FINAL REPORT

Destruction of PFAS and Organic Co-Occurring Chemicals in Water and Soil Present in Investigation-Derived Waste Using Novel Adsorbent and Ultrasound

SERDP Project ER18-1652

MARCH 2020

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
03/25/2020	SERDP Final Report	8/20/2018 - 8/20/2020

4. TITLE AND SUBTITLE
Destruction of PFAS and organic co-contaminants in water and soil present in investigation-derived waste at DoD sites using novel adsorbent and ultrasound

5a. CONTRACT NUMBER
18-C-0078

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
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5d. PROJECT NUMBER
ER18-1652

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
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8. PERFORMING ORGANIZATION REPORT NUMBER
ER18-1652

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Strategic Environmental Research and Development Program
4800 Mark Center Drive, Suite 17D03
Alexandria, VA 22350-3605

10. SPONSOR/MONITOR'S ACRONYM(S)
SERDP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
ER18-1652

12. DISTRIBUTION/AVAILABILITY STATEMENT
DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Per- and polyfluoroalkyl substances (PFAS) have become pollutants of global concern due to their widespread usage and presence in the environment. Investigation of PFAS impacted sites results in investigation-derived waste (IDW). The IDW is a mixture of soil, purge water from groundwater sampling, and fluid from decontamination of drilling equipment, and likely to have PFAS and other co-contaminants. The PFAS are also becoming a subject of environmental regulations.

The broad objective of this proof-of-concept project was to develop an innovative, low cost, simple to use, technology for the treatment of IDW containing groundwater and soil at DoD sites. This project evaluates the use of a novel adsorbent and ultrasound for the decontamination of groundwater and soil, and destruction of PFASs (PFOA, PFOS, PFBA, PFNA, PFHxA, PFBS, PFHxS, 6:2 FtS). The removal of CVOC co-contaminants is also investigated.

15. SUBJECT TERMS
PFAS, ultrasound, per and poly fluorinated substances, IDW

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Dr. Hui (Lisa) Yu
					19b. TELEPHONE NUMBER *(Include area code)*
UNCLASS	UNCLASS	UNCLASS	UNCLASS	48	215-313-8246

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Table of Contents

List of Tables

List of Figures

List of Acronyms

AFFFs	Aqueous Film-forming Foams
CD	Cyclodextrin
COD	Chemical Oxidation Demand
DoD	Department of Defense
GAC	Granular Activated Carbon
IDW	Investigation derived waste
PCE	Tetrachloroethylene
PFAS	Per- and Polyfluoroalkyl Substances
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctanesulfonic Acid
PFBA	perfluorobutanoic acid
PFBS	perflurobutane sulfonic acid
PFHxS	Perfluorohexane sulfonic acid
PFHxA	Perfluorohexanoic acid
PFNA	Perfluorononanoic acid
PFCA	Perfluoroalkyl carboxylic acid
6:2 FtS	Fluorotelomer sulfonic acid 6:2
Ppt	Parts-per-trillion
TCE	Trichloroethylene
TOC	Total Organic Carbon
TOPs	Total Oxidizable Precursors assay
VOC	Volatile Organic Compounds
US	Ultrasound
DI	Distilled water

Keywords

PFAS, ultrasound, per and poly fluorinated substances, IDW

Acknowledgements

Harika Dhanalakota and Rupam Rani of Amriton LLC worked on the project with the PI in conducting the experiments, and Dr. Rominder Suri assisted the PI by providing technical advice on the project and reviewed the reports. Samples for PFAS and other organics were analyzed at Temple University by Dr. Gangadhar Andaluri of Temple University. The adsorbent was synthesized and provided by Dr. Mithil Nayunigari of Temple University. We appreciate Mr. Jason Speicher, NAVFAC Atlantic, for his assistance in obtaining groundwater and soil samples. The financial support from the SERDP program is appreciated.

ABSTRACT

Introduction: Per- and polyfluoroalkyl substances (PFASs) have become pollutants of global concern due to their widespread usage and presence in the environment. Investigation of PFAS contaminated sites results in investigation-derived waste (IDW). The IDW is a mixture of soil, purge water from groundwater sampling, and fluid from decontamination of drilling equipment, and likely to have PFAS and other co-contaminants. The PFASs are also becoming a subject of environmental regulations.

Objectives: The broad objective of this proof-of-concept project was to develop an innovative, low cost, simple to use, technology for the treatment of IDW containing groundwater and soil at DoD sites. This project evaluates the use of a novel adsorbent and ultrasound for the decontamination of groundwater and soil, and destruction of PFASs (PFOA, PFOS, PFBA, PFNA, PFHxA, PFBS, PFHxS, 6:2 FtS). The removal of CVOC co-contaminants is also investigated.

Technical approach: Overall, the technology employs a three-step approach to clean the soil and groundwater and destroy PFASs.

i remove PFAS and co-contaminants from contaminated groundwater using a novel, low cost adsorbent

ii desorb contaminants from the soil and adsorbent with a chemical (desorption) solution in presence of ultrasound

iii destroy PFAS and other co-contaminants in the desorption solution and those sorbed on soil using ultrasound in one reactor

Key Results: In batch system, the novel polymer adsorbent can efficiently remove PFAS from groundwater + soil mixture, and final concentration ranged from non-detect to < 40 ppt. The adsorbent can also remove TCE and PCE co-contaminants from water in presence of PFAS, and PFAS removal was not adversely affected by the presence of CVOCs. The adsorption of PFAS from groundwater was very fast, and equilibrium was reached in approximately 5 minutes. Site contaminated soil was cleaned using ultrasound and a desorption solution. The final PFAS concentrations on the soil were much less than the target level of 10 ug/kg (except for PFOS which was 13 ug/kg). The Site soil had a very high contamination of PFOS (243 ug/kg), and 95% of PFOS was removed from the soil in 4 hours of sonication. Higher removal of PFOS from the soil could be achieved by process optimization. The ultrasound process was able to destroy PFASs (10 ppm each) in the desorption solution in 6 hours to concentrations <100 ppt for all PFAS except PFBS (final PFBS concentration was 3900 ppt). Higher destruction of PFAS could be achieved by process optimization. The sonication process with desorption solution was effective to clean the adsorbent in 6 hours, and the final concentrations of all PFAS were < 10 ug/kg. The initial PFOS loading on the adsorbent (from treatment of site groundwater) was 1725 ug/kg, and the final was 7 ug/kg, representing a cleanup efficiency of 99.6%.

Benefits: Overall, this proof-of-concept project showed that the groundwater and soil (including the spent adsorbent) can be decontaminated for on-site disposal, and the PFAS are destroyed, offering an environmentally sustainable solution to manage IDW at DoD Sites. The technology needs to be tested for different types of groundwater and soils, different soil-water slurry ratios, and optimized. A pilot-scale demonstration would allow the RPMs and stakeholders to evaluate the economic and technical suitability of the technology for IDW management at their Sites. In addition, further optimization of this technology could provide a low cost and environmentally green solution for the management of PFAS contaminated soil, as an alternative to soil incineration or landfilling.

EXECUTIVE SUMMARY

Introduction

Per- and polyfluoroalkyl substances (PFASs) have become pollutants of global concern due to their wide usage, ubiquitous presence in the environment, toxicity, persistence, and bio-accumulative properties. There are many Department of Defense (DoD) sites where groundwater is contaminated with PFAS. Investigation of PFAS contaminated sites results in investigation-derived waste (IDW). The IDW is a mixture of soil, purge water from groundwater sampling, and fluid from decontamination of drilling equipment, and likely to have PFAS and other co-contaminants. In 2015, US EPA issued a guidance of acceptable concentration of less than 70 parts per trillion for PFOA + PFOS in water. Some States have or are considering regulating PFASs. It is desired to develop efficient, low cost, environmentally sustainable treatment technologies that can cleanup groundwater and soil in IDW, and destroy PFAS and co-contaminants present in IDW.

Objectives

The broad objective of this proof-of-concept project was to develop an innovative, low cost, simple to use, technology for the removal and destruction of PFAS and organic co-contaminants from IDW containing groundwater and soil at DoD sites. Both, the contaminated groundwater and soil in IDW will be cleaned and suitable for possible on-site discharge. No secondary waste stream will be generated, and which will be of particular interest to DoD RPMs and regulatory professionals.

The key specific objectives of this proof-of-concept project were:
(I). For IDW groundwater cleanup – evaluate the feasibility of using a novel adsorbent in batch reactor, and determine adsorption kinetics, for the removal of PFAS from a mixture of groundwater and soil. The removal of co-contaminants from water using the adsorbent was also of interest.

(II). For IDW soil cleanup - evaluate the feasibility of using ultrasound and desorption solution to remove sorbed PFAS from the soil. Removal of PFAS adsorbed on the adsorbent was also of interest including the reusability of the adsorbent.

(III). For destruction of PFAS - evaluate the feasibility of using ultrasound to degrade PFAS present in a small volume of desorption solution and sorbed on the soil and the adsorbent.

This was a feasibility study to clean the groundwater and soil mixture. If the feasibility is acceptable, a follow-on project would extensively study the development and optimization of the technology to produce a pilot-scale reactor for decontamination of soil and groundwater in IDW.

Technical Approach

Contaminated soil and groundwater were obtained from NAS JRB Willow Grove Site and characterized. Batch adsorption isotherm experiments were conducted with groundwater, with and without the presence of soil, to examine the removal of PFAS. The PFAS examined in this study were PFOA, PFOS, PFBA, PFNA, PFHxA, PFHxS, 6:2 FtS and PFBS. By using adsorption process, the PFAS are removed from the groundwater and concentrated on the adsorbent. Batch adsorption kinetic experiments were also conducted, with and without the presence of soil, to examine the removal rate of PFAS. Several desorption solutions were examined. The adsorbent

was also treated with ultrasound and desorption solution. With this approach, overall, the PFAS are removed from groundwater and soil and concentrated in a small volume of desorption solution. The destruction of PFAS in the desorption solution was evaluated using high frequency ultrasound. Removal of TCE and PCE, as examples of possible co-contaminants, from water containing PFAS was also tested using batch experiments. For these tests, PCE, TCE and PFAS were spiked in laboratory water to simulate a mixture. The novel adsorbent comprises of a cyclodextrin polymer with ionic liquid coated iron (PILI) that has very high affinity for organic contaminants (Badruddoza et al., 2017). In addition, a newly synthesized polymer adsorbent was also tested.

Overall, the technology employs a three-step approach to clean the soil and groundwater in IDW, and destroy PFASs.

1. remove PFAS and co-contaminants from contaminated groundwater using a novel, low cost adsorbent
2. desorb the contaminants from the soil and adsorbent with a chemical (desorption or regenerant) solution in presence of ultrasound
3. destroy PFAS and other co-contaminants in the desorption solution and those sorbed on soil using ultrasound in one reactor

For possible on-site application of the technology, the novel adsorbent will be mixed in the IDW tank to remove PFAS and co-contaminants from groundwater. The adsorbent and soil will be filtered out and the treated groundwater will be discharged. The contaminants sorbed on the adsorbent and soil will be desorbed and destroyed using ultrasound in one reactor. The iron-based adsorbent is separated from the slurry using magnets and could be reused or disposed off after decontamination. The treated soil could be disposed off at the site.

This limited scope project discusses the proof-of-concept results on adsorption, desorption and destruction of contaminants using ultrasound.

Results and Discussion

Groundwater and soil from NAS JRB Willow Grove site were obtained and PFAS concentrations were analyzed. The ground water was mainly contaminated by PFOS and which was around 52 ppb (Table 1). PFOS contamination in groundwater and soil was significantly higher than other PFASs.

In batch experiments, the adsorbent was combined with groundwater and soil to test the adsorbent efficiency for removal of PFAS from groundwater. The detailed results are shown in Table 2. The groundwater mixture contained 15g/L of adsorbent and 5 g/L of soil. After one-time adsorption, the final concentrations of each PFAS was less than 70 ppt, with PFOA+ PFOS around 31 ppt. The objective was to achieve concentration of PFOA+ PFOS <70 ppt, and which was met. As additional test, the groundwater was separated from the adsorbent, and upon adding another dosage of adsorbent (15 g/L) to it, the final total concentration of all PFASs together was further reduced to less than 91 ppt, with PFOA+ PFOS around 20 ppt. If needed, use of higher adsorbent amount could lead to lower concentrations of individual PFAS. These tests demonstrate that the Site IDW groundwater, in presence of soil, could be treated with our adsorbent in batch mode (i.e. in the

IDW tank) to desired PFAS levels which would allow for onsite discharge of the treated groundwater.

Table 1. NAS JRB Willow Grove site soil and groundwater characteristics.

	Ground water (ng/L)	Soil (ug/kg)
PFOA	920.00	5.35
PFOS	51,935	242.69
PFNA	21.25	8.13
PFBA	212.90	2.29
PFHxA	940.00	3.81
PFHxS	3106.00	10.86
PFBS	583.43	12.41
FTS 6:2	1060	96.46
COD (mg/L)	3	na
moisture content (%)	na	0.8
volatile solids (g/kg)	na	20.8
TOC (mg/L)	2.61	na

na: not applicable or available

Table 2. Removal of PFAS in IDW groundwater and soil mixture. Date reported is for aqueous phase. Initial concentration of PFAS in the groundwater are listed in Table 1.

