Advances in PFAS Monitoring and Remediation Using a Functionalized Material Approach – 20080

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ABSTRACT

The growing global concerns about the effects to public health from human exposure to per- and polyfluoroalkyl substances (PFAS) motivates the development of strategies for reliable monitoring of PFAS in environmental streams, as well as for their rapid, effective removal if detected. For the continuous PFAS monitoring, an inexpensive, field-deployable, *in situ* sensor is urgently needed; yet the prevalent *in situ* techniques often struggle to strike a balance between the practical sensitivity and selectivity demands of the real world. Similarly, for effective PFAS removal, strategies for their fast, selective, and quantitative capture are desired, yet the present commercially available sorbents are unable to meet the requirements of rapid, quantitative capture of all PFAS components, and are notably inefficient in removing the more toxic smaller chains. To address these twin challenges, Pacific Northwest National Laboratory is developing strategies for improved detection and remediation of PFAS. For the rapid, selective, quantitative removal of PFAS from environmental streams, the strategy relies on designing capture probes with exclusively tailored electronic and spatial affinities for the PFAS that are able to selectively capture them from environmental streams. For the *in situ* detection and quantification of PFAS in complex, multicomponent matrices such as groundwater, the approach relies on the targeted capture of specific PFAS by these PFAS-specific capture probes immobilized on a platform. The platform acts as an electrode to directly measure PFAS concentration through a proportional change in electrical response upon their capture. A combination of optimization of platform design and incorporation of additional, sensitive detection modalities have allowed us to achieve detection limits as low as 0.5 ng/L for detection of PFAS compounds (compared to the 70 ng/L Health Advisory Limit of the U.S. Environmental Protection Agency).

INTRODUCTION

PFAS (per- and polyfluoroalkyl substances) are an anthropogenically generated group of ~6500 compounds characterized by a saturated carbon-fluorine tail. Their high thermal stability and resistance to chemical degradation due to the extremely stable C-F bonds (which are the fourth strongest bond in nature) have motivated their use as resistive coatings across multiple applications. Recent studies on the toxicological effects of these compounds have revealed their health impacts, which include elevated cholesterol, obesity, immune suppression, endocrine disruption, and cancer [1-3]. Identification of PFAS-contaminated sites is fast expanding across the globe, and in the United States alone, 620 locations across 43 different states have already been found to be affected; this also includes the drinking water systems serving an estimated 19 million people. These factors have cumulatively dictated the U.S. Environmental Protection Agency (EPA) to set the health advisory level for the most commonly studied PFAS (PFOS and its congener with the carboxylic acid functionality, namely perfluorooctanoic acid [PFOA]) in drinking water to as low as 70 ng/L (either individually or cumulatively).

To address this emerging issue, methodologies are needed for in situ monitoring and remediation of PFAS in water. These methods need to be functional for the wide range PFAS compounds at very low concentrations and address interferences from other constituents in the source waters that are usually present at much higher concentrations. Further, they need be field deployable for fast turnaround. However, existing *in situ* techniques that have been proposed for PFAS detection and monitoring are unable to meet the desired sensitivity requirements of multi-component real-world matrices, and therefore, the dominant methods of their analysis employ *ex situ* laboratory techniques [4] such as liquid chromatography tandem mass spectrometry (LC-MS/MS) for a limited number (up to 24) of compounds, total oxidizable precursor analysis (TOP) [5] as an overall PFAS mass estimate, or total fluorine analysis by particle induced gamma ray emission (PIGE) spectroscopy as an overall PFAS mass estimate [6]. However, results obtained from these techniques are either not adaptable for field deployment or their portable configurations lack the desired sensitivity to meet the recommended health advisory limits.

