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# Synthesis and Characterization of Organically Modified Hectorites for Sequestration of PFAAs from Contaminated Drinking Water

Alexandra Pagano

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Thesis Title: Synthesis + characterization of organically modified halotones for segmentation

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The Synthesis and Characterization of Organically Modified Hectorites for  
Sequestration of PFAAs from Contaminated Water

By

Alexandra Pagano

\*\*\*\*\*

Submitted in partial fulfillment of the requirements for  
Honors in the Department of Chemistry

UNION COLLEGE

June, 2018

## ABSTRACT

PAGANO, ALEXANDRA The Synthesis and Characterization of Organically Modified Hectorites for Sequestration of PFAAs from Contaminated Water.

Department of Chemistry, June 2018

ADVISOR: Laura A. MacManus-Spencer

Perfluoroalkyl Acids (PFAAs), a family of industrial chemicals, are found in household products such as pizza boxes, microwave popcorn bags, and non-stick pans. PFAAs of different carbon chain lengths and ionic head groups exist, such as PFOA (perfluorooctanoic acid) and PFOS (perfluorooctane sulfonic acid). Used without regulation in industry for decades, PFAAs only recently became recognized as contaminants of emerging concern, since they are bioaccumulative in organisms, persistent in the environment, and toxic. PFAAs are known to accumulate in the blood, liver and kidneys, and drinking water contaminated with PFAAs has been linked to certain types of cancer. Therefore, it is highly desirable and necessary that drinking water in PFAA contaminated areas be effectively filtered. Previous research has focused on testing granulated activated charcoal and ion exchange resins on water contaminated with only certain PFAAs. Recently, a montmorillonite material was modified with a specialized surfactant and was demonstrated to selectively adsorb PFOA and PFOS in the presence of other organic contaminants in water. The aim of this work is to expand upon the previous research using hectorite clay and more commonplace and inexpensive surfactants to target PFAAs of all chain lengths and ionic head group type. The modified hectorite materials are synthesized by a simple, aqueous method using various cationic quaternary ammonium salts of different size. These materials are then exposed to different environmentally-relevant concentrations of PFAAs in water, and the resultant aqueous PFAA concentrations are quantified via liquid chromatography-tandem mass spectrometry. Multiple modified Hectorite materials have been synthesized and characterized via infrared spectroscopy and X-ray powder diffraction. Preliminary evidence has shown that hectorite modified with dodecyltrimethyl ammonium bromide is successful at adsorbing PFOA from water. Ongoing work is focused on more extensive testing of this and other modified hectorite materials with other PFAAs, mixtures of PFAAs and real contaminated drinking water samples.

## **Acknowledgements**

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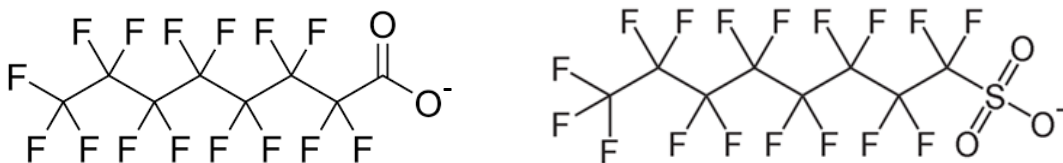
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## Introduction