Adsorbent dosage in groundwater + soil (5 g/L) mixture	**PFAS**	**Final Concentration (ppt or ng/L)**	**PFAS removal (%)**
NI-1 adsorbent, 15g/L, two step adsorption	PFOA	14.83	98.39
	PFOS	4.44	99.99
	PFNA	nd	100.00
	PFBA	37.85	82.22
	PFHxA	nd	100.00
	PFHxS	1.17	99.96
	PFBS	20.63	96.46
	fts 6:2	12.00	98.87

nd: non-detect

The mechanism of our adsorbent for PFAS adsorption is (1) complex formation through host−guest hydrophobic interactions occurring between the cyclodextrins and the hydrophobic carbon chain in PFAS molecules and (2) electrostatic interactions between the negatively charged PFAS anions and positively charged sorbent / ionic liquid functional group. The adsorbent has Fe_3O_4 component, and maybe the reason that the removal of sulfonate PFAS was generally higher than the corresponding carboxylate group of PFAS.

As a secondary objective, batch adsorption isotherm experiments were also conducted to examine the removal of TCE and PCE as co-contaminants, in the presence of PFAS, from water. With a very low dosage of the adsorbent (1.25 g/L), about 40% removal of CVOCs was observed. Higher removal could be achieved using higher dosage of the adsorbent. It was noted that the adsorption of PFAS was higher than the CVOCs. This indicates that PFAS removal will not be affected adversely by the presence of CVOCs. These results provide the proof-of-concept that CVOC co-contaminants could also be removed along with PFAS using the proposed technology.

Batch adsorption kinetic experiments were conducted using laboratory DI water to see how quickly can the PFAS be removed from the water. The effect of Site soil on the adsorption kinetics was also examined by conducting tests with and without the presence of soil in the solution. Figure 1 below shows an example of the adsorption kinetics. In both systems, all the PFAS reached the adsorption equilibrium very quickly and in about 5 minutes. The soil in the solution did not seem to affect the PFAS adsorption kinetic. However, in the soil-water-adsorbent mixture, the PFBA removal was slightly decreased after several hours. It may be possible that with extended time, some of the PFBA sorbed on the soil desorbed into the solution, and hence, the overall removal efficiency reduced slightly with time.

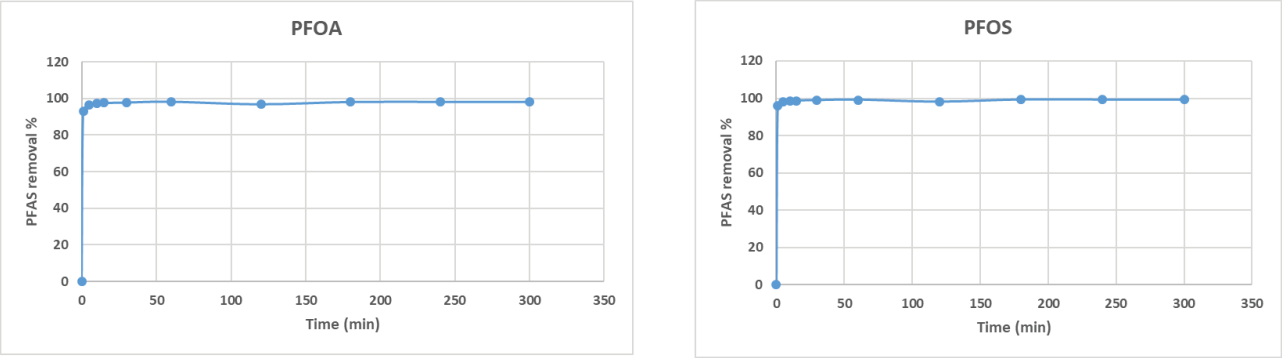

Figure 1. PFAS adsorption kinetic results in mixture of laboratory DI water and soil (PFAS initial concentrations: 50 ppb; PILI adsorbent dosage: 2.5g/L; soil content: 2.5g/L).

A number of desorption solutions (also referred to as regenerant solution) were tested, and 1M NH_4OH solution was selected for further testing in this proof-of-concept project. The 1M NH_4OH solution provided very high desorption, and at the same time did not impede the ultrasound destruction of the desorbed PFAS. High concentration of PFAS (10 ppm of each) were spiked in 1 M NH_4OH solution, and the destruction of PFAS using ultrasound is shown in Figure 2. The removal of most PFAS reached more than 95% within 3 hours of ultrasound reaction (except PFBA and PFBS). On extending the ultrasound reaction to 6 hours, higher removal was achieved, and the final concentration in the solution was <100 ppt for all PFAS except PFBS (PFBS was 3900 ppt). Higher destruction of PFAS could be achieved by process optimization. These results show that the desorption solution containing high concentration of PFASs can be cleaned and PFAS destroyed with ultrasound. The treated desorption solution can be used for the next cycle of desorption or disposed off at the Site. As follow-on work, it is suggested to optimize the ultrasound process, and develop a pilot-scale ultrasound reactor for onsite demonstration.

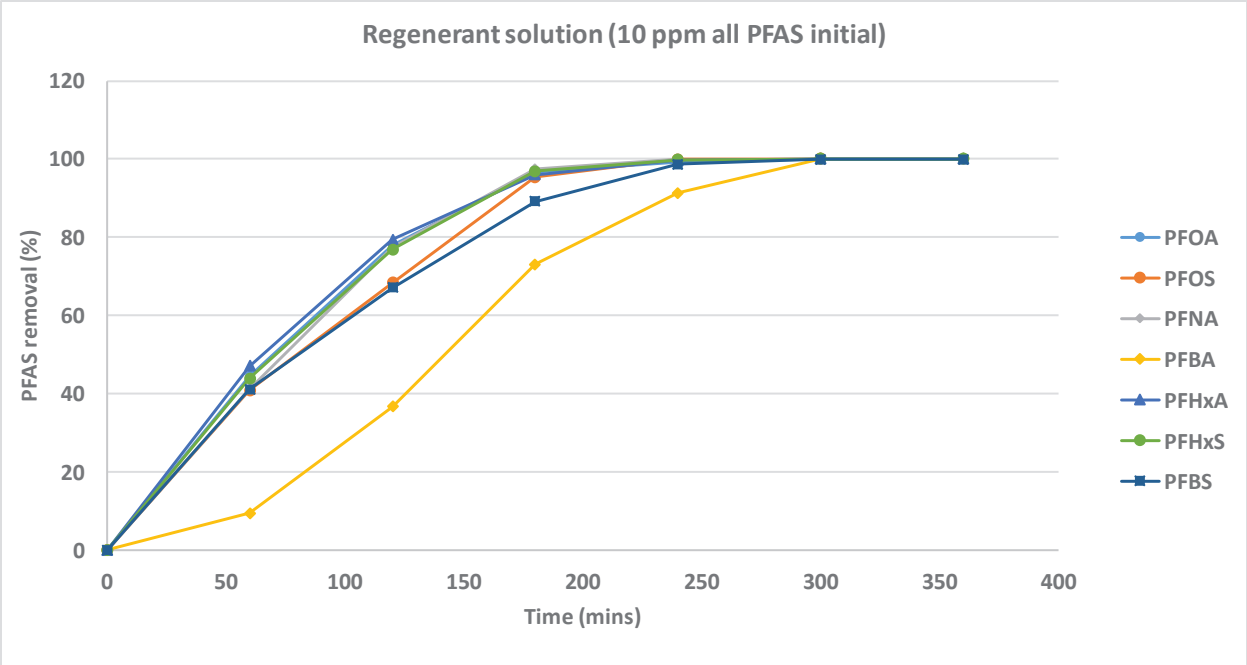

Figure 2. Ultrasound degradation of PFASs (10 ppm of each as initial concentration) in desorption solution.

Ultrasound tests were conducted with the desorption solution used to clean the soil and the adsorbent. The adsorbent was separated from the slurry using a magnet. The remaining slurry containing both soil and concentrated PFAS solution was placed in the ultrasound reactor for the destruction of PFAS. The soil samples were treated with ultrasound process in presence of the desorption solution of 1M NH_4OH. After sonication, the soil sample was processed to determine the PFAS sorbed on it (using 3 step methanol extraction). The final PFAS concentrations in soil samples are shown in Table 3. Comparing with original soil PFAS data, after the ultrasound treatment, all PFAS concentrations significantly decreased. The final concentrations were much less than 10 ug/kg except for PFOS which was 13 ug/kg. Higher removal of PFOS from the soil could be achieved by using additional sonication time, and/or stronger regenerant solution. These proof-of-concept results demonstrate that the PFAS contaminated soil could be cleaned using the ultrasound process.

Table 3. PFAS sorbed on DoD Site Soil, before and after ultrasound processing.

Sample name	Concentration (ug/kg)						
	PFOA	PFOS	PFNA	PFBA	PFH_XA	PFH_XS	PFBS
Untreated Soil (based on 4 replicated soil extraction data)	5.35	242.69	8.13	2.29	3.81	10.86	12.41
Treated Soil; with desorption solution + ultrasound for 4 hours	0.21	12.87	ND	ND	0.35	1.51	6.47
Treated Soil; with DI water + ultrasound for 6 hours	0.52	50.6	ND	ND	0.2	2.5	4.54

The desorption of PFAS from the adsorbent was also examined. The adsorbent was subjected to 6 hours of sonication in presence of 1M NaOH as the desorption solution. The final concentrations of all PFASs was less than 10 ug/kg. The initial PFOS sorbed on the adsorbent was very high (1725 ug/kg), and final concentration of PFOS was 7 ug/kg, representing a cleanup efficiency of 99.6%.

Implications for Future Research and Benefits

This project provides the necessary proof-of-concept data on using novel adsorbent for efficient removal of PFAS from a dual media comprising of DoD Site groundwater and soil simulating IDW. The groundwater was cleaned to target level of <70 ppt (PFOA+PFOS), and individual PFAS were at much lower concentrations. The project also provides proof-of-concept data on decontamination of soil for PFAS removal. For some PFASs, the ultrasound treated soil was already at or below the standards and guidance values of most States. Higher removal or treatment (to reach desired PFAS levels) could be achieved by optimizing the proposed process.

Future research should examine the technology for groundwater and soil from different DoD locations, since the type of soil, PFAS contamination, groundwater chemistry can vary with location. This may affect the operational conditions of the technology. The process should be optimized, and process conditions determined to achieve desired PFAS levels for soil and groundwater to meet State standards. The IDW may contain different ratio of soil and groundwater, and hence, it is important to test the technology with several soil to groundwater ratios in the mixture. The optimized process should be tested at a pilot-scale at a DoD Site for decontamination of IDW. This would allow the stakeholders to evaluate the economic and technical suitability of the technology for their Sites.

Both, the contaminated water and soil particles in IDW can be decontaminated, and PFAS are destroyed by ultrasound in the same reactor. This proposed process will lead to the development of a very simple, low cost, small footprint, easy to operate treatment system having primarily a PVC tank with mixer for IDW, small filter, magnets, pH controller, and a small ultrasound reactor.

It must be pointed out that the proposed approach, with optimization, may also be used to treat PFAS contaminated soil on-site (to desired PFAS concentrations) where PFAS could be desorbed using a desorption solution and ultrasound, and then the desorbed PFAS are simultaneously destroyed by ultrasound. This approach could be a lower cost and environmentally sustainable alternative to thermal treatment or landfilling.

OBJECTIVES

There are many DoD sites where groundwater is contaminated with per- and polyfluoroalkyl substance (PFAS). Investigation of PFAS contaminated sites results in investigation-derived waste (IDW). The IDW is a mixture of soil, purge water from groundwater sampling, and fluid from decontamination of drilling equipment, and likely to have PFAS and other co-contaminants. It is desired to develop treatment technologies that can destroy PFAS and co-contaminants in IDW, and which was the primary focus of SON ERSON-18-L1. The broad objective of this proof-of-concept research was to develop an innovative, low cost technology for the removal and destruction of PFAS and organic co-contaminants from IDW containing groundwater and soil at DoD sites. Both, the contaminated water and soil will be cleaned and applicable for on-site discharge. This will be of particular interest to the RPMs and regulatory professionals.

Overall, the technology uses a three-step approach for PFAS and co-contaminant destruction for soil and water treatment in IDW:

i removal of PFAS and co-contaminants from contaminated groundwater using a novel, low cost adsorbent

ii desorb the contaminants from the adsorbent and soil with a chemical (regenerant) solution, and

iii destroy PFAS and other co-contaminants in the regenerant solution and those sorbed on soil using ultrasound

With this approach, the contaminants are removed and concentrated so that the treated water can be discharged. The concentrated contaminants and the trapped soil are then cleaned by ultrasound. The ultrasound process can destroy organics in the regenerant solution and can also clean the soil in the same operation.

The project objectives were to obtain proof-of-concept data, specifically:
(I). For the adsorption process, evaluate the feasibility, and determine the adsorbent capacity and kinetics for the removal of PFAS and co-contaminants from a mixture of water and soil.

(II). For the desorption process, evaluate and determine the desorption process parameters, applicable to adsorbent and soil mixture; and determine the reusability of the adsorbent.

(III). Evaluate the feasibility of destruction of (1) PFAS in the regenerant water and (2) PFAS sorbed on the soil using the ultrasound process in the same reactor.

This was a feasibility study to simultaneously clean the groundwater and soil mixture in one tank or reactor. If the feasibility is acceptable, a follow-on project will extensively study the development and optimization of the technology, and to produce a pilot-scale reactor for on-site demonstration.

