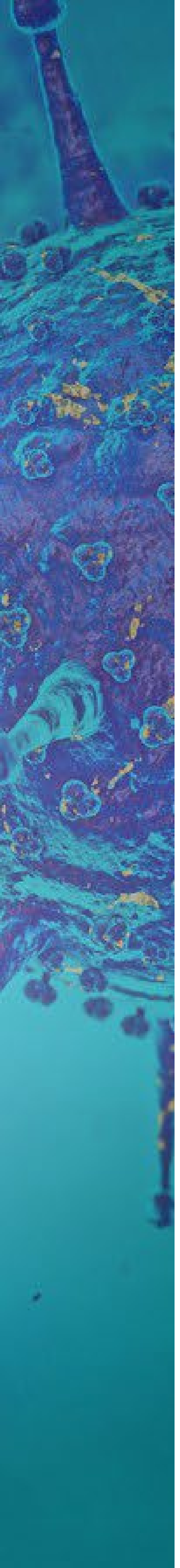

PFAS Remediation:

The Role of Engineered Nanoporous Materials

Dr. Radha K Motkuri
Sr. Principal Chemical Engineer/Scientist
Pacific Northwest National Laboratory
Richland, WA 99352, USA

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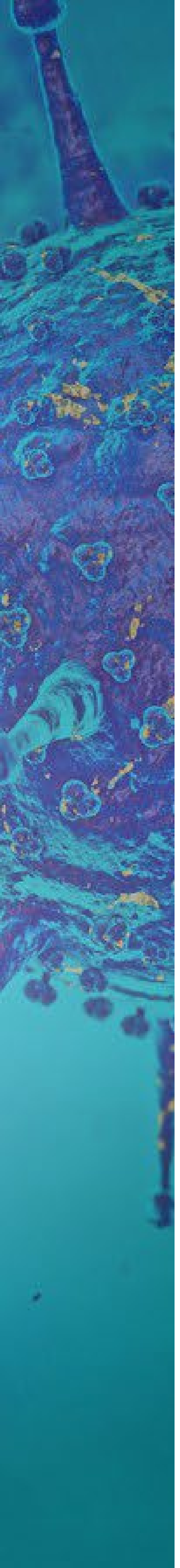


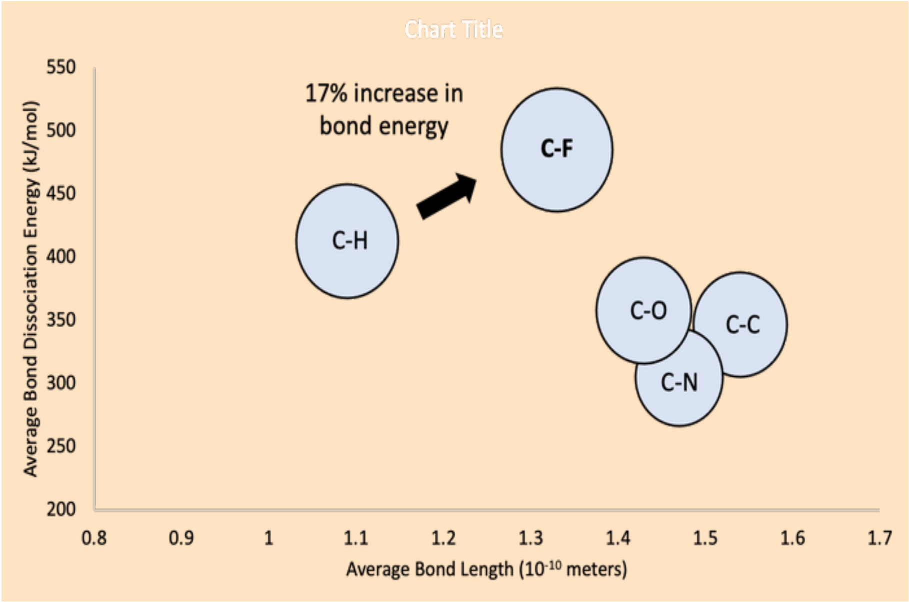
Per- and Polyfluoroalkyl Substances (PFAS)

The Problem:

Organofluorine chemistry: The electron density is concentrated around the fluorine, leaving the carbon relatively electron-poor. This introduces ionic character to the bond through partial charges (**$C^{\delta+}$—$F^{\delta-}$**). The partial charges on the fluorine and carbon are attractive, contributing to the unusual bond strength of the **carbon-fluorine** bond.

- C−H: 413 kJ/mol; C−F: 441 kJ/mol
- Each fluorine brings more stability

O'Hagan, D. *Chem. Soc. Rev.* **2008**, *37*, 308-319



- Unlocking ways to break the bond barrier
- Advancements are needed to find effective ways.

Per- and polyfluoroalkyl substances (PFAS), a group of 4,000+ environmentally stable and bio-persistent anthropogenic compounds found in firefighting foam and many other products

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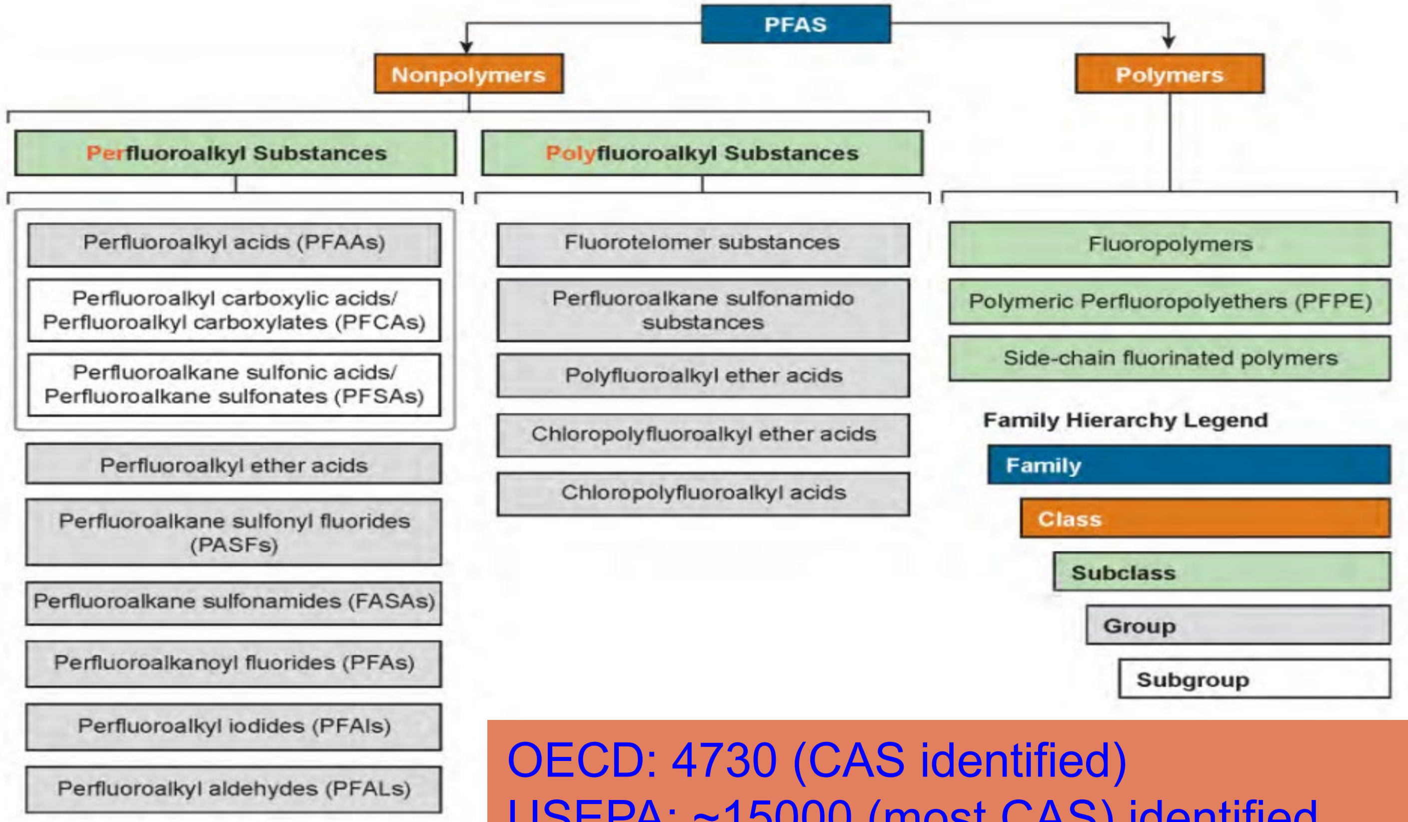
Per- and Polyfluoroalkyl Substances (PFAS)



