EXECUTIVE SUMMARY

Cost-Effective Destruction of Per- and Polyfluoroalkyl Substances from DoD Subsurface Investigation-Derived Wastes Using a New Class of Adsorptive Photocatalysts

SERDP Project ER18-1515

APRIL 2020

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Project: ER18-1515

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ACRONYMS AND ABBREVIATIONS

AC	Activated carbon
AFFF	Aqueous film-forming foam
DoD	Department of Defense
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
Fe/TNTs@AC	Iron doped activated carbon modified titanate nanotubes
FeO/CS	CS-modified iron oxide
Ga/TNTs@AC	Gallium doped activated carbon modified titanate nanotubes
HRT	hydraulic residence time
IDW	Investigation-derived wastes
LC-MS/MS	Liquid chromatography-tandem mass spectrometry
M/TNTs@ac	Metal impregnated TNTs-AC composite
MCL	Maximum Contaminant Level
PFAS	Per- and polyfluoroalkyl substances
PFHxS	Perfluorohexane sulfonate
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
PI	Principal investigator
SDBS	Sodium dodecyl benzene sulfonate
SEM	Scanning electron microscope
SEED	SERDP Exploratory Development
SERDP	Strategic Environmental Research and Development Program
TEM	Transmission electron microscopy
TNTs	Titanate nanotubes
TNTs@AC	Activated carbon modified titanate nanotubes
UCMR 3	Unregulated Contaminant Monitoring Rule 3
UV	Ultraviolet

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1.0 INTRODUCTION

1.1 ENVIRONMENTAL ISSUES WITH PFAS

Per- and polyfluoroalkyl substances (PFAS) have become a class of important contaminants in soil and water due to their wide-spread applications, resistance to environmental degradation, and potential health effects. Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are the most detected PFAS. To mitigate human exposure, in 2016, the Environmental Protection Agency (EPA) established a lifetime health advisory level of 70 ng L^{-1} for combined PFOA and PFOS in drinking water. A recent survey reported that drinking water supplies for 6 million U.S. residents exceeded the advisory level.

Human exposure to PFAS has been linked to cancer, elevated cholesterol, obesity, immune suppression, and endocrine disruption. Health concerns in the early 2000s prompted manufacturers in Europe and North America to phase out production of some long-chain PFAS.

The EPA's third Unregulated Contaminant Monitoring Rule (UCMR 3) requires close monitoring of PFAS. In addition to the EPA health advisory, EPA unveiled a PFAS Action Plan that will move forward with the Maximum Contaminant Level (MCL) process for PFOA and PFOS. As part of the Action Plan, U.S. EPA will continue their enforcement actions, clarify clean-up strategies, and expand monitoring of PFAS in the environment. Meanwhile, many states have initiated stringent drinking water standards on PFAS.

Aqueous film-forming foams (AFFFs) have been a vital tool to fight large hydrocarbon fires. Due to their surface-tension lowering properties, fluorinated surfactants are often added in the formulations to enhance their firefighting capabilities. Historical reports of uncontrolled spills and repeated uses of AFFFs during fire training and for AFFF performance testing have been correlated with elevated concentrations of PFAS in biota, surface water, or groundwater.

AFFF formulations have been used by DoD since the 1970s, and the military use accounted for 75% of the U.S. market. Consequently, hundreds of military sites have been contaminated with PFAS. Groundwater at sites impacted by AFFF uses has the greatest recorded concentrations of PFAS of any aqueous environment. The vast majority of the AFFF formulations used by DoD contain PFOS and related perfluoroalkyl sulfonates such as perfluorohexane sulfonate (PFHxS). As a result, the use of PFOS-based AFFFs has been a major environmental liability of DoD.

In the last decade or so, DoD has been increasingly investigating the extent of PFAS contamination across its portfolio of sites. Consequently, large quantities of investigation-derived wastes (IDWs) were (and will continue to be) generated. Yet, cost-effective technologies are lacking to treat the IDWs including both PFAS-laden water and soil. To a large extent, current practices rely on landfilling and incineration of these wastes, which are both costly and pose additional transportation requirements and secondary contamination issues. As such, SERDP has been looking for *alternative innovative technologies that would permit unrestricted disposal, discharge, and/or reuse of IDW on-site*.

1.2 THE STATE OF THE TECHNOLOGY

Due to the strongly polarized carbon–fluorine bonds and the amphiphilic nature, PFAS are uniquely persistent (biological half-life = ~3 years), mobile, and bio-accumulative in the environment. Conventional treatment technologies are not effective for degrading PFAS, such as standard biological, Fenton, and photochemical processes. Numerous studies have examined remediation methods for treatment of PFASs (mainly PFOA and PFOS). Yet, cost-effective technologies remain lacking. Sorption has been one of the most cited methods to remove PFAS, and various adsorbents have been investigated, including activated carbon (AC), carbon nanotubes, ion exchange resins, synthetic magnetite nanoparticles, and biomaterials. However, these adsorbents come with some critical drawbacks, such as low adsorption capacity, high material cost, costly regeneration, and/or generation of large volumes of process waste residuals. For instances, AC has been tested/used at several sites to remove PFOA and PFOS from contaminated water; however, the cost-effectiveness of AC systems remains questionable due to costly regeneration and disposal of the spent regenerant. Moreover, while adsorption concentrates PFAS, it does not degrade them.

Past efforts to induce photochemical transformations of PFASs employed persulfate ions ($S_2O_8^{2-}$) or TiO_2 particles as sensitizers, but the reactions are very slow. For instance, degradation of PFOA using $S_2O_8^{2-}$ as a sensitizer was found slow and costly due to the large amount of $S_2O_8^{2-}$ required and because persulfate activation is energy demanding. Sonochemical oxidation was also studied, but it is energy-demanding, and its feasibility has not been tested under realistic field conditions.