Therefore, a clear need exists for a highly sensitive *in situ* sensor that is inexpensive and field-deployable. To address this need, a new detection strategy has been developed in collaboration between Pacific Northwest National Laboratory (PNNL) and the New Jersey Institute of Technology that relies on a patent-pending sensor platform technology for rapid, field-deployable, *in situ* detection and quantification of PFAS in complex, multicomponent matrices such as groundwater. The approach relies on the targeted capture of specific PFAS by analyte-specific capture probes immobilized on a platform. The platform acts as an electrode to directly measure PFAS concentration through a proportional change in electrical response upon their capture. Using this methodology and a combination of platform design optimization and incorporation of additional detection modalities, we have achieved detection limits of 0.5 ng/L for PFOS and 1.3 ng/L for PFOA.

Further, once PFAS are detected in ground and drinking water sources, remediation may be necessary. To combat increasing concentrations of PFAS in drinking water, one suggested methodology involves the destruction and degradation of these molecules. Several approaches have been developed and tested for PFAS degradation, which include photo and electrocatalysis [7-10], biological degradation [11-12], plasma cleaning [13-14], chemical oxidation [10], and sonolysis [15-16]; however, these technologies suffer from inherent weaknesses such as inefficiency, high energy consumption, high cost, and inability of complete mineralization of PFAS to benign chemical forms [17-19]. An alternate strategy involves removal of these contaminants via adsorption, which is already a proven cost-efficient and scalable process for general removal of environmental contaminants. Application of this methodology for PFAS removal necessitates selection of candidates with high selective affinity for PFAS, fast uptake rates, large overall capacities, and resistance to PFAS leaching. Depending on the end application, these sorbents may also need to be scalable in terms of both expense and production. The traditional sorbents of choice for this purpose are activated carbons, carbon nanotubes, and ion exchange resins, and have met with moderate success in the removal of the more abundant, longer chains [20-22], namely, PFOS and PFOA; however, they are ineffective for the removal of the shorter chains, some of which have been shown to have higher toxicity (namely PFBS and PFBA).

To address this challenge, an emphasis at PNNL has been the development of a new class of porous sorbents with tailored affinity for PFAS of various chain lengths and functionalities. These sorbents have ultra-high surface area and tuned porosities. The affinities of these materials have been tailored by altering their porosity and electronic affinity such that they can selectively target specific PFAS of choice, or are customized to capture PFAS in general. Initial laboratory testing has shown that these materials have a >10-fold higher uptake capacity and >10-fold faster uptake kinetics than commercial sorbents (namely, granular activated carbon, powdered activated carbon, ion exchange resins) currently used for PFAS treatment commercially or by the U.S. Department of Defense (DoD).

Concurrent with the development of these materials, equilibrium batch testing on the viability of long-term PFAS removal from drinking water systems is underway in collaboration with AVANTech Incorporated.

Individually, these advances in PFAS monitoring and treatment offer substantial advantages over current methods. However, understanding PFAS fate and transport and selecting an appropriate remediation approach must consider the complexities of PFAS contamination issues. Thus, use of these advanced monitoring and treatment methods must be integrated with recent technical guidance and advances in application of system-based characterization and assessment, adaptive site management, exit strategies for active treatment, and determination of remediation end states.

METHODS

A key first step in our methodology was the development of capture probes with targeted PFAS affinity that could potentially be incorporated in an electrochemical platform for selective PFAS detection. The same type of probe could also potentially serve the complementary role as sorbent for PFAS removal from source water streams. Over the last decade, researchers at PNNL have developed a rich, vast and diverse library of nanoporous-material frameworks including metal-organic frameworks (MOFs), covalent organic frameworks (COFs), hierarchical porous carbons (HPCs), and zeolites for the selective sorption and capture of a variety of fluorocarbons (chain lengths C1-C10) with exceptional selectivity, sensitivity, and sorption capacity (representative examples shown in Fig. 1) [23-24]. These materials have shown the highest fluorocarbon sorption capacity reported to date (~180 wt%) [25], while also showing fast uptake kinetics and improved selectivities compared to sorbents adapted by DoD [23, 26].

