

FINAL REPORT

Complete Reductive Defluorination of PFAS by Hydrated
Electrons Generated from 3-Indole-acetic-acid in Chitosan-
Modified Montmorillonite

SERDP Project ER18-1526

MAY 2020

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REPORT DOCUMENTATION PAGE					<i>Form Approved</i> OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) 07-05-2020		2. REPORT TYPE SERDP Final Report			3. DATES COVERED (From - To) 4/13/2018 - 4/12/2021	
4. TITLE AND SUBTITLE Complete Reductive Defluorination of PFAS by Hydrated Electrons Generated from 3-Indole-acetic-acid in Chitosan-Modified Montmorillonite					5a. CONTRACT NUMBER 18-C-0031	
					5b. GRANT NUMBER	
					5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Hailiang Dong					5d. PROJECT NUMBER ER18-1526	
					5e. TASK NUMBER	
					5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Miami University 250 South Patterson Ave Oxford, OH 45056					8. PERFORMING ORGANIZATION REPORT NUMBER ER18-1526	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Strategic Environmental Research and Development Program 4800 Mark Center Drive, Suite 16F16 Alexandria, VA 22350-3605					10. SPONSOR/MONITOR'S ACRONYM(S) SERDP	
					11. SPONSOR/MONITOR'S REPORT NUMBER(S) ER18-1526	
12. DISTRIBUTION/AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT Perfluorinated compounds (PFCs) are extensively utilized industrial compounds with a wide variety of applications (Sznajder-Katarzyńska et al., 2019). They find heavy use due to their hydrophobic alkyl chains which are attached to hydrophilic end groups. These compounds are useful in various industrial applications such as textiles (Supreeyesunthorn et al., 2016), carpet manufacturing (Lau et al., 2007), food packaging (Begley et al., 2005), and leather treatment (Sznajder-Katarzyńska et al., 2019). They are also used as surfactants and fire-fighting foam (Houtz et al., 2013). These compounds have found such prolific use because of the strength of the carbon - fluorine bond, which requires 485 kJmol ⁻¹ to break (O'Hagan, 2008), making PFCs long lasting as they are thermally stable and resistant to oxidation. Because of their widespread applications, PFCs have made into the EPA's list of emerging contaminants as they are persistent, bio-accumulative, and have been shown to be both environmentally hazardous and potentially carcinogenic (Cooke, 2017; Sznajder-Katarzyńska et al., 2019).						
15. SUBJECT TERMS Reductive Defluorination, Poly- and Perfluoroalkyl Substances, PFAS, Hydrated Electrons, 3-Indole-acetic-acid, Chitosan-Modified Montmorillonite						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UNCLASS	18. NUMBER OF PAGES 29	19a. NAME OF RESPONSIBLE PERSON Hailiang Dong	
a. REPORT UNCLASS	b. ABSTRACT UNCLASS	c. THIS PAGE UNCLASS			19b. TELEPHONE NUMBER (Include area code) 513-529-2517	

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Introduction

Perfluorinated compounds (PFCs) are extensively utilized industrial compounds with a wide variety of applications (Sznajder-Katarzyńska et al., 2019). They find heavy use due to their hydrophobic alkyl chains which are attached to hydrophilic end groups. These compounds are useful in various industrial applications such as textiles (Supreeyasunthorn et al., 2016), carpet manufacturing (Lau et al., 2007), food packaging (Begley et al., 2005), and leather treatment (Sznajder-Katarzyńska et al., 2019). They are also used as surfactants and fire-fighting foam (Houtz et al., 2013). These compounds have found such prolific use because of the strength of the carbon - fluorine bond, which requires 485 kJmol^{-1} to break (O'Hagan, 2008), making PFCs long lasting as they are thermally stable and resistant to oxidation. Because of their widespread applications, PFCs have made into the EPA's list of emerging contaminants as they are persistent, bio-accumulative, and have been shown to be both environmentally hazardous and potentially carcinogenic (Cooke, 2017; Sznajder-Katarzyńska et al., 2019).

Perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) are two members of the PFC group. PFOS is a fully fluorinated organic acid, used in a variety of consumer products and can be generated as a degradation product of various other perfluorinated compounds (Paul et al., 2009). While production in the United States has voluntarily been phased out since 2002, PFOS still exists as a legacy product and as an import product (Cooke, 2017). Exposure to PFOS in the United States remains possible, due to its legacy uses, existing and legacy imported goods, degradation from precursor compounds, and extremely high persistence in the environment and in the human body (Sznajder-Katarzyńska et al., 2019). PFAS has been detected in blood serum in up to 99% of the U.S. general population since 2008, however this number is expected to decrease for PFOS and PFOA as their production is phased out domestically (Kato et al., 2011).

Recent degradation methods of these compounds include photocatalytic (Chen et al., 2020; Li et al., 2014; Qu et al., 2010; Tian et al., 2016), plasma reactors (Singh et al., 2019); electrochemical (Schaefer et al., 2019; Trautmann et al., 2015), and sonochemical methods (Cheng et al., 2010; Lee et al., 2016; Rodriguez-Freire et al., 2015). However, these methods often do not completely break down these compounds, require expensive or easily spent electrodes, or introduce other hazardous materials into the environment. While ultrasonic degradation has achieved success in complete defluorination, the required frequency and power along with the generation of bubbles and heat greatly limit the application of this method for wastewater treatment (Fernandez et al., 2016).

Photochemical methods used to breakdown these molecules often rely on hydrated electrons, as these are highly reactive (Hart et al., 1964). The generation of hydroxyl radicals, which is a more common method of photochemical contaminant degradation, is ineffective for PFAS, likely due to the strength of the C-F bond (Javed et al., 2020; Mitchell et al., 2014). However, the highly reductive hydrated electron can break the carbon fluorine bond (Bao et al., 2018; Bentel et al., 2019; Chen et al., 2020; Gu et al., 2017a; Song et al., 2013; Tian et al., 2016). While previous studies have used hydrated electrons, generated through photoionization of iodide or sulfite, for treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), the large-scale

application of this treatment approach may be limited due to: 1) the toxicity of iodide and sulfite, and generation of elevated levels of undesirable products (e.g., sulfate); 2) the practical implementation issue of attaining and maintaining the anoxic and high pH conditions that are required for the defluorination reactions, as both O₂ and protons can quickly consume hydrated electrons (Qu et al., 2014; Qu et al., 2010; Song et al., 2013). These conditions are difficult to maintain at contaminated sites.

Recent studies (Gu et al., 2016; Gu et al., 2017a) have used hydrated electrons to degrade both PFOS and PFOA under partially oxic (DO=5 mg/L) and alkaline pH (9.2) conditions. Loss of hydrated electrons from reaction with O₂ is partially compensated by a high production rate with a high photon flux UV/sulfite system; however, an alkaline pH (9.2) and undesirable sulfite are still required. Gu et al. (2017b) used a vacuum ultraviolet (VUV)/sulfite system to degrade PFOS, and observed that this combination degraded PFOS nearly 7.5- and 2-fold faster than that in sole VUV and UV/sulfite systems, respectively. However, the same problems are apparent: the use of sulfite and an alkaline condition (pH > 9). In addition, in treatment systems with complicated water chemistry containing organic matter, co-contaminants, and anions such as bicarbonate/carbonate, sulfate, and nitrate, hydrated electrons can rapidly react with these species and decrease their efficiency towards PFAS degradation (Buxton et al., 1988; Gu et al., 2016; Gu et al., 2017b).

A recent study (Tian et al., 2016) developed a novel approach to overcome these limitations, where HDTMA was intercalated into the interlayer region of a clay mineral montmorillonite. This HDTMA-montmorillonite nano-composite was highly hydrophobic and even organophilic. PFOA/PFOS and 3-indole-acetic acid (IAA), a common component of natural soil and sediment organic matter (Chen and Kenny, 2007; Miura et al., 2011; Zhang et al., 1999) and a source of hydrated electrons, were intercalated into the interlayer region of HDTMA-montmorillonite. Upon UV irradiation, hydrated electrons were generated from IAA to degrade adjacent PFOA/PFOS in the same interlayer region of the nano-composite. The negatively-charged planar surface of HDTMA-montmorillonite stabilizes indole radical cations, consequently inhibiting their recombination with hydrated electrons. A nearly complete reductive defluorination of both PFOA and PFOS was achieved under mild conditions, e.g., over a pH range of 3-11 and in air (Tian et al., 2016). The authors postulated that the HDTMA in the interlayer region of montmorillonite prevents hydrated electrons from reacting with protons and dissolved oxygen. A more recent study (Chen et al., 2020) reported a near complete defluorination of PFOA by hydrated electrons even without montmorillonite serving as a scaffold. Because PFOA and IAA are both negatively charged, their repulsive interaction makes the degradation of PFOA inefficient. In the presence of positively-charged HDTMA, negatively-charged PFOA and IAA sorb onto HDTMA, this co-localization of PFOA and IAA greatly increases the degradation efficiency of PFOA (Chen et al., 2020).