Treating PFAS-bearing IDW soil is even more challenging because the soil-sorbed PFAS are not directly accessible. For typical IDW soil, the conventional disposal methods have been landfill (upon proper treatment and permission), containment, or incineration. With the rapidly mounting environmental regulations, however, landfill/containment of IDW is facing growing challenges, whereas incineration is cost-inhibitive. In fact, many common soil remediation techniques are ineffective for treating PFAS contaminated soil, including air sparging, soil-vapor extraction, bioremediation, and hydrolysis.

For soil remediation, *in situ* soil flushing or soil washing using a flushing agent has been often practiced. For instance, an anionic surfactant (sodium dodecyl benzene sulfonate [SDBS]) has been used to desorb soil-sorbed chlorinated solvents. However, because desorption of PFAS is often more difficult, more aggressive solvents (e.g., methanol) were used to elute PFAS from soil or other adsorbents, which is not only costly, but environmentally prohibitive. In a prior work, the principal investigator (PI) observed that the addition of 43.4 mg L^{-1} of SDBS increased the water solubility of PFOS by >2 times and lowered the soil adsorption by 31%. These findings suggest that low-cost and nontoxic surfactants or oil dispersants may effectively desorb PFAS from soil in a more cost-effective and environmentally benign manner.

1.3 THE PROPOSED TECHNOLOGY

This project aimed to develop an innovative "Concentrate-&-Destroy" technique that can highly effectively adsorb/concentrate and degrade PFAS in water. The key to this technology is to develop a new class of carbon-modified photocatalysts (iron doped activated carbon modified titanate nanotubes [Fe/TNTs@AC], gallium doped activated carbon modified titanate nanotubes [Ga/TNTs@AC], and iron oxide/carbon sphere [FeO/CS]) that can serve as both an adsorbent and a photocatalyst.

As an adsorbent, the composite materials offer not only rapid adsorption rate, but also high adsorption selectivity towards PFAS, thanks to the concurrent hydrophobic interactions (between the carbons and PFAS tails) and Lewis acid-base interactions (between metals and PFAS head groups) as well as the unique structures of the composite materials. As a photocatalyst, the materials provide superior photocatalytic activity over conventional photocatalysts (e.g., TiO_2) owing to the carbon-mediated electron transfer and enhanced generation of reactive species. **Figure A1** illustrates the core-shell structure of activated carbon (AC) supported/modified titanate nanotubes (TNTs@AC) and shows a high-resolution transmission electron microscopy (TEM) image of the tubular structure of TNTs on AC.

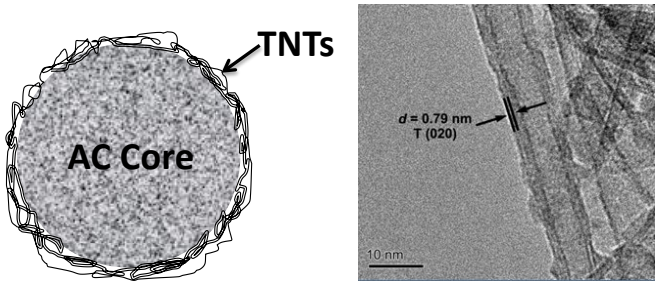

Figure A1. Left: Core-shell Structure of Activated Charcoal Supported Titanate Nanotubes (TNTs@AC); Right: HRTEM Images of TNT Nanotubes on AC.

The effective adsorption concentrates trace levels of PFAS from large volumes of contaminated water onto a small amount of the photocatalyst, facilitating subsequent photochemical destruction of PFAS in a more efficient and cost-effective manner; and the photodegradation not only destroys PFAS, but also regenerates the material, allowing for multiple cycles of operations without invoking costly chemical/solvent regeneration or producing any process waste residuals. **Figure A2** illustrates the process schematic of the "Concentrate-&-Destroy" strategy for treating PFAS in IDW water. First, PFAS in water are concentrated on metal-doped TNTs@AC (M/TNTs@AC) via common fixed-bed adsorption. Second, the PFAS-loaded adsorptive photocatalyst is subjected to ultraviolet (UV) or solar light to destroy the pre-sorbed PFAS, which also regenerates the material. and third, the photo-regenerated material is reused in another cycle of adsorption/photodegradation. Alternatively, the adsorption step may be conducted using the conventional mixer-settler configuration (for powder activated carbon).

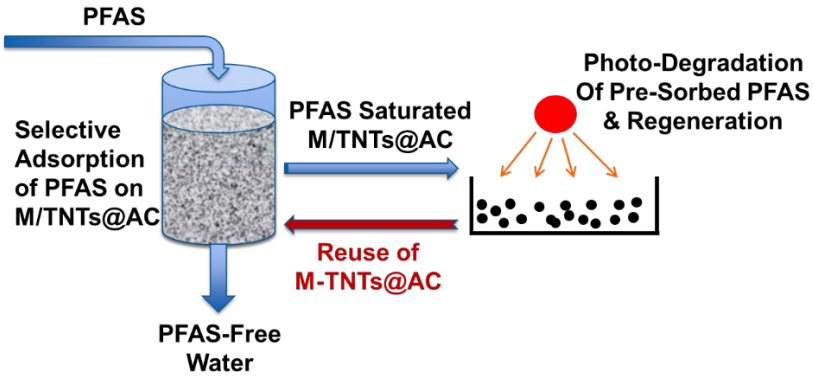

Figure A2. Schematic of the "Concentrate-&-Destroy" Concept for Removal and Destruction of PFAS in Water.