BACKGROUND

Per- and polyfluorinated alkyl substances (PFASs) are persistent organic contaminants. The C-F bond in PFASs makes them one of the most stable compounds and therefore are very difficult to destroy with conventional technologies (Schultz et al., 2006; Sinclair and Kannan, 2006). Even the advanced water treatment technologies such as ozone and advanced oxidation processes (AOPs) are found to be ineffective in degrading such contaminants (Schroder and Meesters, 2005). PFASs have been used as surfactants, emulsifiers, and surface coatings, with specific applications including aqueous film-forming foams (AFFFs). The use of PFASs in AFFFs has resulted in groundwater contamination at a number of DoD sites (Conder et al., 2008; Houtz et al., 2013). Previous work, including research sponsored by DoD, has investigated various remediation and treatment strategies including chemical oxidation, chemical reduction, monitored natural attenuation, bioaugmentation, granular activated carbon, electrooxidation, ion exchange resin, plasma, soil combustion, and sorption enhancement. While limited headway has been made, most in situ remediation approaches result in transformation of larger PFASs into the smaller and more persistent forms (Suthersan et al., 2016).

Granular activated carbon (GAC) has been the technology of choice so far for pump and treat systems, however, it faces the issue of frequent carbon recharge due to quick PFASs breakthroughs leading to high operational costs. Moreover, the spent GAC has to be transported, and either disposed in a landfill or thermally reactivated, at additional cost and liability. For PFAS contaminated soil, thermal destruction or landfill are the current options. Many landfills are reluctant to accept soil, biosolids (sludge from biological wastewater treatment plants), spent GAC and IX resins that are contaminated with PFAS. Given these issues and the recent public attention and the EPA health advisory of 70 ppt (PFOA+PFOS) for drinking water, there is a need to develop advanced strategies to address PFAS contaminated groundwater and soil. Some States have or are considering regulating PFASs, for water and soil (https://pfas-1.itrcweb.org/wp-content/uploads/2020/01/ITRC_PFAS_Sec4Tables_Dec2020.xlsx)

A sustainable technology should be inexpensive, and efficiently remove and destroy PFAS and other co-contaminants present in the soil and water mixture of IDW. Amriton LLC has been working on the development and validation of a sustainable treatment technology for emerging contaminants of concern, including PFASs. The proposed technology uses polymer with ionic liquid coated iron (PILI) as adsorbent material that has very high affinity for organic contaminants (Badruddoza et al., 2017). The adsorbent material has two components: (a) polymer ionic liquid (active component that removes the contaminants such as PFAS, VOCs) and (b) support (inactive component; Fe_3O_4). This adsorbent showed better performance in removing PFOA and PFOS than GAC.

The polymer coat on the iron based PILI adsorbent is composed of beta cyclodextrin (CD) and ionic liquid (Badruddoza et al., 2017). CDs are environmentally benign compounds, and have unique physico-chemical characteristics and excellent selectivity towards organic compounds. The property of CD to form inclusion complexes (Figure S1 in Appendix) with various molecules through host-guest interactions has made it a useful compound for the removal of a number of contaminants from water and other applications (Harada et al., 1996; Crini et al., 1998; Loftssona and Jarvinen, 1999; Crini, 2005; Shao et al., 2010; Xin et al., 2010; Zhang et al., 2010;

Punyapalakul et al., 2013; Sakata et al., 2013; Bhattarai et al., 2014; Kawano et al., 2014; Suri and Bhattarai2014). CDs are glucose-based molecules and the presence of hydroxyl groups at position 2, 3, and 6 in each glucose unit can be used for the structural modifications (Crini, 2005). The commonly available different types of CDs are alpha-cyclodextrin, beta-cyclodextrin (BCD) and gamma-cyclodextrin which consists of six, seven and eight α-1,4 linked D(C)-glucopyranose units, respectively. The PILI adsorbent was primarily used in this project to remove PFAS from the laboratory water and groundwater.

The destruction of PFAS was examined using ultrasound process. The basis of ultrasound technology (Cyr et al., 1999; Loftssona and Jarvinen, 1999; Suri et al., 1999; Suri and Kamrajapuram, 2003; Fu et al., 2007; Suri et al., 2007; Cheng et al., 2008; Suri et al., 2008; Vecitis et al., 2008; Cheng et al., 2010; Suri et al., 2010; Vecitis et al., 2010; Andaluri et al., 2012; Yang et al., 2013; Campbell and Hoffmann, 2015; Rodriguez-Freire et al., 2015; Dietrich et al., 2016; Fernandez et al., 2016; Lin et al., 2016; Rodriguez-Freire et al., 2016) is the passage of high intensity sound waves through water. These sound waves create cavitation (or bubbles) due to oscillating pressures. Cavities grow to a critical size and implode, generating extreme temperatures and pressures at microscopic points. The destruction of organic contaminants can occur either due to thermal degradation or radical oxidation. Sonochemical degradation of PFAS has been reported in the literature (Cheng et al., 2008; Vecitis et al., 2008; Campbell et al., 2009; Cheng et al., 2010; Vecitis et al., 2010; Yang et al., 2013; Campbell and Hoffmann, 2015; Rodriguez-Freire et al., 2015; Fernandez et al., 2016; Lin et al., 2016; Rodriguez-Freire et al., 2016; Shende et al., 2019). PFASs degrade thermally at the cavity interface and via radicals produced in the solution, whereas co-contaminants such as VOCs can degrade thermally inside or at the cavity interface as well as via hydroxyl radicals in the bulk solution. In addition, ultrasound is likely to desorb and destroy the sorbed organics on the soil particles. Ultrasound has been traditionally used for cleaning surfaces and particles, although the frequency of ultrasound is important. The sorbed impurities get desorbed off the surfaces by the sound waves. It is hypothesized that in presence of ultrasound, PFAS and other co-contaminants will desorb from the soil into the bulk solution, and the soil will get cleaned. Moreover, use of a caustic solution will enhance the desorption of organics from soil particles in presence of ultrasound. Previous study (Suri et al., 2008) showed that 2-chlorophenol could be degraded in presence of silica particles. Ultrasound has also been shown to degrade many organic compounds in water. Hence, PFAS and co-contaminants such as TCE in solution are expected to get degraded in presence of soil. This project evaluates the feasibility of cleaning the soil particles in solution by destroying PFAS with ultrasound.

For on-site IDW treatment, our proposed technology approach is to add the adsorbent in the IDW tank and remove PFAS from the groundwater to a desired level so that the treated groundwater could be discharged at the site. The contaminated soil and adsorbent are then subjected to ultrasound in presence of a desorption (also referred to regenerant) solution to desorb the sorbed PFAS to a level where the soil is clean enough to be disposed at the Site. The adsorbent is recovered using magnets and reused, if needed. The desorbed PFAS in the regenerant solution are then destroyed using ultrasound under a controlled environment. With this approach, both groundwater and soil in IDW are decontaminated and discharged at the Site, and the PFAS are destroyed. It offers a low cost, on-site, low footprint, and environmentally sustainable solution to manage PFAS contaminated IDW.

For this proof-of-concept project, the target was to examine whether we could remove PFAS from the groundwater in the IDW to below 70 ppt. This would allow for on-site discharge of the groundwater. The target for the treatment of soil in IDW was of PFAS levels below 10 ug/kg for disposal, although some States may have more stringent limits ((https://pfas-1.itrcweb.org/wp-content/uploads/2020/01/ITRC_PFAS_Sec4Tables_Dec2020.xlsx). However, for this proof-of-concept project, we selected the limit of 10 ug/kg, with an understanding that more stringent levels could be achieved upon process optimization in a follow-on project. Overall, the target was to destroy PFAS in IDW, so that there is no generation of secondary waste stream requiring additional treatment.

For this proof-of-concept project, we wanted to answer the following specific questions:

1. can the PFAS be removed to below 70 ppt in the site groundwater in IDW in a batch reactor
2. how much adsorbent is needed to remove PFAS to below 70 ppt in the groundwater in IDW, as well as the time required for the adsorption process
3. can the site contaminated soil be treated to PFAS levels below 10 ug/kg using ultrasound and desorption solution
4. can the adsorbent be regenerated with the desorption solution and ultrasound, and reused
5. can the PFAS, present in the desorption solution, be destroyed to below 70 ppt by the ultrasound process

MATERIALS AND METHODS

Chemicals

The following chemicals were obtained from Sigma-Aldrich (USA): β-cyclodextrin, 1,2-dimethyl imidazole, p-toluenesulfonyl chloride, 1,4-hexamethylene diisocyanate (HMDI), and dimethylformamide (DMF), Fe_3O_4 nanoparticles (<50 nm), perfluorooctanoate (PFOA), perfluorooctanesulfonate (PFOS, sodium salt), Perfluorononanic acid (PFNA), perfluorobutyric acid (PFBA), perflurobutane sulfonic acid (PFBS), Perfluorohexanoic acid (PFHxA), Perfluorohexane sulfonic acid (PFHxS), Tetrachloroethylene (PCE) and Trichloroethylene (TCE). Fluorotelomer sulfonic acid 6:2 (6:2 FtS) was obtained from Wellington Laboratories (Canada). Other chemicals and reagents were purchased from Fisher Scientific (USA).

Synthesis of the ionic liquid coated iron (PILI) adsorbent

The PILI adsorbent was synthesized at Temple University and provided to Amriton for testing. The details of the synthesis method are described elsewhere (Badruddoza, et al., 2017).

Batch sorption and desorption tests

Batch isotherm experiments were conducted to test the adsorbent efficiency to remove organic contaminants from water. The contaminants of interest are: PFOA, PFOS, PFBA, PFBS, PFHxA, PFHxS PFNA, FtS 6:2, trichloroethylene (TCE) and tetrachloroethylene (PCE). For the initial tests, lab water was used. Later, contaminated groundwater and soil from a DoD site were used to represent IDW.

All the experiments were conducted in 50 mL polypropylene containers for PFAS, and in 40 ml glass vials for TCE and PCE. A pre-determined amount of adsorbent was weighted and placed in the container. A 40 mL of PFAS solution (either laboratory water or groundwater from a DoD Site) was then added to the vial containing the adsorbent and secured on the tumbler for 48 hours. The adsorbent was separated using magnet, centrifuged and the final concentration of each PFAS in the water were measured using LC/MS/MS instrument. In some cases, after the first adsorption cycles was completed, the adsorbent was separated, and the separated adsorbent was added to a new PFAS solution to initiate a new cycle of adsorption. Multiple adsorption cycles were conducted. The kinetic adsorption experiments were conducted with 50 ppb PFAS solution in 250 ml HDPE bottles. The water phase sample was collected at different time and filtered immediately using 0.2µm regenerated cellulose syringe filter (Corning, USA). For the batch isotherm tests with PCE and TCE as co-contaminants, all experiments were conducted in glass vials without any headspace.

For desorption of PFAS adsorbed on soil and adsorbent, different desorption (also referred to as regenerant in this report) solutions were added to vials containing the solid media. The vials were secured on the tumbler for 48 hours. The adsorbent was separated using magnet, centrifuged and the final concentration of each PFAS in the water were measured. In the case of soil, the mixture was centrifuged and separated from water. After separation, the solid media was washed thrice with DI water to remove any desorption solution.

PFAS extraction tests. To quantify PFAS sorbed on the soil (or adsorbent), a one gram sample of the soil (or adsorbent) was placed in a vial and 7 ml methanol was added. The mixture was vortexed for 5 minutes, centrifuged and the supernatant was collected. The procedure was repeated three times, and all the methanol supernatant were mixed. The supernatant was dried and then reconstituted, and analyzed for PFAS on LC/MS/MS instrument following the DoD approved method. From control tests, the average PFAS extraction efficiency of the methanol process was about 100%.

Ultrasound (US) Experiments

A 200 ml sample of PFAS contaminated water, either DI water or groundwater, was added in a glass flask and placed in the 1.5 KW ultrasound (US) reactor. In a control test, after the ultrasound experiment, the solution container was rinsed with methanol and no significant PFAS were measured in the rinsate thereby showing that PFAS were not being removed by sorption on the container. The solution was irradiated with ultrasound of 430 kHz frequency for specific period of time. Water samples were taken periodically and analyzed for the organic compounds of interest. For desorption+US experiments, a desorption solution was added to the solid media in a 200 ml flask and then placed in the US reactor for a specific period of time. Constant temperature was maintained by circulating cold water from a chiller in the US bath. For larger scale treatment operation, the soil water mixture will be placed directly in the US bath and sonicated.

Analytical methods

All the PFAS samples were analyzed using Waters Acquity UPLC coupled with a Xevo TQ-S mass spectrometer (LC/MS/MS, Waters Corps, USA) with a BEH C–18 (2.1 × 50 mm, 1.7µm) column (Waters Corps, USA). The column temperature was maintained at 40 °C. The analytes were eluted using 2mM ammonium acetate in 95/5 water/methanol and methanol mobile phases

at a flow rate of 300µL/min for 8 min. The electrospray ionization capillary voltage was 3.53 kV with source and desolvation temperatures of 150 °C and 350 °C, respectively. The cone gas flow, desolvation gas flow, and collision gas flow were maintained at 150 L/h, 800 L/h, and 0.14 mL/min, respectively. The analysis followed the DoD approved qa/qc procedures.

Quantitative analysis of TCE and PCE was performed using liquid-liquid extraction followed by gas chromatography/mass spectrometry (GC/MS) analysis. The GC/MS analysis is performed using Agilent 7890 GC coupled with 5975C MS. Auto injections are made using splitless mode and the injection volume is 3µL. Injection temperature is 250 °C and the head pressure is 60kPa of helium. The initial temperature of the oven was 45 °C, held for 4.5 minutes and then ramped to 100 °C at a rate of 12°C/min. The temperature was then ramped to 240 °C at a rate of 25 °C/min and held for 1.3 minutes. Transfer line temperature to the MS was maintained at 250 °C and the electron energy was 70eV.