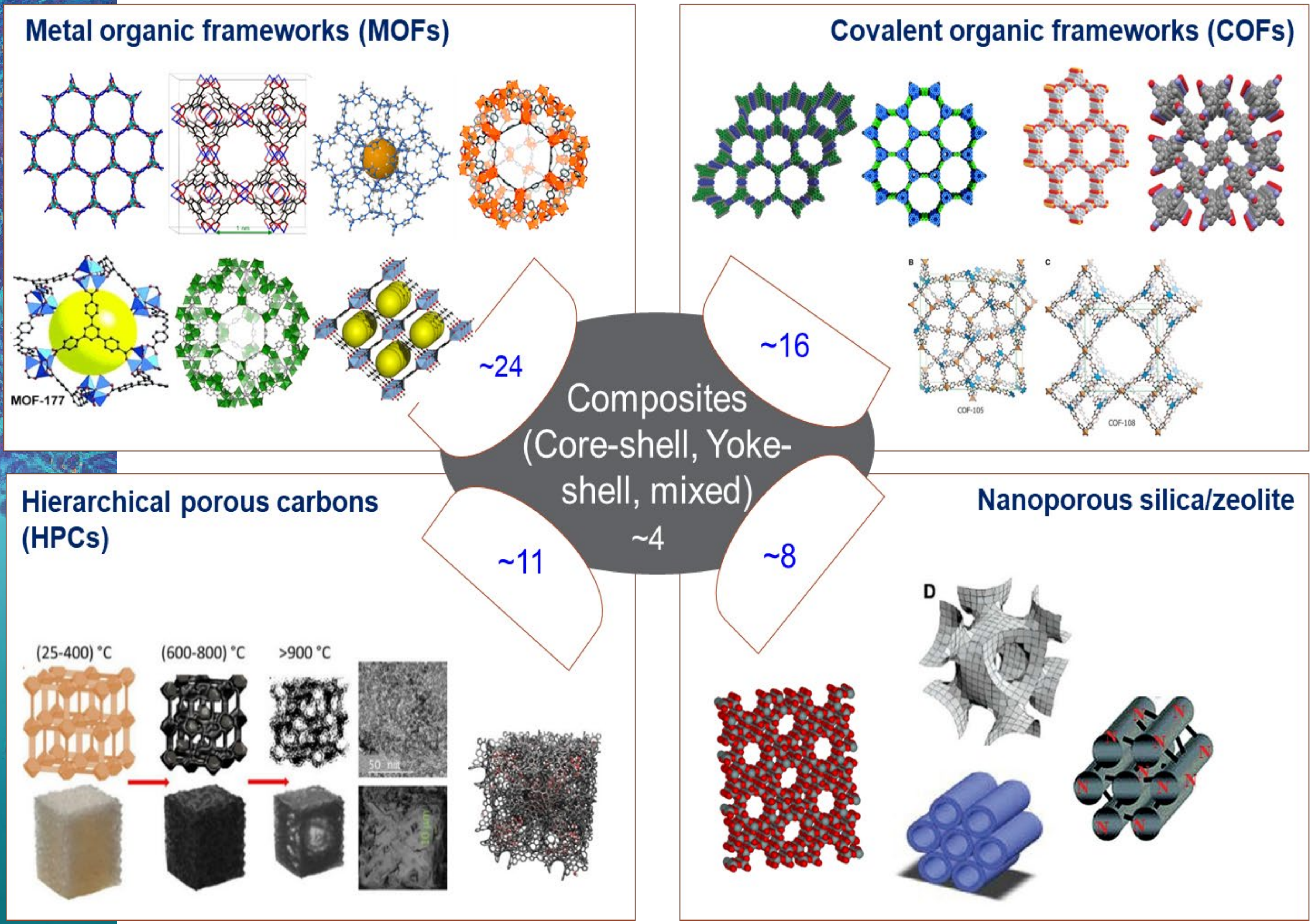
OECD: 4730 (CAS identified)
USEPA: ~15000 (most CAS) identified

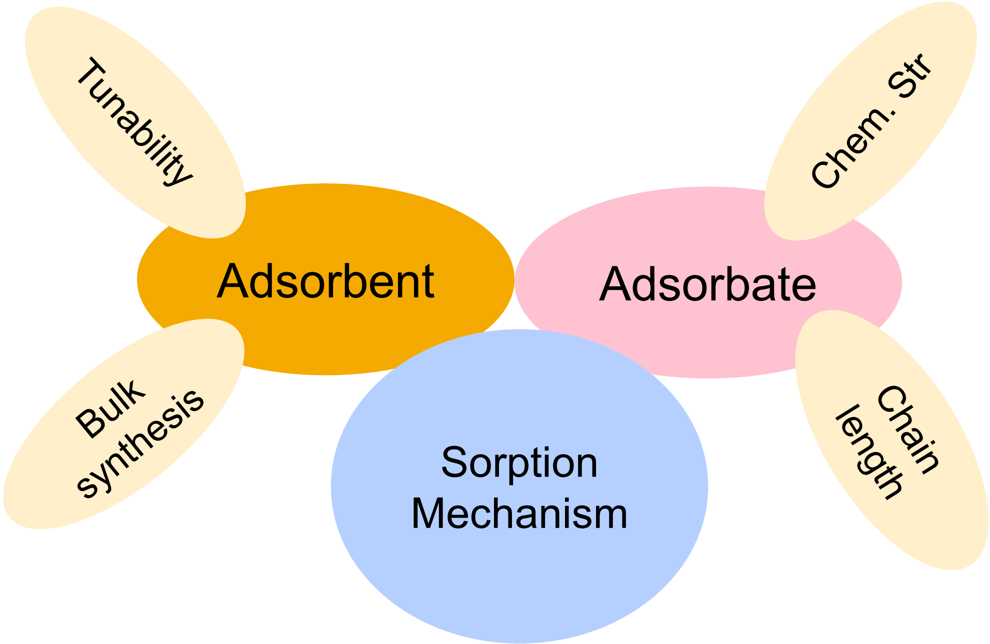
https://www.ewg.org/research/update-mapping-expanding-pfas-crisis

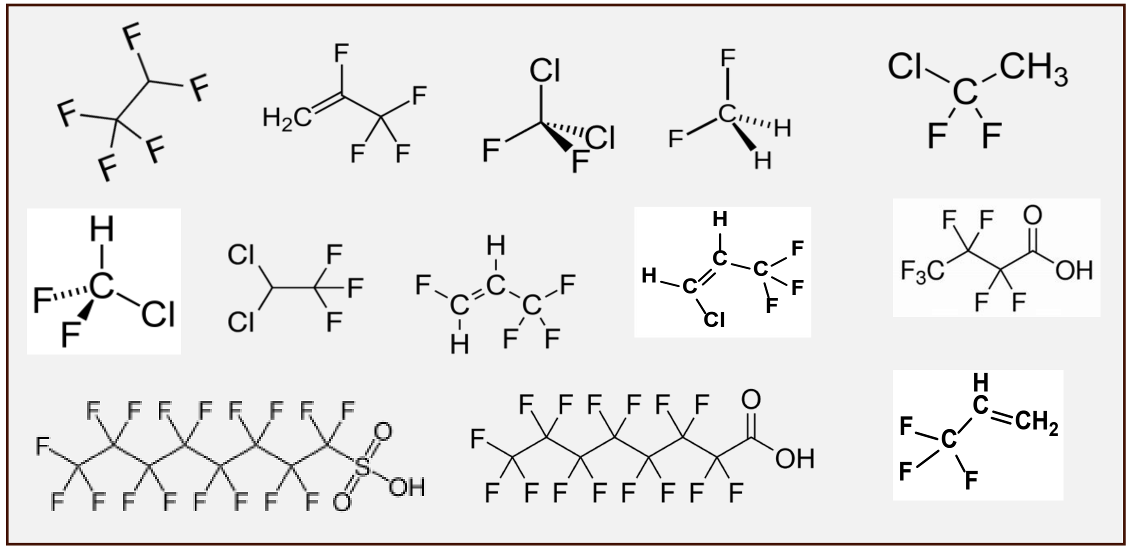
- Sorbent based approach is an efficient method for PFAS remediation
- A fundamental understanding of the guest PFAS and the host SORBENT is crucial for efficient remediation
- Development of Advanced Engineered Nanoporous Sorbents

PFAS Remediation Requirements

A unique database of nanoporous materials, including MOFs, COFs, zeolites, inorganic materials, and hierarchical porous carbon materials towards various fluorocarbons was developed

