A Novel, Nanostructured, Metal-Organic Frameworks-Based Pretreatment Technology for the Remediation of PFAS in Industrial Wastewater

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ABSTRACT

Per-and polyflouralkyl substances, otherwise known as PFAS, are a class of chemicals that include perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). This class of chemcials has a large variety of uses globally, but their utilization has begun to wane due to toxicological concerns and their environmental persistance. As such, remediation of PFAS has gained increasing attention from regulatory and funding agencies.

This research study gives a preliminary overview of a water pretreatment system which combines the use of a novel, nanostructured sorbent for the effective removal of PFAS by levereging the material's selective adsorption and solar light-driven photocatalytic properties. At the heart of the technology are our innovative, chemically stable, metal-organic frameworks (MOFs) which can be tailored for selective PFAS and PFOS capture and host degradation under light irradiation. This novel water treatment solution brings the advantages of high PFAS adsorption capacity in MOFs alongise of the photocatalytic properties of their constituent components.

Keywords: metal-organic frameworks, Per-and polyflouralkyl substances, perfluorooctanoic acid, perfluorooctane sulfonate, solar light-driven photocatalysis.

1 SIGNIFICANCE

Per- and polyflouralkyl substances (PFAS) have increasingly been used in the chemical industry due to their hydrophobic chains. Amongst PFAS, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) have been of tremendous interest in areas such as food production, non-stick cookware, cleaning products, water-repellant fabrics, and commodity synthesis and fabrication. However, due to their environmental persistence and toxicity, alongside their global use, their remediation has gained increasing attention.

In many locations there are already significant levels of PFOA and PFOS contamination in drinking water caused by localized contamination[1]. Processes such as anion exchange, reverse osmosis, microfiltration, granular filtration, sorption, and flocculation have all been found ineffective at removing PFAS from drinking water. Water treatment methods must combine multiple strategies to be effective, as PFAS are commonly found in complex mixtures in the environment. The U.S. Environmental Protection Agency (EPA) Lifetime Health Advisory (LHA) sets a limit of 70 nanograms per liter as a safe limit. This limit can apply to PFOA or PFOS on an individual basis, or in conjunction with each other.[2] In 2015, the EPA passed a Significant New Use Rule that requires manufactures to notify the EPA at least 90 days before starting or resuming new uses of chemicals. In 2006, a Stewardship Program was enacted to reduce emissions of PFAS by 95%. Eight companies from the United States committed to reducing their output, as well as eight international companies.[3]

The process described here utilized MOFs to capture and store PFAS by adsorbing them within their porous surfaces. Compared to leading solid sorbent alternatives, MOFs have several key advantages that allow them to stand out. MOFs are comprised of organic linkers and metallic nodes, often called secondary building units (SBUs), both of which allow for a high level of tunability compared to other adsorbents. Alterations in the organic components can allow MOFs to be either hydrophilic[4], hydrophobic[5], or even contain both hydrophilic and hydrophobic parts.[6] This is in stark contrast to solid adsorbent systems such as activated carbon, which tend to be neither fully hydrophilic nor hydrophobic, resulting in low selectivity for specific compounds.[7] In addition, MOFs have highly tunable pore sizes. Traditionally, MOFs have been known as microporous materials, however, there has been an increased level of interest in hierarchical porosity in MOFs, both with various microporous regimes, and mixed micro and mesoporous regimes.[8]

Amongst the thousands of MOF structures reported so far, the majority are built up from divalent cation based SBUs. MOFs built up from higher valance cations, such as Ti^{4+}, are not very common since their high charge density often results in less control over the crystallization process.[9] For a given linker, especially carboxylic acid-based linkers, increasing the charge of the metal leads to an enhancement of the hydrothermal stability of the MOF. For water treatment applications, the hydrothermal stability is a crucial requirement. Build up from high valent Ti^{4+} clusters, the MOF utilized in this study (AYRSORB™ T-125) is stable in air and at a full range of pH values, covering acidic and alkaline water applications. To add to this advantage, the findings of this study point out that AYRSORB™ Ti-MOFs are photocatalytically active which can be leveraged to initiate reductive reactions to breakdown the adsorbed PFAS within the MOF for effective and prolonged PFAS remediation.