Ion chromatography (IC) analyses for fluoride ions was performed using a Metrohm 930 Compact IC Flex equipped using a Metrosept-a Supp. 150/4 mm column operating at a flow rate of 0.7 mL/min and a column temperature of 30 ˚C. The mobile phase was 0.32M Na_2CO_3/0.1M $NaHCO_3$. The IC instrument LOD for fluoride, nitrite, nitrate, and sulfate anions was 0.3 mg/L. The IC instrument LOQ of fluoride, nitrite, nitrate, and sulfate anions was 0.5 mg/L.

PFAS Total Oxidizable Precursor (TOP) Assay was used to measure the total concentration of PFASs not detectable by direct analysis. The procedure followed the method of Casson and Chiang(2018).

Other analysis: Moisture content for soil samples was analyzed using Standard Method 2540D; Volatile solids for soil samples was analyzed using Standard Method 2540E; TDS for ground water samples was analyzed using ASTM 5907 method; COD was analyzed using Hach kits (USEPA approved Reactor Digestion Method 8000); TOC was analyzed using a TOC analyzer; pH was measured using pH meter (OAKION pH meter).

RESULTS AND DISCUSSIONS

The following sections describe the key results of this proof-of-concept project.

(1) Removal of PFAS from laboratory water

Initially, batch isotherm experiments were conducted to test the removal of PFAS from water. Laboratory DI water was used with a mixture of PFAS at high initial concentrations of 50 ppb of each PFAS, and data is shown in Figure 1. The adsorbent (1.25 g/L) shows very high removal for both long chain and short chain PFAS, including PFBA. The average removal rates were more than 96%. A higher removal could be achieved by using a higher dosage of the adsorbent. Figure S2 in Appendix shows that the adsorbent performs better than GAC for the removal of PFOA and PFOS, and the adsorption equilibrium is well described by Freundlich isotherm model (Figure S3).

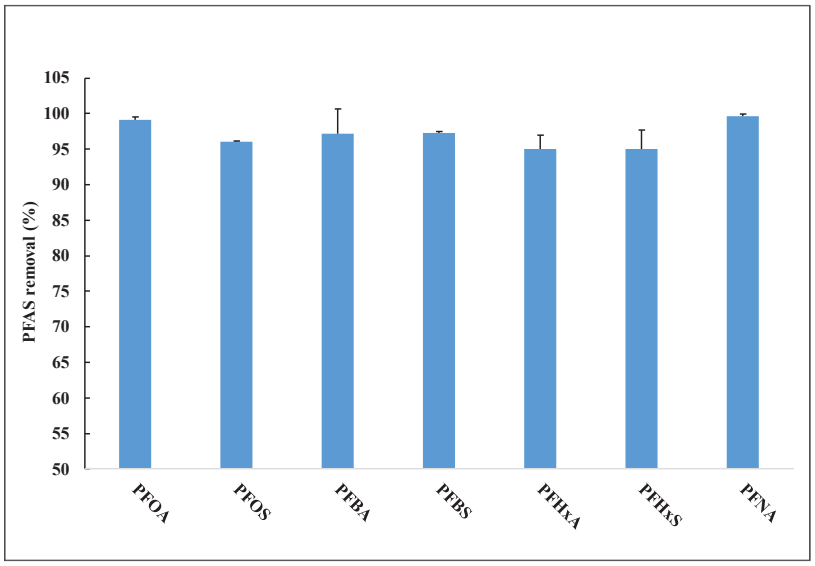

Figure 1. Removal of PFAS from laboratory DI water (1.25g/L PILI adsorbent in 50 ppb of each PFAS in multicomponent solution). Data reported is average of triplicate experiments.

(2) PFAS removal from mixture of contaminated groundwater and soil obtained from DoD Site

Groundwater from NAS JRB Willow Grove site was obtained and PFAS concentrations were analyzed. The ground water is mainly contaminated by PFOS and which was around 52 ppb (Table 1). Table 1 also lists the characteristics of the soil obtained from the Willow Grove site. PFOS contamination in groundwater and soil was significantly higher than other PFASs.

In batch experiments, the PILI adsorbent was combined with groundwater and soil to test the adsorbent efficiency for the removal of PFAS from groundwater. The detailed results are shown in Table 2. In presence of 5 g/L of site soil, 15g/L of adsorbent was added to site groundwater based on our preliminary adsorption data (Table S1 in Appendix). After one-time adsorption, the final concentrations of PFAS were still higher than 70 ppt. The groundwater was separated from the adsorbent, and upon adding another dosage of adsorbent (15 g/L) to it, the final concentration of most PFASs was less than 70 ppt, with the exception of PFBA whose concentration was about 90 ppb. Use of higher adsorbent amount could lead to the desired <70 ppt for all the PFAS.

Table 1. NAS JRB Willow Grove site soil and groundwater characteristics.

	Ground water (ng/L)	Soil (ug/kg)
PFOA	920.00	5.35
PFOS	51,935	242.69
PFNA	21.25	8.13
PFBA	212.90	2.29
PFHxA	940.00	3.81
PFHxS	3106.00	10.86
PFBS	583.43	12.41
FTS 6:2	1060	96.46
COD (mg/L)	3	na
moisture content (g/kg)	na	8
volatile solids (g/kg)	na	20.8
TOC (mg/L)	2.61	na

na: not applicable or available

In further tests, another CD polymer-iron based adsorbent NI-1(obtained from our NSF SBIR project) was used. With only one-time adsorption, the final concentrations of all PFAS were less than 70 ppt, and data is shown in Table 2. A two-step strategy of adsorption was also tested, and the final total concentration of all PFASs together was less than 70 ppt, with PFOA+ PFOS around 20 ppt. As an example, PFOS concentration in groundwater of about 52,000 ppt (Table 1) was reduced to < 40 ppt (Table 2) after treatment. *These tests demonstrate that the Site groundwater, in presence of soil, can be treated with our adsorbent in batch mode (i.e. in the IDW tank) to desired PFAS levels which would allow for onsite discharge of the treated groundwater.* In the follow-on project, additional tests will be done with the NI-1 adsorbent to optimize the process.

Data in Table S1 shows that in the absence of soil, the adsorbents provide higher removal of PFAS from groundwater. Hence, if the soil could be separated from the groundwater, the PFAS removal efficiency would be higher using the adsorption process.

Table 2. Removal of PFAS in IDW groundwater and soil mixture. Date reported is for aqueous phase. Initial concentration of PFAS in the groundwater are listed in Table 1.

Adsorbent dosage in groundwater + soil (5 g/L) mixture	**PFAS**	**Final Concentration (ng/L or ppt)**	**PFAS removal (%)**
PILI adsorbent, 15g/L, one step adsorption	PFOA	113.17	87.70
	PFOS	2966.34	94.29
	PFNA	4.73	77.74
	PFBA	180.15	15.38
	PFHxA	373.12	60.31
	PFHxS	274.68	91.16
	PFBS	163.95	71.90

	fts 6:2	298.68	84.53
PILI adsorbent, 15g/L, two-step adsorption	PFOA	10.98	98.81
	PFOS	66.59	99.87
	PFNA	nd	100.00
	PFBA	98.83	53.58
	PFHxA	20.68	97.80
	PFHxS	6.34	99.80
	PFBS	18.24	96.87
	FTS 6:2	28.98	97.26
NI-1 adsorbent, 15g/L, one step adsorption	PFOA	9.46	98.97
	PFOS	21.28	99.96
	PFNA	nd	100.00
	PFBA	64.24	69.83
	PFHxA	10.78	98.85
	PFHxS	16.15	99.48
	PFBS	18.24	96.87
	fts 6:2	14.05	98.68
NI-1 adsorbent, 15g/L, two-step adsorption	PFOA	14.83	98.39
	PFOS	4.44	99.99
	PFNA	nd	100.00
	PFBA	37.85	82.22
	PFHxA	nd	100.00
	PFHxS	1.17	99.96
	PFBS	20.63	96.46
	fts 6:2	12	98.87

nd: non-detect

The adsorbent showed very good removal of PFAS from groundwater with or without the presence of soil (Figures S4 and S5 in Appendix). It was observed that the removal of PFAS generally has the following order: PFOS>PFOA, PFHxS>PFHxA and PFBS>PFBA. The removal of all sulfonate PFAS was higher than the carboxylate PFAS. According to Pearson's concept of hard and soft acids/bases, the sulfonate group, that is a hard base, could be more readily adsorbed on oxide surfaces. The adsorbent has Fe_3O_4 component, thus the removal of sulfonate PFAS was slightly higher than the corresponding carboxylate group of PFAS. Other mechanisms of the adsorbent for PFAS adsorption are: (1) complex formation through host−guest hydrophobic interactions occurring between the cyclodextrins and the hydrophobic carbon chain in PFAS molecules and (2) electrostatic interactions between the negatively charged PFAS anions and positively charged sorbent / ionic liquid functional group.

These preliminary results show that with appropriate dosage of adsorbent in a batch of IDW, all PFASs could be removed from the groundwater to a desired level so that the treated groundwater could be discharged onsite. This technology approach seems to be very promising for onsite application at DoD sites.

(3) Removal of TCE and PCE co-contaminants in presence of PFAS

As a secondary objective, batch isotherm experiments were also conducted to examine the removal of TCE and PCE as co-contaminants from water using our adsorbent, and the results are shown in Table 3. With a very low dosage of the adsorbent (1.25 g/L), about 40% removal of CVOCs was observed. Note that all organic compounds were at very high initial concentrations (Table 3). Higher removal could be achieved using higher dosage of the adsorbent. It was also noteworthy that the adsorption of PFAS was higher than the CVOCs. This indicates that PFAS removal will not be affected adversely by the presence of CVOCs. In follow-on work, the effort will optimize the removal of CVOC co-contaminants along with PFAS. *These results provide the proof-of-concept that CVOC co-contaminants could also be removed along with PFAS using the proposed technology.*

Table 3. Batch isotherm experiments for removal of TCE and PCE co-contaminants in presence of PFAS; (1.25 g/L PILI adsorbent in TCE/PCE + PFAS solution).

Compound name	Initial concentration (ppb)	Final concentration (ppb)	Removal (%)
TCE	38.45	24.10	37.3
PCE	25.35	13.20	47.9
PFOA	37.94	0.55	98.6
PFOS	32.61	0.90	97.2
PFNA	44.14	0.95	97.9
PFBA	38.92	4.51	88.4
PFHxA	64.68	0.63	99.0
PFHxS	41.07	0.46	98.9
PFBS	29.68	0.60	97.9
FTS 6:2	8.86	0.07	99.2

(4) PFAS Adsorption Kinetic Experiments

Batch adsorption kinetic experiments were conducted using laboratory DI water to see how quickly can the PFAS be removed from the water. The effect of Site soil on the adsorption kinetics was also examined by conducting tests with and without the presence of soil in the solution, and the kinetic results are shown in Figures 2 and 3. In both systems, all the PFAS reached their adsorption equilibrium very quickly and in approximately 5 minutes. This is very promising. The soil in the solution did not seem to affect the PFAS adsorption kinetic. However, in the soil-water-adsorbent mixture, the PFBA removal was slightly decreased after several hours. It may be that, with extended time, the PFBA sorbed on the soil was getting desorbed into the solution, and hence, the overall removal efficiency reduced somewhat with time.

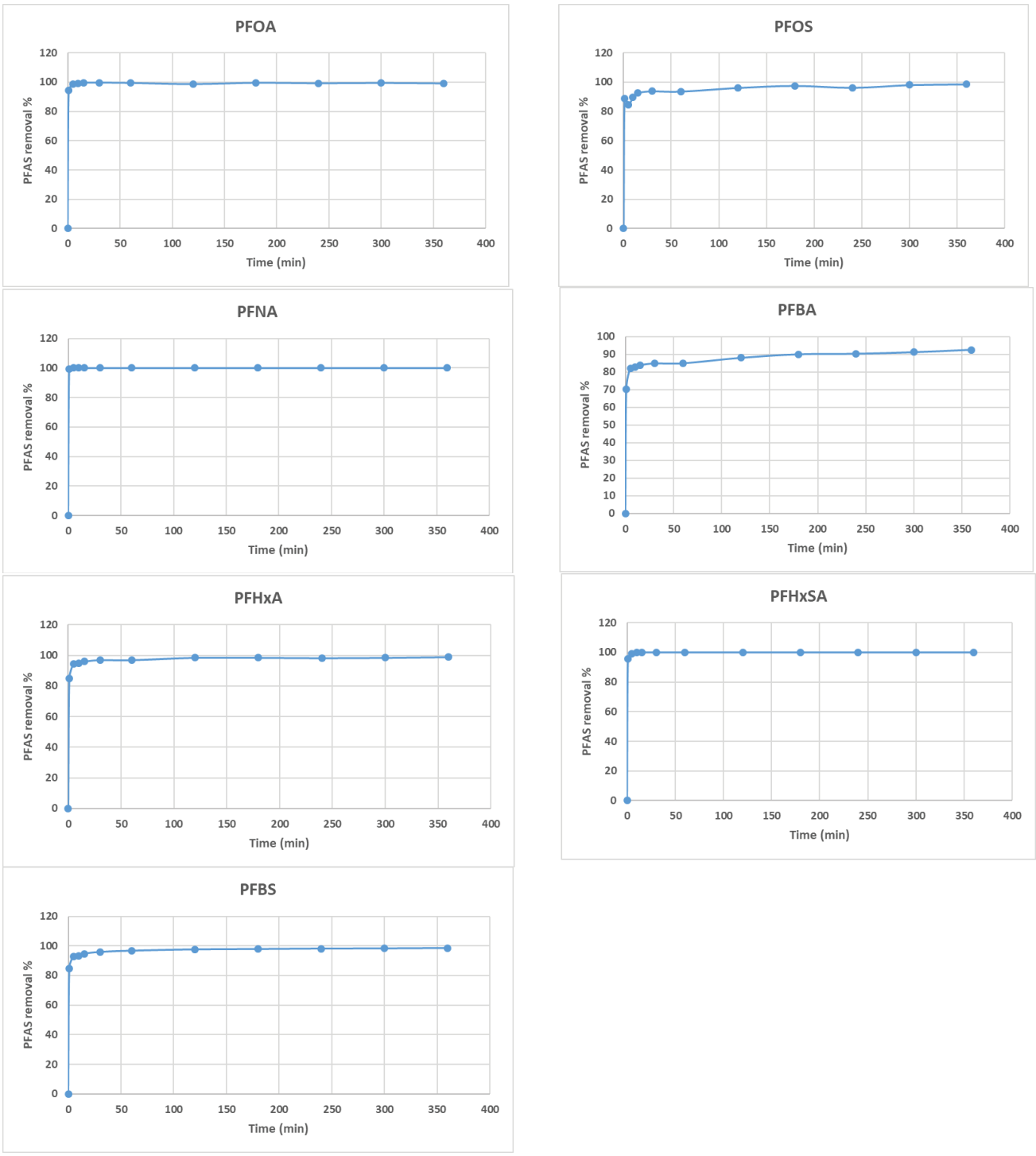

Figure 2. PFAS adsorption kinetic results in lab DI water (PFAS initial concentrations: 50 ppb; PILI adsorbent dosage: 2.5 g/L).