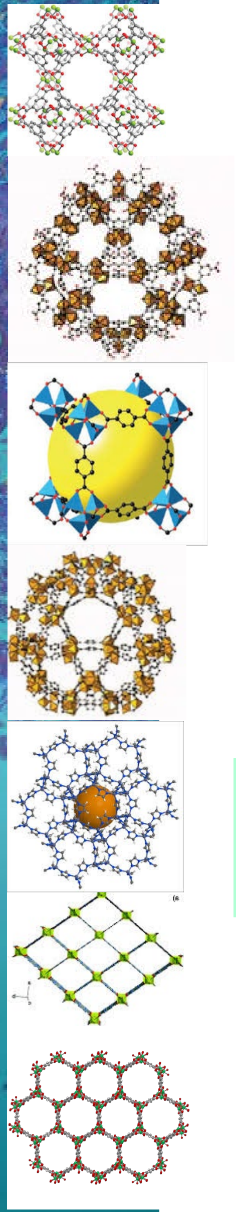


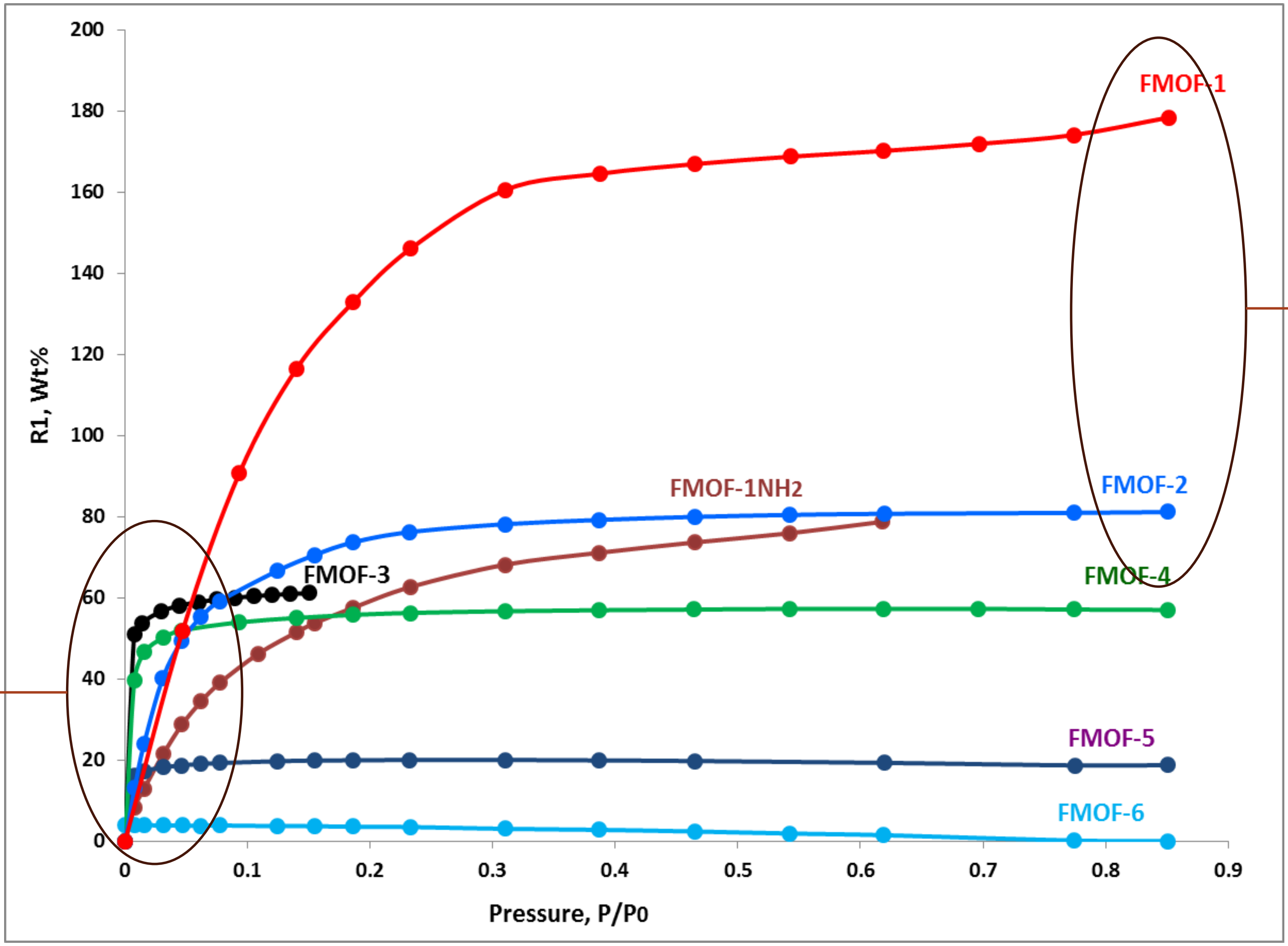




Fluorocarbon Adsorption in Advanced sorbents

A unique database of nanoporous materials including MOFs, COFs, zeolites, inorganic materials, and hierarchical porous carbon materials towards various fluorocarbons was developed

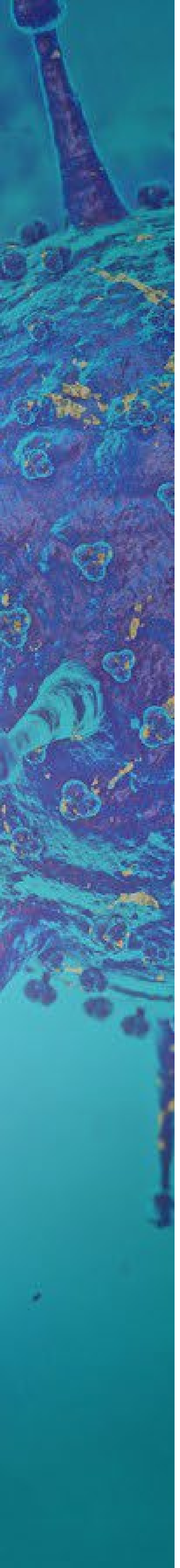




Capture/sorption applications

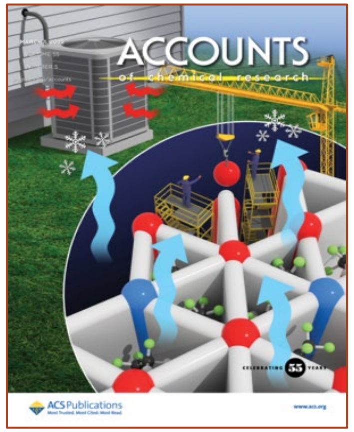
Sensor/detection applications

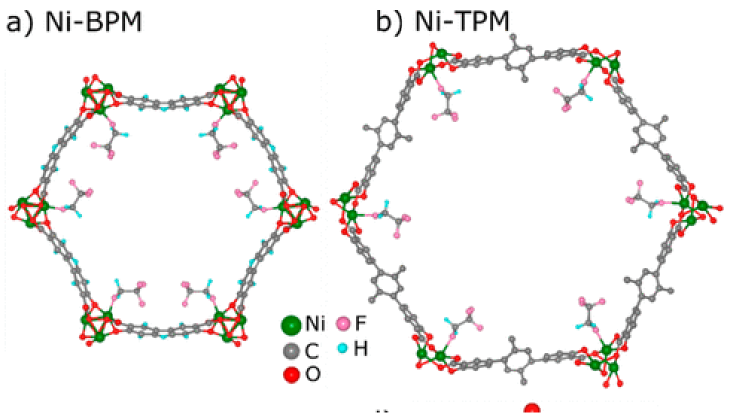
Motkuri *et al.*, *Chemical Reviews. 2024, 124, 12, 7619–7673; Nature Communications* 2014, 5, 4368; *Scientific Reports*, 2016, **6**, 28050, US Patent 10,266,737

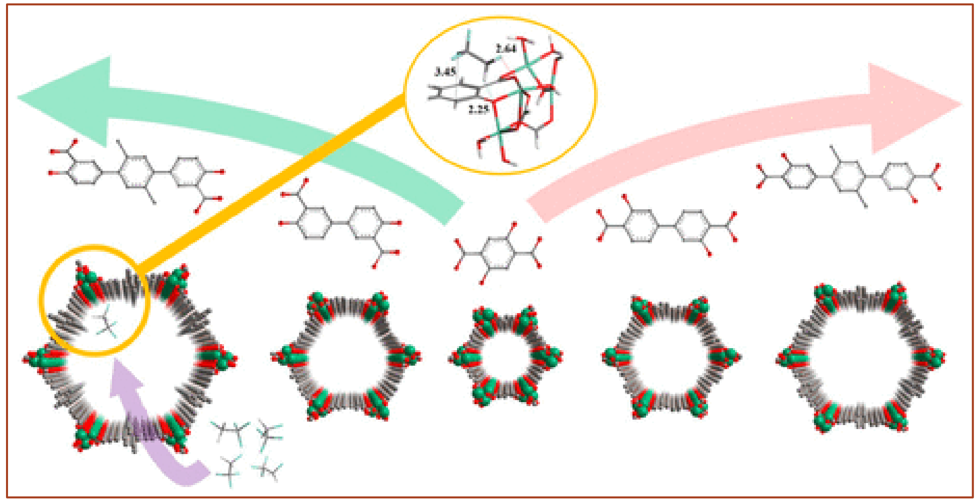


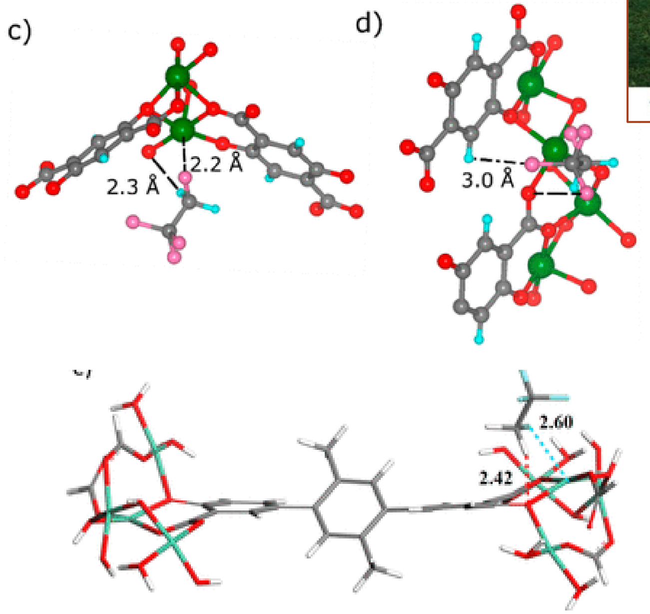
PNNL Advanced Nanomaterials Development

Pore engineering and C-F interactions

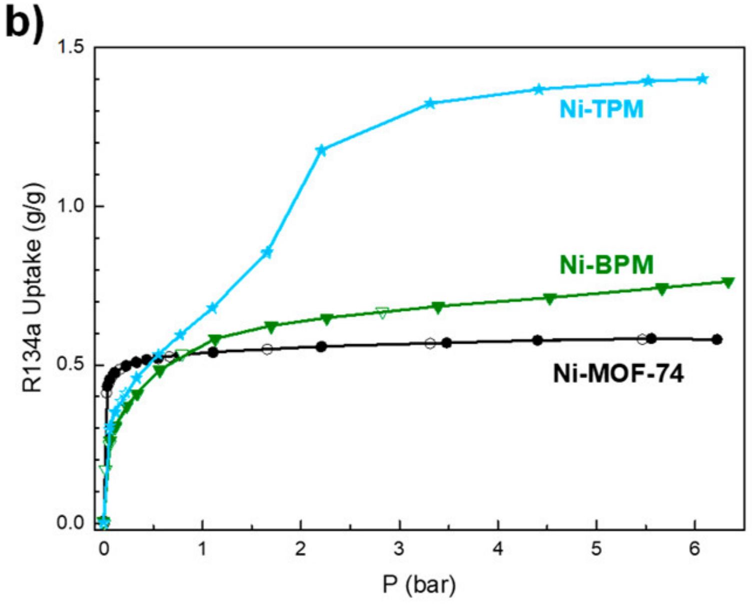








- Pore-engineering for advanced sorbent development for fluorocarbon capture/interactions
- Tuning the porosity (micro and meso) for capture at low and high concentrations;
- Recyclability of the nanoporous sorbent material
- Affinity and pore-filling
- Revealed the coordination of fluorine (e.g., CH2F in C2 fluorocarbon) to the open metal centers at low pressures/concentrations (C-F-----M)
- These interactions provide insight into the affinity and pore-filling mechanisms.
- The tools helped to probe and understand the adsorption mechanisms of CF3-CF2H in advanced nanoporous MOFs



Motkuri et al., J. Am. Chem. Soc. 2017, 139, 10601-10604; J. Am. Chem. Soc. 2020, 142, 6, 3002-3012