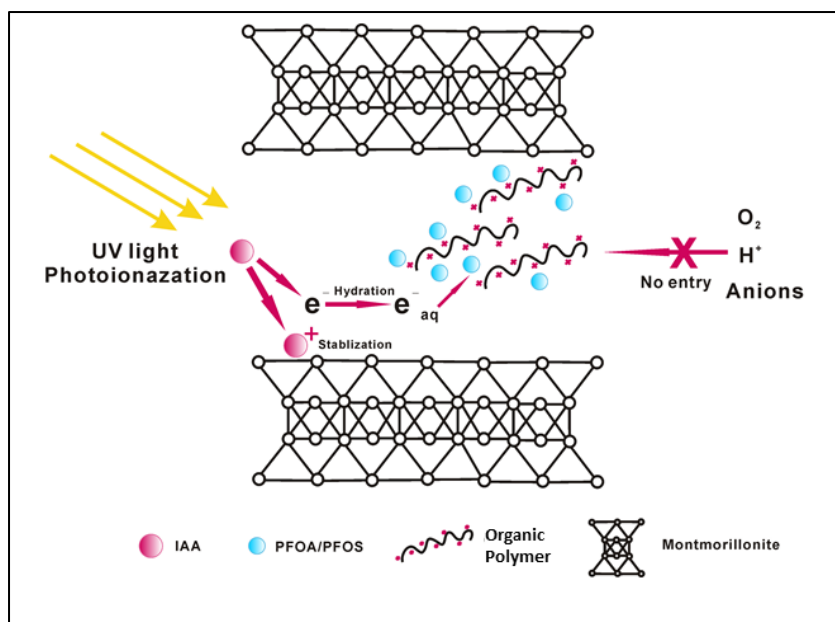


Figure 1. A conceptual model showing the mechanism of PFOA/PFOS degradation by hydrated electrons generated by UV irradiation of 3-indole-acetic-acid (IAA). IAA and PFOA/PFOS are sorbed to the organic polymer HDTMA, which is pre-inserted into the interlayer region of montmorillonite. For better viewing, the interlayer region is not to scale.

Despite these encouraging results, this approach has a few limitations. *First*, HDTMA is toxic. It is well-known that HDTMA is a toxic compound and is often used as an antibacterial agent (Boyd et al., 1988), even when it is intercalated into the interlayer region of montmorillonite (Malachová et al., 2009; Malek et al., 2013; Mondal et al., 2014; Plachá et al., 2014). HDTMA is man-made, very stable, and is not biologically degraded (Boyd et al., 1995). Therefore, once released to the environment, it is difficult to degrade. *Second*, the maximum sorption capacity of HDTMA-montmorillonite is only 277.3 mmol/kg, which is much lower than that by cross-linked chitosan (up to 5500 mmol/kg, Zhang et al., 2011). For these reasons, a more environmentally friendly and highly sorbing material is desirable for treatment of IDW. *Third*, while this hydrated electron based degradation approach has been successful for PFOA and PFOS degradation (Tian et al., 2016), the degradation intermediates have not been identified from PFOS degradation, some of which (i.e., shorter-chain products) may be more toxic than the parent compounds (Brendel et al., 2018; Kabadi et al., 2020; Rice et al., 2020). *Fourth*, the effects of natural organic matter, co-contaminants, and competing anions such as nitrate, sulfate, and bicarbonate on PFOA/PFOS degradation are currently unknown and deserve further study.

A potential replacement of HDTMA, which overcomes all these limitations, is chitosan. Chitosan is a type of biopolymer and the deacetylated form of chitin. Chitin is synthesized by many living organisms such as crab, shrimp, krill, squid, clam, insect, and fungi (Kurita, 2006; Wan Ngah et al., 2011). Chitosan is the most abundant natural biopolymer in the environment after cellulose (Rinaudo, 2006), and it is nontoxic, biocompatible, and biodegradable. Chitosan is used in a wide range of applications such as dietary supplements, water treatment, food preservation, agriculture, textiles, pulp, and paper (Kurita, 2006). A previous study has shown an exceptional

sorption capacity of cross-linked chitosan beads for PFOS, reaching up to 1000, 2000, and 5500 mmol/kg at pH 3, 7, and 9.5, respectively (Zhang et al., 2011). Cross-linked chitosan is believed to have the highest sorption capacity among all known adsorbents for PFOS (Du et al., 2014). At acidic pH, electrostatic and hydrophobic interactions are the dominant sorption mechanisms, but at neutral and alkaline pH, hydrophobic interaction is believed to be the main mechanism. Furthermore, at acidic pH competitive anions such as sulfate and anionic Cr have little effects on PFOS sorption capacity to chitosan, although the sorption rate was slightly lower in the presence of these anions (Zhang et al., 2011), possibly due to the electrostatic interactions between the positively charged amine group of chitosan and these anions.

Our previous study has shown that chitosan can be readily intercalated into the expandable smectite (a general term for montmorillonite) interlayer, and expands the d(001) spacing up to 1.828 nm and reverses the charge of the smectite from overall negative to positive, when the chitosan/smectite ratio is greater than 0.2 (Singh et al., 2017). This chitosan-intercalated smectite has been shown to sorb significant quantities of nitrate (Pentrák et al., 2014) and dichromate anion (Singh et al., 2017). Furthermore, other studies have shown that this type of chitosan configuration, e.g., intercalated into the interlayer region of expandable clay minerals, is effective in sorbing large amounts of organic contaminants including acid fuchsin from wastewater (Cao et al., 2017), pesticides (Celis et al., 2012), various dyes (Vanamudan and Pamidimukkala, 2015; Wan Ngah et al., 2011), and humic acids (Lin and Zhan, 2012).

Another organic compound of interest in the expansion of the montmorillonite and sorption of organic contaminants is 12-amino lauric acid (ALA) (Zeng et al., 2016). 12-aminolauric acid (ALA) is a saturated fatty acid with a 12-carbon atom chain, thus having many properties of medium-chain fatty acids. It is nontoxic and is readily found in many edible plants (Liu et al., 2013). The method of ALA intercalation, however, is simpler and significantly less time consuming, which greatly reduces the cost of the treatment.

While the literature review and our own studies described above prompt us to propose the above conceptual model with respect to *reductive degradation of PFAS via hydrated electrons*, a number of fundamental questions need to be addressed to assess the feasibility of this technology. It is unclear how hydrated electrons generated from IAA within the interlayer region of chitosan- and ALA-intercalated montmorillonite reductively defluorinated PFOA/PFOS with a high efficiency under mild environmental conditions (water chemistry). It is unknown if this approach works when multiple PFASs and co-contaminants are present in IDW. Attainment of answers to these questions will provide insights into active treatment of PFAS-contaminated IDW.

Therefore, the objective this study is to develop a technique which can be used to effectively degrade PFASs under specific conditions in a wastewater facility. Chitosan- or ALA modified-montmorillonite increases the sorption capacity of PFOS, an important type of PFASs, and potentially enhances the degradation potential, while not using or generating any toxic compounds. To maximize the efficiency IAA was selected as the indole compound, a 254 nm UV monochromatic source was used, and the montmorillonite was modified using ALA and chitosan as scaffold materials. Sorption isotherms of PFOA and PFOS onto organo-clay nano-composites

were determined. The rate and extent of PFOS degradation and defluorination were determined, along with identification of daughter products of PFOS degradation.

