Advanced Materials and Technologies for Treatment of Emerging Contaminant PFAS

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Nirupam Aich (Niru) - Background

BSc in Chemical Engineering
Bangladesh University of Engineering and Technology (BUET)

MS in Environmental Engineering
University of South Carolina

PhD in Environmental Engineering
University of Texas at Austin
Austin, TX

Assistant Professor (2016-2022)
University at Buffalo (SUNY)

Associate Professor, 2023-Present
University of Nebraska - Lincoln

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Ph.D. (Current)


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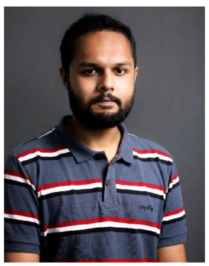
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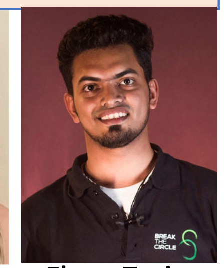
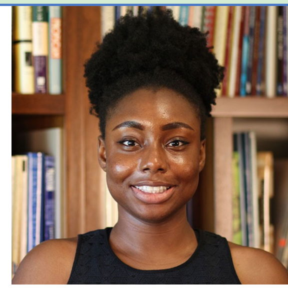

Ehsan Tanim

Undergrad Researchers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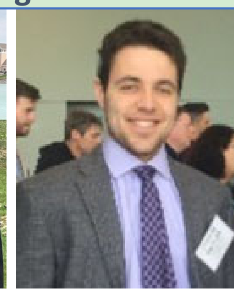
Mourin Jarin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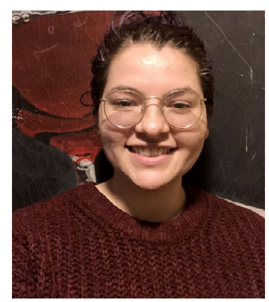
Mollika Urmi


Dao Sysouvanh


Anusha Gupta


Lillian Baker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Collaborators

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- Dr. Rajib Saha (UNL CBE)
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- Dr. Diana Aga (UB Chemistry)
- Dr. Chi Zhou (UB Industrial Engg)
- Dr. Haiqing Lin (UB Chem. Engg)
- Dr. Toufiq Reza (Florida Tech)
- Dr. Isabel Escobar (U Kentucky)
- Dr. Olga Tsyusko (U Kentucky)
- Dr. Tara Sabo-Attwood (U Florida)
- Dr. Carla Ng (U Pittsburgh)
- Dr. Mario Reidt (U Texas Dallas)
- Dr. Michelle Crimi (Clarkson U)
- Dr. Nafisa Islam (BUET, Dhaka, Bangladesh)
- Dr. Daesung Kyung (U Ulsan, Korea)
- Dr. Chandra Sekhar Tiwari (IIT Kharagpur)

NSF CAREER Award

NIH National Institute of Environmental Health Sciences
Superfund Research Program

USGS science for a changing world

USDA NIFA
United States Department of Agriculture
National Institute of Food and Agriculture

SERDP DOD ▪ EPA ▪ DOE

United States Environmental Protection Agency

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Department of Environmental Conservation • New York State •

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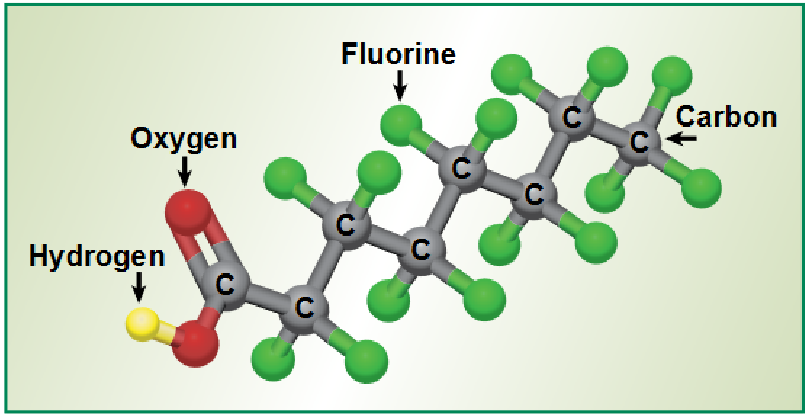
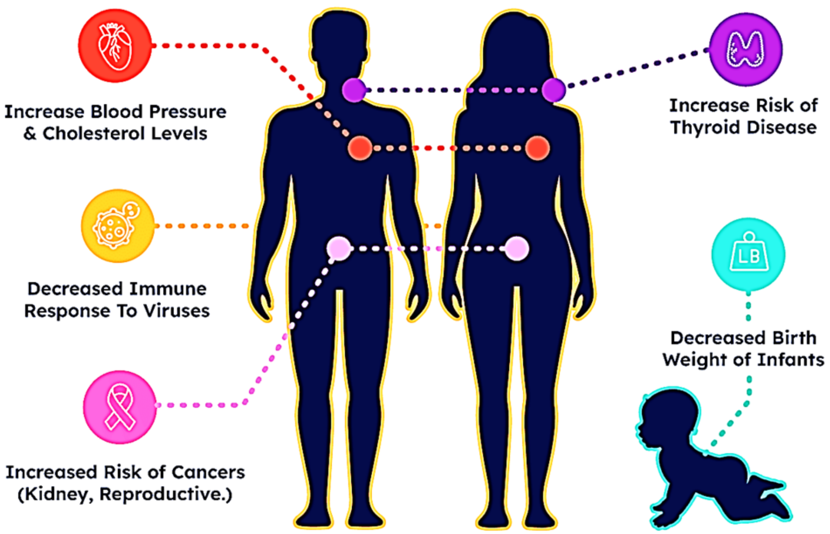
Per- and Polyfluoroalkyl Substances (PFAS)

- Anthropogenic *fluorinated organic compounds* commercially used in many industries since 1940's
- *Persistent*, *bio-accumulative* and *ubiquitous* in environment
- *Complex toxicity* profile including endocrine disruption, immunotoxicity, developmental disorder
- Despite restriction for production in western countries, ***>8000** PFASs* are prevalent in present global market
- ***C-F bond is very strong*** and difficult for breakdown





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Per- and Polyfluoroalkyl Substances (PFAS)

The New York Times

E.P.A. Says 'Forever Chemicals' Must Be Removed From Tap Water

The rule applies to a family of chemicals known as PFAS that are linked to serious health effects. Water utilities argue the cost is too great.

Share full article 166

The new measure will require utilities to reduce PFAS substances in drinking water to near-zero levels. Justin Sullivan/Getty Images

By Lisa Friedman

April 10, 2024

EPA United States Environmental Protection Agency

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Safe Drinking Water Act

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Per- and Polyfluoroalkyl Substances (PFAS)

Final PFAS National Primary Drinking Water Regulation

Compound	Final MCLG	Final MCL (enforceable levels)
PFOA	Zero	4.0 parts per trillion (ppt) (also expressed as ng/L)
PFOS	Zero	4.0 ppt
PFHxS	10 ppt	10 ppt
PFNA	10 ppt	10 ppt
HFPO-DA (commonly known as GenX Chemicals)	10 ppt	10 ppt
Mixtures containing two or more of PFHxS, PFNA, HFPO-DA, and PFBS	1 (unitless) Hazard Index	1 (unitless) Hazard Index

>200 Billion Capital Cost

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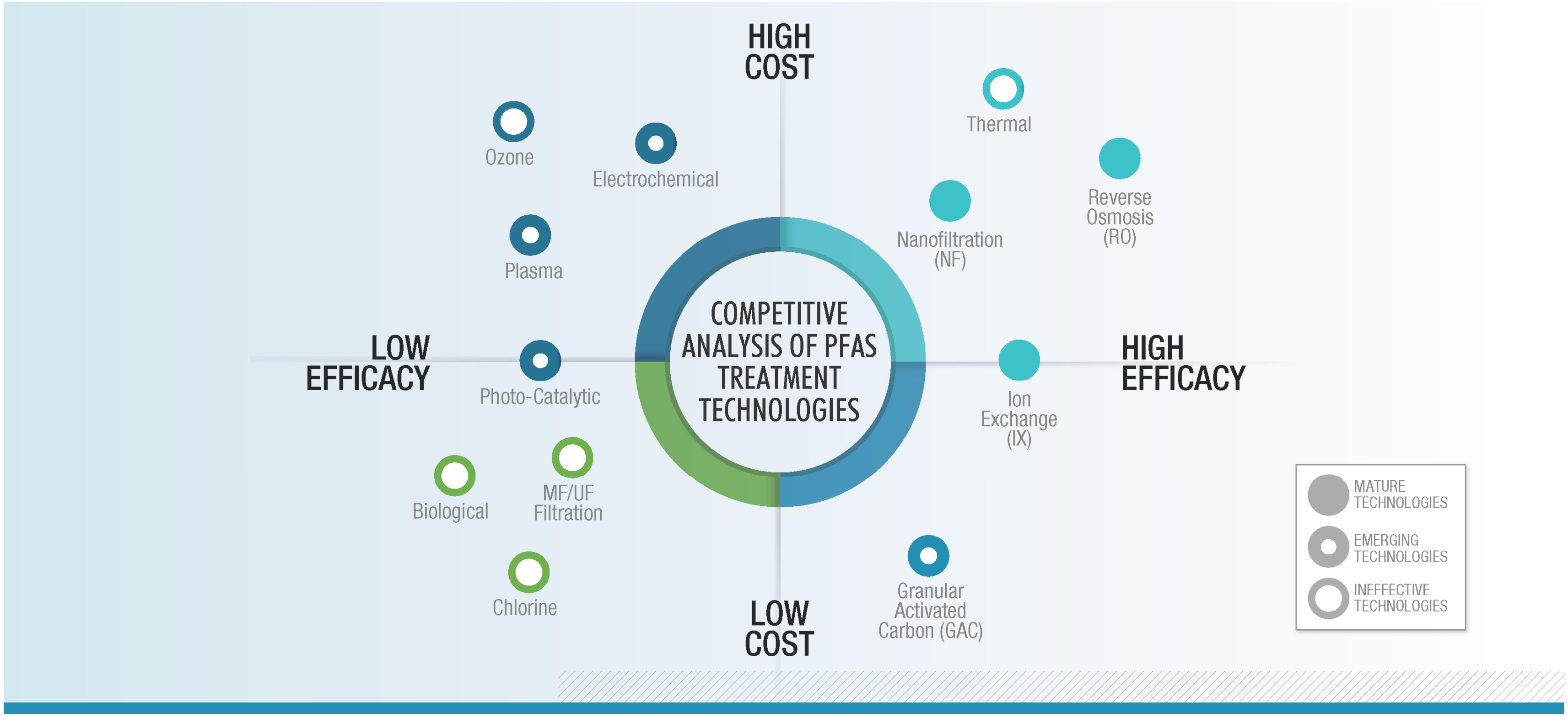
PFAS Treatment: Current Approaches & Future Considerations