PNNL Advanced Nanomaterials Development

Pore functionalization and Defects for C-F interactions

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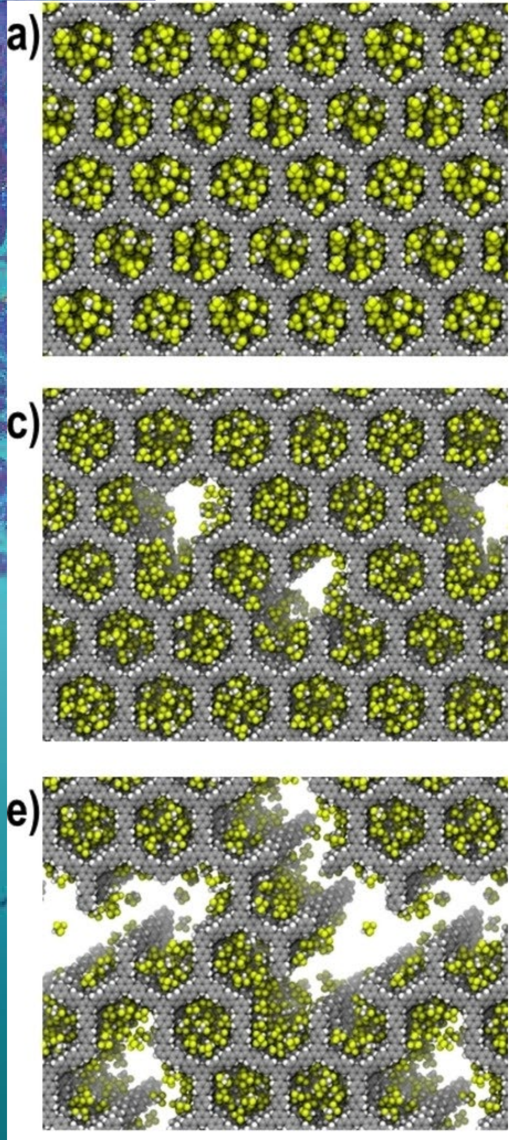

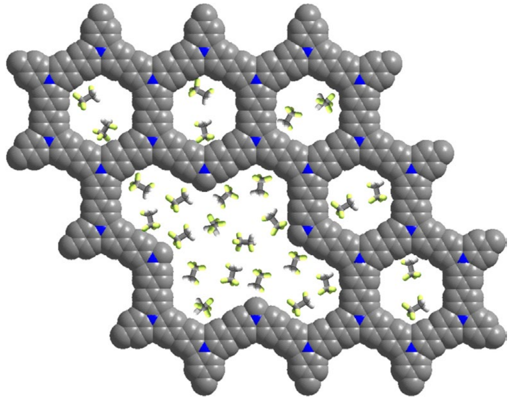

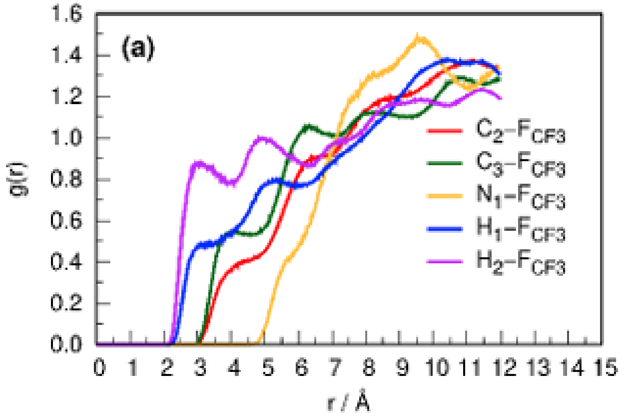

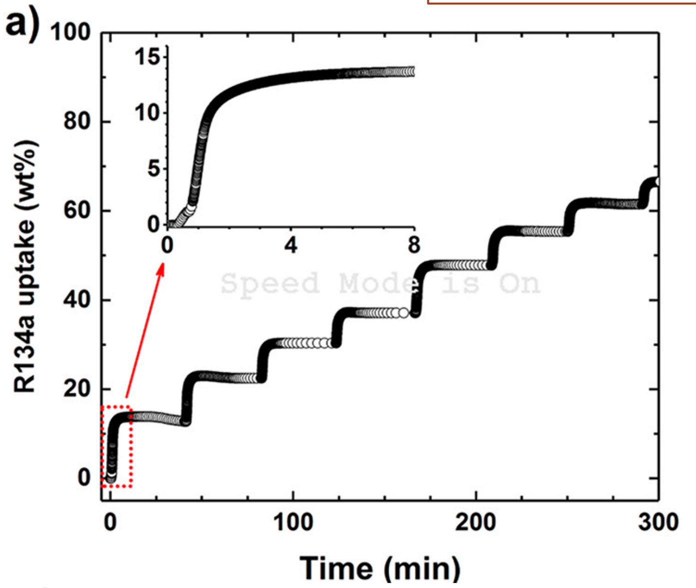

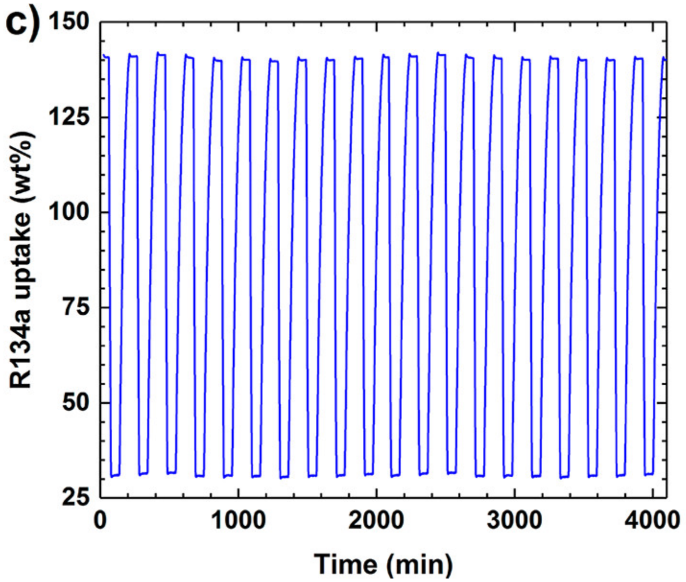

- Fluorocarbon adsorption affinity (in terms of mass loading and isosteric heat of adsorption)
- Optimizing the capture by introducing the defects
- Defect Engineering in COFs and tuning towards the C-F----Pi interactions for improved sorption capacities
- Pore morphology and functionalization
- Overview of C-F interactions with advanced sorbents
- Advanced characterization tools for C-F----M and C-F---Pi interactions
- Supporting molecular modeling studies
- These interactions provide insight into the affinity and pore-filling mechanisms.
- Recycling the sorbent

Motkuri et al., Angew. Chemie Int. Ed. 2021, 60 (33), 18037; ACS Appl. Energy Mater. 2018, 1, 11, 5853

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PFAS Remediation Advances

Capture/Adsorption

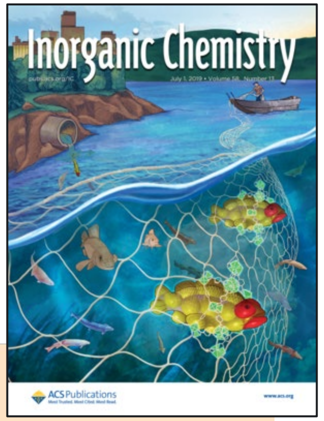
- *Advanced sorbent developed with tunable pore structures, morphologies, and functionalities developed.*
- *high surface area, sorbents for large sorption capacities*
- *Structure property correlation*
- *Host-guest interaction*
- *Selectivity for shorter chains/longer chains;*
- *Scalable sorbent synthesis*
- *Gas-phase capture of PFAS*

Destruction

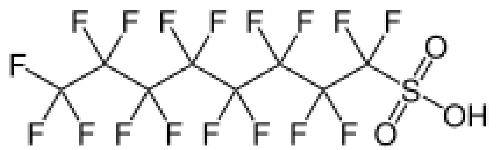
- *Preliminary studies on thermocatalytic destruction and enzymatic destruction*
- *Combining capture and destruction*
- *Gaseous phase sorption of short-chain PFAS for incineration*

Detection/Sensing

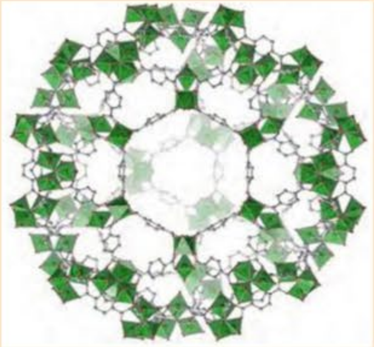
- *Electrical impedance-based sensor*
- *in situ* method
- Short turnaround times (~hours vs days current)
- Inexpensive compared to traditional methods
- Detection limits are low (in the ppt range)
- Currently, PNNL is working on improving accuracy and precision