Materials and Methods

Chemicals. All chemicals used were of laboratory grade or higher and procured from Fisher Scientific unless specified elsewhere. Hexadecyltrimethylammonium (HDTMA) bromide, PFOA and PFOS were all purchased from Sigma-Aldrich. No additional purifications or modifications were made to any chemicals purchased.

Synthesis of Organoclay Nano-composites

Montmorillonite SWy-3 was procured from the Source Clays Repository of the Clay Minerals Society (West Lafayette, IN). SWy-3 is sourced from Crook County, Wyoming, USA. Bulk SWy-3 was ground and soaked overnight in 0.5 mM NaCl solution, which was followed by centrifugation to collect the 0.02–0.5 μm size fraction. Chloride was removed by repeated washing and its complete removal was confirmed with an AgNO_3 test.

The chitosan-montmorillonite nanocomposite was synthesized in accordance with the methodology described by Singh et al. (2017). In short, a stock solution of chitosan (60 gL^{-1}) was made in 2% v/v acetic acid. Chitosan to clay ratio of 3:1 was mixed overnight, washed and lyophilized. The 12-aminolauric acid (ALA) -montmorillonite suspension was prepared according to a previous method (Zeng et al., 2016). A protonated ALA solution was made by dissolving it in a diluted HCl (0.07 N) solution at 80 °C under vigorous stirring conditions until the ALA was fully dissolved. The ALA-montmorillonite nano-composite was synthesized by adding the ALA solution to the clay suspension followed by vigorous stirring at 80 °C. After 30 minutes the solid was collected via centrifugation and washed with 80 °C 18.2 Mohm•cm ultrapure water three times to remove any residual aqueous ALA. The solid was then air-dried. The HDTMA-montmorillonite complex was prepared in accordance with the methodology described by Boyd et al. (1988). In short, 50 g of the 0.02-0.5 μm SWy-3 was suspended in an aqueous solution containing 38.5 mmol HDTMA bromide to equal the cation exchange capacity of the clay. The HDTMA-montmorillonite was then washed and lyophilized.

Analysis of Organoclay Nano-composites

Powder X-ray Diffraction (XRD) and Brunauer–Emmett–Teller (BET) analyses were performed on each of the four clays: SWy-3, HDTMA-modified SWy-3, chitosan-modified SWy-3, and ALA-modified SWy-3. Smear mounts were prepared on glass slides. XRD patterns were collected on a Scintag X1 X-ray powder diffractometer with CuK α radiation and a fixed slit scintillation detector at 1400 W (40 kV, 35 mA). Samples were scanned from 2 to 32 degree 2-theta. BET analysis was collected using a Micromeritics TriStar II Surface Area and Porosity Analyzer. Samples were degassed prior to analysis, and nitrogen gas was used for adsorption.

Batch Sorption Experiments of IAA, F⁻ PFOA, and PFOS.

Batch equilibrium experiments were carried out to determine the sorption of IAA, F⁻, PFOA, and PFOS to SWy-3 clay and organoclay nanocomposites. All glassware, metal, or reusable plastic containers were washed in isopropanol and methanol to prevent cross contamination. For each experiment 22 mg of clay or organo-clay nanocomposites were suspended in 10 mL water. The initial concentration of IAA ranged from 0.05 mM to 2.25 mM. Fluoride time-course sorption experiments were performed at a concentration of 1 ppm, due to the lack of adsorption no other concentrations were examined. The concentration range for PFOA and PFOS was from 0 to 2.2 mM. Samples were shaken at 150 rpm in the dark to avoid light degradation, and then centrifuged at 6000 g for 10 minutes. Preliminary experiments and previous research (Tian et al., 2015) demonstrated that equilibrium was reached within 8 hours and thus all batch sorption experiments were carried out overnight. All sorption experiments were carried out in duplicate.

IAA, F⁻, PFOA, and PFOS Analyses

IAA was analyzed spectrophotometrically using a method modified after Tang and Bonner (1948) using a Thermofisher Genesys 10vis (Waltham, MA). Reagent one has a final concentration of 12 g of FeCl₃ L⁻¹ in 7.9 M H₂SO₄. One milliliter of this reagent was added to 1 mL sample and incubated in the dark at room temperature for 20 minutes. The samples were analyzed at 540 nm wavelength. F concentration was analyzed using the SPADNS colorimetric method, which is based on the reaction between fluoride and a zirconium-dye lake (Marier and Rose, 1966). Fluoride reacts with the dye lake, dissociating a portion of it into a colorless complex anion ZrF₆²⁻; and the dye. As the amount of fluoride increases, the color produced becomes progressively lighter.

PFOA and PFOS during sorption experiments were determined using an HPLC system (Waters Alliance 2695, Milford, MA) with a 4.6 × 250 mm Waters X-Bridge Shield C18 column and a Waters conductivity detector. The mobile phase consisted of 40% acetonitrile and 60% 0.02 M ammonium acetate at a flow rate of 1 mLmin⁻¹ (Tian et al., 2016).

Experimental Setup of PFOS degradation

The degradation experiments of PFOS were conducted in a photochemical reactor (model XPA-7, Xujiang Electromechanical Inc., Nanjing, China) equipped with an internal quartz photoreactor (height = 400 mm; internal diameter = 40 mm). In each of the degradation experiments the concentration of PFOS, IAA, and the organoclay nanocomposite was 10 mg L⁻¹, 1 mM and 2.2 g L⁻¹, respectively in 18.2 Mohm•cm water. The UV source was a low-pressure mercury lamp (Philips; 254 nm, 36 W) which was fully immersed into the reaction solution. Previous measurements of this reaction cell using a radiometer (CEL-NP2000-10, Ceaulight Inc., Beijing, China) reported the light intensity at the surface of the sheath as 4.5 mW cm⁻² (Tian et al., 2016). The reaction vessel was cooled using a recirculating water bath, and the pH was adjusted to circumneutral using 1 N HCl or NaOH as appropriate. Samples were taken at predetermined time intervals without disturbing the light apparatus.

To determine the effects of competing anions and complex mixtures of PFASs in natural groundwater on PFOS degradation (Cheng et al., 2010; Schaefer et al., 2019), these experiments were repeated in the presence of 1 mM sodium bicarbonate or sodium nitrate. Degradation experiments were also performed in natural groundwater (procured from CDM Smith, Seattle, see Table 1 for initial water chemistry). In this experiment, 10 ppm PFOS was spiked into the groundwater in the presence of 1 mM IAA, and 2 gL⁻¹ of ALA-modified clay. The pH of the groundwater remained at ~6.5 throughout the experimental duration.

Table 1. Real impacted groundwater chemistry prior to experimentation.

pH	TOC (mg/L)	PFBA (ng/L)	PFBS (ng/L)	PFHpA (ng/L)	PFHxA (ng/L)	PFHxS (ng/L)	PFOA (ng/L)	PFOS (ng/L)	PFPeA (ng/L)	Chloride (mM)	Sulfate (mM)	Nitrate (mM)
7.9	0.574	4.66	3.38	2.98	3.96	1.14	8.56	3.7	4.63	3.1	0.11	0.15

Analysis of PFOS degradation products

Samples were analyzed via LC/MS/MS under conditions similar to those previously reported (Higgins et al., 2005) at the Center for Environmental Risk Assessment (Colorado School of Mines). Chromatography was performed using an aqueous ammonium acetate (2 mM) and methanol gradient. Samples and standards were injected into a C18 column. The percent methanol was increased from initial 5% to 60% in 0.75 min, ramped to 100% by 10 min, held at 100% for 1.5 min, and reverted to 5% at 12.5 min. A triple quadrupole mass spectrometer operating in negative electrospray ionization multiple reaction monitoring (MRM) mode was employed for sample analysis. To maintain adequate peak resolution without loss of sensitivity, each sample was injected twice, with data collected for the perfluorocarboxylates (PFCAs) and the perfluoroalkyl sulfonyl-based chemicals (PFASs) separately.

Results

Characterization of organo-clay nanocomposites

The surface area and d-spacing of montmorillonite SWy-3 greatly increased due to the intercalation of the different organic compounds (Table 2), with chitosan increasing surface area and d spacing the most, by a factor of 9 and 1.5 respectively. HDTMA increased the surface area and d spacing the least, by only a factor of 5 and 1.2, respectively. ALA's enhancements were between these two compounds.

Table 2. Physical Characteristics of the Organo-clay nanocomposites.