These materials were further modified and tailored for PFAS targeted PFAS affinity with rapid sorption kinetics from environmental matrices. The advanced sorbent design uses specific surface functionalities in the nanoporous materials for adsorption of multiple specific PFAS from aqueous solutions effectively even in the presence of common interferences in groundwater applications. The effectiveness is due to the combined effect of the metal-centered framework of the material, associated surface functionalities, and the overall treatment particle porosity. The enhanced effectiveness of these treatment materials enables high-capacity treatment systems that are more robust to interferences and are more certain in terms of preventing breakthrough of PFAS in the system effluent than the current commercial sorbents. Given the extremely low PFAS treatment standard, the new sorption materials offer a potential solution to many PFAS treatment needs.

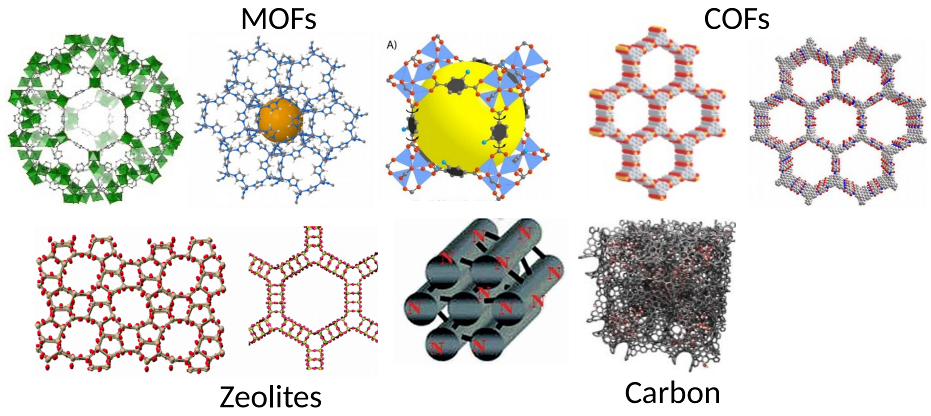

Fig. 1. Representative porous frameworks

After development of the capture probes, they were integrated within an electrochemical platform to detect PFAS in source water streams using voltammetric methods (cyclic voltammetry and differential pulse polarography) or electrical impedance spectroscopy. The targeted capture of the PFAS resulted in a change in the electrical response (change in redox, decrease in current, or increase in impedance). Further, multiple approaches such as optimization of the platform configuration and design and incorporation of additional, sensitive detection modalities have been incorporated in our design strategy to enhance the device sensitivity. Using this methodology and a combination of platform design optimization and incorporation of additional detection modalities, we have achieved detection limits of 0.5 ng/L for PFOS and 1.3 ng/L for PFOA. These detection limits are significantly lower than the Health Advisory Limit of 70 ng/L recommended by EPA. The detection limit is comparable to quantification limits for state-of-the-art laboratory techniques.

The key benefits of this platform are (1) the ability to eliminate matrix interferences; (2) highly sensitive, accurate, and precise quantification; and (3) responsiveness to dynamic ranges of PFAS concentrations. The approach has been demonstrated for the detection of multiple PFAS compounds in simple and complex matrices. Given the recognized difficult and cost of laboratory analyses for PFAS in water, these sensors have the potential to radically enhance the ability of sites to quantify PFAS contamination and develop suitable remediation approaches**.**

DISCUSSION

Development of capture probe with targeted PFAS affinities: A diverse range of porous-framework materials designed at PNNL were tested as potential capture probes for PFAS uptake. These materials consisted of mesoporous materials as well as MOFs, COFs, zeolites, and HPCs. The initial selection of the porous materials was based on high surface area with functional groups or metal centers with super fluorophilicity and high stability under aqueous conditions The uptake of a diverse range of PFAS with varying functionalities and chain lengths by the PNNL designed probes was tested in both deionized (DI) water and groundwater. For sorption studies, batch contact experiments were performed with either DI water or groundwater from U.S. Department of Energy (DOE) well 299-W19-36 at the Hanford Site (composition of groundwater given in TABLE I). The water was spiked with select PFAS and contacted with a given mass of the chosen porous-framework materials for 24 hours. PFAS' sorption was monitored using ^{19}F nuclear magnetic resonance (NMR) of the solution pre- and post- contact. We have also made progress in demonstrating the comparative uptake of nine different PFAS (shown in Fig. 2) by porous-frameworks. The PNNL-designed materials were observed in general to demonstrate significantly higher uptake capacity from groundwater compared to the sorbents adapted by DoD or elsewhere [namely granular activated carbon (GAC), hydrophilic-lipophilic balance [27], or weak anion exchangers (WAX) [28]]. This higher capacity was presumably due to incorporation of tailored electronic affinity, superfluorophilicity, and porosity in these probes to allow specific PFAS selectivity.