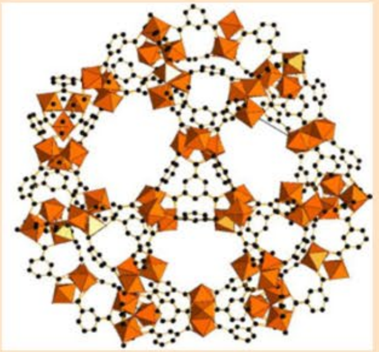


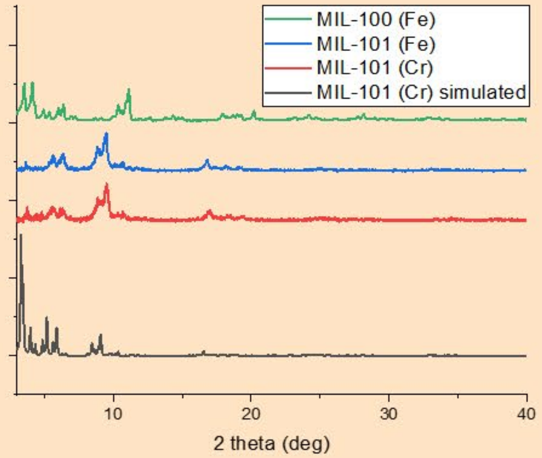
PFAS capture by Advanced sorbents



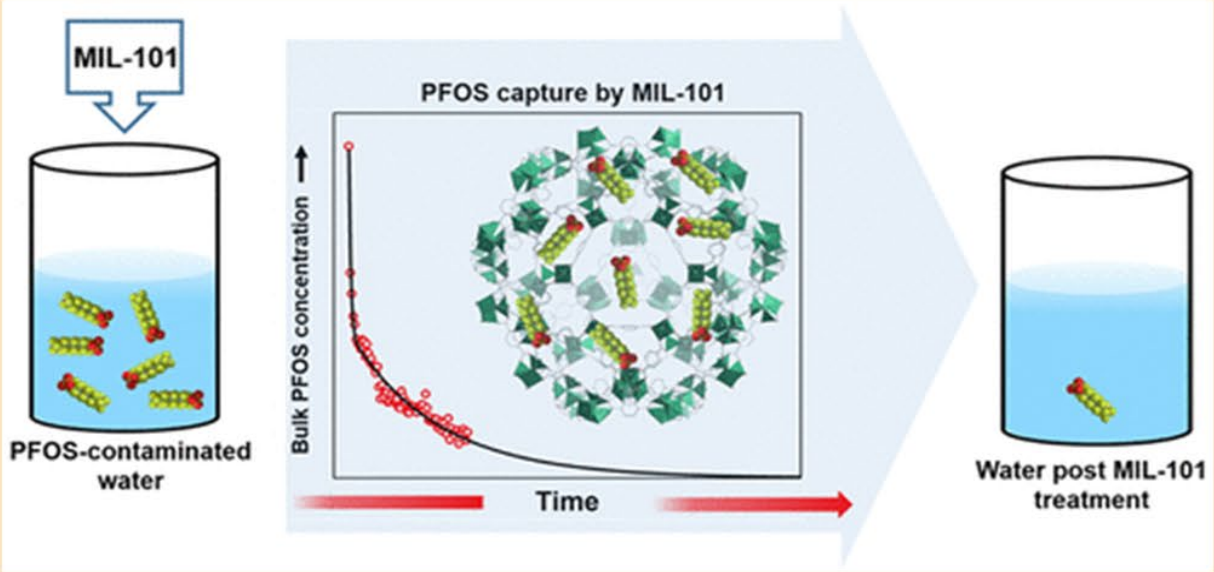
E.g., MOF based sorbents







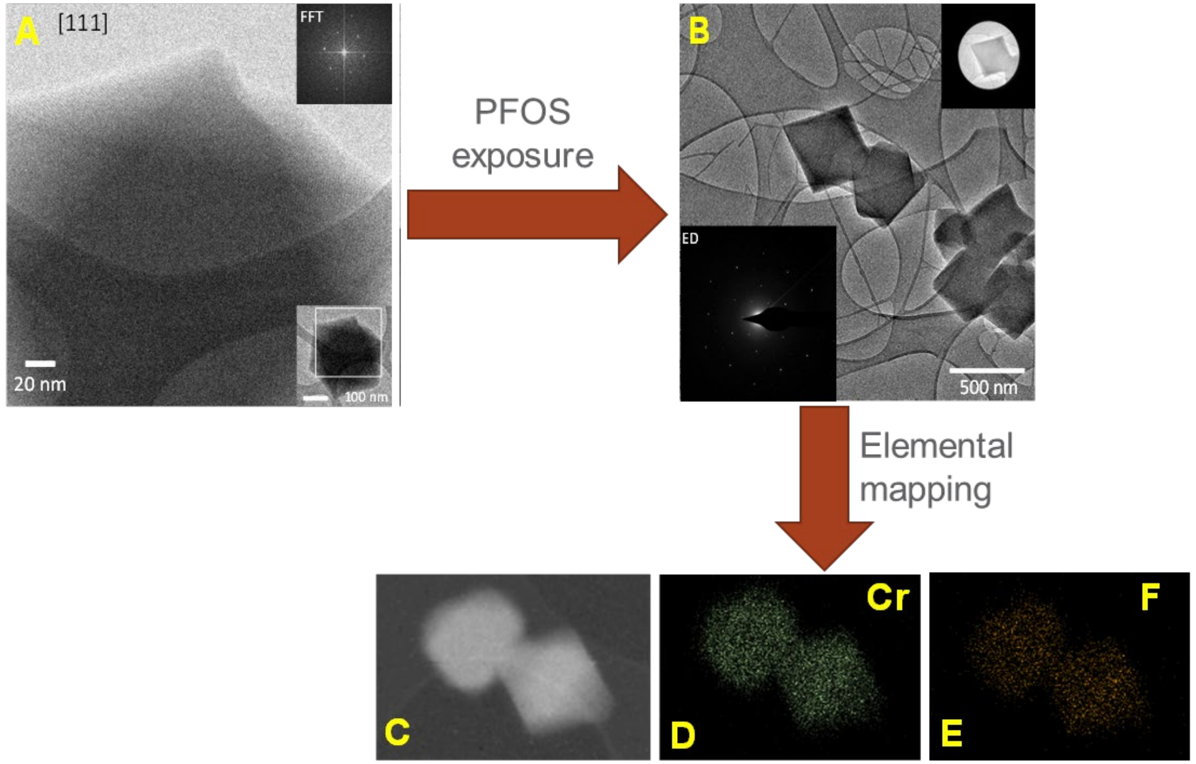
- **Cr-MIL-101 and Fe-MIL-101: Trimeric Cr/Fe^{3+} octahedral clusters interconnected by terephthalic acid linkers**
- **Fe-MIL-100: Trimeric Fe^{3+} octahedral clusters interconnected by trimesic acid linkers**

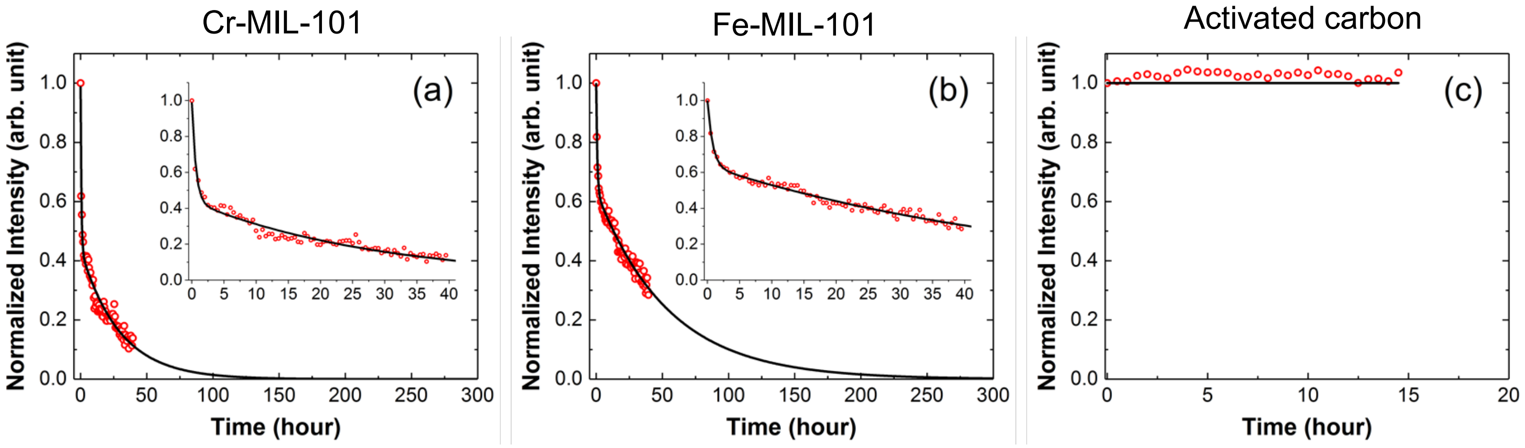


❖ PFOS solution contacted with sorbent
  ❑ PNNL-designed MOF sorbents compared with commercial GAC
❖ PFOS concentration periodically monitored using ^{19}F nuclear magnetic resonance (NMR)

Motkuri et al., Inorganic Chemistry 2019, 58 (13), 8339– 8346; *US Patent 11,518,689*

PFAS capture by Advanced sorbents





- Measure decay in bulk PFOS concentration (i.e., sorption kinetics for 10mM PFOS) for each sorbent
- Fe-MIL-101 has slower sorption rates than Cr-MIL-101
- Activated carbon shows negligible sorption
- Characterization tools, TEM and XPS revealed the sorption

Motkuri, et al., Inorganic Chemistry 2019, 58 (13) 8339-8346

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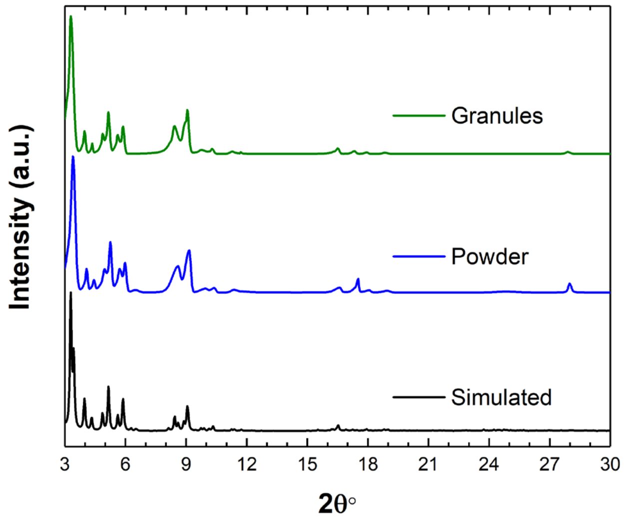
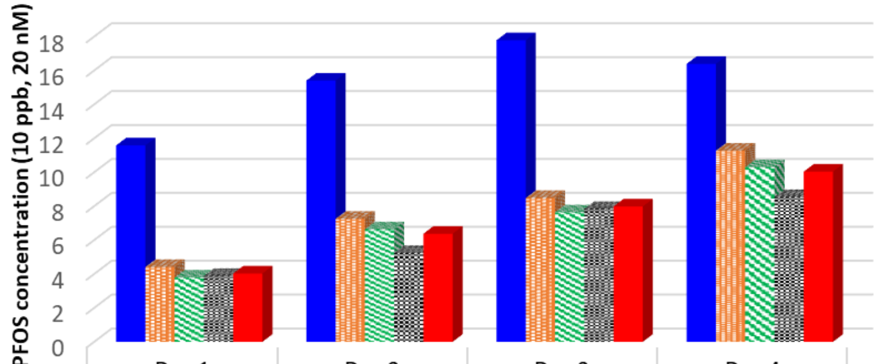
PFOS remediation



- Developed and processed the MOF material in the engineering form (granules) on a gram scale.
- PFOS sorption tests were performed by flowing a known concentration of PFOS solution in tap water through a tube packed with MOF granules.
- Triplicate samples were collected from the outlet, and PFOS concentration was tested using LC-MS/MS at PNNL.
- The preliminary testing of PFOS at low concentrations (10 ppb) in tap water showed a decent performance in PFAS removal of up to 65% from the water within 24h.
- The saturation was not reached even after 8 days after flowing 60-liter solution, indicating more optimization is required.
- Further studies are required to optimize and understand sorption for such industrial-scale applications.