To treat PFAS in soil, the project team tested a novel three-step approach (desorption, concentrate and destroy). As shown in **Figure A3**, soil-sorbed PFAS are first desorbed using a dilute solution of a low-cost and nontoxic oil dispersant, known as Corexit 9500A, and the "Concentrate-&-Destroy" technique is applied to treat the PFAS in the dispersant solution. The treated dispersant solution is then reused in another desorption cycle, and the concentrated PFAS are then destroyed via the photodegradation.

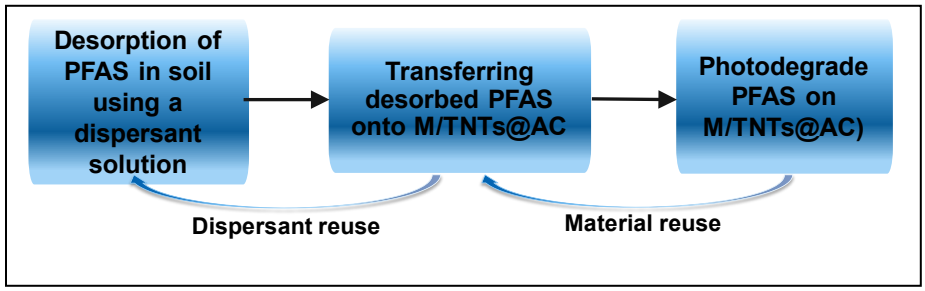

Figure A3. Schematic for Treating PFAS in IDW Soil.

2.0 OBJECTIVES

The overall goal of this project was to develop an innovative, cost-effective and "green" technology for destruction of PFAS from DoD's IDWs including both PFAS-contaminated water and soil. The specific objectives were to do the following:

1) Develop a new class of novel composite materials based on commercially available, low-cost AC, TiO_2, and CS-modified iron oxide (FeO/CS), which can offer both rapid and high-capacity adsorption and high photocatalytic degradation of PFAS.
2) Test the effectiveness of the new materials for adsorption and photocatalytic degradation of PFAS in water under UV or solar light.
3) Examine reusability of the materials for repeated adsorption and photodegradation of PFAS without chemical regeneration.
4) Explore a "green" and cost-effective approach for eluting PFAS from IDW soil using dilute surfactants or oil dispersants.
5) Test the effectiveness of the new materials for adsorption and photodegradation of PFAS in the spent desorbing solution, and reusability of the treated solution.
6) Carry out a preliminary cost-benefit analysis.

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3.0 TECHNICAL APPROACH

The research objectives were accomplished by carrying out five interconnected tasks (**Figure A4**). In the screening experiments, PFOA and PFOS were used as the model PFAS, and deionized water or synthetic water was used in the water treatment tests. In addition, the material performance was preliminarily probed using groundwater from the Willow Grove site. For soil treatment (PFAS desorption), the field soil from Willow Grove was used.

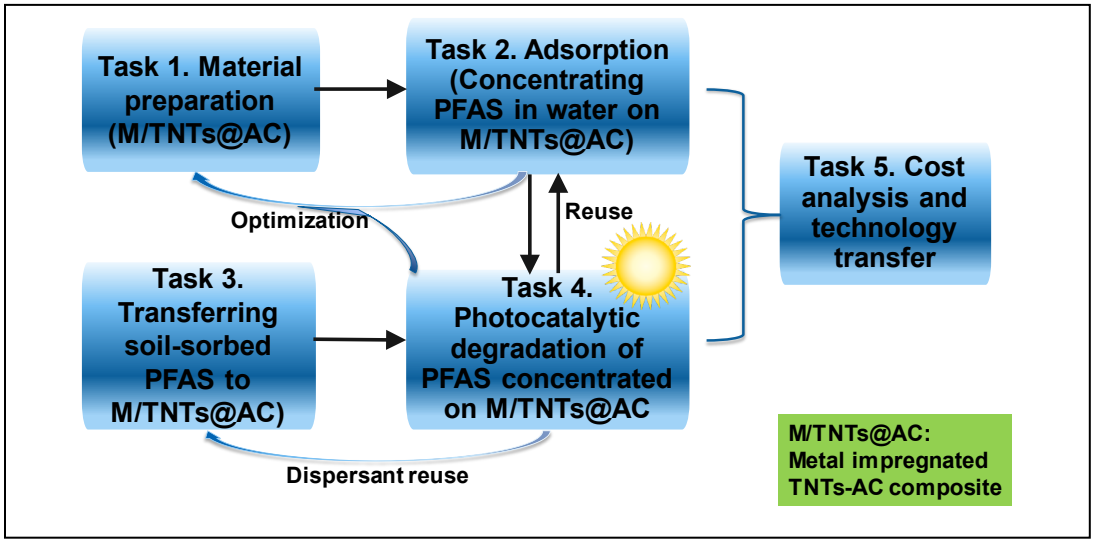


Figure A4. Flow Chart of the Research Approach and Tasks.

First, the project team prepared two metal-doped TNTs@AC composites (Fe/TNTs@AC and Ga/TNTs@AC) through a facile hydrothermal treatment approach by thermal impregnation of iron or gallium onto TNTs@AC. In addition, the project team prepared a new iron oxide/CS composite, referred to as FeO/CS, through a one-step hydrothermal treatment of Fe (III) and glucose precursors. While Fe/TNTs@AC and Ga/TNTs@AC were photoactive under UV light, FeO/CS was designed to degrade PFAS under solar light. The new adsorptive photocatalysts were then characterized with respects to morphology, particle size, surface area, elemental composition, crystal type and structure, pore size distribution, surface functional groups, element oxidation states, light absorbance, band energy gap, and zeta potential. The characterization information, along with the adsorption and photodegradation data, is then used to polish the material synthesis and elucidate the underlying adsorption and photocatalytic degradation mechanisms.

