

EXECUTIVE SUMMARY

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

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ACRONYMS AND ABBREVIATIONS

COD	Chemical Oxidation Demand
CVOC	Chlorinated Volatile Organic Compounds
DI	Distilled [water]
DoD	Department of Defense
FtS	Fluorotelomer sulfonic acid 6:2
IDW	Investigation derived waste
NAS/JRB	Naval Air Station/Joint Reserve Base
NAVFAC	Naval Facilities Engineering Command
PCE	Tetrachloroethylene
PFAS	Per- and Polyfluoroalkyl Substances
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctanesulfonic Acid
PFBA	perfluorobutanoic acid
PFBS	perfluorobutane sulfonic acid
PFHxS	Perfluorohexane sulfonic acid
PFHxA	Perfluorohexanoic acid
PFNA	Perfluorononanoic acid
PFCA	Perfluoroalkyl carboxylic acid 6:2
PILI	polymer with ionic liquid coated iron
PI	Principal Investigator
ppt	parts-per-trillion
TCE	Trichloroethylene
TOC	Total Organic Carbon
TOPs	Total Oxidizable Precursors assay

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1.0 INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) 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. Investigations of PFAS contaminated sites result in the identification of investigation-derived waste (IDW). The IDW is a mixture of soil, purge water from groundwater sampling, and fluid from decontamination of drilling equipment. The IDW is likely to contain PFAS and other co-contaminants. In 2015, the US Environmental Protection Agency (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.

2.0 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 this will be of particular interest to DoD Remedial Project Managers and regulatory professionals.

The key objectives of this proof-of-concept project were the following:

1. 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.
2. 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.
3. 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.

3.0 TECHNICAL APPROACH

Contaminated soil and groundwater were obtained from Naval Air Station/Joint Reserve Base (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 the 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 of after decontamination. The treated soil could be disposed of at the site.

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

4.0 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 an 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 PFASs. These tests demonstrate that the Site IDW groundwater, in presence of soil, could be treated with the 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 the 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 a Fe₃O₄ component, and that may be 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 Chlorinated Volatile Organic Compounds (CVOCs) was observed. Higher removal could be achieved using a 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 distilled (DI) water to see how quickly the PFAS can 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: in about five 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.

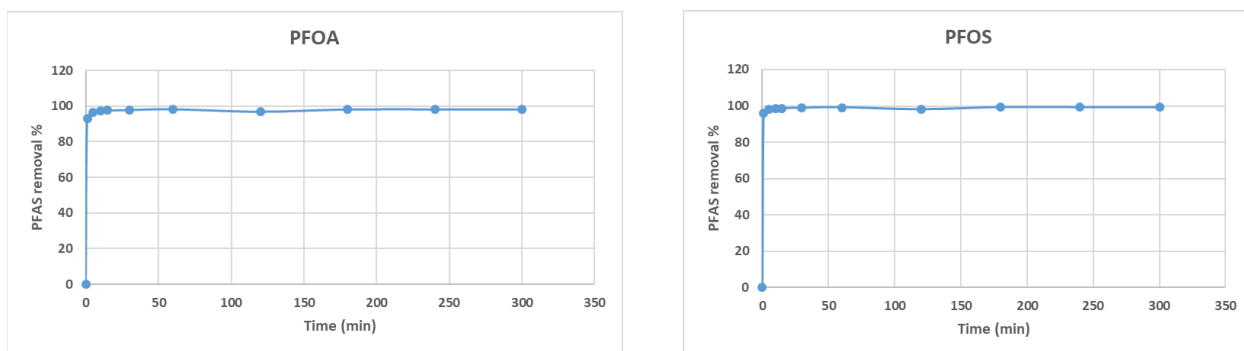


Figure 1. PFAS Adsorption Kinetic Results in Mixture of Laboratory DI Water and Soil.

(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 the 1M 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 three hours of ultrasound reaction (except PFBA and PFBS). On extending the ultrasound reaction to six 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 a 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 be disposed of 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.

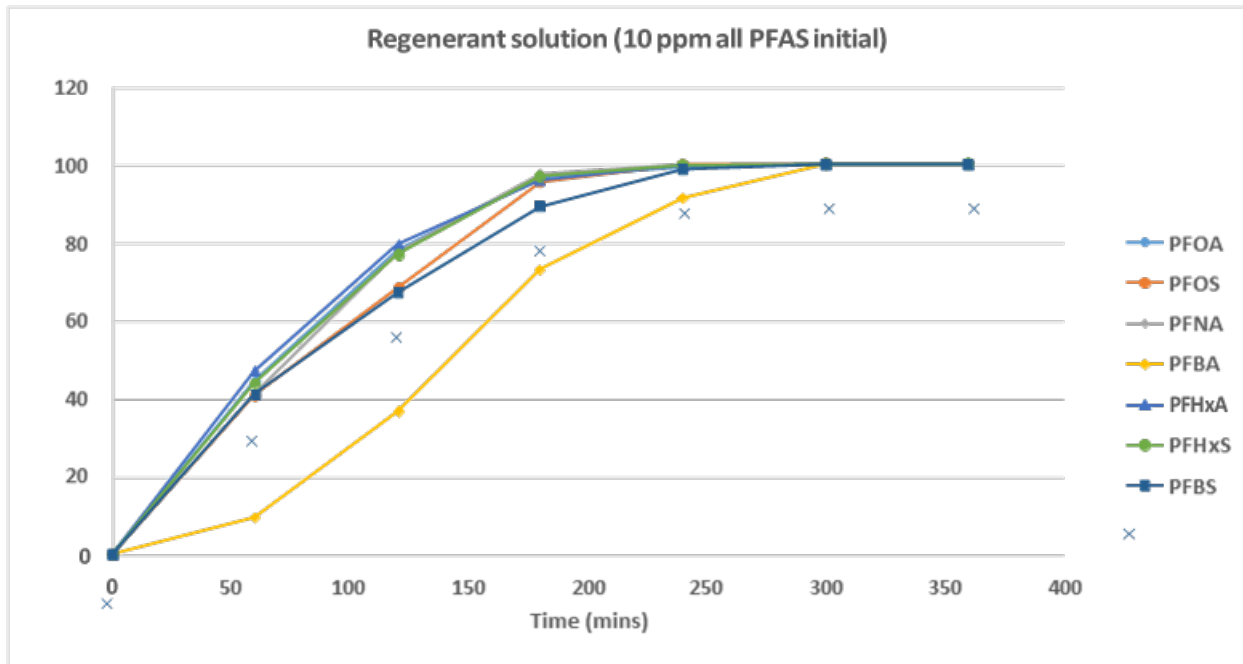


Figure 2. Ultrasound Degradation of PFASs (10 ppm of Each as Initial Concentration) in Desorption Solution.

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 NH₄OH. 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. Compared with the 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	PFHxA	PFHxS	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

nd: non-detect

The desorption of PFAS from the adsorbent was also examined. The adsorbent was subjected to six 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%.

5.0 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 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, and 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 ratios 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, and 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.

6.0 LIST OF PUBLICATIONS REFERENCED

Badruddoza, A.M., Bhattarai, B., Suri, R.P.S., 2017. Environmentally Friendly beta-Cyclodextrin-Ionic Liquid Polyurethane-Modified Magnetic Sorbent for the Removal of PFOA, PFOS, and Cr(VI) from Water. *Acs Sustain Chem Eng* 5, 9223-9232.