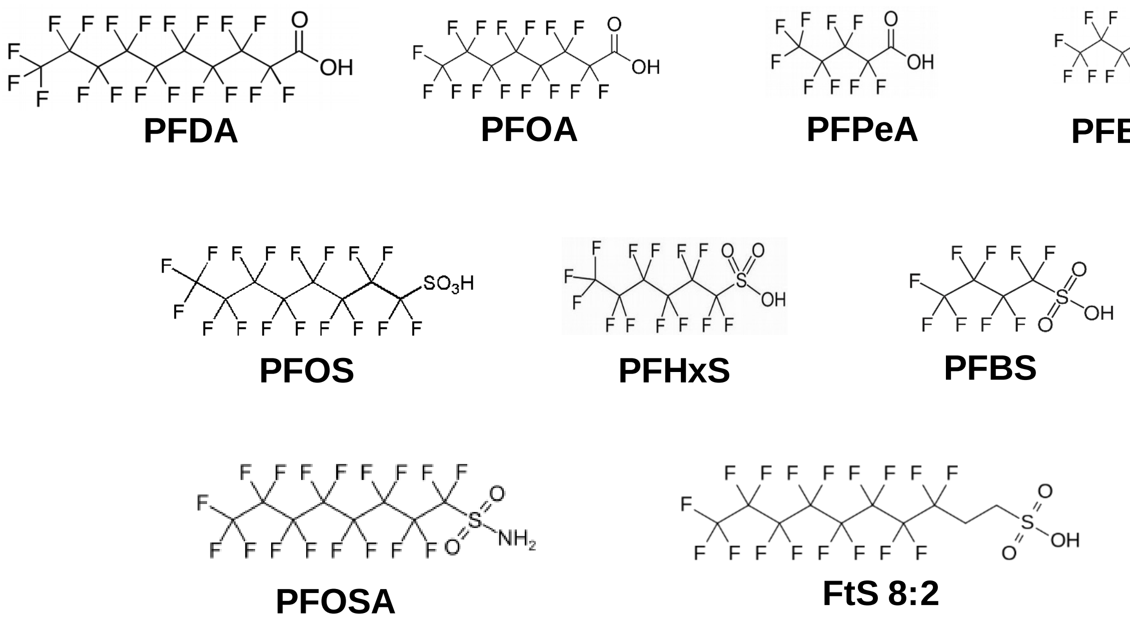

Fig. 2. Molecular structures of PFAS used in this work

TABLE I. Composition of groundwater from DOE well 299-W19-36 at Hanford, WA

Constituent	µg/L	Constituent	µg/L
Calcium	122,000	Nitrate	317,000
Chloride	181,000	Sodium	118,000
Total CR	17.3	Potassium	7,010
CR(VI)	0.05	Carbonate	116,000
Magnesium	36,400	Organics	123,000

It is noteworthy that while the designed probes in general demonstrated superior affinities toward the chosen PFAS compared to the commercial GAC, they could be further tailored to show greater preferential selectivities toward selected PFAS. Thus, the mesoporous MOF Cr-MIL-101 based on Cr(II/III) metal center showed a high affinity toward the PFAS; this is presumably due to the affinity of the Cr toward both the F and S [29-30]. On the other hand, the affinity of the Fe-MIL-101 based on softer Fe metal centers is considerably lower for PFAS, while they show significantly higher affinity toward the softer Lewis bases consisting of perfluorocarboxylic acids.