Second, the project team tested effectiveness of the new materials for adsorption of PFAS through batch adsorption kinetic and equilibrium experiments.

Third, for treating PFAS in soil, batch desorption tests were carried out to elute soil-sorbed PFAS using various desorbing agents (Corexit 9500A and SPC1000). Based on the screening results, Corexit 9500A was selected as the best dispersant, and PFAS in the dispersant solution was then reloaded onto the photocatalyst (Ga/TNTs@AC) and destroyed subsequently.

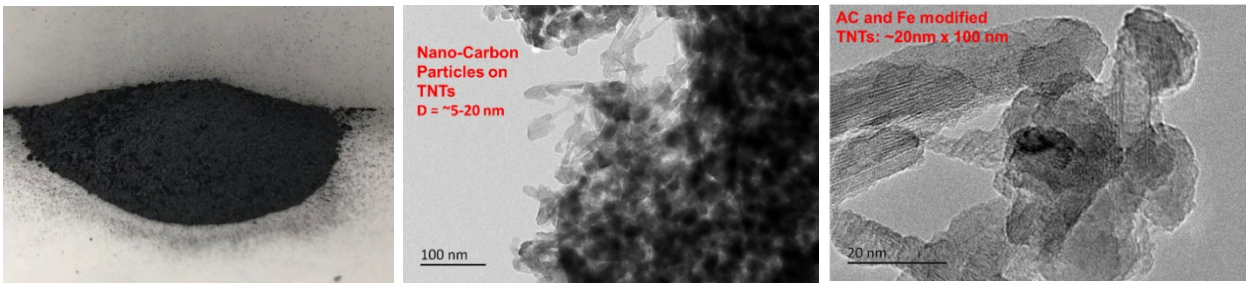
Fourth, photodegradation of pre-concentrated PFAS on the photocatalysts was tested in batch reactors under UV or solar light (with 95% of water removed from the batch adsorption tests), and factors affecting the effectiveness were examined. The photo-regenerated materials were then reused in another cycle of adsorption-photodegradation to gauge reusability of the materials.

Lastly, a preliminary cost-benefit analysis was carried out.

4.0 RESULTS AND DISCUSSION

4.1 SYNTHESIS AND CHARACTERIZATION OF FE/TNTS@AC

Figure A5a shows the as-prepared iron-doped, AC-supported titanate nanotubes (Fe/TNTs@AC). The physical size and shape mimic those of typical powder AC, though the surface is functionalized with the photoactive Fe-doped TNTs. **Figure A5b** shows that upon the alkaline hydrothermal treatment, some carbon broke into nanoscale carbon particles that are attached on TNTs, and **Figure A5c** presents a close-up of the Fe- and carbon modified TNTs. The iron and carbon modifications are expected to enhance both adsorption and photodegradation of PFAS.

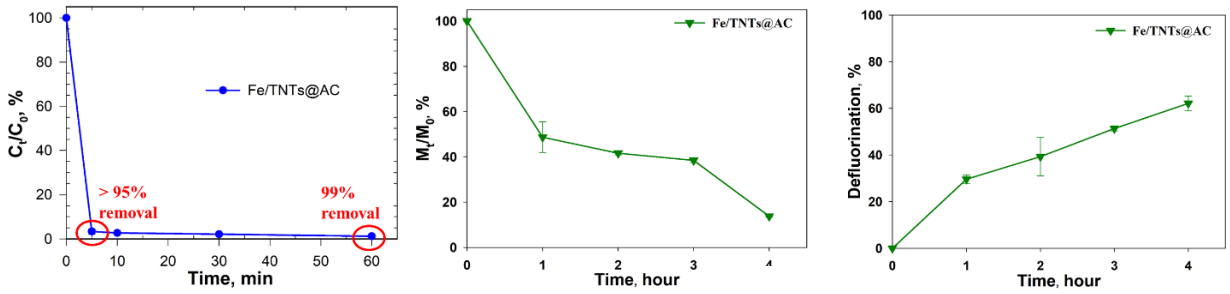


(a) **(b)** **(c)**

Figure A5. (a) A Digital Image of Fe/TNTs@AC Prepared Based on Commercial Activated Carbon (AC) and TiO_2 through an Alkaline Hydrothermal Process (AC:TiO_2 mass ratio = 1:1, Fe = 1 wt.% of TNTs@AC); (b) TEM Images of Nanoscale AC Particles Attached on Titanate Nanotubes (TNTs); and (c) A Close-up of Iron- and AC-Modified TNTs with FeO Patched on TNTs.