Sample (Swy-3 Intercalation)	BET Surface Area (m ² g ⁻¹)	Interlayer Spacing (Å)
No Intercalated Material	2.44	12.6
HDTMA	10.14	14.7
Chitosan	22.89	18.3
12-Aminolauric Acid	21.57	16.1

Batch Sorption Experiments

Two types of sorption experiments were carried out. Time course experiments were first carried out to determine the amount of time required to reach equilibrium. These preliminary experiments (Figure 2) demonstrated that sorption reached equilibrium within 24 hr and in many cases much shorter.

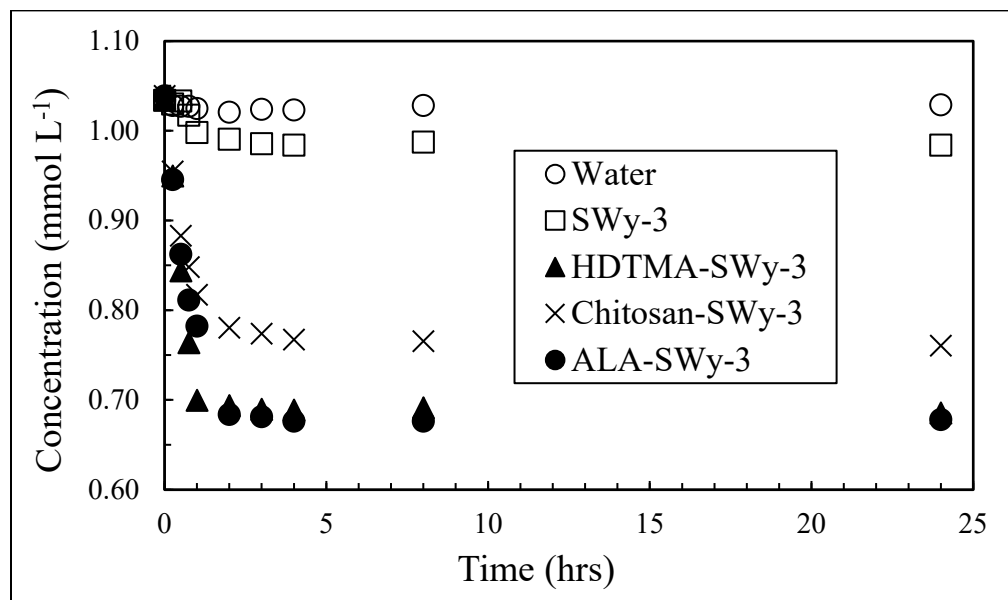


Figure 2. Time course sorption of IAA in the dark. Sorption of IAA to all four materials ceases beyond the four-hour mark. Concentrations started at approximately 1 mM and decreased over time, all clay concentrations were 2.2 g/L. Error bars from duplicate experiments are smaller than the symbol sizes shown.

Similar time course sorption curves were observed for PFOA and PFOS (Figure 3), while the fluoride showed little to no sorption over the same time interval (Figure 4).

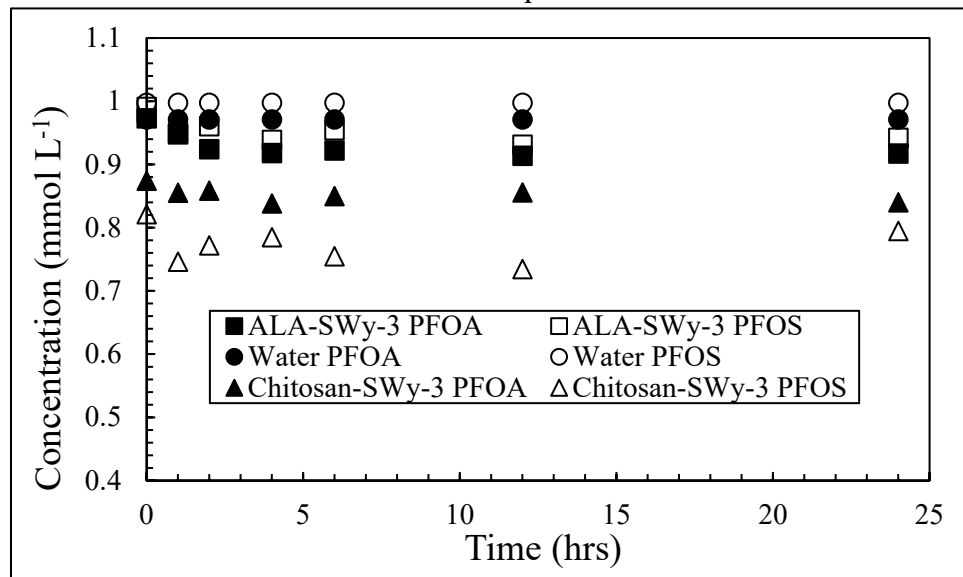


Figure 3. Time course sorption of PFOS/A in the dark. Sorption of PFOS to all organoclay nanocomposites ceases beyond the four-hour mark. Concentrations started at 1 mM and decreased over time; all clay concentrations were 2.2 gL⁻¹. Error bars from duplicate experiments are smaller than the symbols shown.

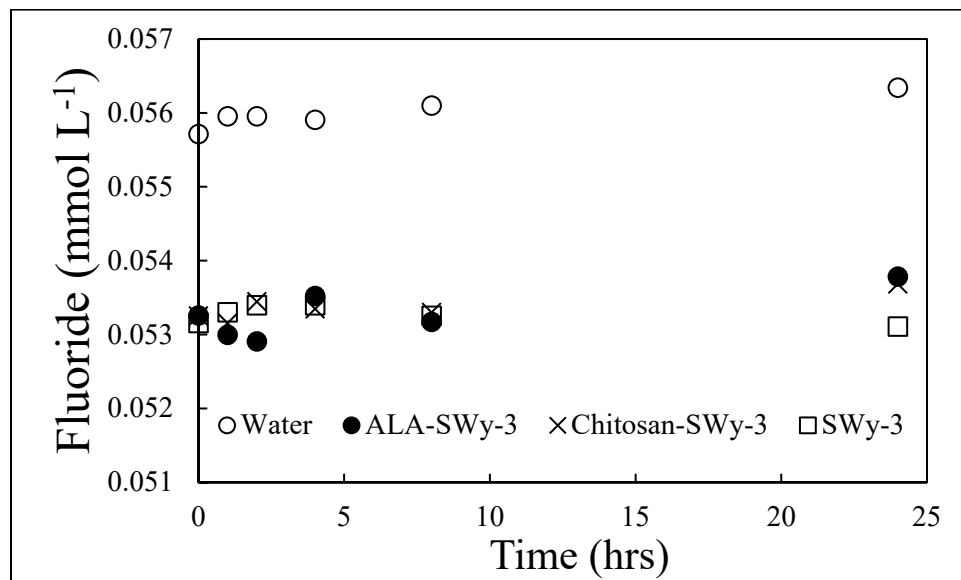


Figure 4. Time course sorption of fluoride in the dark. Little to no sorption is observed. Concentrations started at 1 ppm and remained stable. All clay concentrations were 2.2 gL⁻¹. Error bars from duplicate experiments are smaller than the symbols shown.

Sorption isotherms of IAA to unmodified montmorillonite, HDTMA-montmorillonite, Chitosan-montmorillonite, and ALA-montmorillonite were conducted. All the isotherms were described using the Langmuir isotherm equation ($R^2 \geq 0.68$). The sorption of IAA by all organoclay nanocomposite clays were much greater than that to the unmodified clay (Table 3 and Figure 5). As shown in Table 3, the maximum sorption capacity ($C_{\max}$) of IAA on unmodified montmorillonite, HDTMA-montmorillonite, Chitosan-montmorillonite, and ALA-montmorillonite is 6, 140.0, 266.0, and 168.0 mmol kg⁻¹, respectively. The Langmuir constant, K_L , is a measure of the affinity for sorption and follows the same trend showing that chitosan has a very high affinity for IAA.