Evidence of this affinity comes from our X-ray photoelectron spectroscopy (XPS) studies on the MOF before and post-exposure to PFOS [30]. For Cr-MIL-101, the Cr region of the photoelectron spectrum of the pristine sample shows two Cr environments, as demonstrated by the $3p_{3/2}$ region being resolved into two species. MOF exposure to PFOS resulted in chromium oxidation. It should be noted that a detectable change in the Cr binding energies upon adsorption is in itself quite significant because the relative abundance of Cr from the MOF framework compared to PFOS molecules adsorbed is so large. This alone suggests strong adsorption affinities of PFOS on the MOF. For Fe-MIL-101, the Fe center is observed to get oxidized as well, albeit to a lesser magnitude, as shown in Fig. 3.

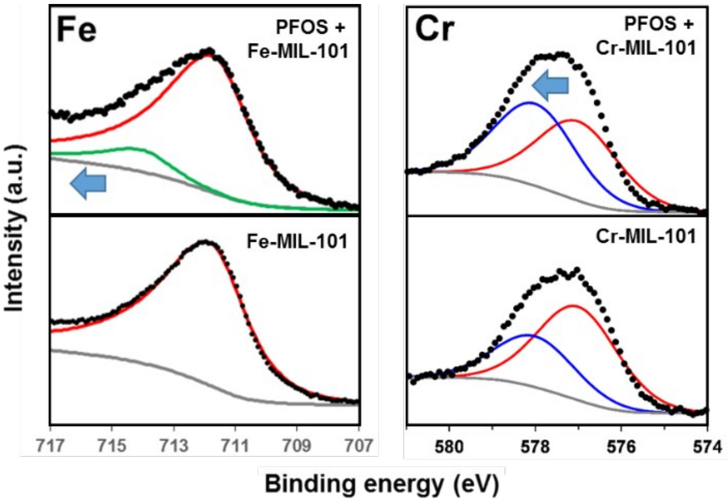

Fig. 3. X-ray photoelectron spectra showing binding energy changes of the metal node of the MOF framework for both Cr-MIL-101 and Fe-MIL-101 before and after exposure to PFOS. The circles represent the experimental data and the solid lines represent the Gaussian-Lorentzian fits for each different chemical environment of an element. The arrows indicate the direction of the shift going from pristine MOF to MOF exposed to PFOS [30].

Accordingly, the F region of the XPS spectrum (Fig. 4) of PFOS-loaded MOFs shows an opposite shift, as expected. When compared to pure PFOS, the PFOS sorbed onto Cr-MIL-101 showed reduction of F through the appearance of a second F environment with lower binding energy compared to pristine PFOS, suggesting the F center is gaining electron density. A similar, yet more pronounced, reduction of the F atoms is observed for Fe-MIL-101. In both cases, this reduction is suggestive of a synergistic redox process with the F atoms pulling electrons away from the metal center, and thereby being reduced. Based on the fluorine spectrum alone, PFOS-exposed Fe-MIL-101 has a more reduced F environment, suggesting stronger interactions with the fluorinated hydrophobic tail compared to those with Cr-MIL-101.

Ultimately, the S region of the photoelectron spectrum must be probed since high concentrations of PFOS (past the critical micelle concentrations) are expected to have more sulfur-containing moieties exposed to adsorption sites. This S region of the spectrum shows a similar, albeit significantly larger, shift in the same direction as the F spectrum. This observation confirms the expectation that the sulfur-containing head groups would be forced to interact more with adsorption sites of the MOF frameworks compared with the hydrophobic tails. This indicates a significantly reduced S environment after sorption compared to free PFOS. This also suggests a slightly stronger interaction with Cr-MIL-101 compared to Fe-MIL-101, suggesting Cr-MIL-101 likely has a more favorable interaction with PFOS.