4.2 ADSORPTION AND PHOTODEGRADATION OF PFOA AND PFOS BY FE/TNTS@AC

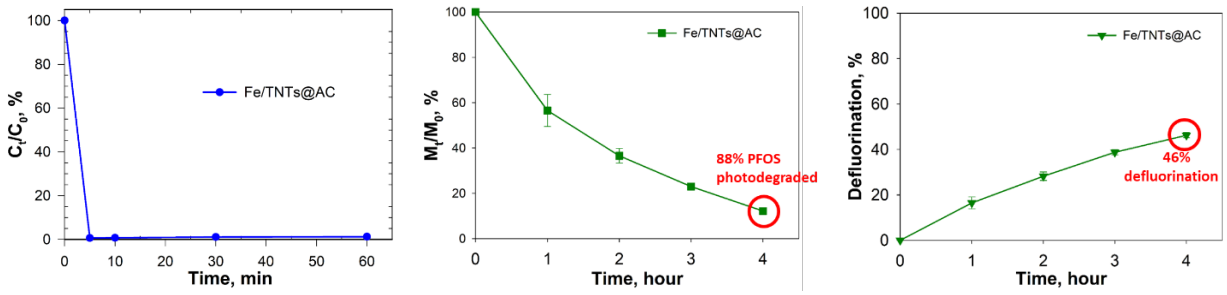
Fe/TNTs@AC exhibited excellent adsorption rate and photocatalytic activity for both PFOA and PFOS. **Figure A6a** shows adsorption kinetics of PFOA. More than 99% was adsorbed after 60 min. The rapid adsorption allows for efficient removal of PFOA from bulk water with a small hydraulic residence time (HRT) (i.e., a small reactor). Moreover, the adsorption pre-concentrates PFAS from a large volume of water onto a small volume of Fe/TNTs@AC, enabling the subsequent photocatalytic degradation to be carried out in a much smaller volume of photo-reactor with much less energy consumption compared to directly treating the bulk raw water. **Figure A6b** shows that Fe/TNTs@AC was able to highly efficiently degrade (i.e., break down into other compounds) >90% of pre-concentrated PFOA in 4 h. Moreover, **Figure A6c** shows that 62% of PFOA was completely destroyed or defluorinated (i.e., converted into F^- ions). It should be noted that in this preliminary study, the adsorption was carried out in batch reactors, where the material capacity was not fully utilized. In practice, the treatment can be further optimized. For instance, the adsorption can be performed using fixed-bed columns, which may treat much more volumes of water. Likewise, the photodegradation can be further improved by optimizing factors such as material synthesis, dosage, and reaction chemistry. PFOS has been known to be more persistent and adsorptive than PFOA. **Figure A7a** shows that Fe/TNTs@AC removed >99% of PFOS from water within just 5 min of contact time. When subjected to the UV irradiation, ~88% of preloaded PFOS was degraded within 4 h (**Figure A7b**), of which 46% was defluorinated (**Figure A7c)**.



(a) **(b)** **(c)**

Figure A6. (a) Adsorption, (b) Photodegradation, and (c) Defluorination Kinetics of PFOA by Fe/TNTs@AC.

Experimental conditions: initial [PFOA] = 100 μg L^{-1}, material dosage = 1.0 g L^{-1}, solution volume = 40 mL, and pH = 7.0 ± 0.3. Photodegradation conducted under UV (λ=254 nm, 21 mW cm^2). Degradation: transformation or breakdown of PFAS into other compounds; Defluorination: conversion of fluorine into fluoride ions. M_0: initial mass of PFOA in the material, and M_t: PFOA remaining at time t.



(a) **(b)** **(c)**

Figure A7. (a) Adsorption, (b) Photodegradation, and (c) Defluorination Kinetics of PFOS by Fe/TNTs@AC.

Experimental conditions: initial [PFOS] = 100 μg L^{-1}, material dosage = 2.0 g L^{-1}, solution volume = 40 mL, and pH = 7.0 ± 0.3. Photodegradation conducted under UV (λ=254 nm, 21 mW cm^{-2}).

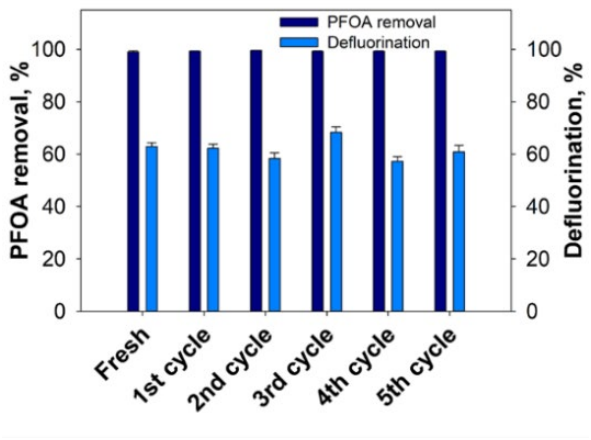


Figure A8. Reusing Fe/TNTs@AC in Six Consecutive Cycles of Adsorption-Photodegradation of PFOA.

Experimental conditions are the same as in Figure A6.

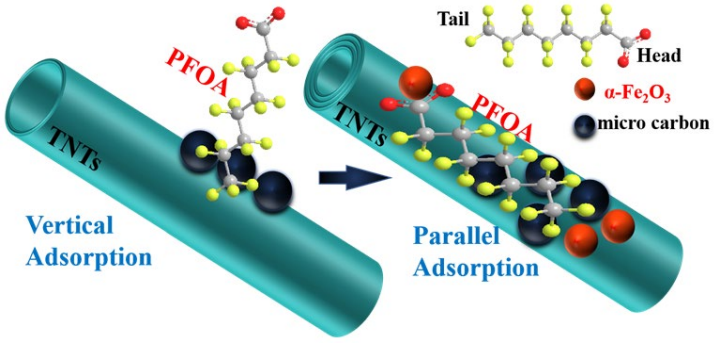


Figure A9. Conceptualized Illustration of PFOA Adsorption by Fe/TNTs@AC.

Carbon nanoparticles interact with the tail, and FeO nanoparticles attract the head groups, setting up for subsequent photodegradation.