- Separation vs Destruction is an issue; Consideration of cost vs efficacy
- Improvement of efficiency and developing advanced materials



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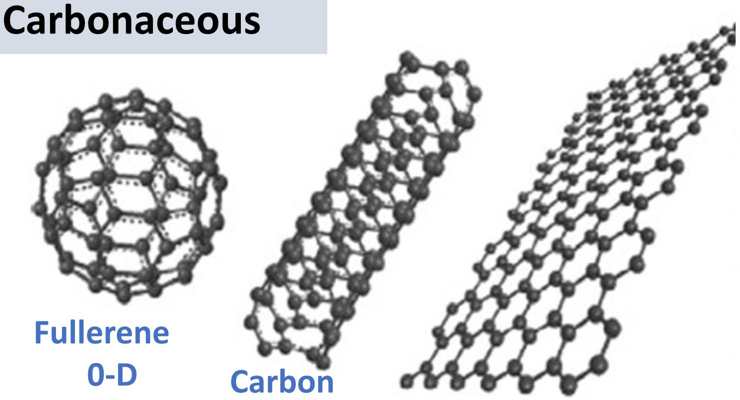
Perspective of Nano-Scale: 1 nm = 10^{-9} m

Nanotechnology: Material Manipulation in Nano-Scale

Nanomaterials: At least one-dimension is within 1-100 nm

Carbonaceous

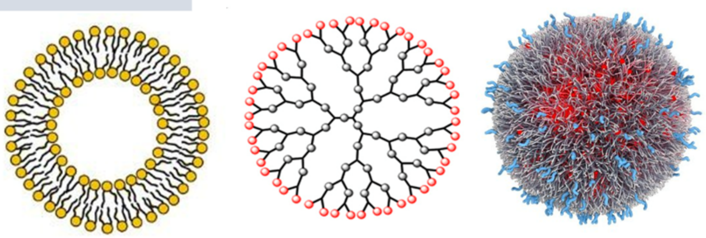


Fullerene
0-D

Carbon
Nanotube
1-D

Graphene
2-D

Organic

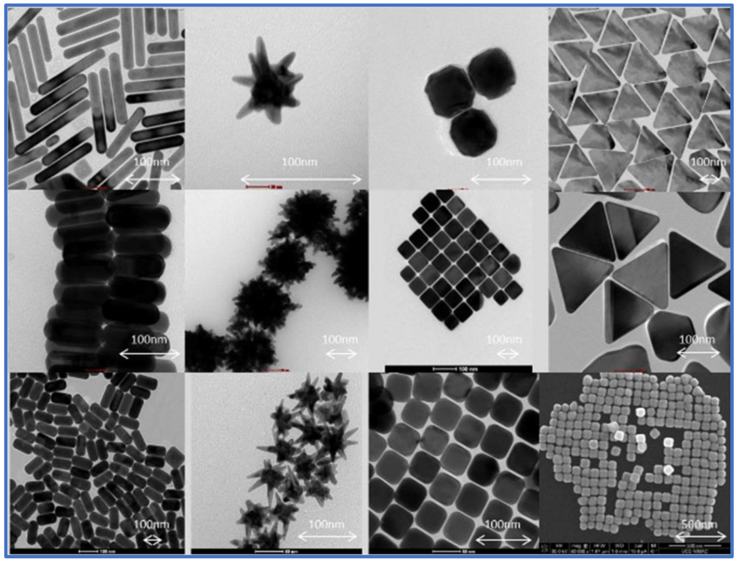


Liposome

Dendrimers

Polymeric Nanoparticle

Metallic: Iron, Gold, Silver, TiO_2, ZnO, MoS_2, Quantum Dots (CdSe), Pt



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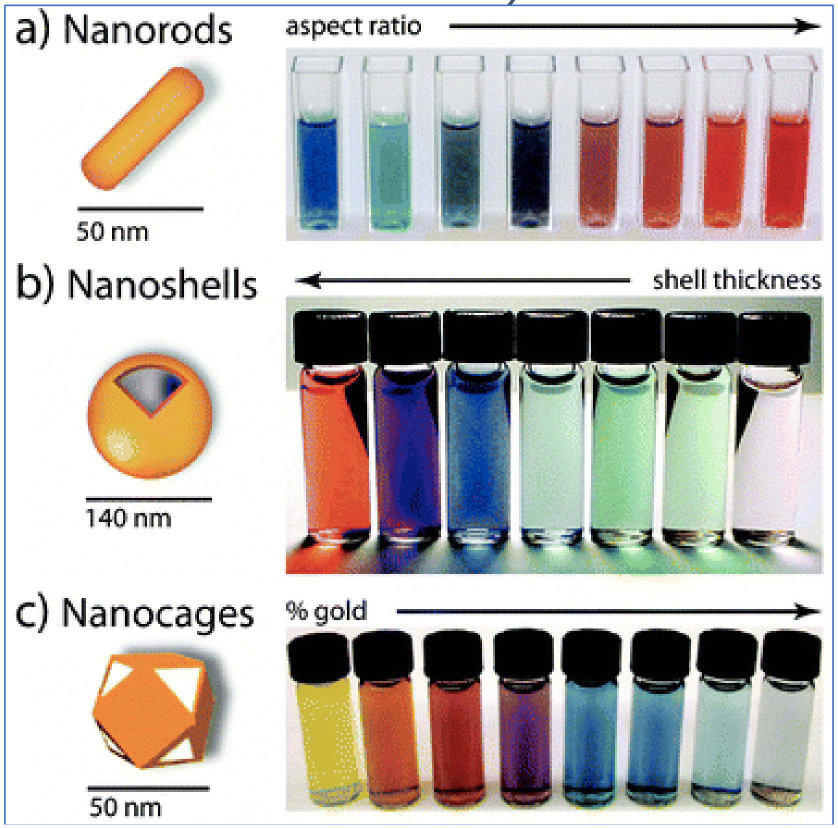
Advantage?