2 OBJECTIVES

The objectives of this study were: *(i)* reduction of concentration of PFAs in aqueous environments to <70 ppt using Ti-MOF adsorbents, and *(ii)* photodegradation of PFAs in aqueous solutions enough to reduce the concentration of large PFAs to <70 ppt. This study focused on the efficiency of the photodegradation pathway, and further kenetic loading studies will be needed to fully prove our thesis. TiO_2 based photoreduction of perfluoroalkanes has already been well demonstrated in the literature, typically through incorporation of TiO_2 into graphene oxide sheets.[10-11] However, material such as these can only engage in the degradation of perfluoroalkanes, they cannot capture the resulting degradation products, typically lower molecular weight perfluoroalkanes, which can still cause bioaccumulation issues. By combining degradation with capture processes, we can ensure that even the smallest of components stain out of the medium.

3 TECHNICAL APPROACH

The microporous environment of one of framergy's Ti-MOFs, AYRSORB™ T-125 – also known as MIL-125-NH_2, represents the ideal platform to achieve this process. MIL-125-NH_2 consists of titanium oxo clusters bridged by 2-aminoterephthalic acid. The titanium oxo clusters are known to act as analogues to titanium dioxide, facilitating photocatalysis, while the incorporation of the amino functional group into 2-aminoterephthalic acid has been observed to help shift the absorption band of the material from the UV to the visible region,[12-13] with MIL-125-NH_2 showing a clear absorption in the 400-425 nm range due to this effect (Figure 1).

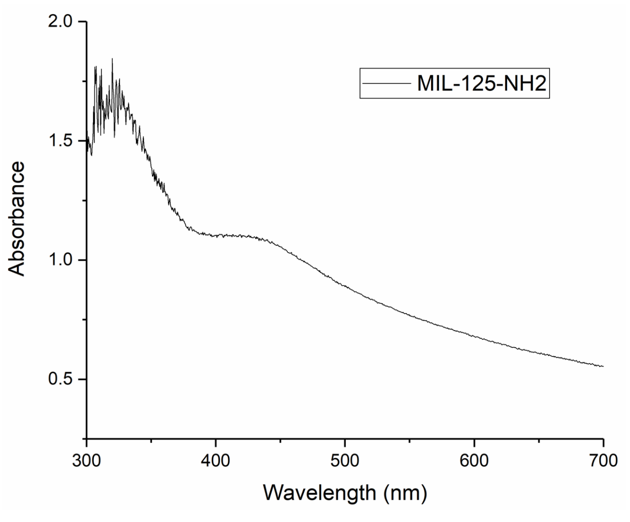

Figure 1 *framergy* – synthesized MIL-125-NH_2 slurry UV-Vis spectrum, photocatalytically-active from the UV to the visible region (see the absorption peak at 400-425 is due to ligand effects)

MIL-125-NH_2 has already been observed to engage in photocatalysis, with both H_2 generation[14] and CO_2 reduction[13] known to occur.

MIL-125-NH_2 is a largely microporous material, with a pore aperture approximately 8.2 Å across. The micropore environment is ideal for trapping small molecules inside the pores, preventing desorption back into the environment. In particular, many perfluoro compounds have atomic sizes that are similar to MIL-125-NH_2, a situation that is ideal for performing one-way capture.

3.1 Adsorptive Separation Studies

Separation studies were conducted using MIL-125-NH_2 and 500 ppm aqueous solutions of PFOA, and PFOS. After agitating the MOF in the stock solution, the total uptake of the perfluoroinated compounds in MIL-125-NH_2 was quantified via ^{19}F NMR, using 2-fluoroaniline as an internal standard (Table 1).

Compound	Uptake (mg/g)
PFOA	42
PFOS	17

Table 1: Total uptake of the perfluoroinated compounds in *framergy* – synthesized MIL-125-NH_2

3.2 Photocatalytic Degradation Studies

In addition, photocatalytic degradation studies were performed using PFOS in an aqueous solution with triethanolamine (TEOA) as a sacrificial reductant, the results show that MIL-125-NH_2 is capable of degrading PFOS, with 9% conversion visible via ^{19}F NMR. (Figure 2). This data represents the first known example of photoactive degradation of PFAs using a MOF.