4.3 REUSABILITY OF FE/TNTS@AC

Figure A8 shows that when Fe/TNTs@AC was repeatedly used in six consecutive cycles of adsorption-photodegradation without chemical regeneration, PFOA adsorption remained high (>99% removal), and defluorination kept at ~60%. Evidently, Fe/TNTs@AC can be reused in multiple cycles without additional regeneration need. This important feature represents a great advancement of conventional adsorbents (AC or ion exchange resins), which require costly regeneration and subsequent treatment of the spent regenerant wastes. The slight increase in defluorination with the cycle time is attributed to the additional defluorination of intermediate products from the previous cycles. Indeed, short-chain PFAS were detected on Fe/TNTs@AC during the photodegradation process.

4.4 MECHANISMS OF ENHANCED PFAS ADSORPTION AND PHOTODEGRADATION BY FE/TNTS@AC

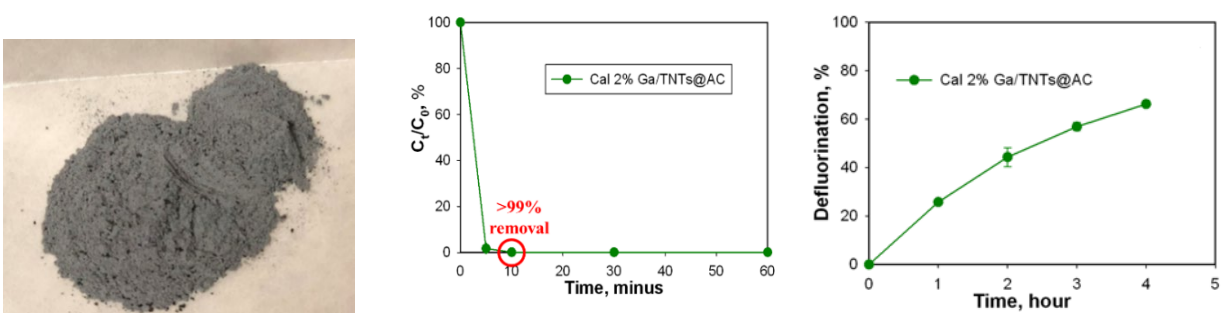
The adsorption rate, capacity and photocatalytic activity of Fe/TNTs@AC far exceed those of conventional Ti-based photocatalysts such as TiO_2 or TNTs. The PFOA photodegradation starts with decarboxylation of the head (COO^-) group through oxidation by the photo-generated holes (h^+), i.e.,

$$h^+(\mathrm{VB}) + C_7F_{15}COO^- \rightarrow C_7F_{15}COO^{\bullet}, \qquad C_7F_{15}COO^{\bullet} \rightarrow {}^{\bullet}C_7F_{15} + CO_2$$

The resulting ${}^{\bullet}C_7F_{15}$ radicals are decomposed via reactions with $OH^{\bullet}$ radicals and hydrolysis, resulting in cleavage of the C-F bond and release of fluoride ions. The shorter-chain products undergo the same decarboxylation/defluorination cycle, each of which eliminating one carbon and two fluorine atoms (CF_2). In addition to this standard pathway, Fe/TNTs@AC can also directly induce the decarboxylation reaction, thanks to the iron impregnation which is not only photoactive, but can directly withdraw electrons from the PFOA.

The enhanced adsorption and photodegradation are attributed to the following: 1) the carbon nanoparticles facilitate hydrophobic interactions with the PFOA tail, 2) the carbon coating also facilitates electron transfer and prevents electron-hole recombination in the photocatalyst, 3) the Fe(III) coating suppresses surface negative potential and enhances the interactions between the holes and the PFOA head groups (carboxylate), 4) the presence of Fe(III) also facilitates production of more ${}^{\bullet}OH$ radicals and prevents e-h recombination.

Lastly, because of the lower band energy gap of iron oxide, the Fe-doping enhances absorption of more visible light. **Figure A9** illustrates the modes of the interactions, where both the head and tail are involved in the adsorption process, resulting in a molecule orientation that is more conducive to the subsequent photocatalytic cleavage of the head groups and the C-F bonds.



(a) **(b)** **(c)**

Figure A10. (a) Ga/TNTs@AC Prepared Based on Commercial AC and TiO_2 (AC:TiO_2 Mass Ratio = 1:1, Ga = 2 wt.% of TNTs@AC); (b) Adsorption, and (c) Defluorination Kinetics of PFOS by Ga/TNTs@AC.

Experimental conditions: initial [PFOS] = 100 μg L^{-1}, Ga/TNTs@AC = 3.0 g L^{-1}, solution volume = 40 mL, and pH = 7.0 ± 0.3; UV: λ = 254 nm, 21 mW cm^{-2}). C_0 and C_t: PFOS Concentrations at time 0 and t, respectively.

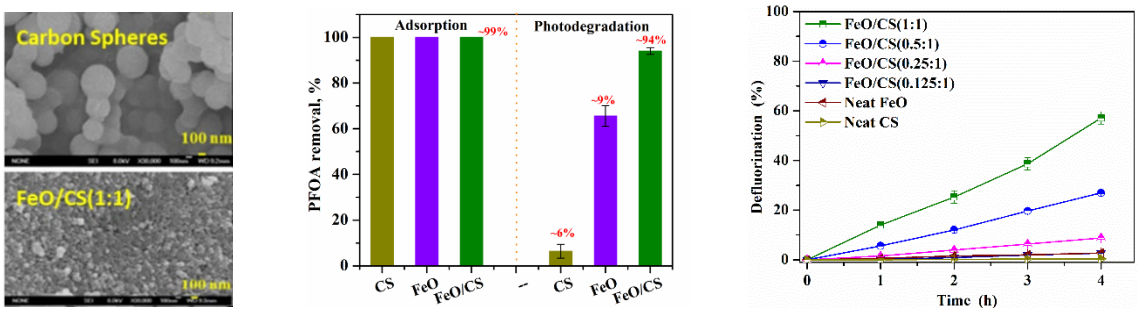
4.5 PREPARATION AND TESTING OF GA/TNTS@AC FOR ADSORPTION AND DESTRUCTION OF PFOS

