media would work for your technology?** Our technology could be tuned to address any other persistent halogenated contaminant. **Combined Remedy: Would this technology work well with other treatment approaches?** This technology could be implemented as part of a treatment chain to address PFAS concentrates (e.g. from membrane filtration).
Sites/Samples	This project does not have a specific site for collecting real-world samples.

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Technology Readiness Level	TRL 3 — Experimental proof of concept
Update of Progress	**Aga Laboratory for Environmental Research and Testing (ALERT)** (Trainees: John Michael Aguilar and Karla Rios) We have developed an LC-MS/MS method that can target potential transformation products of PFAS during bacterial degradation and nano-enabled oxidative degradation. To quantify ultra-short chain PFAS, we also developed other methods, such as supercritical fluid chromatography/mass spectrometry (SFC/MS) and fluorine nuclear magnetic resonance spectroscopy (F-NMR), in addition to LC/MS/MS. Using ion chromatography that measures the amounts of fluorine, acetate, and formate produced during degradation of PFAS, we showed that degradation of PFAS leads to nontoxic byproducts. **Aich Lab (#AichLENS)** (Trainee: Md Arafat Ali) We evaluated how, and to what extent, different environmental and operational parameters, such as initial PFAS concentration, oxidant (H2O2) dose, pH, ionic strength, and natural organic matter (NOM), could influence the removal and degradation of PFOS and PFOA by rGO-nZVI (manuscript under review). We also developed photocatalytic rGO-TiO2 nanohybrid and evaluated its efficacy and extent to which it could remove/degrade multiple PFAS, including PFOS, PFOA, GenX, and 6:2 FTS under UV irradiation. **Ng Lab** (Trainee: Melissa Marciesky) We have performed computational studies using density functional theory (DFT) in Gaussian 16 and calculated the bond dissociation energies (BDEs) of two current-use PFAS: perfluorobutanoic acid (PFBA) and perfluorobutanesulfonic acid (PFBS). We then created multiple PFAS-metal complexes in both gas and water phases and confirmed the lowest-energy conformations using multiple DFT methods and the MP2/Aug-cc-PVTZ level of theory. We then calculated homolytic and heterolytic BDEs for the carbon-fluorine and carbon-carbon bonds in PFBA and PFBS with a variety of metal ions, including Mg(II), Ag(II), Fe(II)/(III), Cu(II), and V(V).

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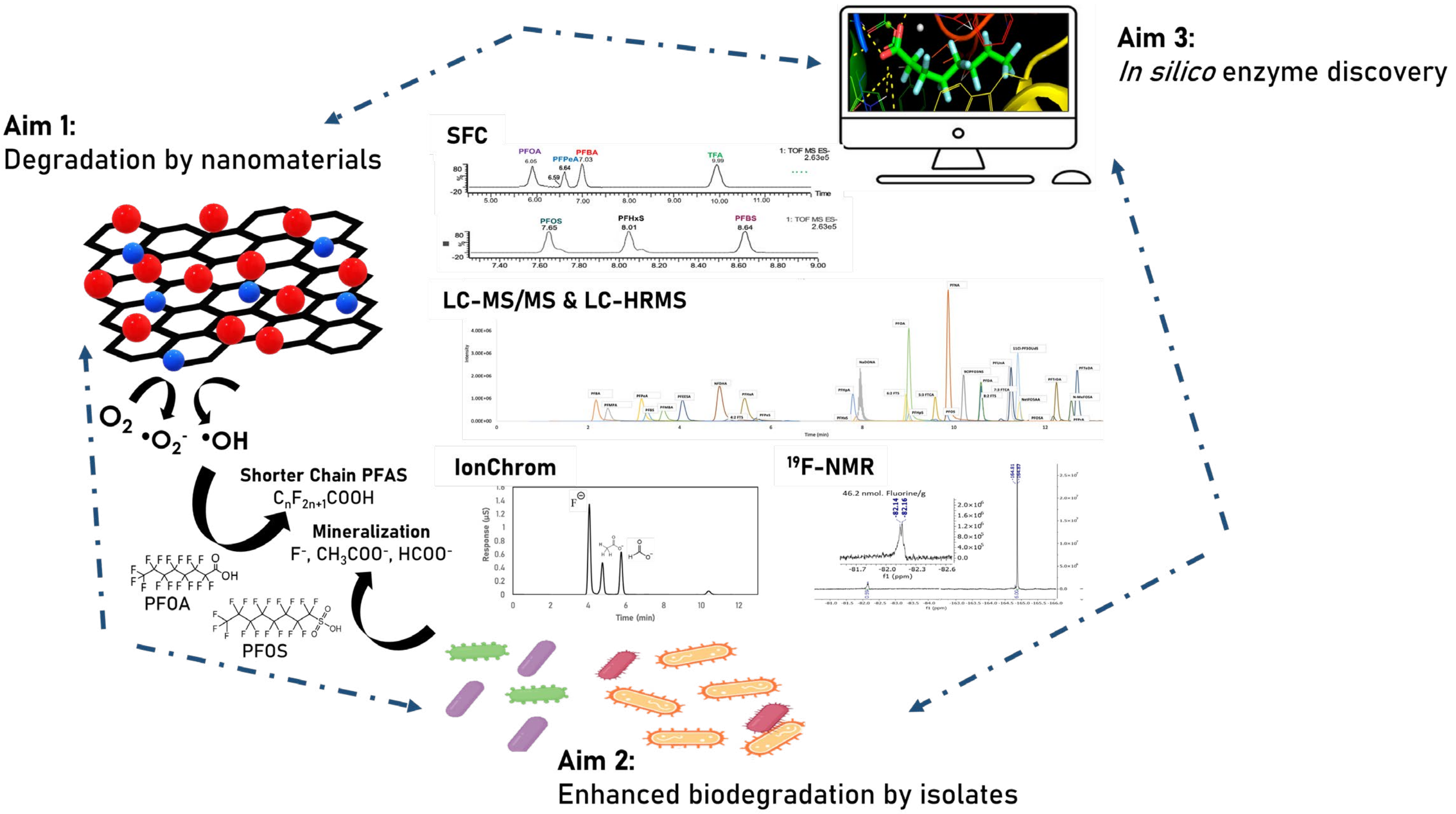

Aim 1:
Degradation by nanomaterials
Aim 2:
Enhanced biodegradation by isolates
Aim 3:
In silico enzyme discovery
SFC
LC-MS/MS & LC-HRMS
IonChrom
19F-NMR
Shorter Chain PFAS
CnF2n+1COOH
Mineralization
F-, CH3COO-, HCOO-
PFOA
PFOS
O2 •O2- •OH