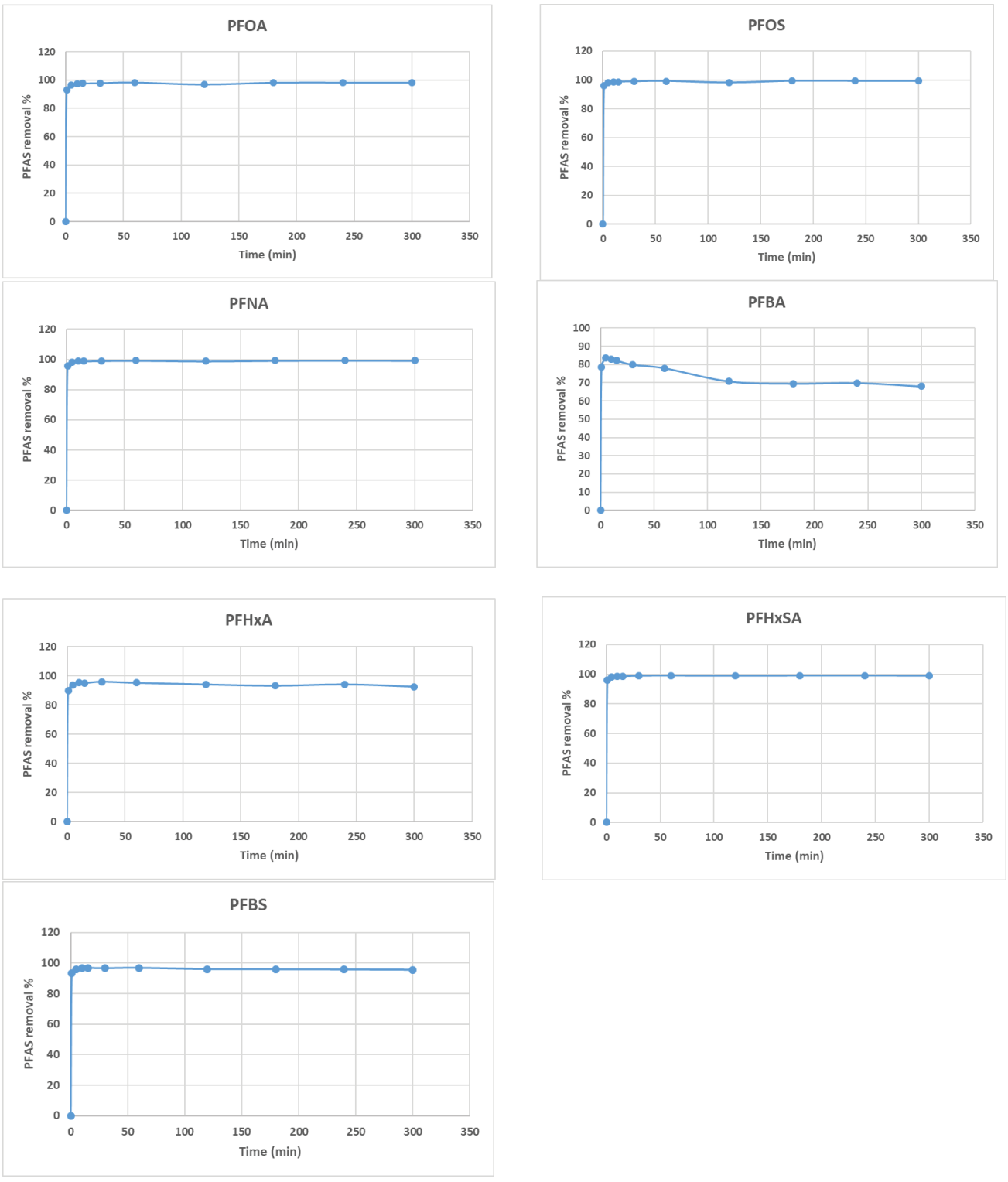

Figure 3. PFAS adsorption kinetic results in mixture of laboratory DI water and soil (PFAS initial concentrations: 50 ppb; PILI adsorbent dosage: 2.5g/L; soil content: 2.5g/L)

(5) Destruction of PFAS in desorption solution using Ultrasound

A number of desorption solutions (also referred to as regenerant solution) were tested, and data is presented in Tables S2 and S3 in Appendix. The 1M NH_4OH solution provided very high PFAS desorption, and at the same time did not impede the ultrasound destruction of the desorbed PFAS (unlike high concentration of organic solvents such as methanol, ethanol or isopropanol that were also tested; Table S4 in Appendix). Therefore, 1M NH_4OH solution was selected as the desorption solution for this proof-of-concept project.

High concentration of PFAS (10 ppm of each) were spiked in 1 M NH_4OH solution, and the destruction of PFAS using ultrasound is shown in Figure 4. The removal of most PFAS reached more than 95% within 3 hours of ultrasound reaction (except PFBA and PFBS). If we extend the ultrasound reaction to up to 6 hours**,** higher removal was achieved and the final concentration was less than 100 ppt for all PFAS except PFBS (final PFBS concentration was 3900 ppt). *These results show that the desorption solution containing high concentrations of PFAS could be cleaned to a desired level, and PFAS are destroyed with ultrasound.* The treated desorption solution could be used for the next cycle of desorption or disposed off at the Site. In the follow-on project, further optimization of the ultrasound process will be conducted.

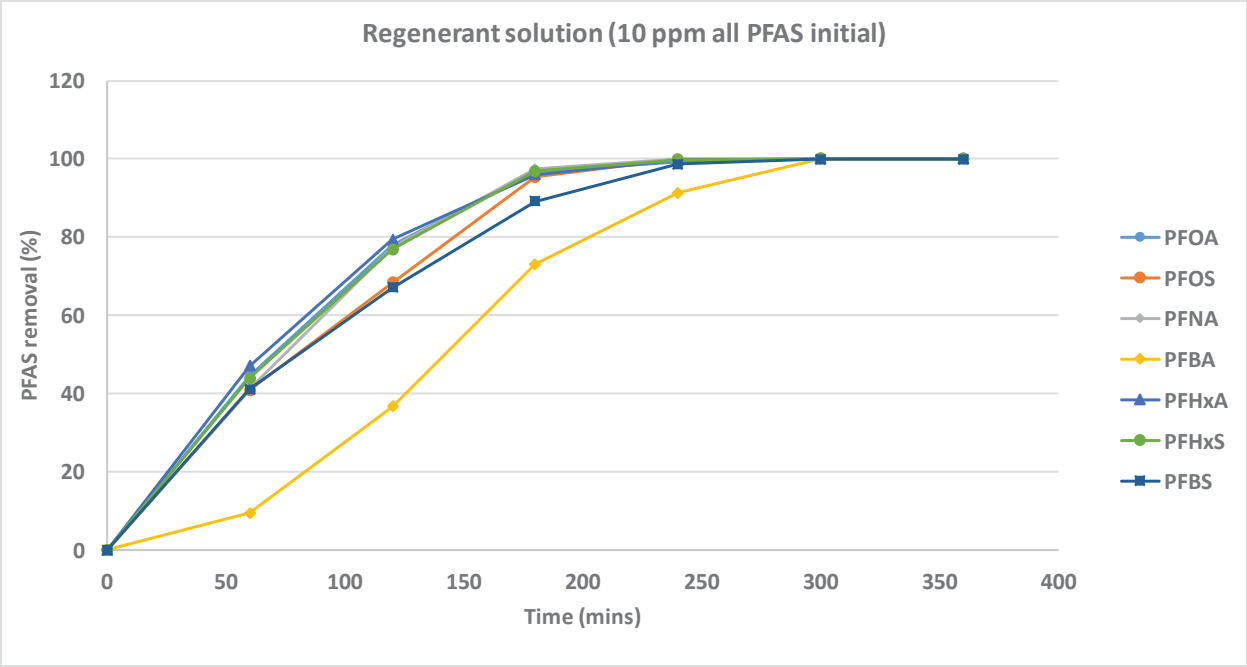

Figure 4. Degradation of PFAS in desorption solution (1M NH_4OH; ultrasound frequency: 430 kHz; solution volume: 200 mL).

(6) Cleanup of PFAS Contaminated Soil from DoD Site using Ultrasound

Ultrasound tests were conducted with the desorption solution that was used to clean the soil and the adsorbent. The adsorbent was separated from the slurry using a magnet. The remaining slurry containing both soil and concentrated PFAS solution was placed in the ultrasound reactor for the

destruction of PFAS. The soil samples were treated with ultrasound process in presence of the desorption solution of 1M NH_4OH. After sonication, the soil sample was processed to determine the PFAS sorbed on it (using 3 step methanol extraction). The final PFAS concentration in soil samples are shown in Table 4. Comparing with original soil PFAS data, after the ultrasound treatment, all PFAS concentrations significantly decreased. The final concentrations were much less than 10 ug/kg (except for PFOS which was 13 ug/kg). Higher removal of PFOS from the soil could be achieved by using additional sonication time, and/or stronger regenerant solution. The soil samples were also treated with ultrasound for 6 hours using DI water and the final concentrations of PFOA, PFOS and PFHxS were higher than those with 1M NH_4OH and ultrasound for 4 hours. The PFOS concentration of 51 ug/kg on soil was significantly higher with DI water even after 6 hours of sonication. However, 4 hours of sonication with 1M NH_4OH provided a much lower PFOS concentration of 13 ug/kg on soil. Even lower concentrations could be achieved by process optimization.

These proof-of-concept results demonstrate that the PFAS contaminated soil could be cleaned using the ultrasound process. A follow-on project needs to examine different soil-water slurry ratios; optimize the regenerant concentration, sonication time, ultrasound intensity and frequency; examine different types of contaminated soils from DoD Sites with different characteristics (sandy, clay, loamy, different organic content, co-contaminants, etc.); and the potential of using water as desorption solution with ultrasound with optimization. The process should be demonstrated at pilot scale for onsite management of soil in IDW.

Table 4. PFAS sorbed on DoD Site Soil, before and after ultrasound processing.

Sample name	Concentration (ug/kg)						
	PFOA	PFOS	PFNA	PFBA	PFH_XA	PFH_XS	PFBS
Untreated Soil (based on 4 replicated soil extraction data)	5.35	242.69	8.13	2.29	3.81	10.86	12.41
Treated Soil; with desorption solution + ultrasound for 4 hours	0.21	12.87	ND	ND	0.35	1.51	6.47
Treated Soil; with DI water + ultrasound for 6 hours	0.52	50.6	ND	ND	0.2	2.5	4.54

(7) **Clean up of used adsorbent with ultrasound and desorption solution, for its disposal**

To examine if the adsorbent can be cleaned with ultrasound and desorption solution, tests were conducted with the adsorbent that had been used for the adsorption of PFAS in groundwater. Desorption solution was added to the adsorbent and the mixture was placed in the ultrasound reactor for specific time, following which the PFAS sorbed on adsorbent was determined using the methanol extraction process and mass balance.

The PILI adsorbent underwent 6 hours of ultrasound with 1M NH_4OH desorption solution. As shown in Table 5, the final concentrations of PFOA, PFNA, PFBA and PFHxA on the adsorbent were below 10 ug/kg. However, the process was not very effective to remove PFOS from the

adsorbent, as the final PFOS concentration was 1224 ug/kg, and the cleanup percentage was very low (29%) for PFOS.

In another test, PFAS desorption from the NI-1 adsorbent was examined. The adsorbent was subjected to 6 hours of sonication in presence of 1M NaOH as the desorption solution. The final concentrations of all PFAS were less than 10 ug/kg. The final concentration of PFOS was 7.14 ug/kg, representing a cleanup efficiency of 99.6%. The initial PFOS sorbed on the adsorbent was very high (1725 ug/kg). The cleanup percentage for all PFAS was very high, and which is very promising. *This demonstrates that the NI-1 adsorbent could be cleaned using ultrasound and desorption solution.* Hence, after its use, the spent adsorbent would be cleaned with the ultrasound process and disposed off. In the follow-on project, additional test will be done using the NI-1 adsorbent to optimize the process.