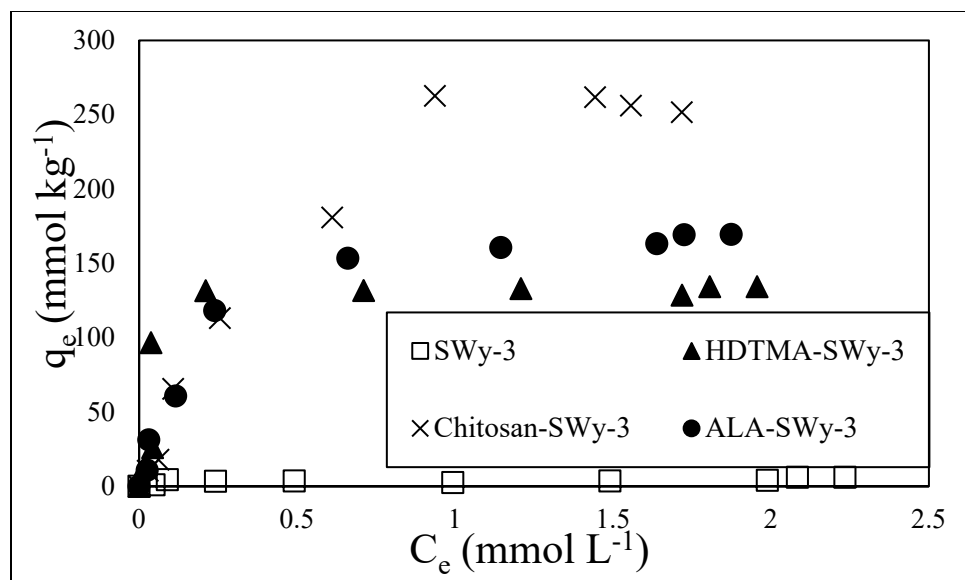


Figure 5. Sorption isotherm of IAA. q_e is the amount of IAA sorbed to various clay minerals, and equilibrium C_e is the equilibrium concentration of IAA. Error bars from duplicate experiments are smaller than symbols shown.

Table 3. Langmuir Isotherm Parameters of IAA

Clay	K_L (L mmol ⁻¹)	C_{max} (mmol Kg ⁻¹)	R^2
Unmodified	4.9	6.0	0.6876
HDTMA	208.3	140.0	0.8183
Chitosan	909.1	266.0	0.9681
ALA	230	168.0	0.8034

The adsorption of PFOA to chitosan-modified clay is shown on Figure 6. It shows very little sorption at low concentrations but with a large spike at an equilibrium concentration (C_e) of around 2 mmolL⁻¹. This large spike is not indicative of Langmuir or any other common type of adsorption. This type of adsorption behavior is likely due to micelle or semi-micelle formation (Noskov, 2002).

The sorption of both PFOA and PFOS to ALA-modified clay are shown in Figures 7 and 8. The maximum sorption capacity of PFOA to ALA-modified clay is just over 100 mmolkg⁻¹, but its sorption to unmodified clay is only 20 mmolkg⁻¹. Likewise, the maximum sorption of PFOS to the same organoclay nanocomposite is much higher, reaching as high as 1400 mmolkg⁻¹, compared to only 10 mmolkg⁻¹ to unmodified clay, suggesting that the intercalated ALA served as an effective adsorbent.

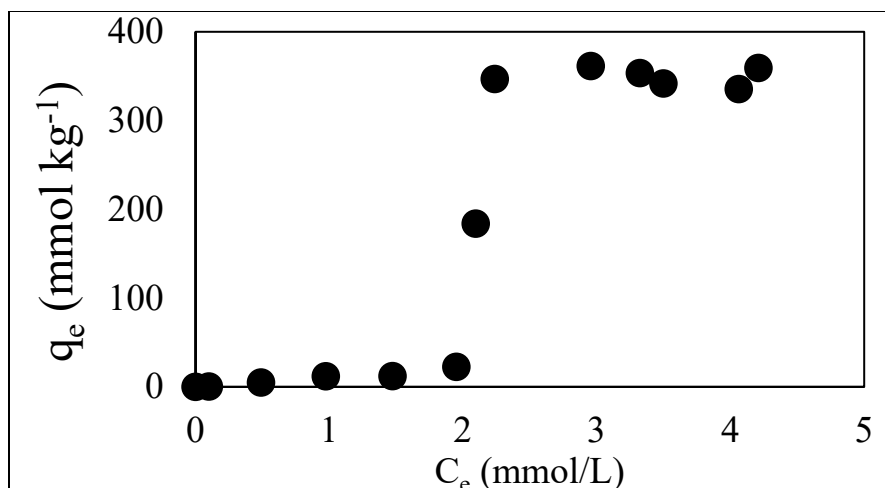


Figure 6. Sorption isotherm of PFOA. q_e is the amount of PFOA sorbed to chitosan-modified clay, and C_e is the equilibrium concentration of PFOA in solution. Error bars from duplicate experiments are smaller than symbols shown. The sorption does not fit a typical Langmuir isotherm.

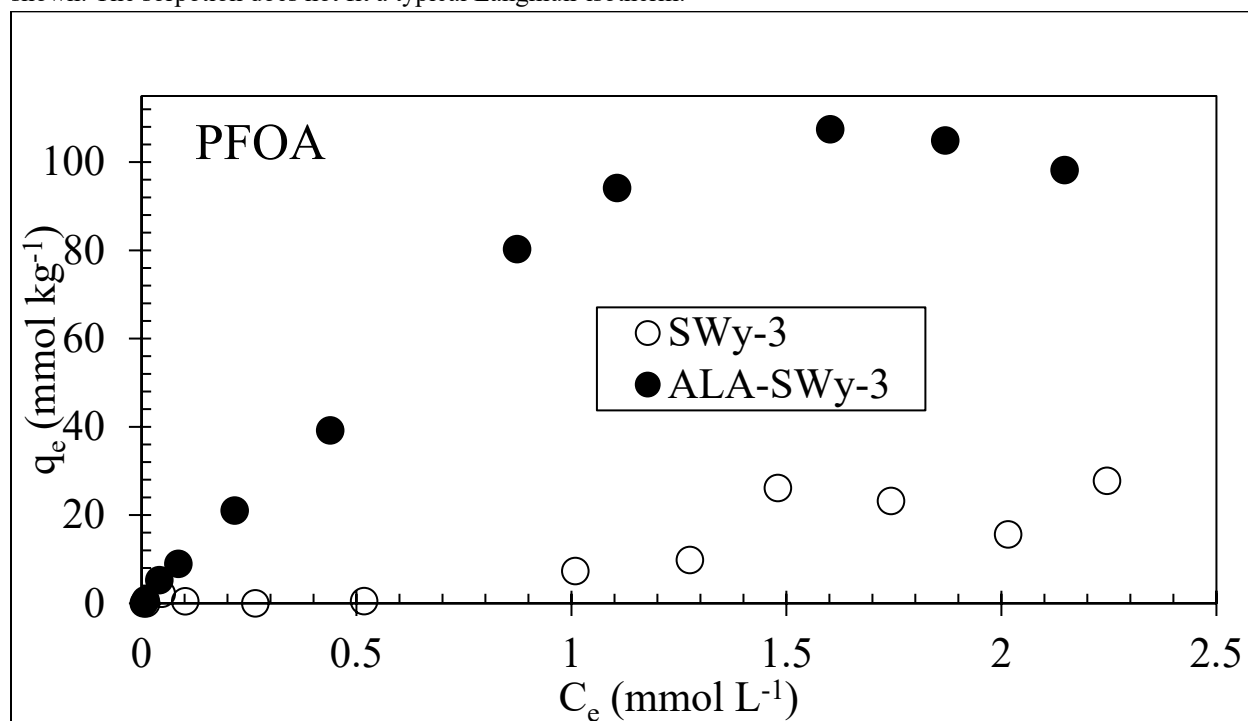


Figure 7. Sorption isotherm of PFOA. q_e is the amount of PFOA sorbed to ALA-modified clay, and C_e is the equilibrium concentration of PFOA in solution. Error bars from duplicate experiments are smaller than the symbols shown.