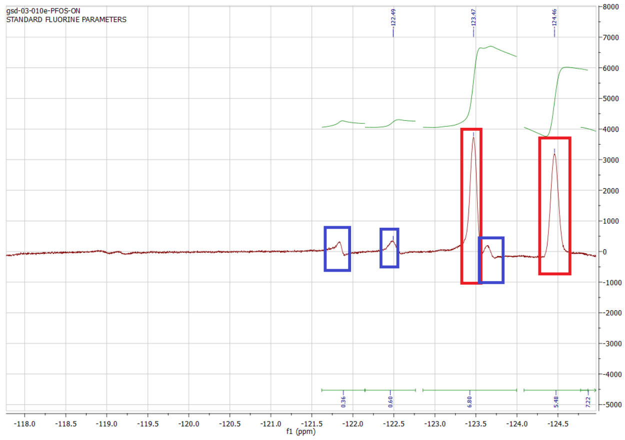

Figure 2 ^{19}F NMR of PFOS degradation in the presence of MIL-125-NH_2. The blue boxes represent new peaks, while the red boxes represent peaks of the parent PFOS.

Supporting the findings of the ^{19}F NMR analysis, liquid-chromatography-mass spectrometry (LC-MS) of 500 ppm PFA water solutions after incubation with MIL-125-NH_2 under UV light showed that both perfluorooctane (PFO) and PFOS did undergo degradation. LC-MS of the PFO reaction mixture showed that three distinct peaks were present after irradiation, all of them coming through with low retention times, 0.9 – 2.07 min, (Figure 3a). The potential identities of the detected compounds are given in the mass spec. window, with identified species potentially being the result from the cleavage and hydrolysis of the parent perfluorooctane (Figure 3b and d) in the presence of excess water.

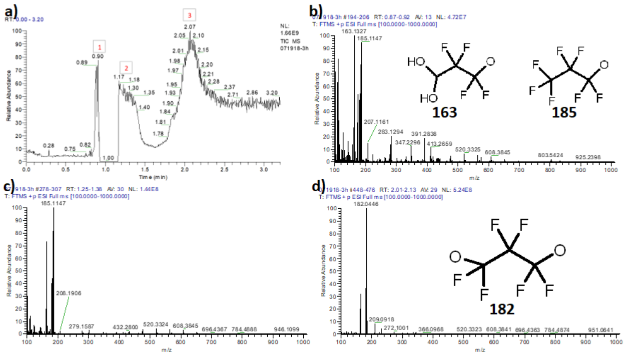

Figure 3 a) LC of PFO degradation in the presence of MIL-125-NH_2 b) Peak one MS c) peak two MS d) peak three MS. Peak one and two appear to be the same species, MS of peaks one and three have the potential chemical species of the main mass peak illustrated.

PFOS degradation still resulted in clean LC-MS signal, again with three peaks, with peak one being the major species and peak two and three representing minor components (Figure 3). We concuded, similar to the PFO degradation results, due to water hydrolysis the tentative structures contained extra O and OH functionalities. It should be noted that there is no evidence for the molecular or ionic peak of PFOS (exact mass 537.89 and 498.93 respectively).

In the light of these findings, it can be concluded that PFO and PFOS photocatalytic degradation can be achieved with MIL-125-NH_2.

3.3 Life Cycle Analysis (LCA)

To evaluate the feasibility of using Ti-MOFs, for PFAS remediation, the lifecycle environmental impacts of the proposed technology were analyzed including MIL-125-NH_2. The considerations included:

- Minimizing Resource Use and Efficient Use of Energy: MIL-125-NH_2 is photocatalytically-active in the visible light region which means that it can be activated under sunlight. Use of solar energy can significantly reduce the need for resources, especially for a photocatalytic water remediation method.
- Minimizing Toxicity of Material and Minimizing Pollution: As shown in Figures 3 and 4, MIL-125-NH_2 can photocatalytically degrade PFO and PFOS, paving the path to the reducing and ultimately minimizing the toxicity caused by PFAS in the environment.