Table 5. Clean up of adsorbent using desorption solution and ultrasound.

Adsorbent name and ultrasound time		PFOA	PFOS	PFNA	PFBA	PFHxA	PFHxS	PFBS
PILI adsorbent, 6 hours	Initial conc. (ug/kg)	30.41	1724.06	0.61	7.10	31.13	102.51	19.08
	Final conc. (ug/kg)	7.82	1223.50	ND	0.90	5.30	55.40	23.32
	Clean up (%)	74.29	29.03	100	87.32	82.97	45.96	-22.19*
NI-1 adsorbent, 6 hours	Initial conc. (ug/kg)	30.15	1725.43	0.62	5.87	30.60	101.97	18.68
	Final conc. (ug/kg)	1.21	7.14	ND	ND	ND	0.74	5.08
	Clean up (%)	95.98	99.59	100	100	100	99.27	72.83

ND: non-detect; *the final concentration was slightly higher than the initial, the reason for which is not well understood at this time.

(8) **Reusability of the Adsorbent to remove PFAS**

To examine the reusability of the adsorbent, multiple cycles (12) of adsorption of PFAS were conducted using the same adsorbent and without any adsorbent regeneration (i.e. no desorption of adsorbates was performed). Figure S8 shows PFAS removal for 12 cycles of adsorption. Interestingly, after 12 cycles of adsorption isotherms, the removal efficiency for PFOA, PFOS, PFNA and PFHxS was almost the same as the first cycle, implying that the adsorbent maintained a high capacity to adsorb these PFAS. The removal efficiency for PFHxA and PFBS was slightly

decreased, while that for PFBA was significantly decreased after 12 cycles of consecutive adsorption. The results demonstrated that the adsorbent has very high capacity for most PFAS in our analyte list. It must be mentioned that no regeneration of the adsorbent was conducted during these experiments.

CONCLUSIONS AND IMPLICATIONS FOR FUTURE RESEARCH

We proposed using a strategy of (1) adding the novel adsorbent in the IDW tank to clean up the groundwater for on-site discharge, (2) cleaning the soil and adsorbent using ultrasound in a small volume of desorption solution, and (3) destroying the desorbed PFAS using ultrasound process in the small volume of desorption solution. Results from this proof-of-concept project were very promising. Overall, the groundwater, soil and spent adsorbent could be cleaned for on-site disposal, and the PFAS are destroyed, offering an environmentally sustainable solution to manage IDW at DoD Sites. Specifically, this proof-of-concept project demonstrated the following:

1. The magnetic polymer adsorbent can efficiently removal PFAS from DoD Site groundwater and soil mixture to very low concentrations. The total of PFOA+PFOS concentration was below 70 ppt, and concentration of all PFASs ranged from non-detect to < 40 ppt. If needed, higher removal of specific PFAS could be achieved using higher dosage of the adsorbent. The treated groundwater could be disposed off at the site. The magnetic adsorbent can be easily separated from the mixture by using magnets. In the follow-on project, optimization tests should be done with groundwater and soil from different DoD Sites, and with different ratio of soil to groundwater slurry. The objective would be to determine the required adsorbent dosage based upon the amount of groundwater volume and contamination in the IDW tank.
   Criteria for success. The technology evaluation goal (PFOA+PFOS <70 ppt) for treating PFAS contaminated site groundwater with the novel adsorbent was achieved, with the potential of reaching lower levels to meet various State limits.

2. As an added benefit, the adsorbent can also remove TCE and PCE co-contaminants from water in presence of PFAS. It is noteworthy that the adsorption of PFAS was higher than the CVOCs. This indicates that PFAS removal will not be adversely affected by the presence of CVOCs. In follow-on work, we will optimize the removal of CVOC co-contaminants, along with PFAS, to a desired level. Contaminated groundwater and soil from different DoD Sites will be used, so we can generate information on simultaneous removal of PFASs and different co-contaminants.

3. The adsorption of PFAS from groundwater was very fast, and equilibrium for all PFASs was reached in about 5 minutes. The presence of soil in the solution did not seem to significantly affect the PFAS adsorption kinetics. This offers a very attractive solution for on-site treatment of groundwater in IDW. Site personnel could add the adsorbent in the IDW tank directly, mix it using a mechanical mixer, and after 5 minutes or so could discharge the treated groundwater. The follow-on project should further examine the adsorption time required in different ratios of groundwater-soil slurry.

4. The contaminated soil from DoD Site was cleaned using ultrasound and 1M NH_4OH desorption solution. The final PFAS concentrations on the soil were much less than the target level of 10 ug/kg, except for PFOS which was 13 ug/kg. The Site soil had a very high contamination of PFOS (243 ug/kg), and 95% of PFOS was removed from the soil in 4 hours of sonication. Higher removal of PFOS from the soil could be achieved by process optimization.
   Criteria for success. For the proof-of-concept, the technology evaluation goal (10 ug/kg) of cleaning the soil was met for all PFASs except for PFOS (although it was very close to the target). The project showed the potential of reaching lower levels to meet the soil screening levels/standards of various US States.

5. The ultrasound process was able to destroy PFAS in the desorption solution. In this proof-of-concept project, all PFAS (10 ppm each) in 1M NH_4OH were degraded in 6 hours of sonication, and the final concentration in the solution was less than 100 ppt (except PFBS). These results show that the desorption solution containing high concentration of PFAS can be cleaned, and PFAS destroyed with ultrasound. The treated desorption solution could be used for the next cycle of soil treatment or disposed off at the Site. The sonication time could be reduced with process optimization. The follow-on project will optimize the ultrasound process, and develop and demonstrate a pilot-scale system at a DoD site. The pilot-scale ultrasound reactor (same one that is mentioned in Conclusion #4 above) will simultaneously clean the soil and the adsorbent, and destroy the desorbed PFAS.
   Criteria for success. The technology evaluation goal of destroying PFAS in the desorption solution were met (PFOA+PFOS <70 ppt), with the potential of reaching even lower levels.

6. After cleaning the groundwater, the adsorbent could either be reused or cleaned for disposal. The NI-1 adsorbent was subjected to 6 hours of sonication in presence of 1M NaOH. The final concentrations of all PFAS were less than 10 ug/kg. The initial PFOS loading on the adsorbent was 1725 ug/kg from the treatment of Site groundwater, and the final was 7.14 ug/kg after 6 hours of sonication, representing a cleanup efficiency of 99.6%. The cleanup percentage for all PFAS was very high, and which is very promising. Hence, after its use, the spent adsorbent could be cleaned with the ultrasound process and disposed off. The follow-on project would further optimize the process, and examine the disposal options of the cleaned adsorbent and any related environmental impacts, along with the option to reuse the adsorbent.
   Criteria for success. The technology evaluation goal (10 ug/kg) of cleaning the spent adsorbent was met for all PFASs.

Outline of next steps and objectives for follow-on research:

Given the success of this proof-of-concept project, there is a need to perform additional research work. The follow-on project will include a wider variety of PFASs, different types of soils from DoD sites with different characteristics (PFAS contaminants and their levels; sandy, clay, loamy, different organic content, co-contaminants, etc.). Samples of IDW, or samples of soil and groundwater, will be obtained from several DoD sites. The process will be examined for different soil-water slurry ratios. The research will further optimize the ultrasound process (time, frequency and intensity), regenerant solution (type, strength, volume), and determine necessary conditions for target soil cleanup goals. In addition, laboratory soil will be spiked with PFASs and tested for

their cleanup. The adsorption and degradation mechanisms of different types of PFAS will be examined, along with any byproducts formed during the ultrasound degradation process. One goal would be to have a convenient process guidance for field technicians regarding what process conditions should be used based upon the soil type, PFAS concentration and target goal. A pilot scale reactor will be designed, constructed and demonstrated at a DoD Site (preferably at Willow Grove, PA since it is less than 5 miles from our lab). The pilot unit will be designed to treat 100 – 200 kg of soil in each batch.

The detailed study of the technology would also result in detailed scientific project report, manuscripts for publication in peer reviewed journals, and technical presentations.

Some specific tasks are:

1. Test the technology, and identify optimum conditions, for cleanup of different types of soil and groundwater (in IDW) from several PFAS contaminated DoD Sites. A larger number of PFAS compounds would be included in the study. An iron based and a silica/sand based adsorbents will be evaluated for quick removal of PFAS from groundwater and fast desorption to clean the adsorbent. The disposal options and reuse of adsorbent will also be evaluated.

2. The IDW may contain different ratio of soil and groundwater. Hence, it is important to test the technology with several different ratio of soil to groundwater in the mixture.

3. Design, construct and demonstrate a pilot-scale process at a DoD Site for decontamination of IDW. It is important to develop scaling models to scale-up the technology from bench to pilot scale, and which could be optimized for full-scale design.

4. Determine any by-products in the desorption solution from the ultrasound degradation process, and perform a mass balance on PFAS. The PFAS removal mechanisms by the adsorbent, desorption mechanisms of PFAS from soil and adsorbent, and degradation mechanism of PFAS by ultrasound process will be elucidated. This will also be useful to other researchers.

5. Based upon pilot tests, determine the cost of the process, and process design to manage IDW. This would allow the RPMs and other stakeholders to evaluate the suitability of the technology for their Sites.

Figure 5 shows a schematic of a possible on-site treatment of IDW with this technology. The follow-on project will lead to the development of a very simple, low cost, small footprint, easy to operate treatment system having primarily a PVC tank with a mixer for IDW, small filter, magnets, pH controller, and a small ultrasound reactor. For possible on-site application of the technology, the novel adsorbent will be mixed in the IDW tank to remove PFAS and co-contaminants from groundwater. The adsorbent and soil will be filtered out and the treated groundwater will be discharged. The contaminants sorbed on the adsorbent and soil will be desorbed and destroyed using ultrasound in one reactor. The iron-based adsorbent is separated from the slurry using magnets and could be reused or disposed off after decontamination. The treated soil could be

disposed off at the site. The option of first separating soil from groundwater, and then treating them separately will also be examined. In this case, the groundwater will be treated with adsorption process. The soil will be treated with the ultrasound process. The spent adsorbent will be cleaned for reuse or disposal, using ultrasound process. The PFAS will be destroyed simultaneously in the ultrasound reactor while cleaning the soil and the adsorbent.

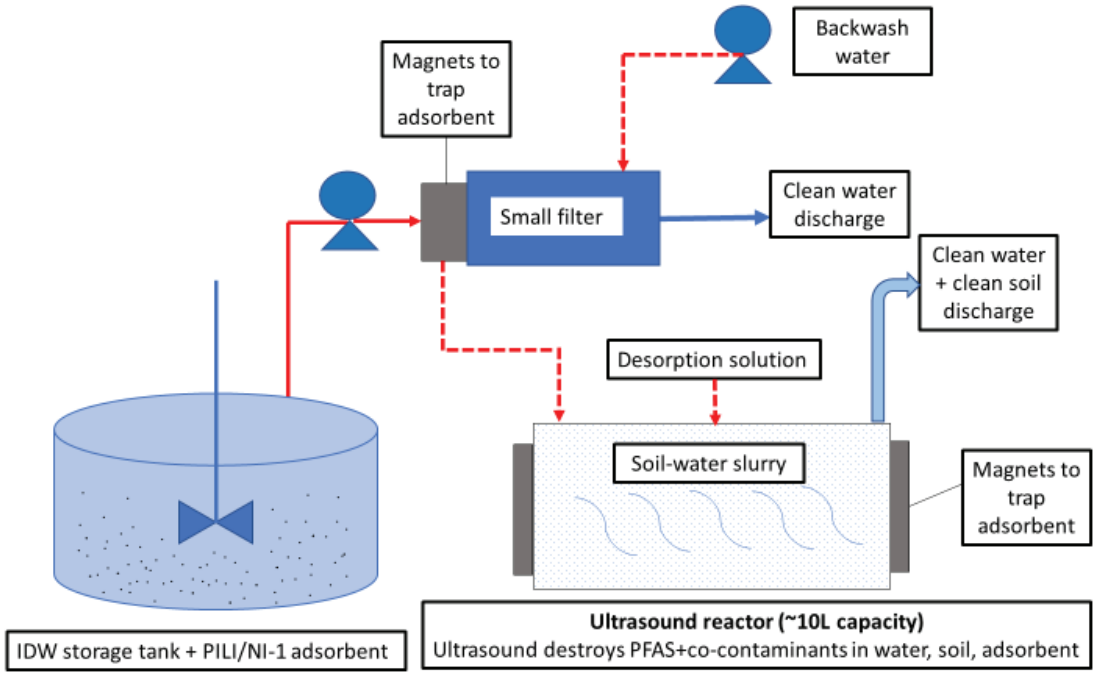

Figure 5. Schematic of the adsorption-ultrasound technology for IDW management.