	Day 1	Day 2	Day 3	Day 4
Inlet Sample	11.58	15.4	17.78	16.39
Outlet-Sample1	4.41	7.25	8.48	11.27
Outlet-Sample2	3.79	6.63	7.63	10.3
Outlet-Sample3	3.88	5.23	7.83	8.53
Average	4.026666667	6.37	7.98	10.03333333

Days

Inlet Sample | Outlet-Sample1 | Outlet-Sample2 | Outlet-Sample3 | Average

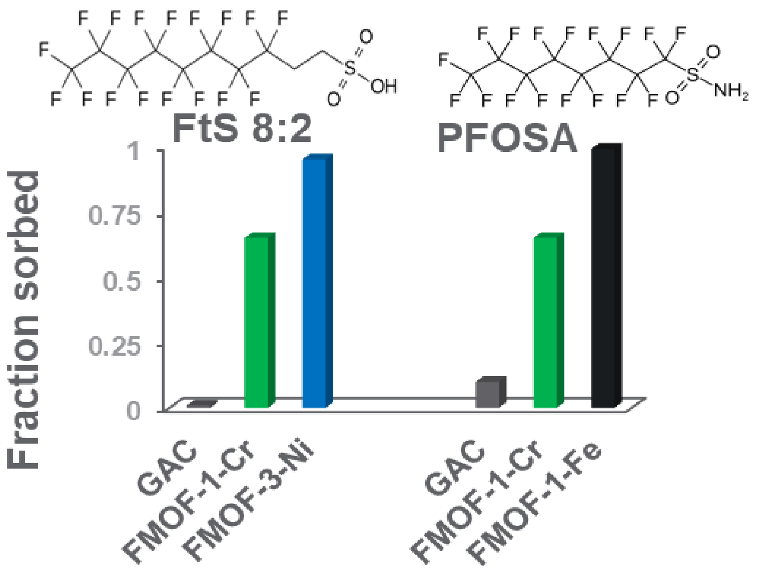
PFOS (10 ppb) sorption results in Tap water under a flow system using Cr-MIL-101 over 8 days (60-liter).

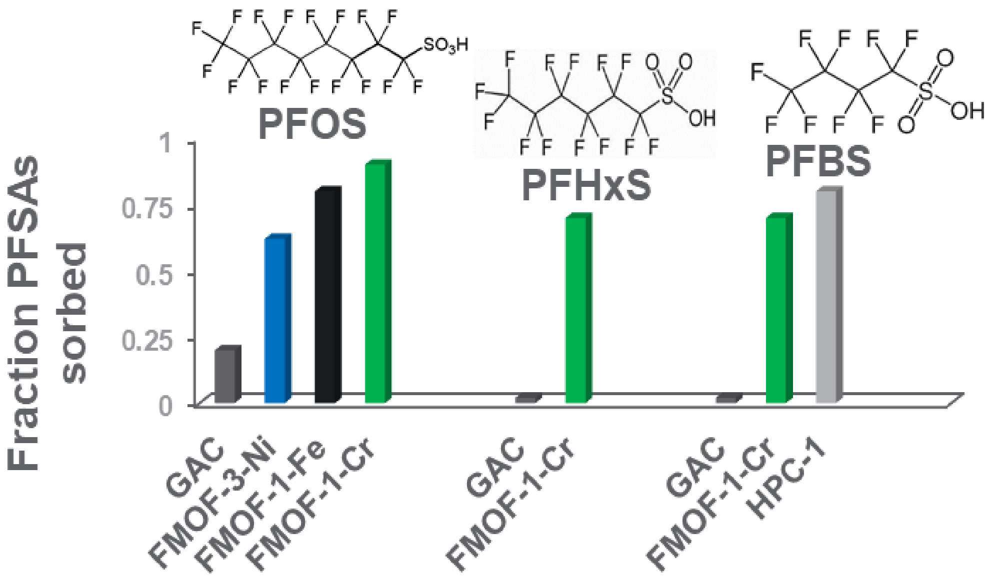
Motkuri et al., https://www.osti.gov/servlets/purl/1984699

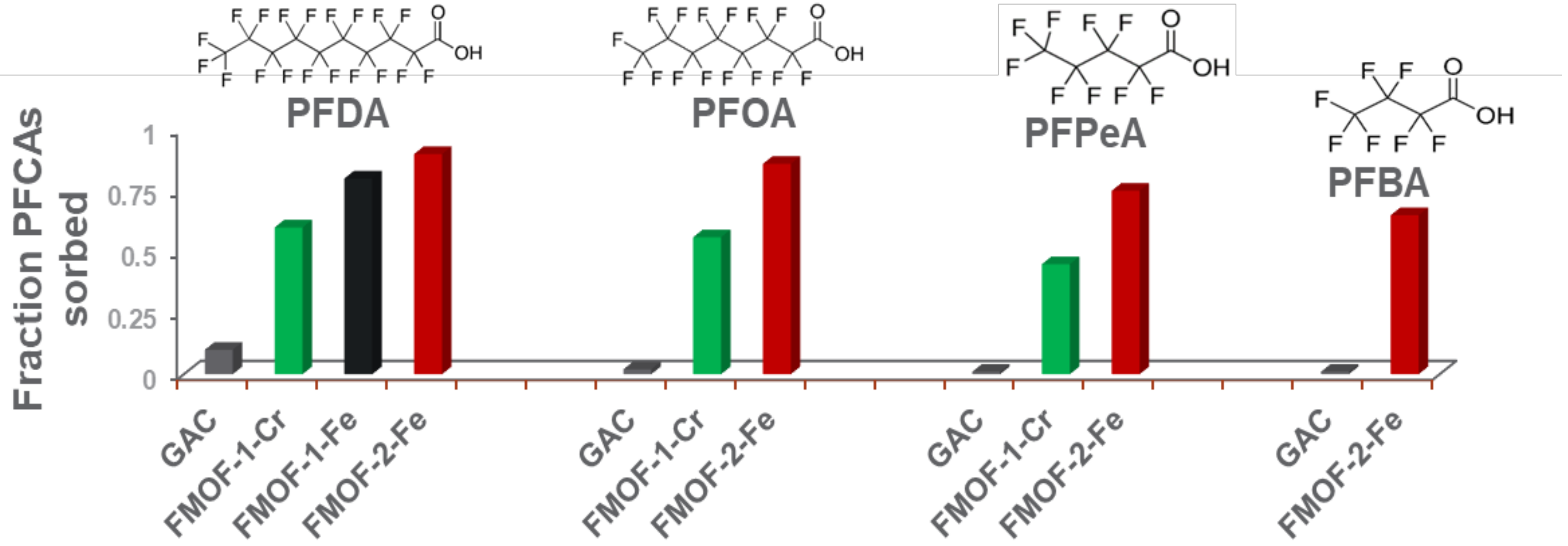
Fluorophilic Sorbent Development (PNNL)

All the sorbent materials were synthesized, characterized, and tested.

Capture from water in ppm, concentrations using ^{19}F NMR







- Sorption of various PFAS molecules in ppm from DI water and analysis using ^{19}F NMR
- Comparison of sorption capacities using commercial GAC

Motkuri et al., *US Patent 11,518,689*

PFAS CAPTURE

Fluorophilic Sorbent Development (PNNL)

All the sorbent materials were synthesized, characterized, and tested.