Nanoscale Properties are Remarkably Different than Bulk Properties

Properties change with *Size, Shape, Surface Chemistry*

*Bulk Gold: **Inert***

*Nano Gold: **Catalytic***



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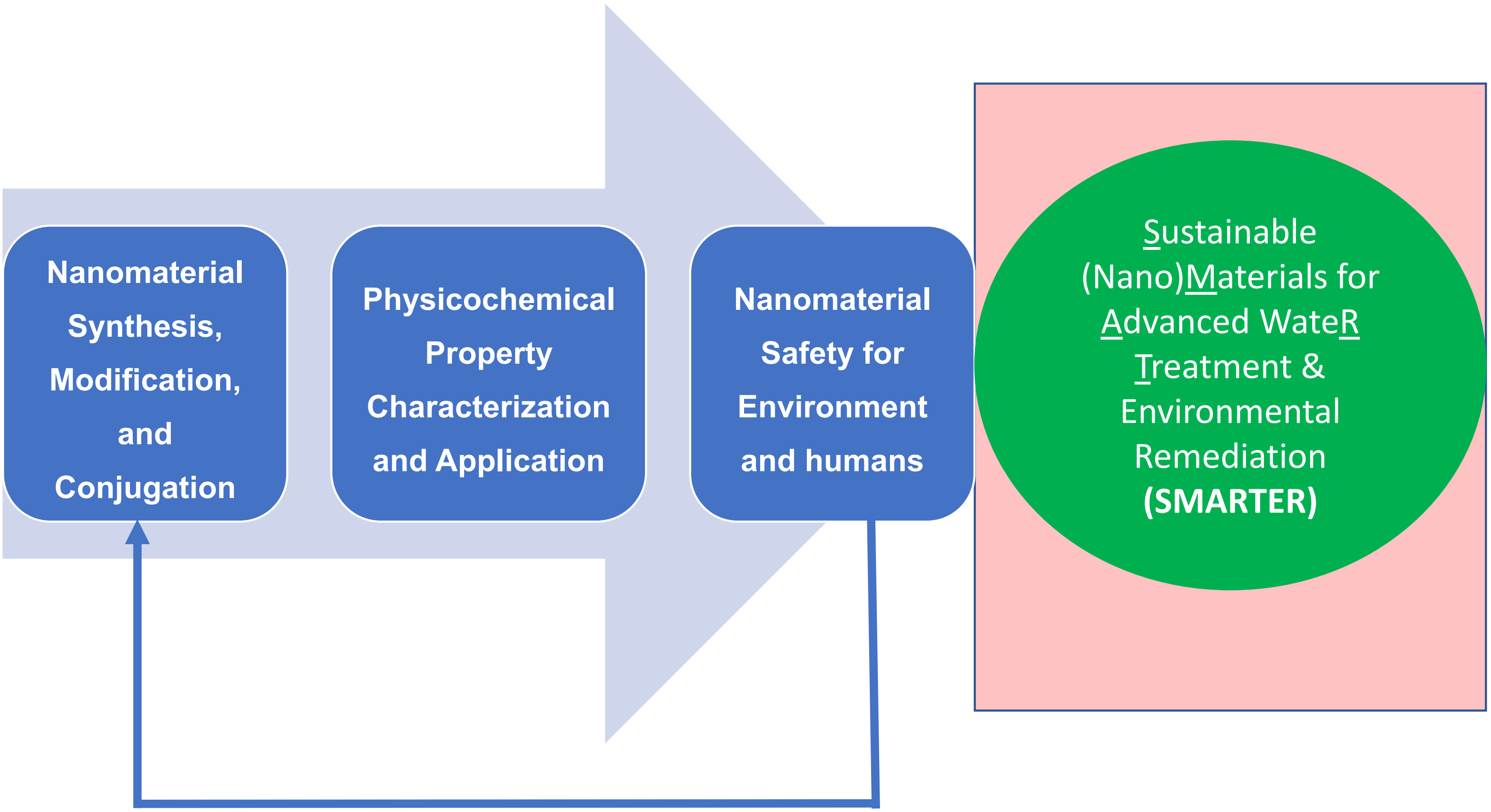

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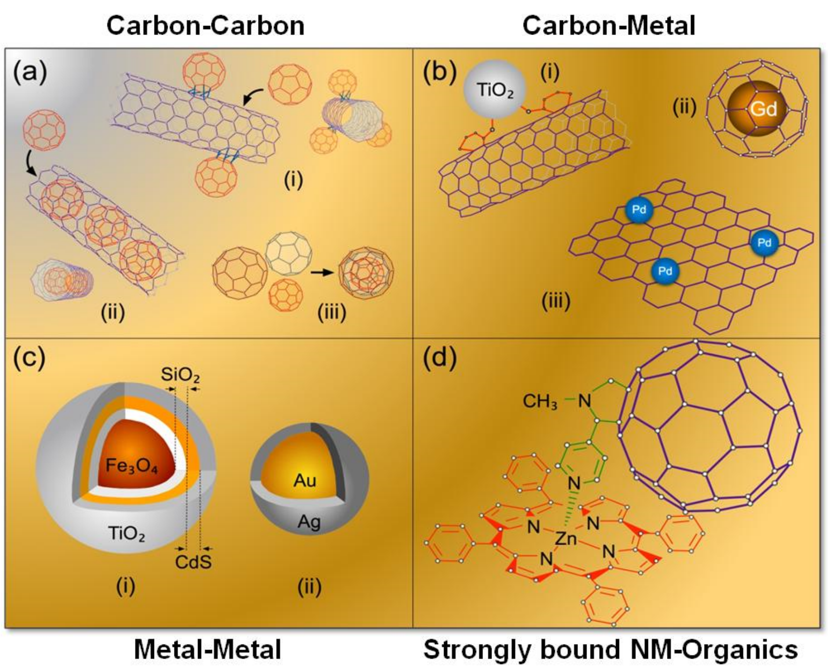
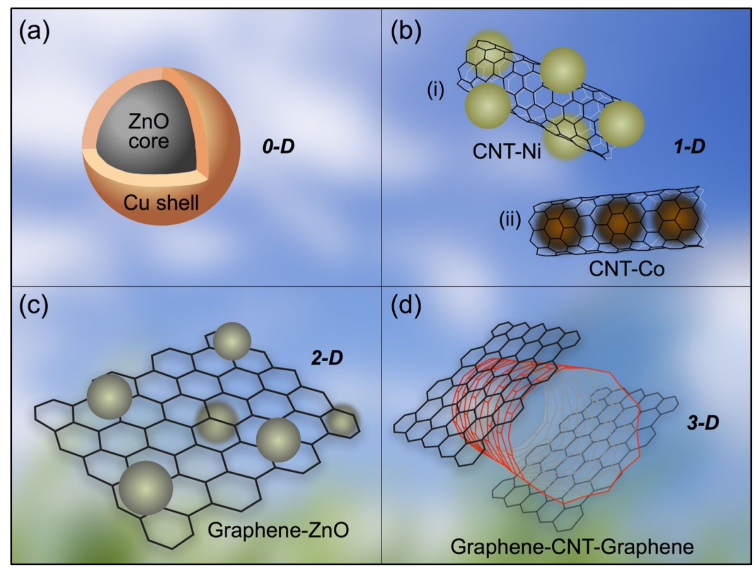
Nanohybrids: Definition & Types

- **Conjugate** multiple nanoscale materials of **unique** chemical origin
- Unique **property manifestation** – Different from **Parent Materials**
- **Enhanced-** or **Multi-functionality** – Purpose





Aich et al. Environ Chem 2014; Saleh and Aich et al. ES:Nano 2015, Nanomaterials 2015; Wang and Aich et al. ES&T 2019.

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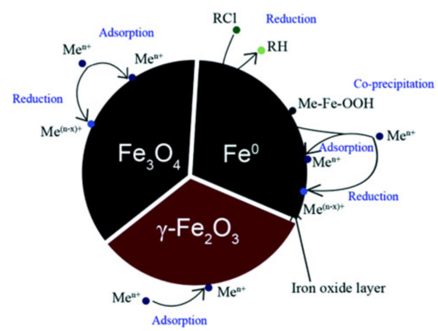
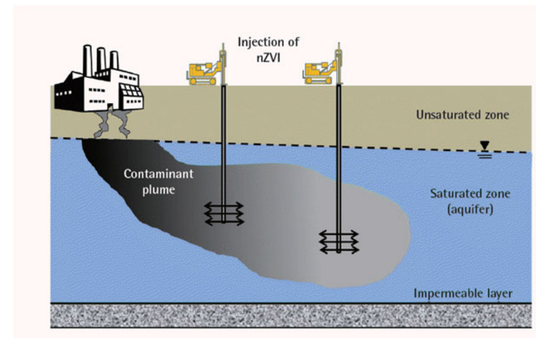
Graphene for Metal (Fe) Nanoparticle Support

- **Fe** NP is the most used engineered nanomaterial for soil and groundwater remediation
- **Nano zero valent iron (nZVI) is the most used form**
- Applied to ***77 pilot & field scale*** sites worldwide
- Industrial waste water and drinking water treatment

Fe NPs ***agglomerate*** due to van der Waals and magnetic attraction forces, ***decreasing reactivity and adsorption***





nZVi

1-D ***carbon nanotube (CNT)*** and 2-D ***reduced graphene oxide*** (rGO) are good solid supports

- Large ***accessible specific surface area***
- High ***electron mobility***
- Mechanical durability
- High ***contaminant adsorption***

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Aich et al. Sanford Publishing, 2018

Graphene for Metal (Fe) Nanoparticle Support

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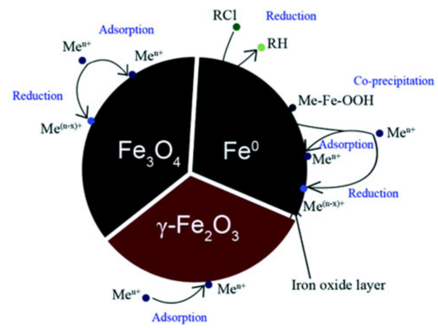

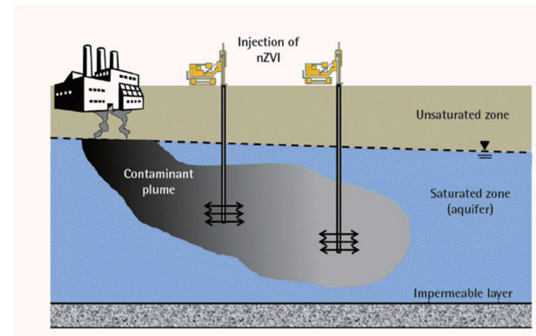

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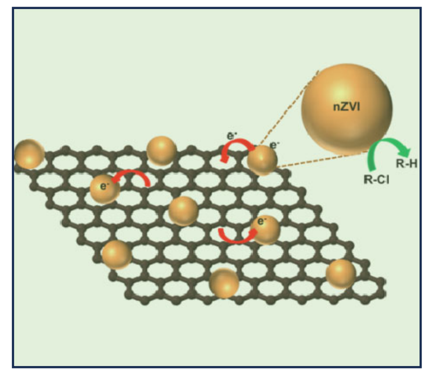
nZVi