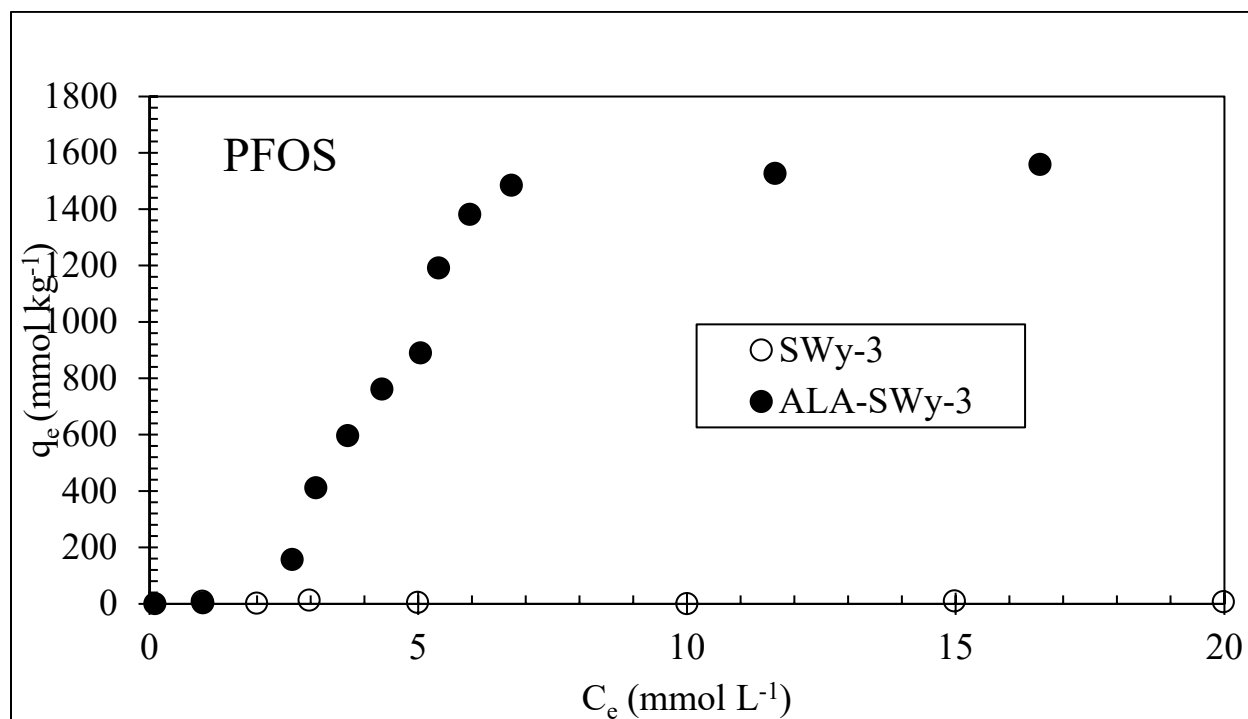


Figure 8. Sorption isotherm of PFOS to SWy-3 and ALA-SWy-3. q_e is the amount of PFOS sorbed to clay, and C_e is the equilibrium concentration of PFOS. Error bars from duplicate experiments are smaller than the symbols shown.

Degradation of PFOS

The degradation experiments focused on the degradation of the more persistent compound PFOS. Because of the ease of determining fluoride concentration with a spectrophotometric method, PFOS degradation was first monitored by determining fluoride generation, along with various controls (Figure 9). Without UV radiation, <0.5% fluoride was generated in any combinations of IAA, SWy-3, ALA, and chitosan (data not shown). However, in the presence of UV radiation, various amounts of fluoride were generated. PFOS itself was stable in water and defluorination was not observed. In the presence of IAA and SWy-3 alone or in combination, little fluoride generation (approximately 5%) was observed. However, much higher percentages of defluorination were observed in ALA- and chitosan-modified SWy-3 experiments, reaching 41% and 62% by ALA-SWy-3 and chitosan-SWy-3, respectively.

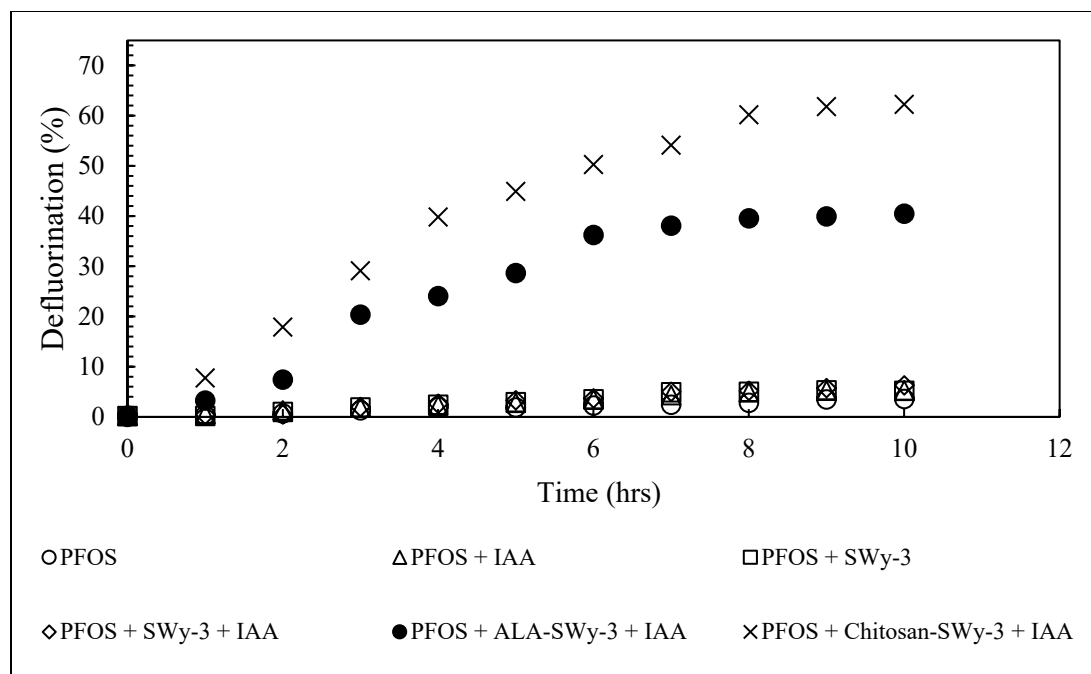


Figure 9. Generation of fluoride after exposure of PFOS to UV radiation at 254 nm. Chitosan-SWy-3 is the most efficient in fluoride generation, ALA-SWy-3 is the second, with unmodified clay showing a negligible amount of fluoride generation. Limited amounts of fluoride (<5%) were generated from PFOS with UV only, in the presence of IAA and SWy-3 alone, or in their combination. All PFOS starting concentrations were 10 ppm, all IAA concentrations were 1mM, and all clay concentrations were 2.2 gL⁻¹.

Because ALA-SWy-3 showed a normal Langmuir sorption behavior and was much easier to synthesize than chitosan-SWy-3. In addition, ALA is reliable, and nontoxic (Baldrick, 2010; Liu et al., 2013). For these reasons, the extent of PFOS defluorination was determined using ALA-SWy-3 only, in the presence of competing anions (bicarbonate and nitrate), and natural groundwater (Figure 10). As expected, the presence of these competing anions decreased both the initial rate and final extents of the defluorination reaction, nitrate appeared to have a greater inhibitory effect than bicarbonate. The presence of the natural groundwater did not affect the rate and extent of defluorination. In addition, the effect of PFOS concentration was also examined, and within the range of 1-10 ppm, the amount of fluoride generation was proportional to the initial PFOS concentration, but the percent of defluorination was independent of initial PFOS concentration (data not shown).