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APPENDIX: SUPPORTING DATA

1. Mechanism of organic removal by CD:

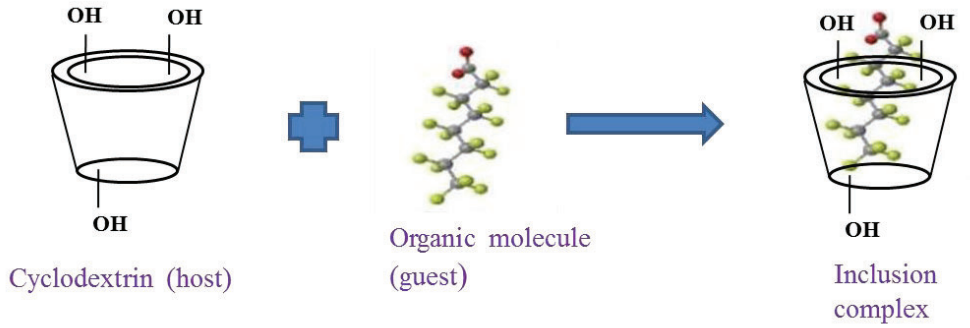
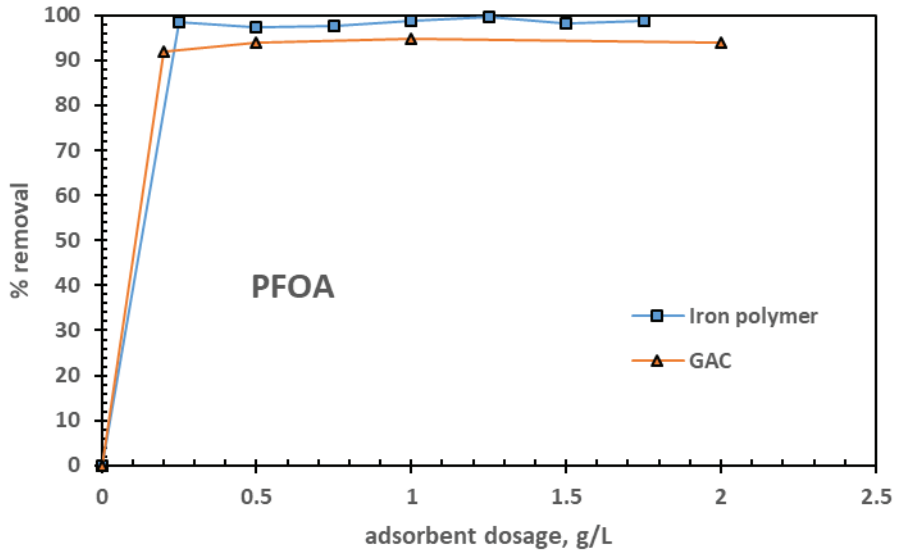


Figure S1. Mechanism of organic compound removal with beta cyclodextrin in the PILI adsorbent.

2. Adsorbent comparison with GAC and effect of adsorbent dosage:

Batch isotherm tests were conducted with F-400 GAC and PILI adsorbent using different dosages for the removal of PFOA and PFOS, and results are shown in Figures S2 (a) and (b). These were initial tests. The PILI adsorbent performed better than the GAC, and both adsorbents showed high capacity. Figure S3 shows that the adsorption of PFOA and PFOS can be well described by the Freundlich adsorption isotherm model.



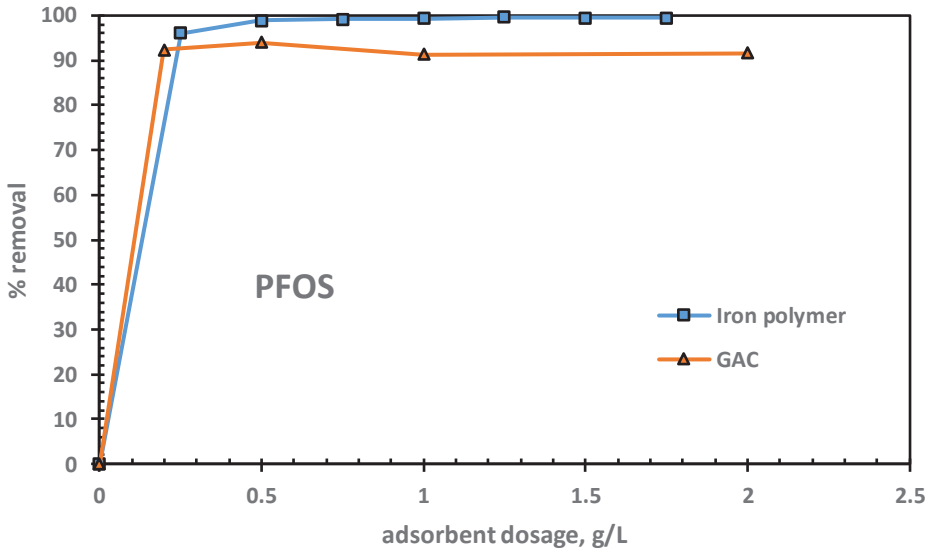


Figure S2. Batch isotherm tests with F-400 GAC and PILI adsorbent using different dosages for the removal of (a) PFOA and (b) PFOS.

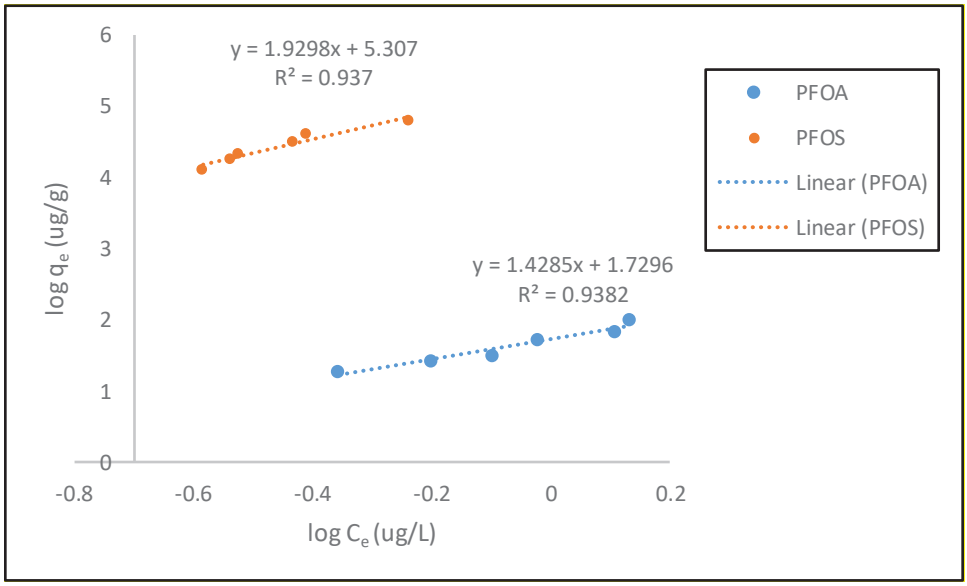


Figure S3 Removal of PFOA and PFOS fitted with Freundlich adsorption isotherm model.

3. PFAS removal from Site groundwater by adsorption process:

Table S1. Removal of PFAS from groundwater using adsorption process (in absence of soil).

	Groundwater initial (ppt)	**Groundwater final (ppt)**	**PFAS removal (%)**	**Adsorbent dosage in groundwater**
PFOA	1270	470	62. 99	5g/L with PILI adsorbent
PFOS	50290	630	98.75	
PFNA	44.9	16.9	62.36	
PFBA	522.2	83.1	84.09	
PFHxA	1210	52.5	95.66	
PFHxS	3040	50.4	98.34	
PFBS	380	1	99.74	
PFOA	1270	11. 8	99. 07	10g/L with PILI adsorbent
PFOS	50290	99	99.80	
PFNA	44.9	6	86.64	
PFBA	522.2	24	95.40	
PFHxA	1210	7.3	99.40	
PFHxS	3040	14.3	99.53	
PFBS	380	4.6	98.79	
PFOA	1270	5	99.61	15g/L, two step adsorption strategy with NI-1 adsorbent
PFOS	50290	5.9	99.99	
PFNA	44.9	1.5	96.66	
PFBA	522.2	1.4	99.73	
PFHxA	1210	0.2	99.98	
PFHxS	3040	2.3	99.92	
PFBS	380	22.9	93.97	

4. Effect of Soil on Adsorbent Performance:

The effect of presence of soil on the performance of the adsorbent was examined in limited experiments. Batch adsorption isotherm tests with a mixture of water and soil system were conducted. We first kept the adsorbent mass constant and varied the soil amount in the batch reactors. The purpose of these experiments was to test if soil in the groundwater mixture will affect the adsorbent efficiency for PFAS removal, and the results are shown in Figure S4. Control experiment conducted with only soil present (no adsorbent) in groundwater, showed no significant removal of PFASs (< 20%). In presence of adsorbent, the soil in the system did not seem to significantly promote or inhibit the removal of long chain PFASs (PFOA, PFOS and PFNA) by the adsorbent. For the median chain PFAS (PFHxA and PFHxS) the removal by adsorbent was slightly decreased with increase of soil mass in the system. For example, with 1 g soil in the system,

compared with no soil system, the PFHxA removal was 15% less and the PFHxS removal was 5% less. The presence of soil affects the sorption of short chain PFASs more than that for medium and long chain PFAS. The presence of 1 g of soil reduced PFBA removal by 19% and PFBS removal by 17%.

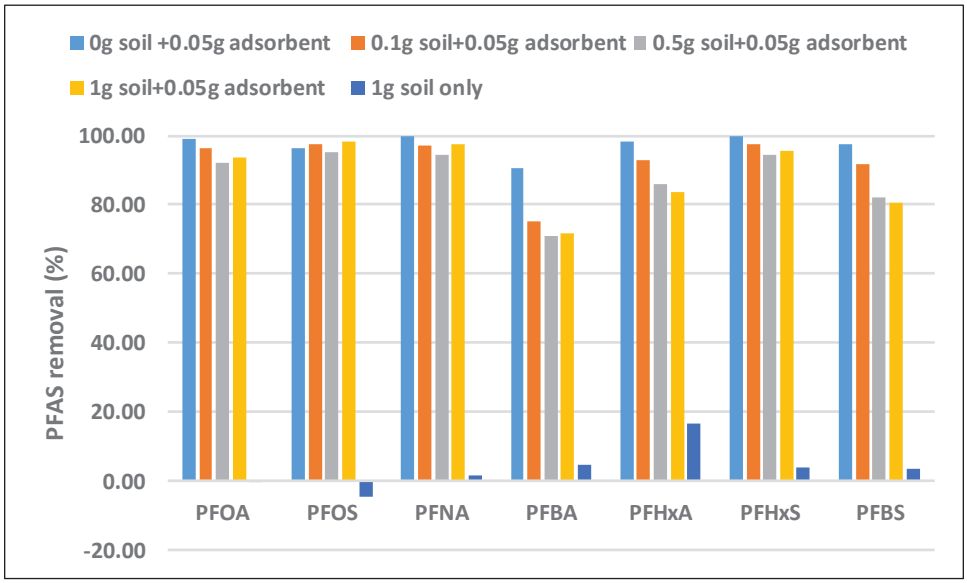


Figure S4. PFAS removal in mixture of water and soil with different amount of soil (40 ml of 50 ppb PFAS multicomponent solution, PILI adsorbent:0.05g).

In the next set of adsorption experiments with groundwater, the mass of soil was kept constant at 12.5 g/L, and mass of adsorbent was varied. The PFAS removal percent with different dosage of adsorbent are shown in Figure S5. The percentage removal of all PFASs increased with the increase of adsorbent dosage. At highest adsorbent dosage tested, which is 5g/L, except PFBA, the removal percent for other PFASs were at least 99%. It may be observed from Figure 5, that the removal of PFAS has the following order: PFOS>PFOA, PFHxS>PFHxA and PFBS>PFBA. In the same system, the removal of all sulfonate PFAS was higher than the carboxylate PFAS. According to Pearson's concept of hard and soft acids/bases, the sulfonate group, that is a hard base, could be more readily adsorbed on oxide surfaces. Our adsorbent has Fe_3O_4 component, thus the removal of sulfonate PFAS was slightly higher than the corresponding carboxylate PFAS. The mechanism of our adsorbent for PFAS adsorption is (1) complex formation through host−guest hydrophobic interactions occurring between the cyclodextrins and the hydrophobic carbon chain in PFAS molecules and (2) electrostatic interactions between the negatively charged PFAS anions and positively charged sorbent.

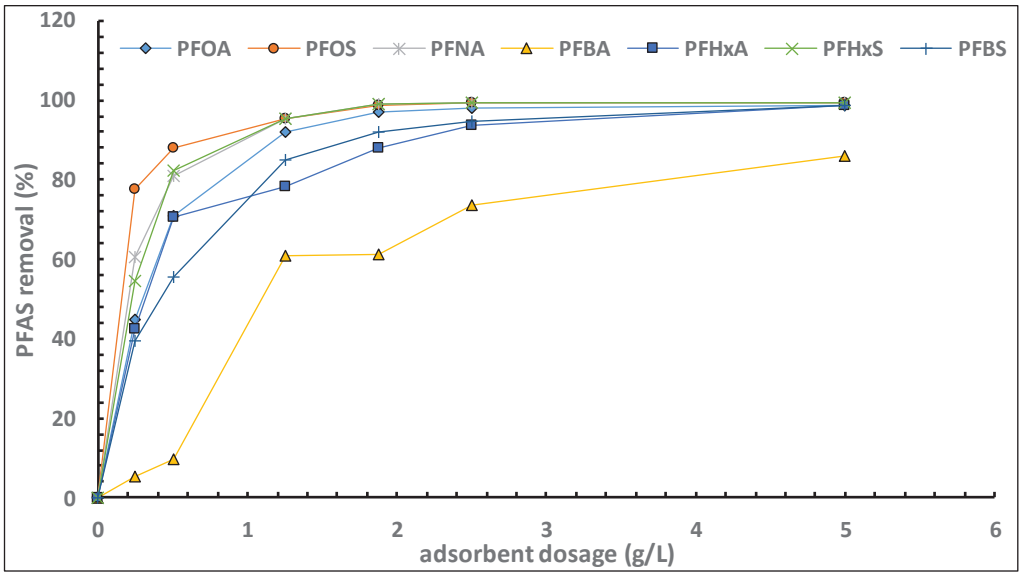


Figure S5. PFAS removal in mixture of water and soil with different amount of PILI adsorbent (soil amount was constant as 12.5g/L; 40 ml of 50 ppb PFAS multicomponent solution).