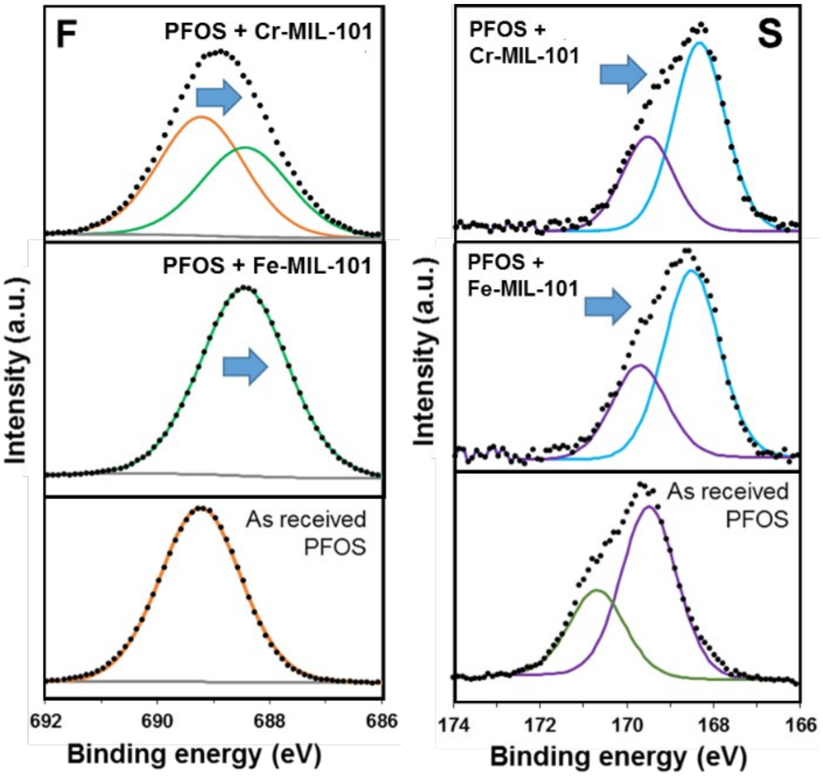

Fig. 4. X-ray photoelectron spectra showing binding energies changes of the fluorine atoms from the hydrophobic tail and the sulfur atom from the polar head group for both Cr-MIL-101 and Fe-MIL-101 before and after exposure to PFOS. The circles represent the experimental data and the solid lines represent the Gaussian-Lorentzian fits for each different chemical environment of an element. The arrows indicate the direction of the shift going from as received PFOS to PFOS captured on MOFs [30].

While more detailed studies are required to gain a comprehensive understanding of these effects, the observed trends do suggest that these materials can be judiciously tailored for targeted PFAS selectivity based on functionalities [31]. For future efforts, pore engineering will also be used to vary micro/mesoporosity for enhancing molecular sieving to separate varying chain lengths and sizes.

The uptake kinetics of our chosen materials were also observed to be significantly better compared to commercial GAC, as shown in Fig. 5, presumably due to a combination of the electronic affinities mentioned above with the high surface area and huge pore volumes that elevate high sorption capacities and rapid kinetics due to high amount of active site density in the pores.

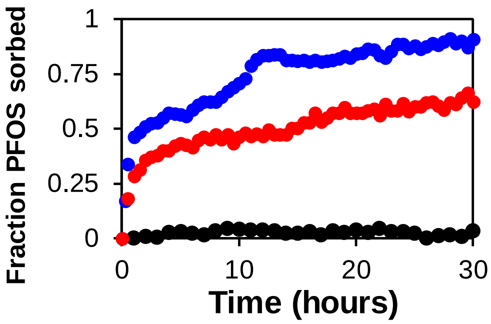

Fig. 5. Kinetics of uptake of 10 mM PFOS solution by 10 mg of different probes from groundwater (PFOS: probe = 1:1 w/w): (black symbols) commercial GAC, (red symbols) Fe-MIL-101, (blue symbols) Cr-MIL-101 [30].

Developing an electrochemical probe for targeted PFAS detection: After development of capture probes, they were incorporated within an electrochemical sensor platform for the rapid, selective detection. The detection of PFAS was done electrical impedance spectroscopy (EIS) via two steps: (1) first, a recognition step that preferentially and selectively captures the target PFAS from a sample matrix using specific affinity based interactions; (2) second, a transduction step that converted this targeted binding event into a unique, measurable electrochemical response.