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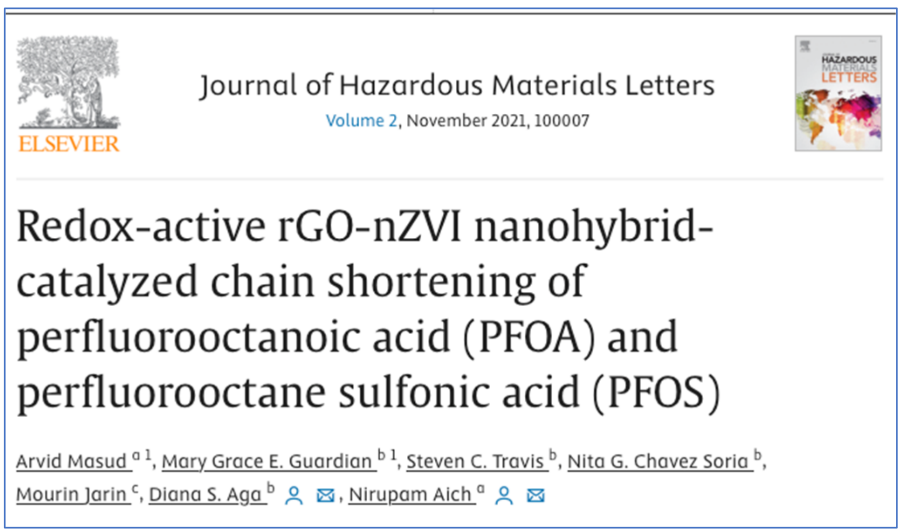
Aich et al. Sanford Publishing, 2018

PFAS Treatment by rGO-nZVI Nanohybrids (NHs)

Use **reduced graphene oxide-nanoscale zero-valent iron nanohybrid (rGO-nZVI NH)** to

- Treat PFASs with different head groups and chain-length
- At environmentally relevant concentration (sub-ppm)
- Exploiting both **adsorption** and **advanced oxidation process (AOP)**
- Determine if any **degradation** is happening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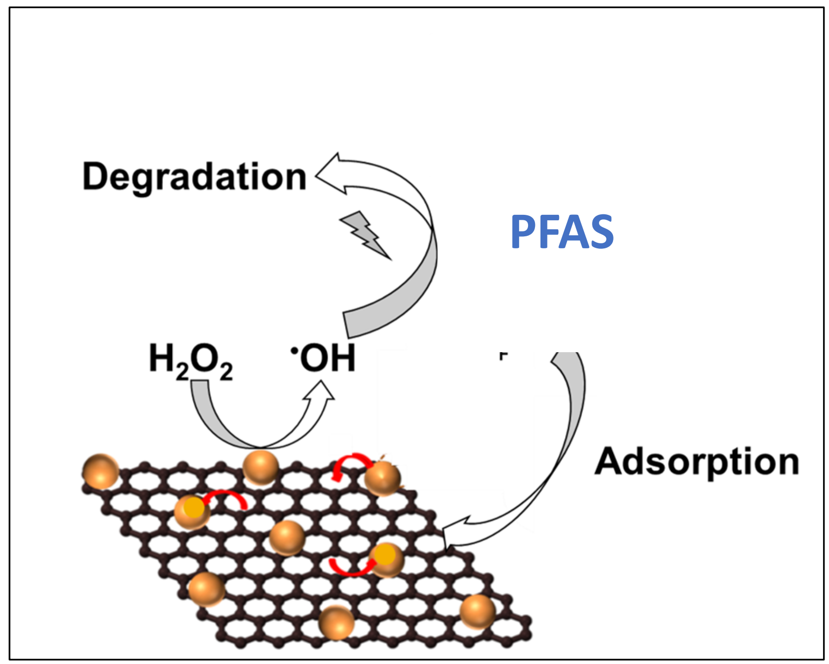
Journal of Hazardous Materials Letters
Volume 2, November 2021, 100007

Redox-active rGO-nZVI nanohybrid-catalyzed chain shortening of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS)

Arvid Masud [a,1], Mary Grace E. Guardian [b,1], Steven C. Travis [b], Nita G. Chavez Soria [b], Mourin Jarin [c], Diana S. Aga [b], Nirupam Aich [a]



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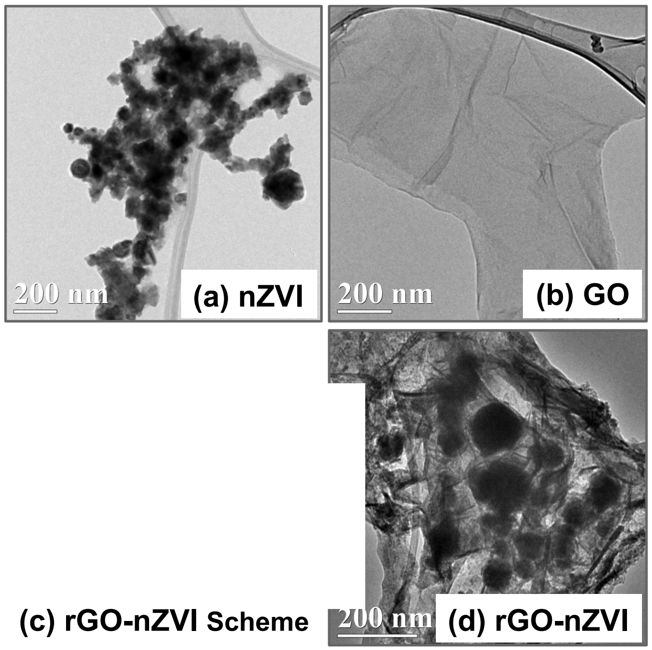
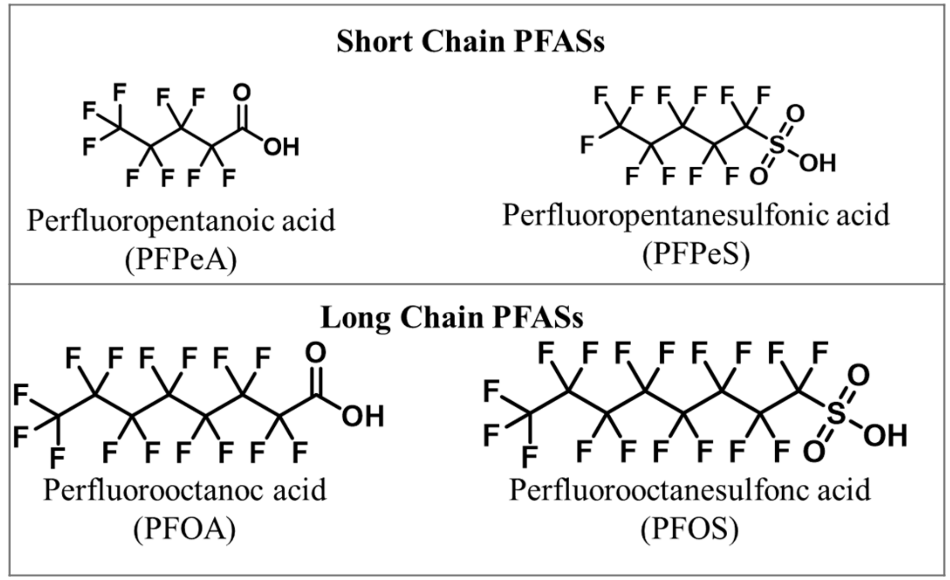
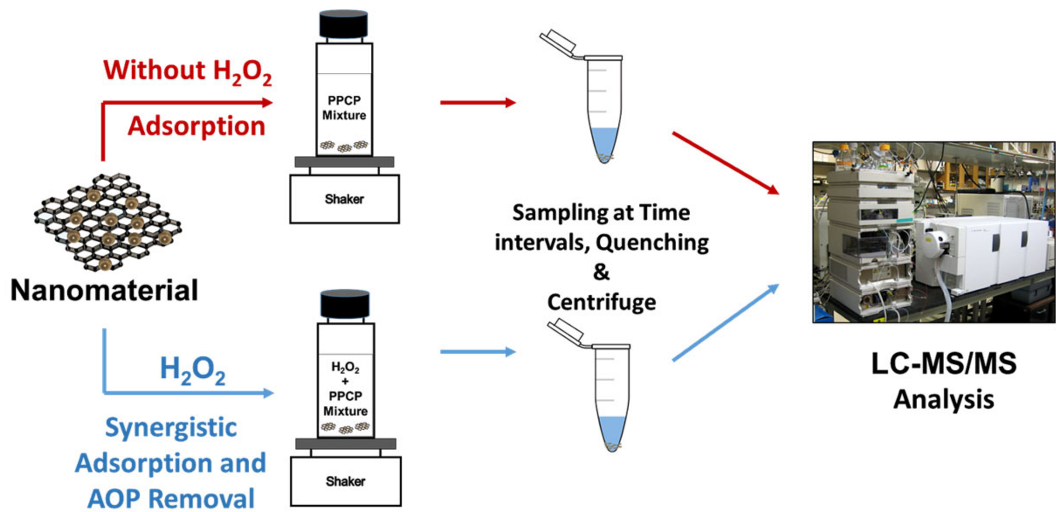
PFAS Treatment by rGO-nZVI NH