5. Regeneration of Adsorbent using different desorption solutions

The PILI adsorbent was used for the removal PFAS from laboratory water, following which different desorption solutions were applied to regenerate the adsorbent. The regeneration percentage of the adsorbent for each PFAS was calculated based on mass balance. In some cases, the regenerated adsorbent was again used for another cycle of adsorption to test its capacity for PFAS adsorption. Among all the desorption solutions (Table S1), 30% isopropanol(v/v) +1M NH_4OH showed best regeneration. The removal of long chain PFAS was higher than short chain PFAS.

Table S2. Regeneration tests for PILI adsorbent using different desorption solutions. Note- In some cases the PFBA regeneration efficiency was very low even though it is a relatively weakly adsorbing compound. This may be due to analytical issues, and more work is needed to understand the reasons.

PFAS name	Regeneration (%)	Regenerant (or desorption solution)	PFAS adsorption (cycle 2) after regeneration (%)
PFOA	81.46	1 M NH_4OH	98.51
PFOS	60.32		98.22
PFNA	64.33		98.97
PFHxA	98.67		94.11
PFHxSA	46.52		99.42
PFBS	61.69		95.90

PFOA	70.55	1M NaOH	99.44
PFOS	33.08		99.41
PFNA	34.63		99.66
PFHxA	113.45		98.74
PFHxSA	38.96		100.00
PFBS	77.07		99.02
PFOA	93.75	30% Isopropanol+1M NaOH	99.26
PFOS	79.25		98.62
PFNA	47.03		99.14
PFHxA	163.55		98.32
PFHxSA	58.73		100.00
PFBS	102.44		98.83
PFOA	102.46	30% Isopropanol+1M NH_4OH	98.98
PFOS	83.20		98.80
PFNA	112.35		98.79
PFHxA	64.48		98.07
PFHxSA	49.71		99.16
PFBS	43.15		100.00

6. Cleanup of soil using different desorption solutions

Experiments were conducted with site contaminated soil and high pH desorption solutions, without the use of ultrasound. After the desorption test, the soil underwent the PFAS extraction procedures using methanol to determine the amount of PFAS remaining on the soil, and results are showed in Table S3. Compared with the PFAS concentrations in original soil, after desorption, the final PFAS concentrations remaining on the soil were significantly lower. With 30% isopropyl + 1M NaOH and 1M NH_4OH+ 0.1 M NaCl as desorption solutions, the final PFAS concentration on the soil was less than 10 ug/kg for all PFASs. Hence, we considered that the soil can be cleaned with this desorption process. In follow-on project, we will examine soil of different characteristics obtained from several DoD Sites, and the process will be optimized for different types of soil.

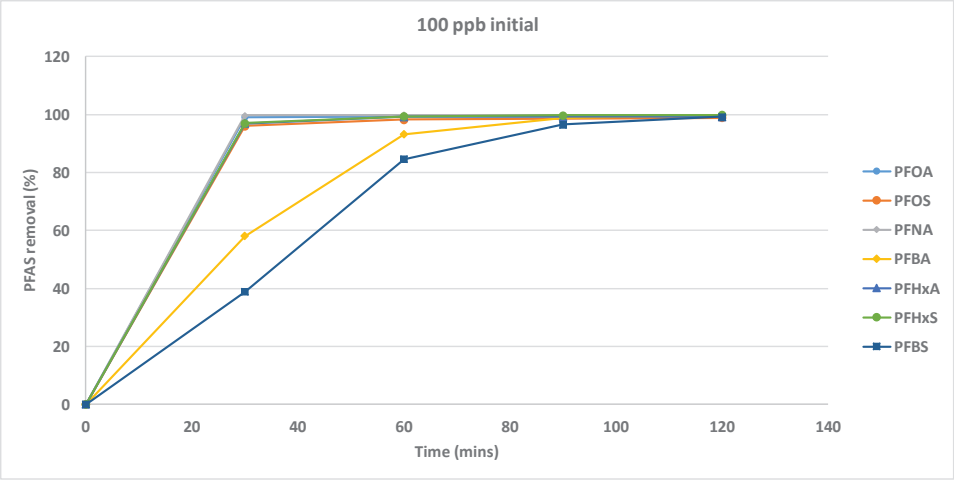
Table S3. Desorption of PFAS from soil using different solutions. The data reported is how much amount of PFAS desorbed from the soil as ug/kg. For comparison, the initial PFAS sorbed on the soil is also included in the last row of the Table (not subjected to desorption).

Desorption solution	Amount of PFAS desorbed from soil, ug/kg						
	PFOA	PFOS	PFNA	PFBA	PFHxA	PFHxS	PFBS
1M NH_4OH	1.44	41.94	1.94	0.3	0.58	5.1	3.48
30% Isopropyl + 1M NH_4OH	5.68	11	10.56	0.72	nd	1.12	5.4
30% Isopropyl + 1M NaOH	3.24	7.4	5.16	nd	nd	0.76	3.56
1M NH_4OH+ 0.1 M NaCl	3.72	7.48	7.08	0.32	nd	0.72	3.88
1M NaOH+ 0.1M NaCl	2.6	13.24	4.96	nd	nd	0.88	11.08
Initial PFAS sorbed on soil	5.35	242.68	8.12	2.29	3.81	10.85	12.40

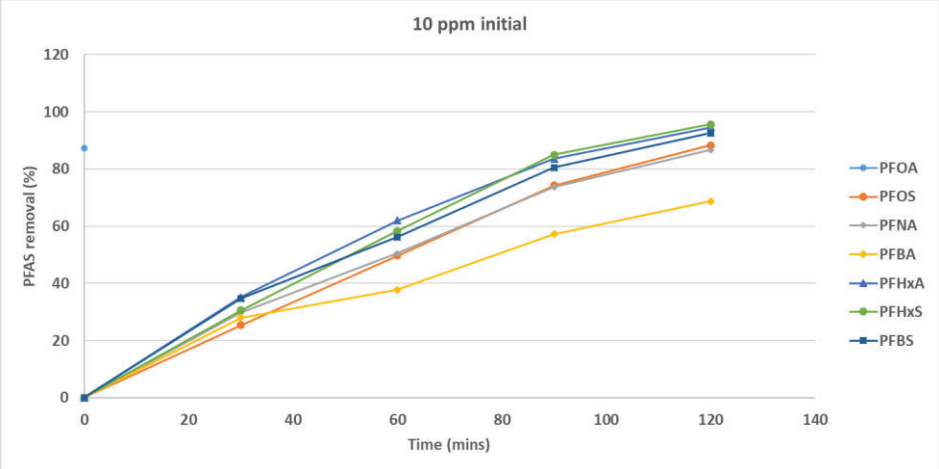
nd: non-detect

7. Feasibility of degrading PFAS in laboratory DI water using ultrasound

We first tested our ultrasound process for the destruction of all PFAS in DI water. The initial concentration of all PFAS was 100 ppb and 10 ppm, respectively (Figure S6). For 100 ppb initial PFAS solution, the degradation for PFNA, PFOA and PFOS was more than 99% in 30 mins reaction. The degradation of short chain PFAS (PFBA and PFBS) was slower, but it increases with extended sonication time. For 10 ppm initial PFAS solution, more than 95% of PFAS was removed in 120 mins of ultrasound. Fluoride ions were also measured for the 10 ppm experiment. The destruction of PFAS can be observed by fluoride data (Figure S7). The F ions in the solution increase with increase in sonication time. At 120 min, the fluoride ions represented about 54% destruction of total PFAS (calculated from mass balance). Higher destruction could be achieved by extending the sonication time.



(a) PFAS concentration of 100 ppb



(b) PFAS concentration of 10 ppm

Figure S6. Degradation of PFAS in DI water.

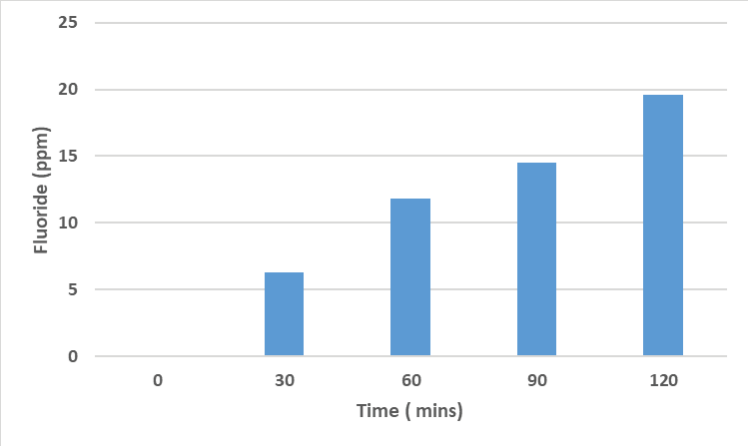


Figure S7. Fluoride ion concentration for 10 ppm PFAS solution destruction.

8. Effect of organic solvent (desorption solution) on ultrasound destruction of PFAS

The organic solvent solution used to desorb PFAS from adsorbent, was placed in the ultrasound reactor to degrade PFAS. However, insignificant destruction of PFAS was observed. Sonication tests were done by spiking PFAS (10 ppm) in various organic solvent solutions, and data is shown in Table S4. The PFAS removal with organic solvent solutions was significantly lower than with ammonium water and DI water. The organic solvent in the solution interferes with the ultrasound destruction process. Based upon these results, we selected 1M ammonium hydroxide as the desorption solution for further testing with soil and adsorbent.

Table S4. PFAS destruction in different organic solutions using ultrasound (PFAS initial concentration = 10 ppm).

Solution time	Removal (%)						
	PFOA	PFOS	PFNA	PFBA	PFHxA	PFHxSA	PFBS
60% methanol solution, 90 mins	6.36	-5.13*	14.38	3.50	7.09	-15.88*	2.97
60% Isopropanol solution, 90 mins	10.86	36.90	25.76	20.06	0.31	-80.91*	10.63
30% acetone solution, 120 mins	17.12	34.20	19.35	12.80	14.68	6.64	15.22
1 M ammonia water, 120 mins	68.21	70.68	62.84	32.46	68.26	75.91	64.04
DI water, 120 mins	87.21	88.35	86.66	68.75	94.52	95.63	92.58

*the final concentration was higher than initial, the reason for which is not clear at present.

9. Adsorbent Reusability:

To examine the reusability of the adsorbent, multiple cycles of adsorption of PFAS were conducted using the same adsorbent and without any adsorbent regeneration (i.e. desorption of adsorbates). The PFAS removals are shown in Figure S8. A total 12 cycles of adsorption experiments were done. Interestingly, after 12 cycles of adsorption isotherms, the removal efficiency for PFOA, PFOS, PFNA and PFHxS was almost the same as the first cycle, which means that the adsorbent still had good capacity to adsorb those PFAS. The removal efficiencies for PFHxA and PFBS were slightly decreased, and the removal efficiency for PFBA was significantly decreased after 12 cycles of consecutive absorption. It must be mentioned that no regeneration of the adsorbent was conducted during these experiments, these were only successive batch adsorption cycles. It appears that the adsorbent could be used for 3 successive adsorption cycles, after which it would require regeneration.

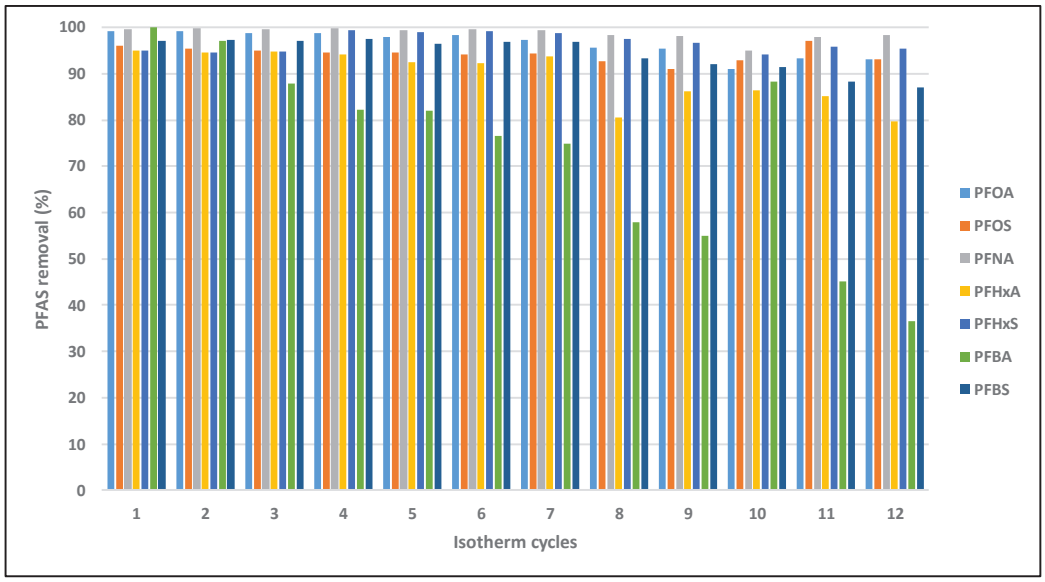


Figure S8. Multiple cycles of adsorption of PFAS (0.05 g adsorbent in 40 ml of 50 ppb PFAS multicomponent solution), without any regeneration or desorption process.