In search for even more reactive photocatalysts, the project team prepared the gallium-doped TNTs@AC, i.e., Ga/TNTs@AC. **Figure A10a** shows the as-prepared powder Ga/TNTs@AC, whose size, shape and morphology resemble those of Fe/TNTs@AC. **Figure A10b** shows that Ga/TNTs@AC was able to rapidly and nearly completely remove PFOS from water, with >99% of PFOS adsorbed within 10 min. Moreover, **Figure A10c** shows that >66% of defluorination of PFOS was achieved in 4 h under UV irradiation.

4.6 PREPARATION AND TESTING OF FEO/CS FOR DESTRUCTION OF PFOA UNDER SOLAR LIGHT

Ferrihydrite (Fh) is a common mineral, which is not only "green" and low-cost, but also has a narrow band gap energy (2.7 eV), stretching its photoactivity into the red region of the solar spectrum. On the other hand, nanoscale carbon spheres (CS) can facilitate efficient PFAS adsorption and electron transfer. Taking advantage of these properties, the project team prepared a new Fh-CS composite (FeO/CS), which was able to offer decent photocatalytic activity under solar light, representing significant energy saving.

Figure A11a shows scanning electron microscope (SEM) images of CS prepared without Fe and FeO/CS composite prepared at an Fe:C molar ratio of 1:1, displaying intermingled FeO and CS nanoparticles. **Figure A11b** shows that FeO/CS(1:1) and neat CS or FeO were all able to adsorb >99% of PFOA in 2 h, however, FeO/CS(1:1) showed much greater photodegradation rate than either CS or FeO alone, with 94% of the pre-adsorbed PFOA degraded in 4 h under solar light, unveiling the strong synergistic effect of FeO and CS. **Figure A11c** shows that FeO/CS(1:1) completely mineralized ~60% of PFOA (based on fluoride production) in 4 h of solar light irradiation. Increasing the Fe:C molar ratio from 0:1 to 1:1 increased photocatalytic mineralization of PFOA from almost 0 for neat FeO or CS to ~60%. Moreover, when repeatedly used for three cycles of adsorption-photodegradation, the adsorption rate and photodegradation rates remained high, though defluorination was decreased to ~50% (data not shown).



(a) **(b)** **(c)**

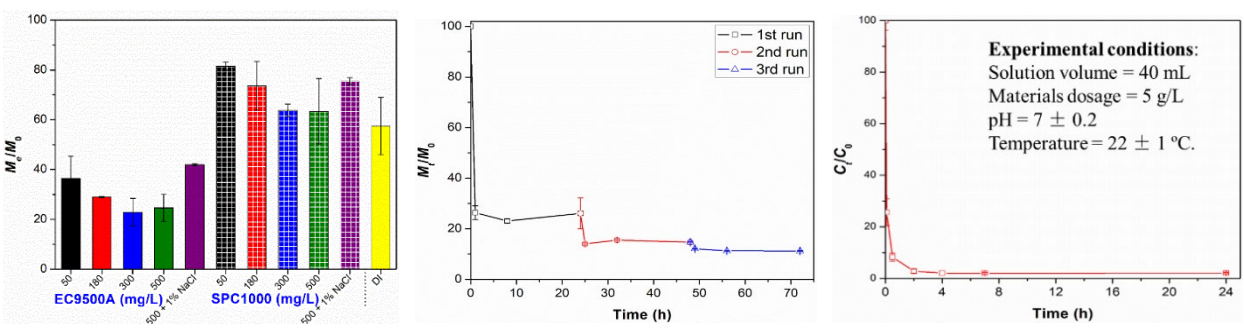
Figure A11. (a) SEM Images of Carbon Spheres (CS) Prepared without Fe and FeO/CS Composite Prepared at an Fe:C molar ratio of 1:1 and through a Hydrothermal Process at 180 °C; (b) Equilibrium Adsorption of PFOA by FeO/CS(1:1) at 2 h, and Degradation of Pre-concentrated PFOA after 4 h of Solar Light Exposure, and (c) Defluorination Kinetics of PFOA by FeO/CS Prepared at Various Fe:CS Molar Ratios (indicated in the brackets).

Experimental conditions: initial [PFOA] = 200 μg L^{-1}, FeO/CS = 1.0 g L^{-1}, pH = 7.0 ± 0.3. Photodegradation conducted under simulated solar light (100 mW cm^{-2}).

4.7 DESORPTION OF PFOS FROM WILLOW GROVE SOIL USING OIL DISPERSANTS

PFOS was the major contaminant in the Willow Grove field soil (PFOS = 1507.7 ± 37.6 ng g^{-1}; PFOA = 21.4 ± 6.8 ng g^{-1}). In search for a "green," low-cost and efficient eluent for desorbing PFOS from soil, the project team tested two common EPA-approved dispersants (Corexit EC9500A and SPC1000), which are composed mainly of surfactants. **Figure A12a** compares the batch equilibrium desorption data using deionized water or the dispersants at various concentrations with or without NaCl for desorption of PFOS from the soil. Evidently, Corexit EC9500A at 50 mg L^{-1} was able to effectively remove PFOS, while SPC1000 actually retarded the desorption due to the different compositions. It is also noteworthy that the addition of NaCl (1 wt.%) also retarded the desorption process, which is attributed to the suppression of the soil surface negative potential.