Masud et al. Journal of Hazardous Materials Letters, 2021



(c) rGO-nZVI Scheme





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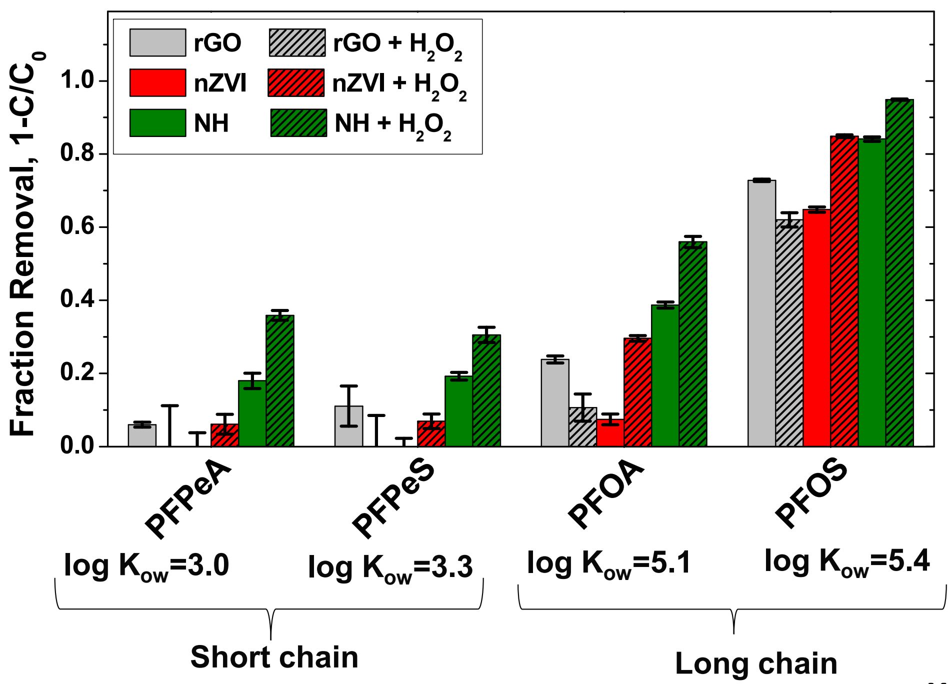
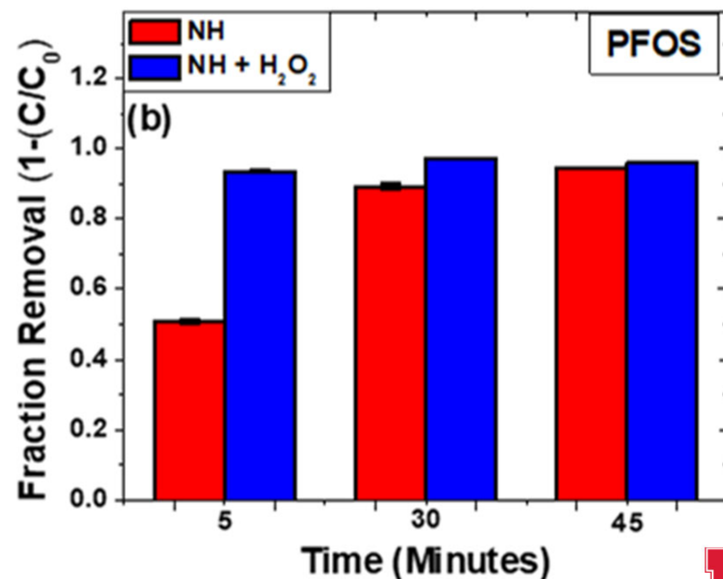
PFAS Treatment by rGO-nZVI NH: Effect of Hybridization & PFAS structure

- Long chain PFAS (PFOS and PFOA) are removed more than short chain ones (PFPeA and PFPeS): **Hydrophobicity (logk$_{ow}$)** dictated the removal efficiency
- rGO-nZVI NHs remove PFAS faster than rGO and nZVI
- AOP removes PFAS better and faster than adsorption





*Masud et al. Journal of Hazardous **Materials** Letters, 2021*

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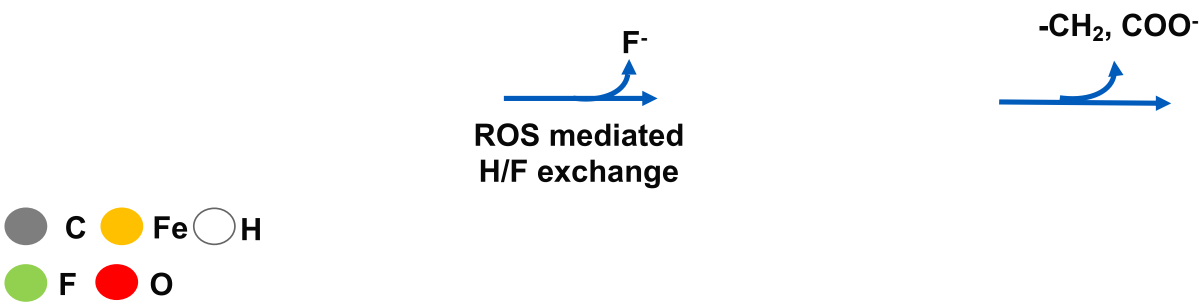
PFAS Treatment by rGO-nZVI NH: Evidence of PFAS Degradation

Is PFAS Degradation Happening?

- PFHxA, PFHpA, PFHxS, PFHpS, PFBS identified
- Non-target analyses using LC-HRMS identified two unique **PFAS-Fe complexes** than the tested PFASs
- $C_7H_4O_2F_{13}Fe$ and $C_6H_2OF_{13}Fe$



Masud et al. Journal of Hazardous Materials Letters, 2021

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PFAS Treatment by rGO-nZVI NH: More Questions

- Is this method suitable for wide range of water chemistry & PFAS?
- Can we understand their altered fate and transport?
- Are these applicable for groundwater remediation or water/wastewater treatment?
- Fate of PFAS transformation products: bio-degradation or photocatalysis?

National Institute of Environmental Health Sciences
Superfund Research Program

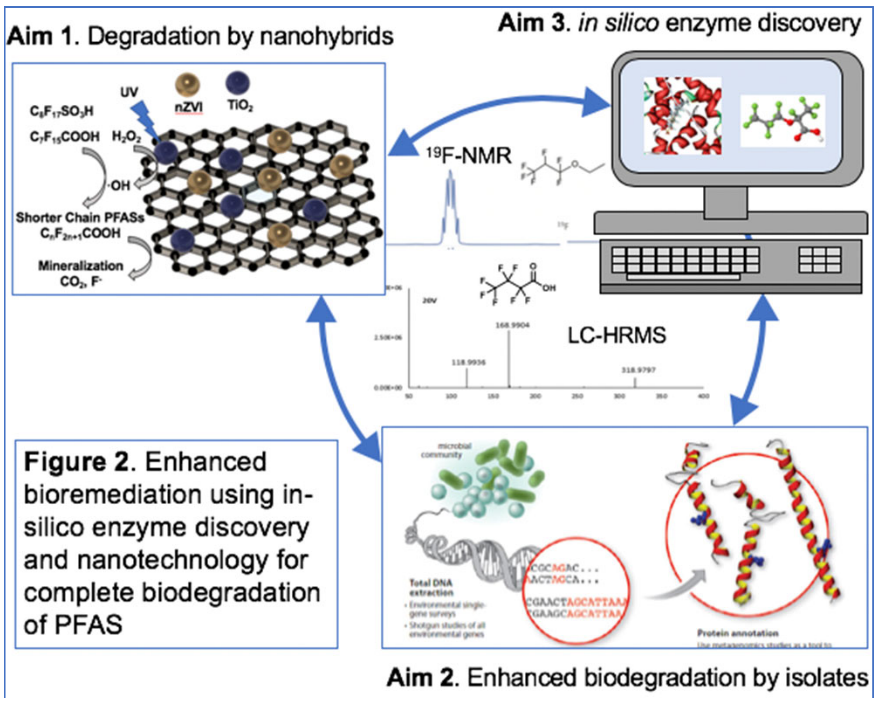
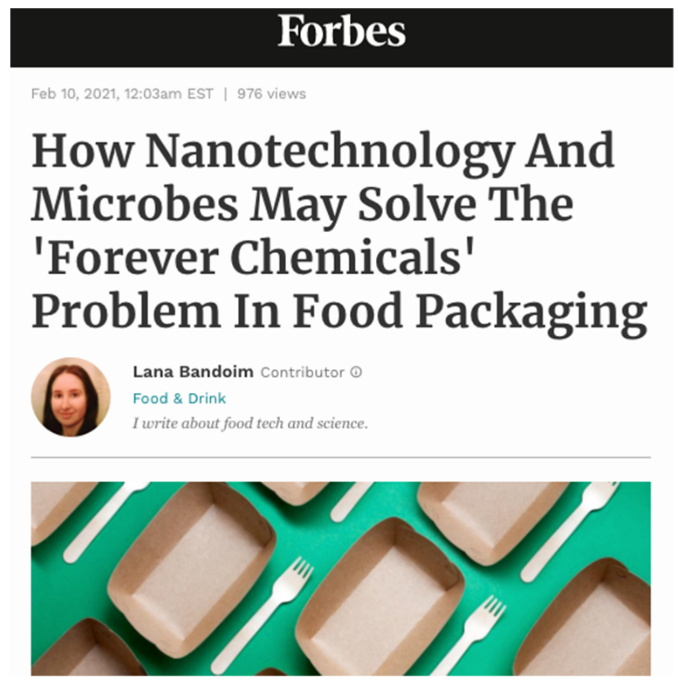


Figure 2. Enhanced bioremediation using in-silico enzyme discovery and nanotechnology for complete biodegradation of PFAS


Forbes

Feb 10, 2021, 12:03am EST | 976 views

How Nanotechnology And Microbes May Solve The 'Forever Chemicals' Problem In Food Packaging

Lana Bandoim Contributor
Food & Drink
I write about food tech and science.