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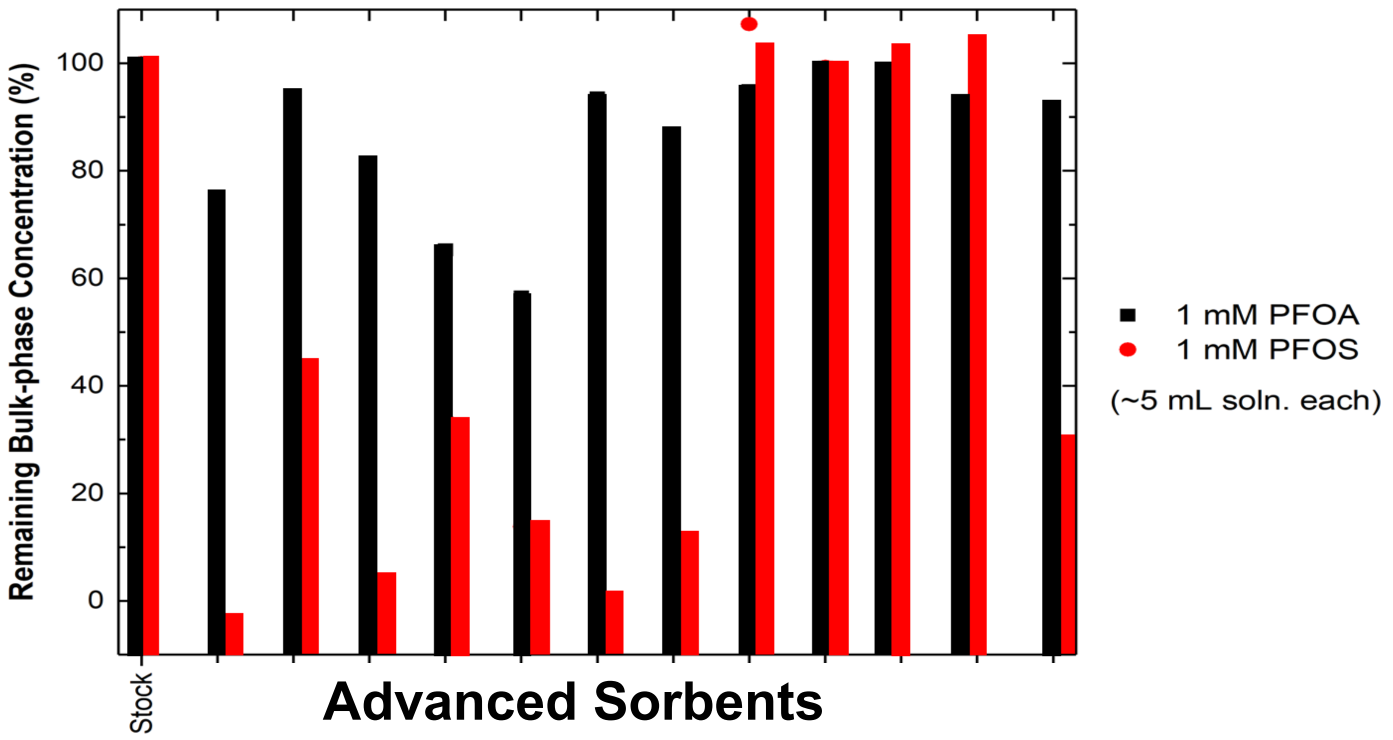
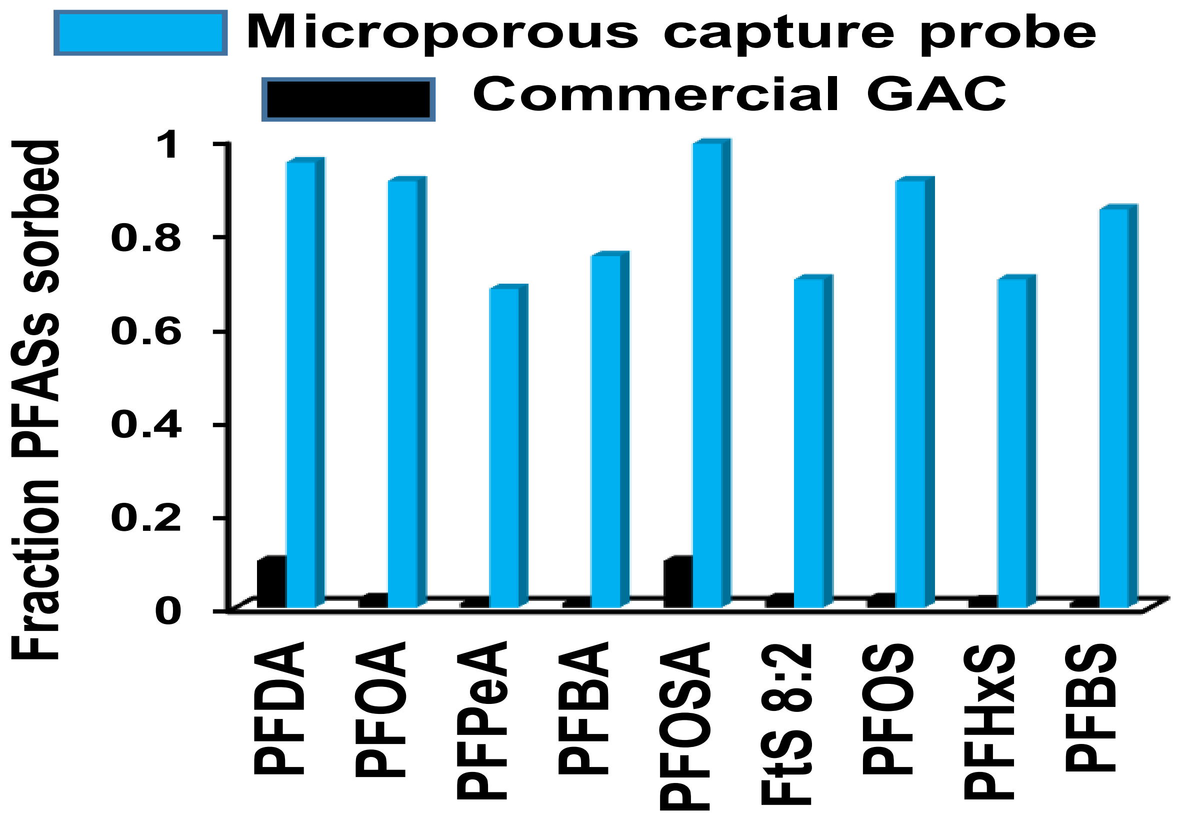
PFOS and PFOA capture in various advanced engineered sorbents

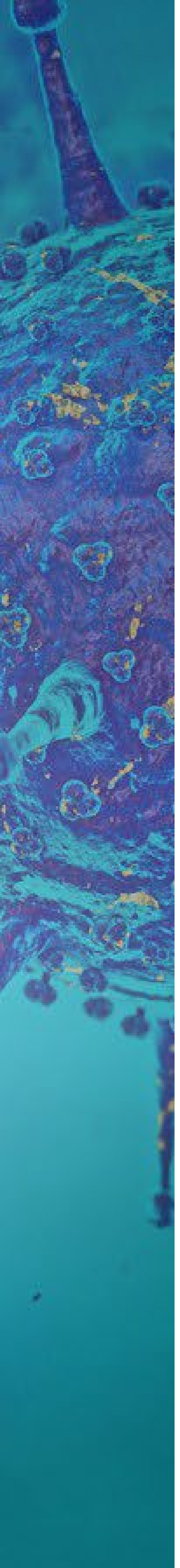


Various PFAS molecules captured in FMOF-1 and comparison with GAC



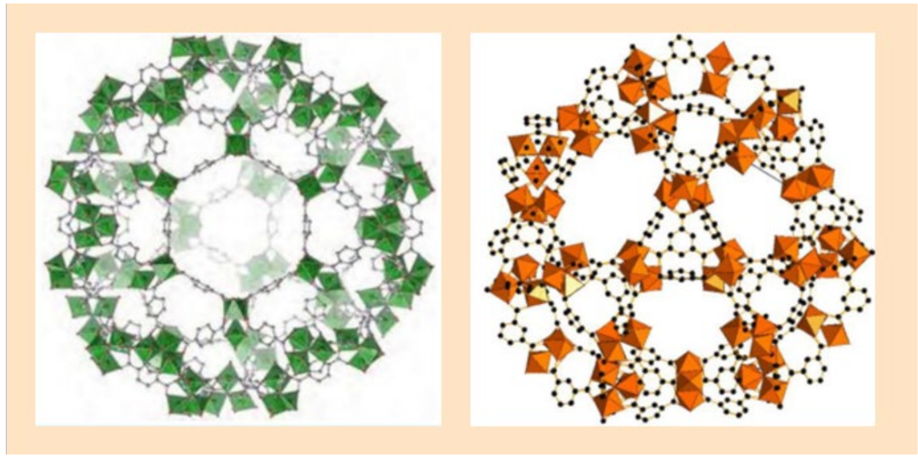
- Capture from DI water in ppm concentrations and testing/analysis using ^{19}F NMR
- Stock solutions are freshly prepared, and sorption was performed

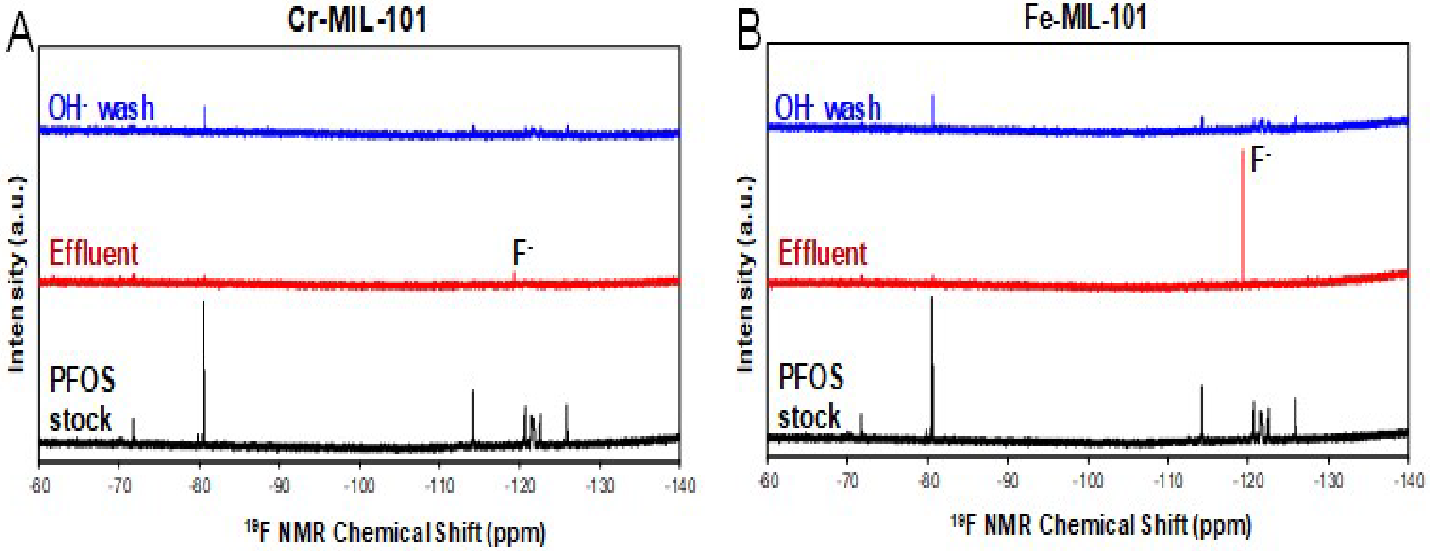
Motkuri et al., *US Patent 11,518,689*



Catalytic hydrothermal PFAS destruction

PFAS Destruction





^{19}F NMR spectra of PFOS solution upon stock, (—) effluent post hydrothermal treatment with the MOFs and NaOH.