One important aspect is the life-cycle of photocatalytically-active Ti-MOFs under UV light. Particularly, would the MOF degrade under UV light and release any toxic components into the environment. To address this, the chemical stability of *framergy*-synthesized MIL-125-NH_2 was tested after PFO, PFOA and PFOS degradation studies under UV light (Figure 4).

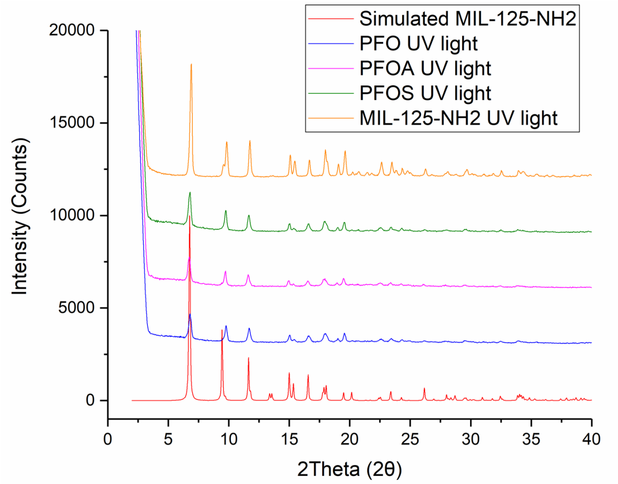

Figure 4 pXRD of all four samples showed up as MIL-125-NH_2, proving that the MOF is stable under the tested remediation conditions.

For this test, MIL-125-NH_2 was dispersed in a 500 ppm water solution of different PFAs (PFO UV light, PFOA UV light, PFOS UV light) alongside a sacrificial reductant (TEOA) and was irradiated under UV light. One last sample, sample (MIL-125-NH2 UV light), was placed in just water under UV light overnight.

The powder X-Ray Diffraction (pXRD) of all four samples showed up identical as MIL-125-NH_2 before UV irradiation, proving that the MOF is stable under the tested remediation conditions without degrading or releasing any toxic components (Figure 4).

This preliminary LCA points out several environmental benefits including reduced use of resources and efficient use of energy. Minimized toxicity and pollution are the other environmental benefits. The low toxicity of titanium coordination compounds is a great starting point for a new catalyst,[15] and for a photocatalytic water treatment technology using Ti-MOFs, including MIL-125-NH_2.

4 CONCLUSION

Water treatment is a significant sector of overall adsorbent use, and granular activated carbon is the dominant product. But PFOA and PFOS adsorption efficiency of current sorbents is considered too low to commercialize. Granular activated carbon has been used for remediation over the years, however its use requires frequent replacement and leaves a substantial environmental footprint. Through the use of both a photocatalyst and an adsorbent, MOFs can greatly increase the adsorption efficiency of PFOA and PFOS.

Due to its high PFAS adsorption capacity and photocatalytic reduction performance under visible light spectrum, Ti-MOFs combine the advantages of leading PFAS remediation technologies. This directly translates to low operating expenditure (OPEX) requirements due to less frequent changeouts and low-energy activation.

The advantage of Ti-MOFs is the elimination of reaction retention time requirement. The PFAS species can be adsorbed and photoreduced within the same medium, this means that MOFs can serve as a PFAS capture agent and a photodegradation catalyst at the same time. Reduced retention time directly translates to higher throughput. This lowers the capital expenditure (CAPEX) requirement of this novel remediation technology compared to the competing chemical oxidation/reduction only systems for a given treatment remediation rate.

Although the current cost of MOFs is higher than activated carbons, the savings from on-going changeout cost justifies switching to a MOF based water remediation system. In addition, framergy is continuously improving its AYRSORB™ MOFs from a cost reduction point. These activities should also help reduce the upfront costs of these novel and alternative remediation agents to levels that will make them cost competitive with existing technologies. More studies are need on kinetic loading of PFAS species and post cyclic material versification through BET and SEM to determine long-term suitability.

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