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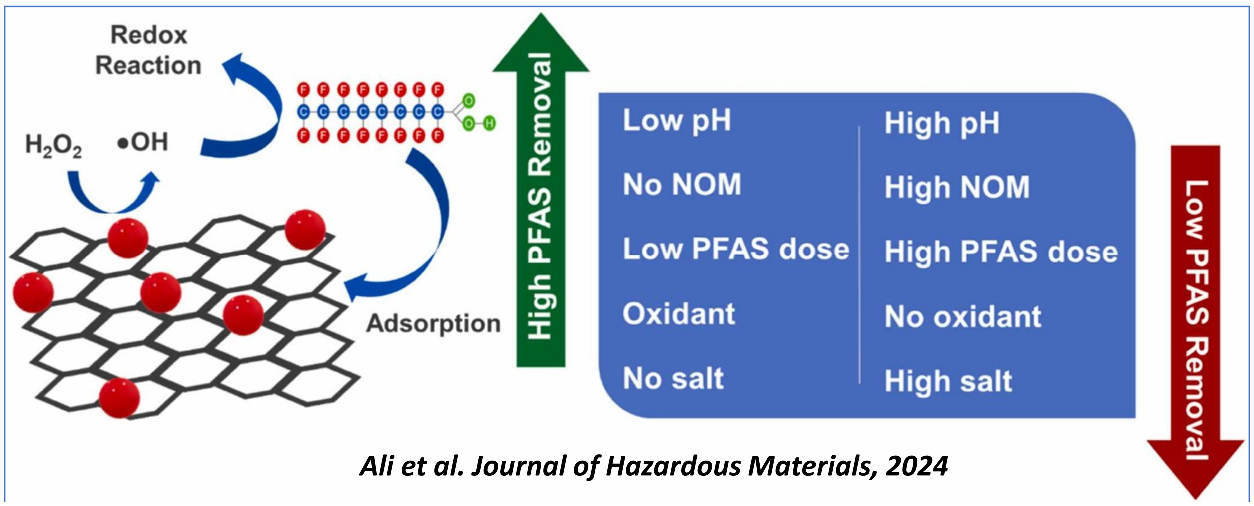
PFAS Treatment by rGO-nZVI NH: Water Chemistry Effects

- Proof-of-concept study had fixed water chemistry
- *pH=3, fixed PFAS conc. at 400 ppb, no salt or NOM*
- *But water chemistry changes along with oxidant and PFAS concentration can have a significant impacts*
    - *Materials surface chemistry*
    - *Reactivity of chemical species n water*
    - *Speciation of PFAS and other compounds*

ELSEVIER
Journal of Hazardous Materials
Volume 469, 5 May 2024, 133912

Influence of water chemistry and operating parameters on PFOS/PFOA removal using rGO-nZVI nanohybrid

Md. Arafat Ali [a], Utsav Thapa [b], Jonathan Antle [b], Ehsan Ul Hoque Tanim [a], John Michael Aguilar [b], Ian M. Bradley [a], Diana S. Aga [b], Nirupam Aich [a c]



Ali et al. Journal of Hazardous Materials, 2024

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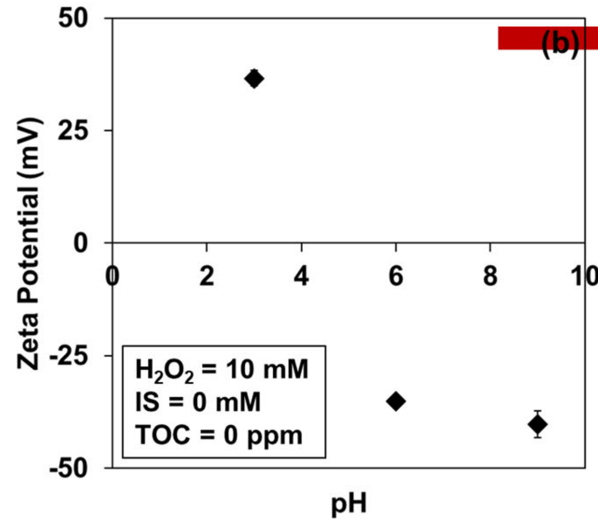
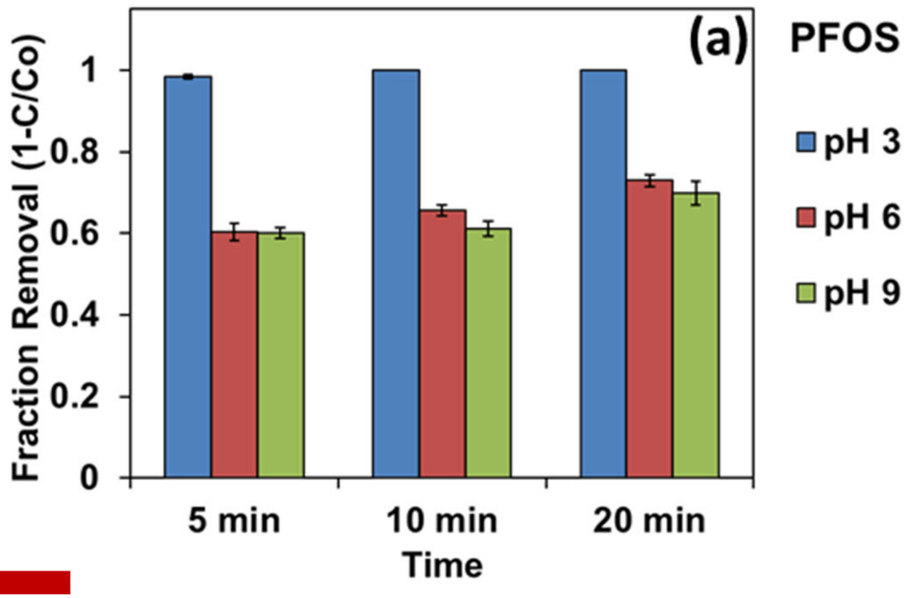
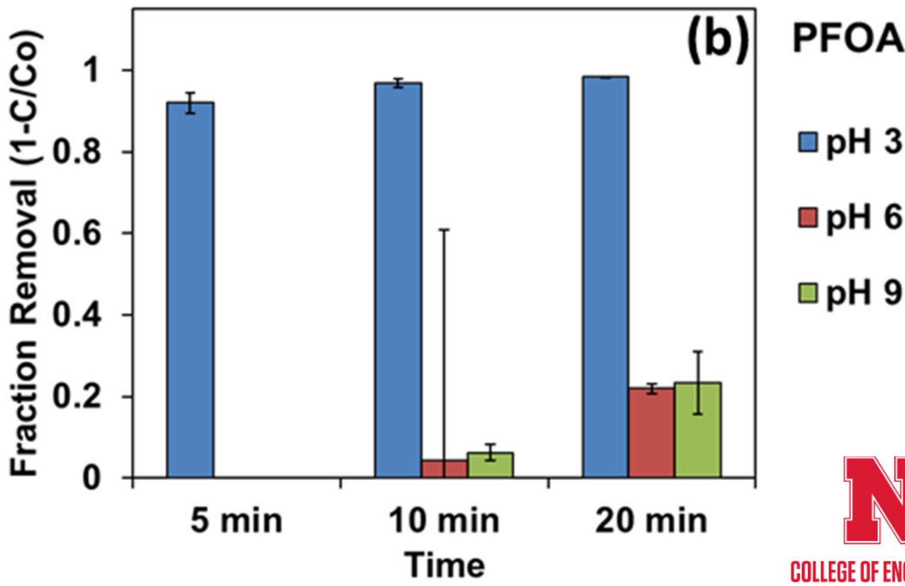
PFAS Treatment by rGO-nZVI NH: pH Change

- PFOA/PFOS removal decreased with increasing pH
- Optimal pH for Fenton reaction is 3
- At higher pH Fe^{2+} from Fe^{0} is compromised
- Surface charge (zeta potential) becomes negative with increased pH