The desorption was not exhaustive because desorbed PFOS in solution prevents further desorption. When the tests were carried out in the successive desorption mode (i.e., replacing the solution with fresh dispersant solution after each batch), >90% of PFOS was desorbed at a dispersant concentration of 300 mg L^{-1} (**Figure A12b**). When the PFAS-laden dispersant solution was treated with 5 g L^{-1} of Ga/TNTs@AC, ~98% of PFOS was rapidly re-adsorbed on the photocatalyst (**Figure A12c**), setting up for subsequent photodegradation. Moreover, the treated dispersant solution was then reused for desorption.



(a) **(b)** **(c)**

Figure A12. (a) Batch Equilibrium Desorption of PFOS from Willow Grove Soil Using Two Dispersants at Various Concentrations; (b) Successive Desorption of PFOS from Willow Grove Soil Using Corexit 9500A (300 mg L^{-1}); (c) Adsorption of PFOS from Spent Dispersant Solution from (b) by Ga/TNTs@AC.

M_0: initial PFOS mass in soil, M_t: PFOS mass in soil at time t, M_e: PFOS mass in soil at equilibrium.

4.8 COST ANALYSIS

A preliminary cost analysis for a hypothetical 0.1 million gallons per day (MGD) treatment system indicates that the overall cost for the "Concentrate-&-Destroy" process is $2.23 for complete degradation of PFOA in 1,000 gal of water, which is 9.1 and 6.5 times lower than those by AC adsorption followed by incineration and landfill, respectively.

5.0 IMPLICATIONS FOR FUTURE RESEARCH AND BENEFITS

In this SEED project, the project team proposed and extensively tested a novel innovative "Concentrate-&-Destroy" strategy for cost-effective and complete destruction of PFAS in IDWs. The key findings are summarized as follows:

- Three reusable adsorptive photocatalysts were prepared based on low-cost and well-accepted commercial materials (AC and TiO_2).
- As an adsorbent, the materials can effectively adsorb/concentrate PFAS from water through commonly used reactor configurations (fixed-bed column or batch reactor); as a photocatalyst, the materials can rapidly and completely degrade PFOA and PFOS under UV or solar light.
- The carbon and metal modifications of TNTs or iron oxide not only facilitate selective adsorption of PFAS, but greatly enhance the photocatalytic degradation.
- The *in situ* efficient photodegradation of PFAS also regenerates the materials, allowing for repeated uses of the photocatalysts without incurring costly chemical regeneration and without generation of waste residuals.
- Dilute Corexit EC9500A can serve as an effective, environmentally safe and low-cost extractant for removing PFOS and PFOA from field soil, and the "Concentrate-&-Destroy" technique can be applied to treat the spent dispersant solution so as to reuse the solution and destroy the PFAS.

The "Concentrate-&-Destroy" strategy offers some unprecedented advantages over conventional approaches, such as adsorption, landfill, and incineration, to treat persistent organic pollutants, including the following:

- It treats low concentrations of PFAS in large volumes of water using low-cost and easy-to-operate adsorption process, and then completely destroys the concentrated PFAS *in situ* through highly efficient photocatalytic approach, representing significant cost savings.
- It eliminates the need for costly and toxic chemical/solvents for regeneration and generates little or no process waste residual.
- The system can be easily applied on site and is easier to operate, and can be made mobile and deployed easily, minimizing the spatial footprint and mobilization time and effort.
- It holds the potential to achieve unrestricted disposal, discharge, and/or reuse of IDW on-site upon some follow-on studies and will greatly aid DoD Remedial Project Managers in more effective management of the PFAS-contaminated sites.

This intensive SEED effort directly addressed the SERDP's critical need to develop "more cost-effective and efficient technologies for treatment of IDW from PFAS investigations". The findings provide compelling evidence for a brand-new strategy for "green", cost-effective and efficient destruction of PFAS. The "Concentrate-&-Destroy" strategy meets the DoD's preference "for destructive technologies...so as to avoid potential future environmental liability" associated with PFAS.

Based on the findings, the project team anticipate that the new technology will potentially equip the DoD Remedial Project Managers with a powerful on-site treatment approach in treating PFAS at hundreds of the DoD sites. To this end, the following follow-on research activities are warranted:

- The adsorptive photocatalysts can be further optimized in terms of selectivity for PFAS and photoactivity by tuning the parent materials, the dopants, and synthesis conditions towards more efficient mineralization of PFAS, especially for PFAS in soil extracts.
- Composite materials that are more reactive under solar light should be further explored.
- Further investigations are needed to test the effectiveness under DoD field water/soil conditions to identify potential inhibitions of the water matrix and find out ways to overcome these inhibitive effects and to optimize the water chemistry conditions.
- Pilot-scale experiments should be carried out to facilitate more realistic assessment of the technical and economic effectiveness and to guide field application design.
- Desorption of PFAS from soil can be further optimized by adjusting the solution recipe and chemistry to facilitate more efficient desorption of PFAS and to promote subsequent photodegradation.
- Water chemistry conditions can be optimized to promote photocatalytic degradation of more persistent PFAS or PFAS from the dispersant solutions, including addition of proper photosensitizers and elevation of reaction temperature.
- To promote earliest possible field adoption, various technology transition/transfer measures should be taken immediately following the pilot-testing, first towards the DoD end users, and then the market at large (e.g., landfill leachate and groundwater sites).