- Thermal catalytic degradation approaches were investigated for complete mineralization of PFAS loaded in engineered sorbents,
- Initial optimization studies were done with the C-8 chained PFOS and PFOA, respectively.
- Various amendments (NaOH, $Na_2S_2O_3$, $Na_2S_2O_8$, Na_2CO_3, H_2O_2) were studied.
- The $S_2O_8^{2-}$ contacted solution showed a ~70% PFOS degradation.
- The reactions were monitored using ^{19}F liquid NMR spectroscopy on the supernatant solutions where Fe-MIL-101 demonstrated the highest amount of mineralization with NaOH amendment.
- More optimization studies are required.

Motkuri et al., *US Patent 11,518,689*

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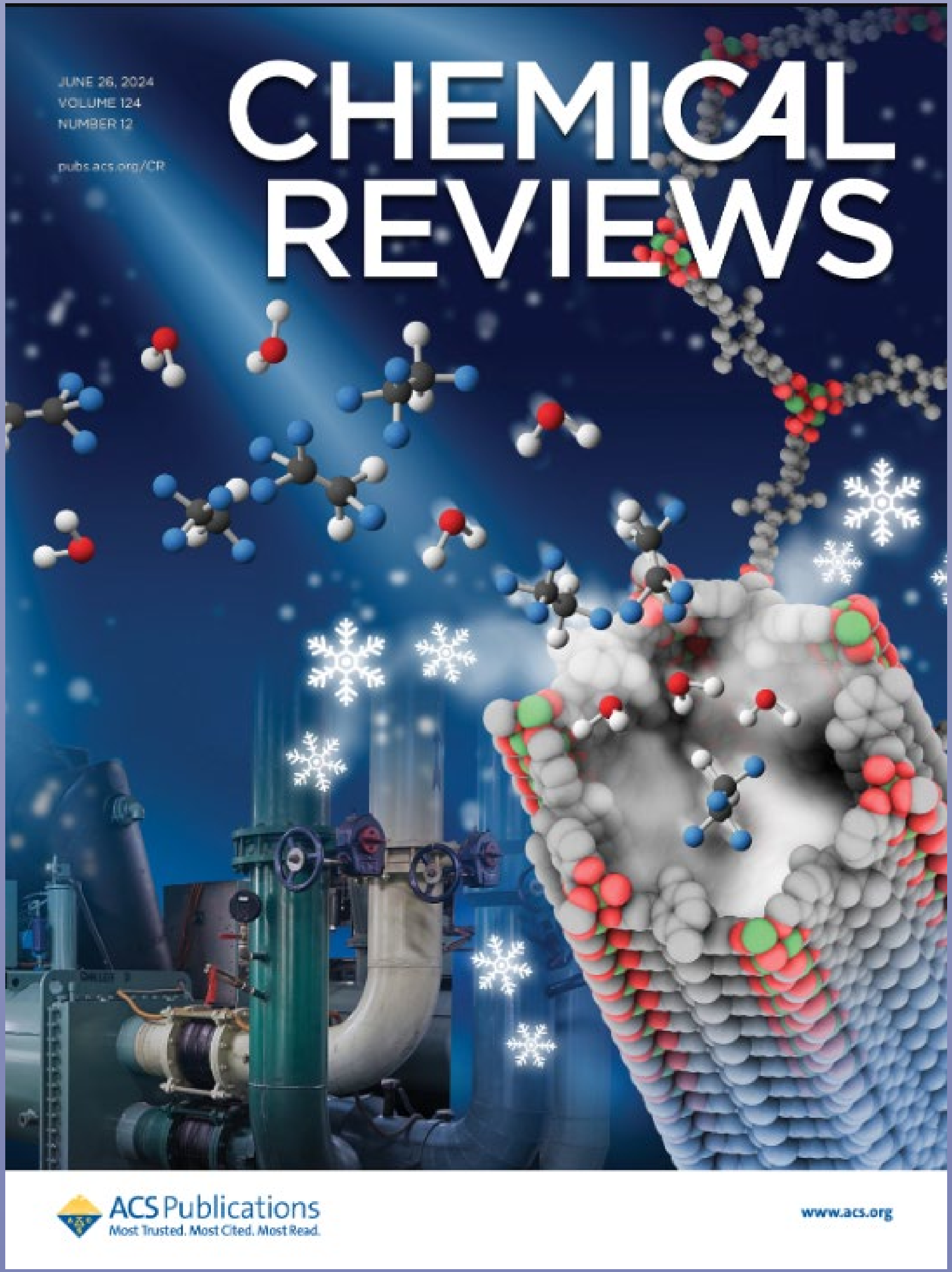
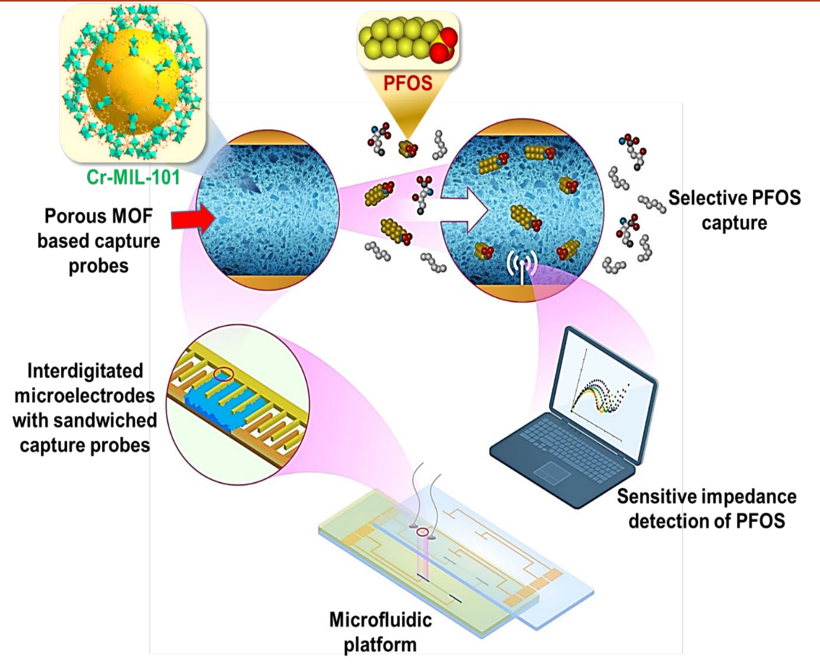
Thank you



June 2024

PNNLPFAS Sensor Technology

PFAS SENSOR



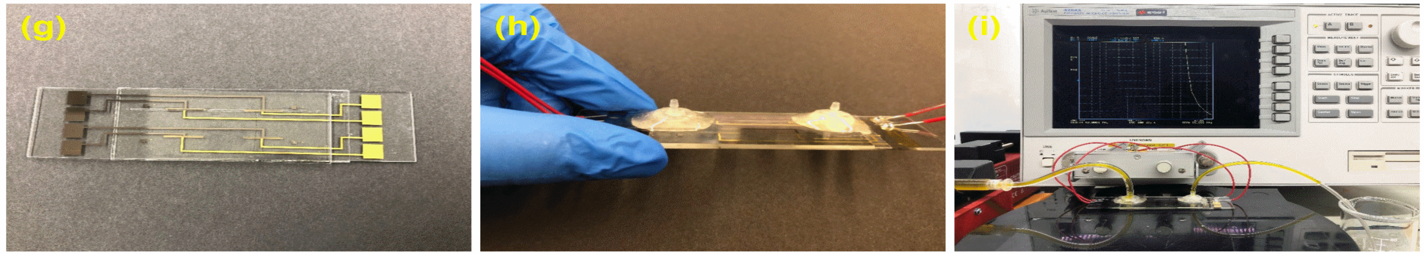
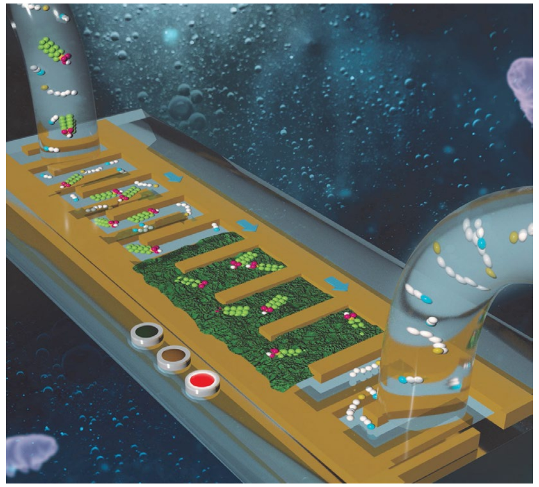


Figure. Actual Chip with the EIS Set-up



Common Techniques for PFAS Analysis	Limit of Detection
LC-MS/MS	~1 ng/L
TOF MS	1-10 ng/L
Ex situ IC-MS	1-10 pg/L
PIGE	~10 nmol/cm^2
NMR	10 μg/L
TOP	1-10 ng/L
Reported electrochemical techniques	25 ng/L
PNNL lab-on-a-chip electrochemical technique	TBD

- Microfluidic channel sandwiched by non-planar interdigitated microelectrode array (NP-μIDE)
- High-density packing of receptors (MOF) in the microfluidic channel
- Impedance spectroscopy used for the detection of PFOS capture
- Detection and measurement of PFAS compounds, including PFOS, PFOA, PFBS, PFBA, PFHxS
- Measures ultra-low PFOS levels – in ng/L (ppt) ranges
- Currently, PNNL is working on improving accuracy and precision

Motkuri et al., *US Patent 11,518,689, US Patent App. 17/613,807; ACS Appl. Mater. Interfaces 2020, 12, 9, 10503–10514*