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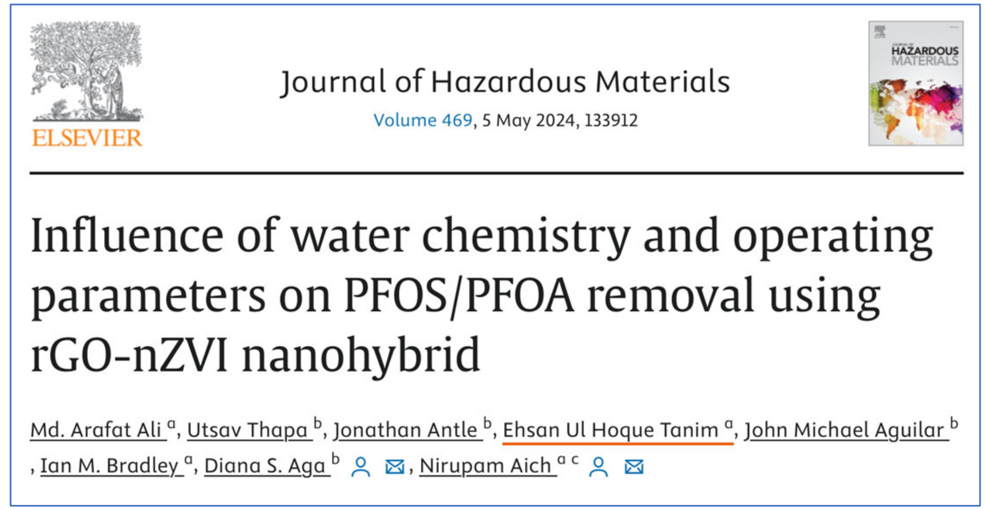
PFAS Treatment by rGO-nZVI NH: Water Chemistry Effects

- PFAS & H_2O_2 concentration, pH, and NOM had the major effects
- Ionic strength (salt amount) had less effects
- Optimization for different water systems will require these considerations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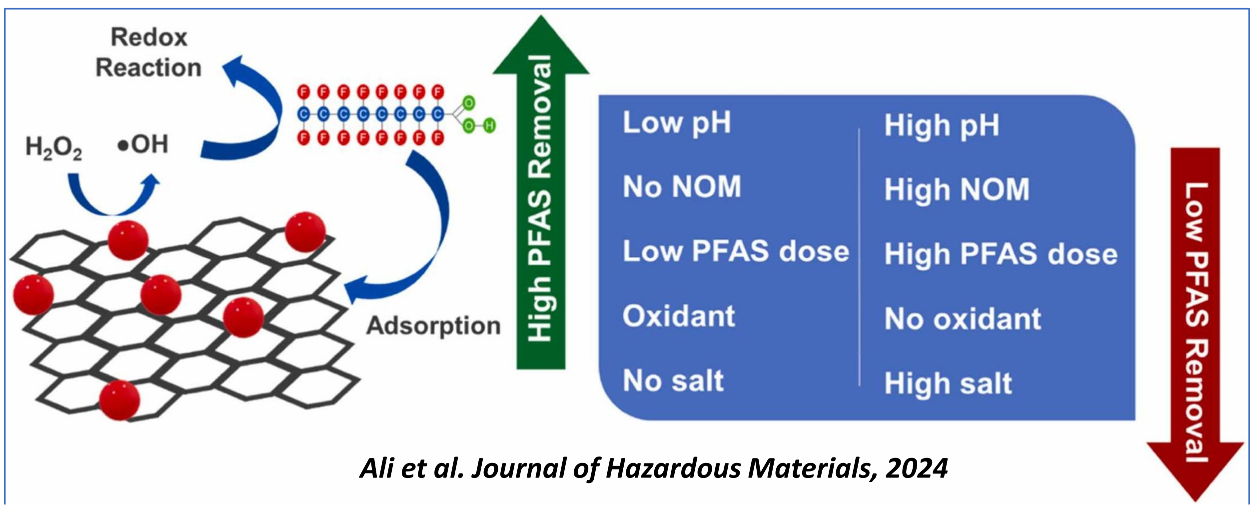

Ali et al. Journal of Hazardous Materials, 2024

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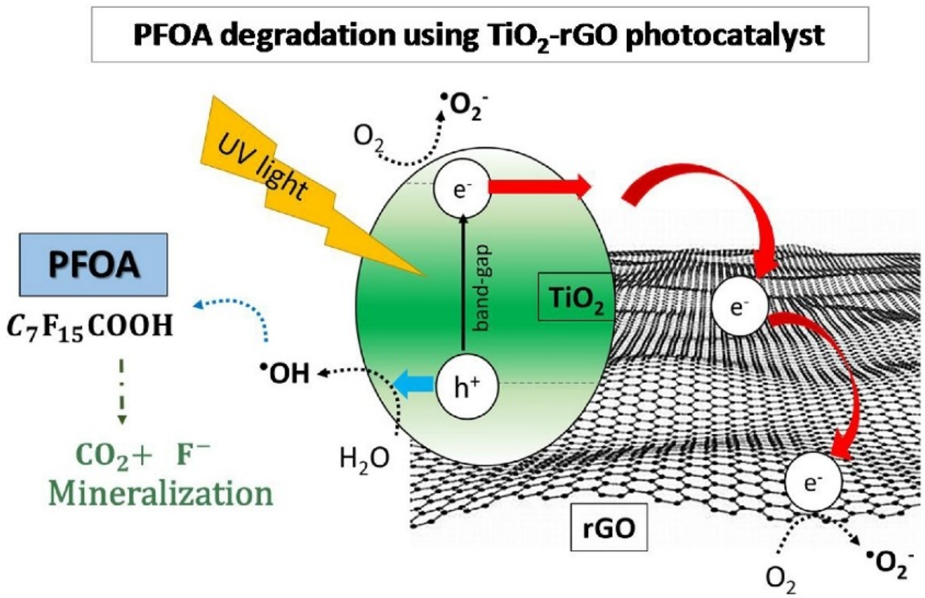
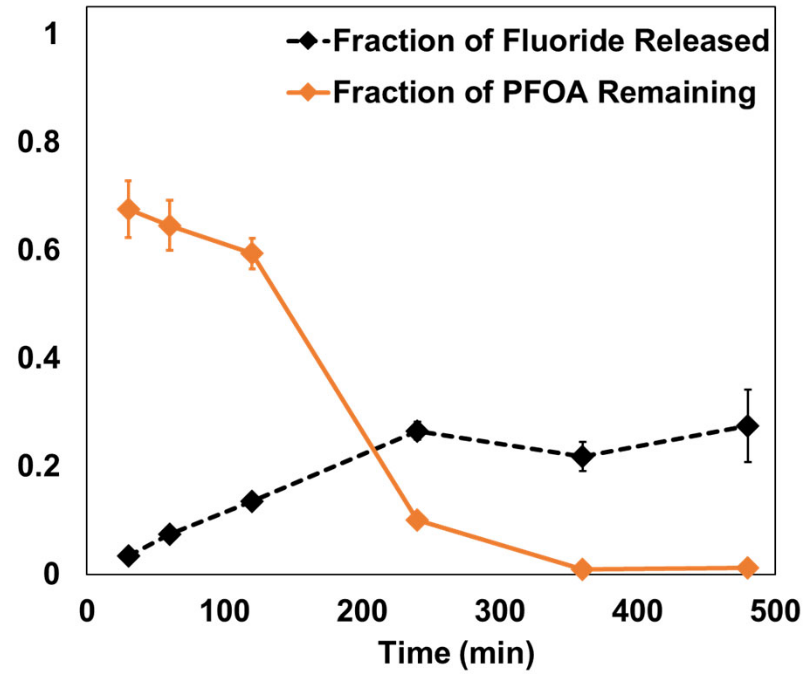
Nanomaterials for Photocatalysis: PFAS Removal

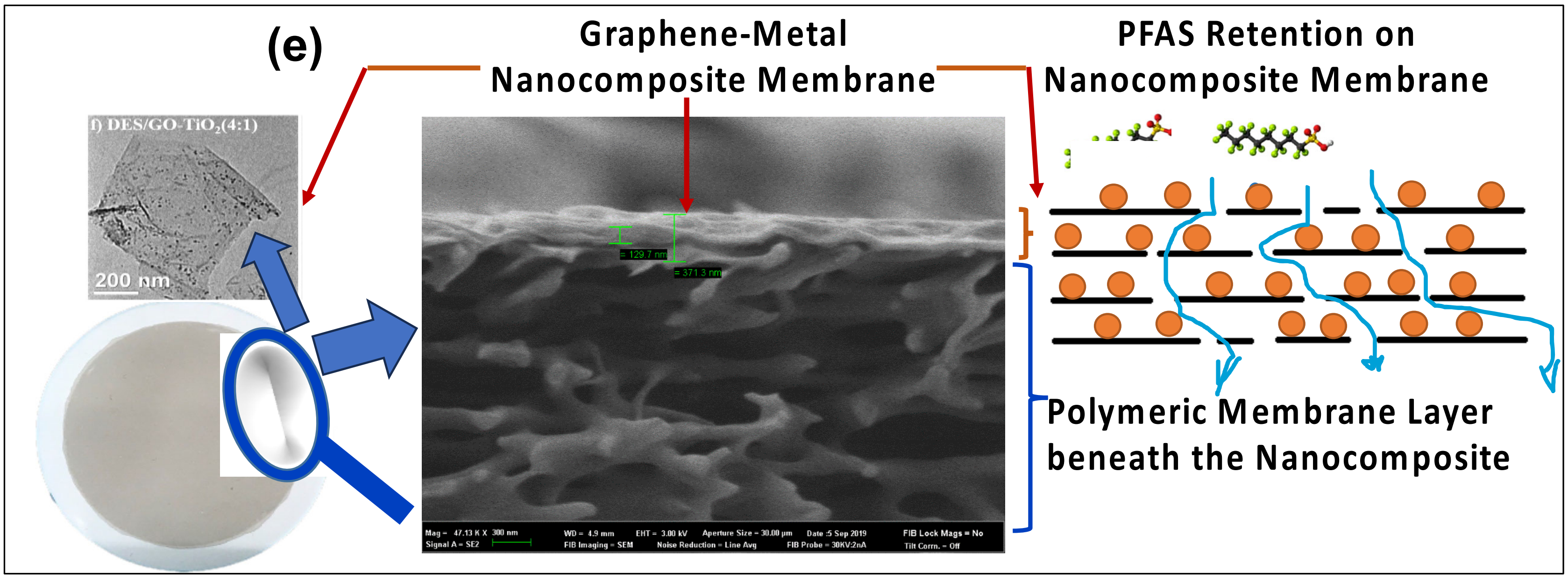
- Semiconductor nanomaterials generate reactive oxygen species under UV-Vis Irradiation (Sunlight)
- rGO-**TiO_2** can be used for the photocatalysis