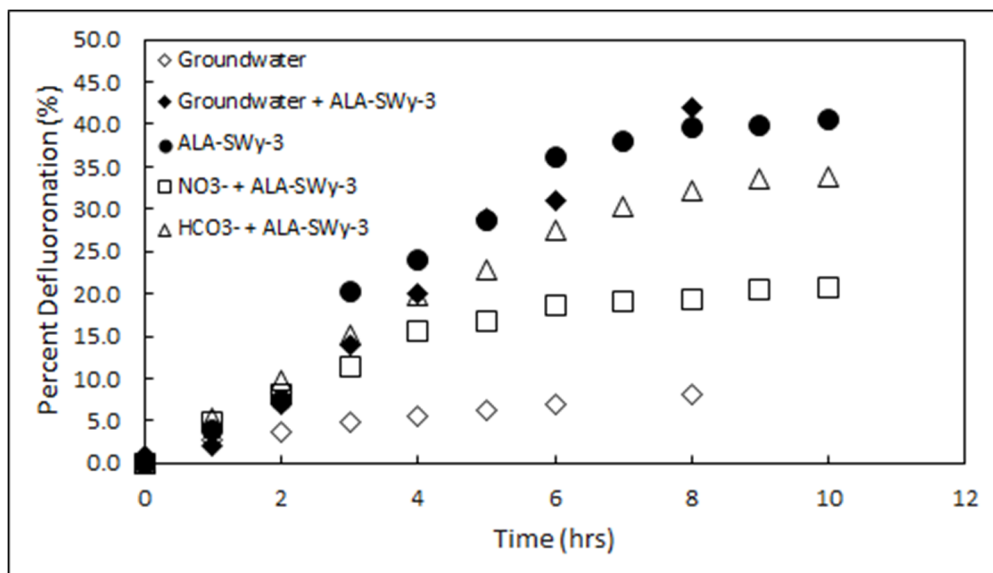


Figure 10. Time-course PFOS defluorination in various treatments. The presence of competing anions decreases both the rate and extent of defluorination. Groundwater slightly inhibits the initial rate of defluorination.

MS-LC analysis was able to quantify PFOS and its daughter products. PFOS exists as both a linear and branched molecule. Interestingly, nearly all branched PFOS were degraded in both pure water and bicarbonate solution within two hours of UV irradiation, but it took much longer to degrade linear PFOS (Figure 11). By the end of 10 hours, over 90% of the linear and nearly 100% of the branched PFOS were degraded, even in the presence of bicarbonate, a competing anion. However, relative to water only, the presence of bicarbonate slightly inhibits the degradation rate of both linear and branched PFOS (Figure 11).

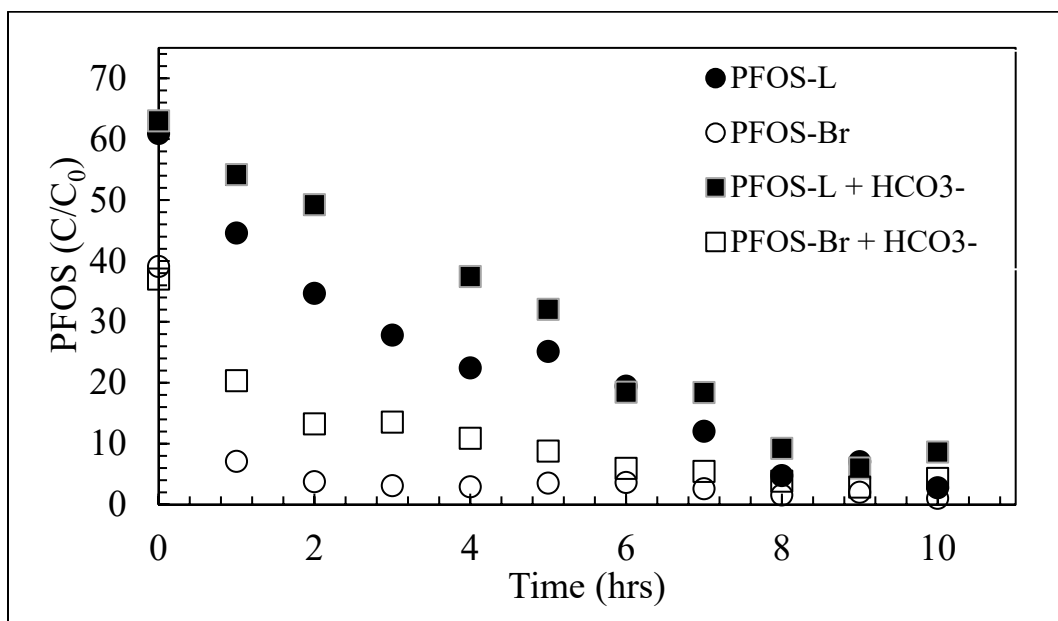


Figure 11. Degradation over time of PFOS in water with and without bicarbonate co-contaminant. Data have been separated into linear and branched isomers of PFOS. The three-hour time point for linear PFOS with bicarbonate has

been removed as the concentration was anomalously high. All PFOS starting concentrations were 10 ppm, IAA concentration was 1mM, and ALA-modified clay concentration was 2.2 gL⁻¹. Sodium bicarbonate was added at a concentration of 1mM.

The concentrations of different breakdown products over time are shown in Figure 12 and 13. The three most prevalent degradation products, C₈H₂O₃SF₁₆, C₈H₃O₃SF₁₅, and C₈H₄O₃SF₁₄, accumulated over time. There was not significant difference in the types and relative amounts of these degradation products in the presence of bicarbonate, other than some inhibitory effect of PFOS degradation.

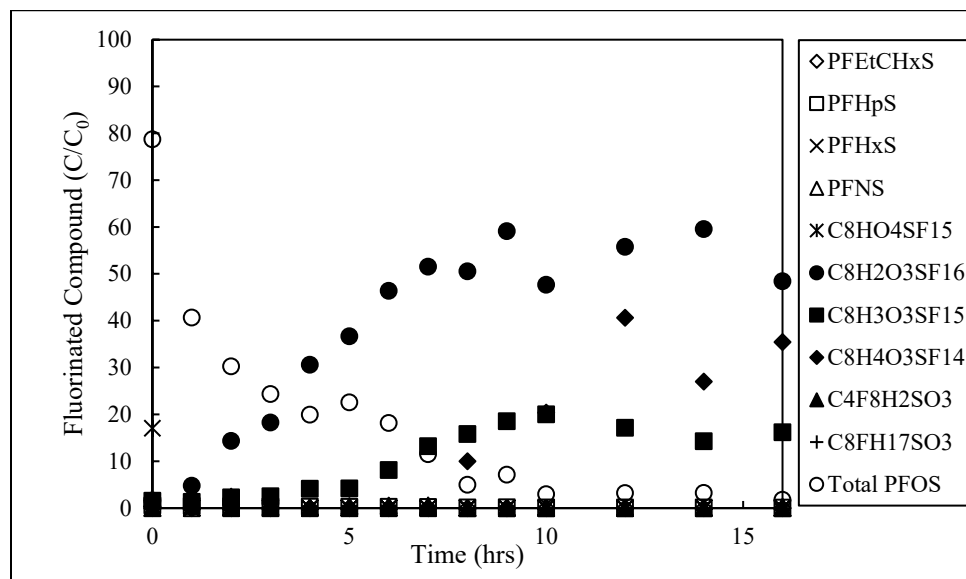


Figure 12. Degradation of PFOS and production of intermediate products over time in a solution of 10 ppm PFOS, 1 mM IAA, and 2.2 gL⁻¹ ALA-modified SWy-3. Concentrations (C) are shown as percentages of the starting PFOS concentration, C₀.

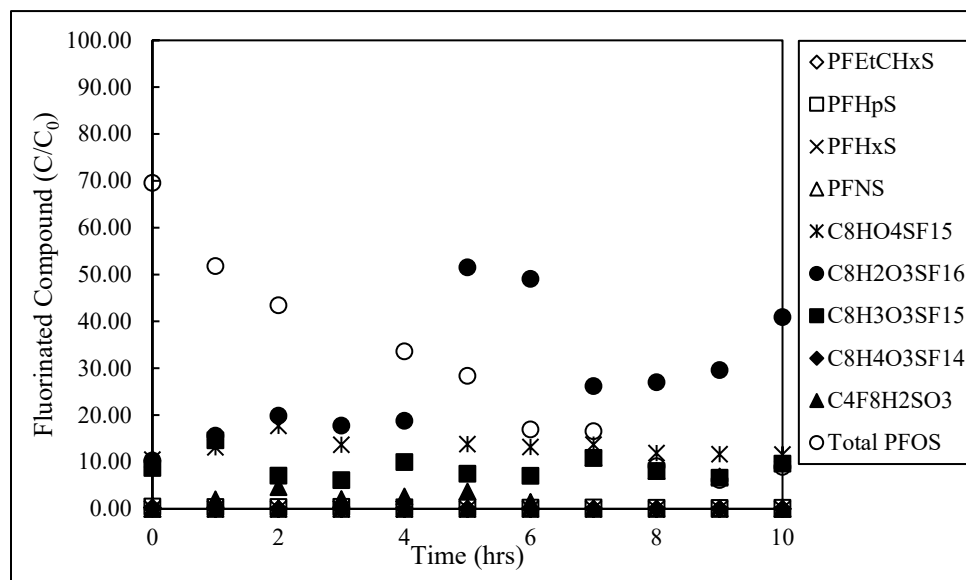


Figure 13. Degradation of PFOS and production of intermediate products over time in a solution of 10 ppm PFOS, 1mM IAA, and 2.2 gL⁻¹ ALA-modified SWy-3 in the presence of 1 mM bicarbonate. Concentrations (C) are shown as percentages of the starting PFOS concentration, C₀.