One of the detection modes was EIS, where a microfluidic platform was used. Here, the select capture probe was directly incorporated in the electrochemical platform, and the capture of PFOS was analyzed using EIS. This allowed us to obtain a limit of quantification of ***1 ng/L which, to our knowledge, is unprecedented for portable approaches for PFOS detection and quantification.***

An additional detection modality was also designed in case a lower detection limit needed to be achieved. In this instance, a secondary, more-sensitive detection mode was incorporated, based on the monitoring of the luminescence intensity during a simultaneous redox conversion of a non-luminescent molecule (**NL**) to its luminescent form (**L**) at the electrode contact solution. In this mode, PFAS capture would passivate the electrode inhibiting the conversion, proportionately reducing luminescence intensity (Fig. 6). Availability of the two modes will provide operational flexibility across a dynamic range of PFAS concentrations, making the platform useful at both minimally contaminated and highly contaminated sites. The ability of this mode was demonstrated on a Ca^{2+} surrogate target and showed a limit of detection **three orders of magnitude lower than the electrochemical impedance modes** [32].

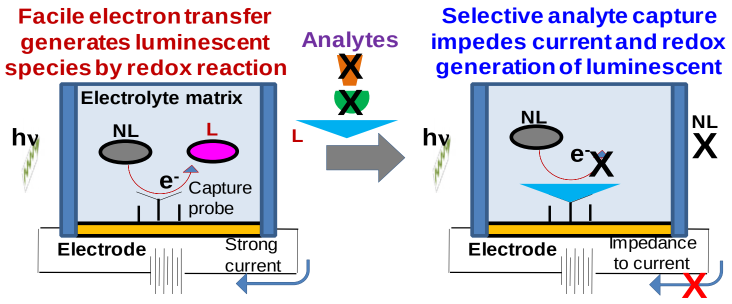

Fig. 6. Schematic representation of bimodal analyte detection with the incorporation of the additional luminescence mode in addition to the impedance mode [32].

For comparison, the detection limits achieved in our methodology are compared to state of the art *ex situ* detection techniques (TABLE II).

TABLE II. A comparison the limits of detection (LOD) for PFOS with our portable electrochemical technique relative to various state-of-the art lab based *ex situ* techniques.

Technique	**LOD**
LC-MS/MS	~1 ng/L
Time-of-flight mass spectrometry	1-10 ng/L
ex situ ion chromatography mass	1-10 pg/L

Particle induced gamma-ray	~10 nmol/cm^2
NMR	10 µg/L
TOP	1-10 ng/L
Our electrochemical technique	1 ng/L

CONCLUSIONS

Our preliminary studies show significant benefits of our approach in developing technologies for PFAS detection and capture. In terms of capture, our approach provides advantages in terms of both speed and capacity of PFAS capture compared to the commercial sorbents (namely GAC and WAX). This, coupled with the ability of select materials to capture the major representative PFAS from waste streams, can offer significant benefits in the long-term removal of PFAS.

In terms of sensing, the work has broad implications for environmental monitoring given that this monitoring approach can be readily expanded to other targets as well. This design can also be extended to other challenging contaminants of interest through design and selection of appropriate receptor probes, and can also be synergized with alternate approaches of contaminant capture [33], recognition, and detection [34], opening promising new opportunities in the diverse areas of CBRNE (chemical, biological, radiological, nuclear, and explosives) detection. With regard to PFAS, while current health advisory focus is on PFOS, or its carboxylate analog PFOA, there are a total of ~6500 different PFAS molecules known with recent studies showing that the smaller chains can be more toxic (namely GenX). This work provides a proof-of-concept of the detection of PFOS and its quantification at levels significantly lower than the health advisory limits. It also provides a strategy by which similar techniques can be designed for the detection and quantification of other PFAS targets (such as GenX) through the design of the capture probe.

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