Nanocomposite Membranes for PFAS Separation and Destruction

- Functionalizing graphene-metal nanocomposite membranes with **green solvents** to achieve superior membrane performance – high water flux and selectivity
- Control surface chemistry and interlayer spacing
- Selectivity for different PFAS



National Science Foundation

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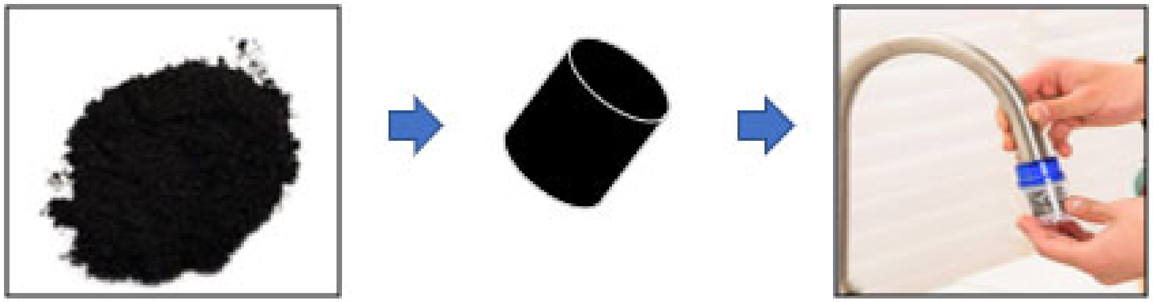
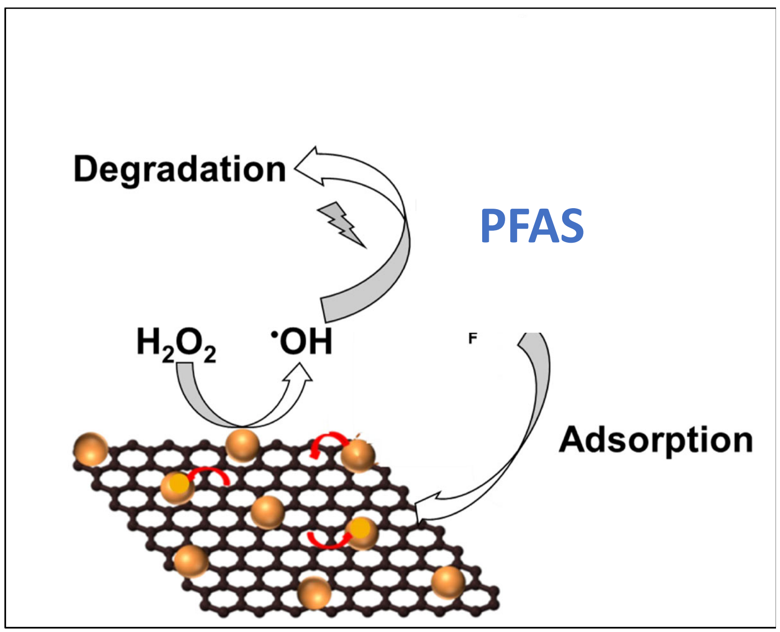
Mehrabi et al., Chemical Engineering Journal, 2021 & ., J Environmental Chemical Engineering, 2023

3D Printed Nanomaterials for PFAS Filters





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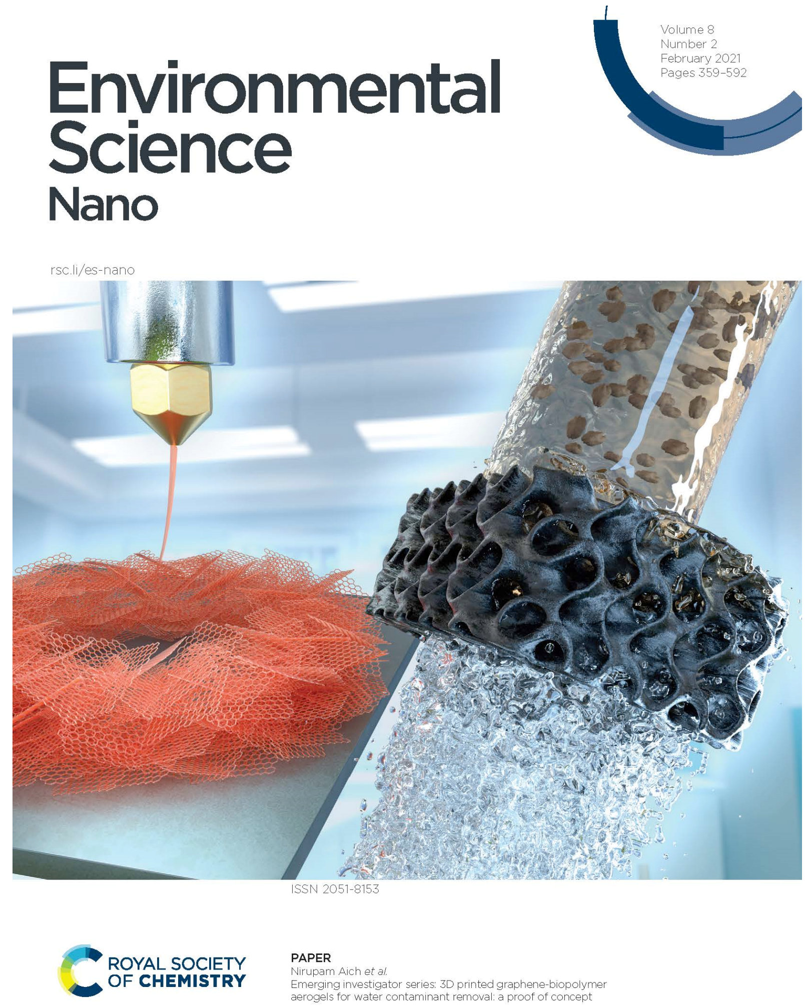
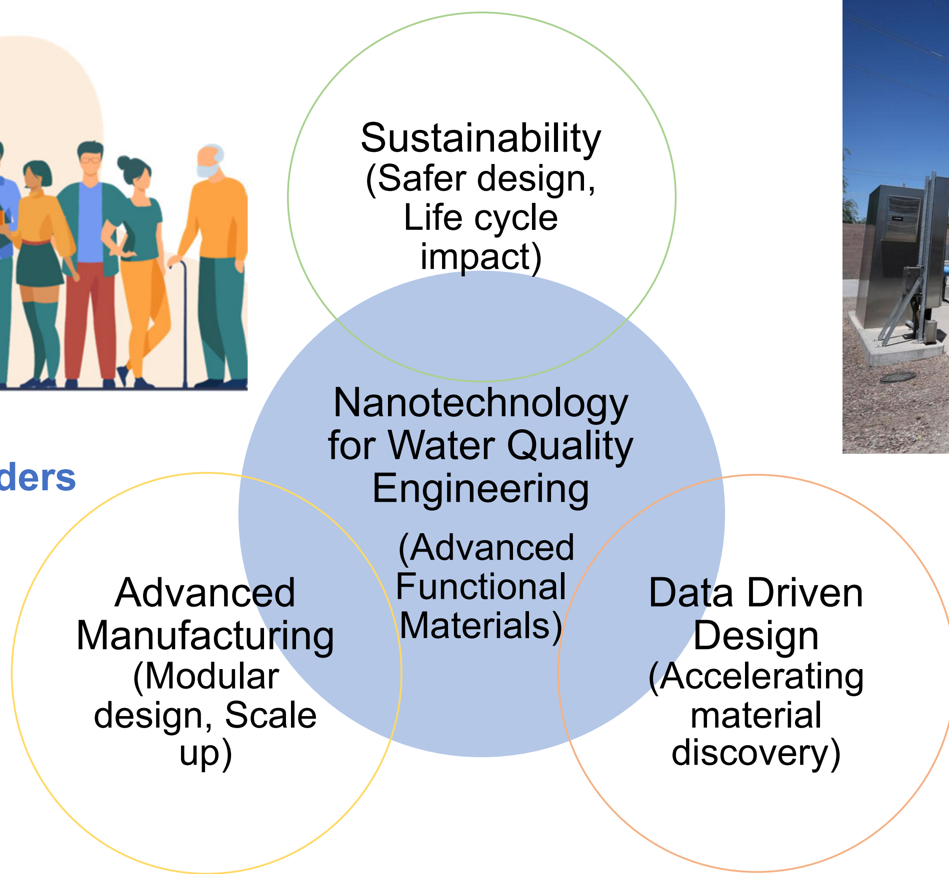


The SMARTER Future

Convergence of Nanotechnology, Sustainability, Additive/Advanced Manufacturing, and Data Science

Communities & Stakeholders



Industry/Utility Partners

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