Discussion

The batch sorption experiments data show that chitosan modified montmorillonite SWy-3 was capable of adsorbing a considerable higher amount of IAA than unmodified, HDTMA-modified, and ALA-modified montmorillonites, likely due to increased surface area of the clay and the number of sorption sites (Solin, 1997). Previous research suggests that the proposed reaction of PFOA with hydrated electrons takes place primarily in the interlayer region (Boyd et al., 1988; Qu et al., 2010; Tian et al., 2016; Tian et al., 2015), which would suggest that the expansion of the interlayer region would yield increased efficiency of the reaction.

Relative to HDTMA both chitosan and ALA have several advantages. First, both compounds are environmentally friendly. HDTMA is toxic and is often used as an antibacterial agent (Boyd et al., 1988), and has also been reported to be antimicrobial even when intercalated (Malachová et al., 2009; Mondal et al., 2014). Second, both chitosan and ALA have considerable sorption capacity for PFOS and possibly other PFASs, as reflected in Figures 5-7, orders of magnitude higher than PFAS sorption to soils (Milinovic et al., 2015) and mineral surfaces (Johnson et al., 2007; Wang et al., 2012; Wang and Shih, 2011; Zhao et al., 2014). This level of sorption is on the scale of custom resins which, based on the affinity and pH of solution, have the amount of sorption ranging anywhere from 1000 to 5000 mmolkg⁻¹ of substrate (Deng et al., 2010; Yu et al., 2009; Zaggia et al., 2016). However, many of these systems require optimization of pH to ranges outside that of circumneutral, meaning that further remediation would be required before the water could be sent into the waste stream (Zhang et al., 2019).

Finally, there is minimal interference from competing anion bicarbonate, which is in contrast to PFOS degradation by hydrated electrons without clay scaffold (Gu et al., 2017). Organomodified montmorillonite forms a framework, and IAA and PFOS (and other PFASs) sorb to either chitosan and ALA. This decreases the overall path that the hydrated electrons must travel and prevents competing anions from interfering with the degradation process. This is reflected in the defluorination in the presence of bicarbonate anion and natural groundwater sample (Figure 10). While the reaction did not initially proceed as quickly in the natural groundwater the extent of defluorination was nearly the same as in deionized water. However, the presence of nitrate inhibited both the rate and extent of PFOS defluorination. The reasons for such inhibition could include competitive sorption such that less PFOS sorbs to ALA in the presence of nitrate. Additional work is required to explore the exact reasons for such inhibitory effect. While 1 mM nitrate is far above the action limit set by the USEPA (Ward et al., 2018) the bicarbonate is not yet at the action limit. These results suggest that although natural groundwaters may contain various combinations of anions, total organic carbon, and other compounds, they are unlikely to significantly interfere with the PFOS degradation reaction.

PFAS decay and defluorination are controlled by both the head group and also the length of the fluoroalkyl chain (Cui et al., 2020). This photoreductive pathway for PFOS degradation is a sequential defluorination which has been demonstrated in previous work using hydrated electrons and matches with the accumulation of 15 and 16 fluorine intermediates presented herein (Bentel et al., 2019; Gu et al., 2017a; Tian et al., 2016). The reductive power of the hydrated electrons breaks the C-F bonds, which results in the generation and accumulation of fluoride. This method has demonstrated the ability to degrade considerable concentrations of PFOS, both branched and linear, within a few hours of its application and cause the generation of a considerable amount of fluoride.

There is also a measurable amount of $C_4F_8H_2SO_3$ which indicates that there is also a breaking of the C-C bond in some of the PFOS molecules, similar to biodegradation of PFOS (Huang and Jaffé, 2019), however there were no short chain fluoroalkyl compounds detected throughout the degradation, suggesting that either there were short chained fluoroalkyl compounds adsorbed onto the clay composite, which were not measured by LC-MS, or once the carbon backbone of the PFOS is broken the remaining small chain fluoroalkyls are rapidly degraded leaving the remaining sulfonic head in solution.

While many of the degradation daughter products were detected via LC/MS and the fluoride was detected via spectrometry, there were most likely small chain or novel compounds which were generated but not identified. Several impurities in the stock PFOS were also identified and they were also destroyed via this method. The $PF_{Et}CH_xS$ and $PFNS$ were completely removed from the solution while the concentration of $PF_{Hp}S$ was reduced by 50%, but the $PF_{Hx}S$ was not affected. These minor impurities (less than 50 ppb) within the PFOS stock solution suggest that this method would be viable against other recalcitrant PFASs, not just PFOS. The degradation of these compounds could account for a small amount of the generated fluoride. However, it is difficult to determine which degradation products are generated in a complex solution as multiple pathways exist for a single compound as shown in the recent study (Bentel et al., 2019). The pathways described in Bentel et al., (2019) show that there were still unknown products when hydrated electrons were applied to PFOS degradation and that several sulfated PFASs, such as $PFBS$ and $PFPrS$ were highly recalcitrant even in the presence of hydrated electrons.

This method effectively removed ~95% of PFOS in solution using the ALA modified clay and a 36W UV bulb. While the chitosan modified clay may have proven to be more effective the time required to manufacture the chitosan clay is significantly larger than that of the ALA clay. Chitosan is not soluble in water and requires the addition of acetic acid to solubilize the polymer, this adds extra steps to the synthesis as well as additional ingredients. A single batch of the chitosan modified clay required upwards of 10 man-hours while the ALA modified clay required as little as 4. This would generate considerable cost savings, even if the efficiency is slightly lower than

that of the chitosan modification. Additionally, this method degraded the PFOS over a period of eight hours. Over a period of eight hours a 36-watt bulb uses approximately 0.3 kWh of electricity. Over the same 8 hours, approximately 6500 ppb of PFOS was degraded, which means that per kilowatt hour 7 mg of PFOS was degraded. According to the US Energy Information Administration the average cost of a kilowatt hour is \$0.1319 meaning that for each dollar of energy input, up to 50 mg of PFOS could potentially be degraded.

Unfortunately, there is not a complete defluorination as expected, which suggests that this method is not yet optimized as other similar methods have reported complete defluorination following similar methods (Bentel et al., 2019; Song et al., 2013; Tian et al., 2016). One possible limiting factor may be the amount of IAA. As the sole source of hydrated electrons, its amount is certainly important to ensure adequate supply of hydrated electrons. However, because its limited solubility at neutral pH, it may not be sufficient. One way to get around this limitation is to add IAA dropwise over the course of the degradation experiment. Another possibility will be to dissolve more IAA in alkaline solution to increase its solubility. Another limiting factor may be time-course desorption of ALA from the clay interlayer, in which case, continuous addition of ALA-clay may improve the defluorination efficiency. Future work will focus on optimization of this method for more complete defluorination of PFOS and other possible PFASs.

Conclusions to Date

This method reports a unique green chemistry approach that achieves degradation of the PFOS compound over the course of several hours, with similar results for PFOA. The photogenerated hydrated electrons, which are generated via 3-indole-acetic-acid hosted by an organomodified clay scaffold induced the defluorination of the co-sorbed PFCs by utilizing the reductive power of the hydrated electrons. The near complete degradation of PFOS occurred within the first few hours of irradiation, costing less than a dollar worth of electrical power. The use of the ALA and chitosan modified montmorillonites promoted the degradation process by stabilizing the reaction during photolysis, which prolonged the half-life of the hydrated electrons. This green chemistry approach provides the framework for the reductive remediation of PFCs using an easily made, robust, organomodified clay which does not require the application or use of hazardous chemicals either in the clay composite or as the source of the hydrated electrons.

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