Perfluoroalkyl acids (PFAAs) are a class of industrial chemicals that have recently been classified as environmental contaminants of emerging concern. Since PFAAs exhibit unique physical properties which render them ideal surfactants, such as water and oil repellency, they can be found in over 200 industrial and commercial products such as non-stick cookware, waterproof fabrics, leather, upholstery, carpets, paints, adhesives, waxes, polishes, aviation hydraulic fluids, popcorn bags, and pizza boxes.<sup>1-5</sup> Major contributors of PFAAs to the environment are aqueous film forming foam (AFFF), which is used to fight large chemical or fuel fires, and the production of Teflon coatings, namely for non-stick pans.<sup>3-5</sup> PFAAs were first synthesized in 1947.<sup>5</sup> However, until recently, the monitoring of PFAAs in the environment was completely neglected. This is a source of concern, since PFAAs have been shown to be persistent in the environment, bioaccumulate in organisms and exhibit toxicity that is attributed to a variety of adverse health effects, including certain cancers.<sup>3-8</sup> PFAAs exist with varying carbon chain lengths (the structures of two eight-chain PFAAs are shown in Figure 1), and chain length has an effect on the properties of the particular PFAA.<sup>6</sup> Due to recent environmental and toxicological concerns, companies that use PFAAs in manufacturing, such as DuPont and the 3M company, have phased out the use of longer chain PFAAs (seven or more fluorinated carbons) for shorter chain (six or fewer fluorinated carbons).<sup>6</sup> Considering the presence of PFAAs in the environment, and the threat they pose to human health, it would be beneficial to develop a filter to remove PFAAs from drinking water.

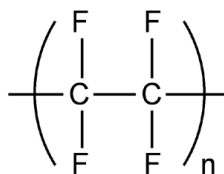




**Figure 1.** Structure of perfluorooctanoic acid (PFOA) (left), and perfluorooctane sulfonic acid (PFOS) (right).

### *PFAA Regulation*

Historically, the two eight carbon-chain PFAAs, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) have been most widely used as emulsifying agents in the production of polytetrafluoroethylene (teflon) (structure is shown in Figure 2) as well as other fluoropolymers, due to their similar carbon-fluorine chain structure. The production



**Figure 2.** Repeated structure of polytetrafluoroethylene or "teflon".

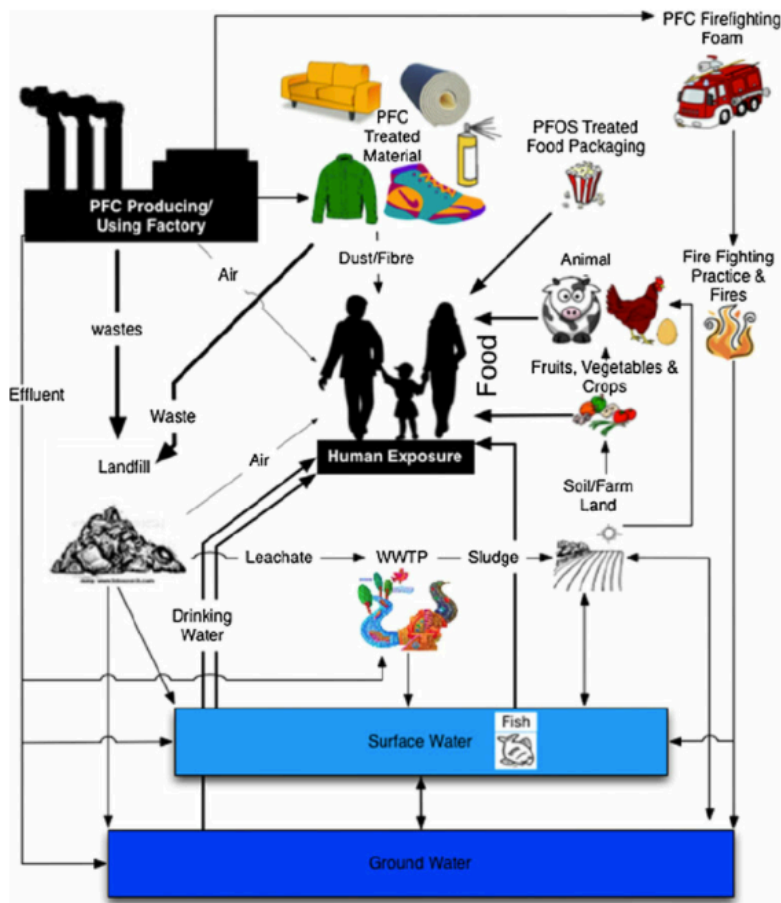
and use of PFOS and PFOA for the year 2000 was estimated at 3500 and 500 metric tons, respectively.<sup>4</sup> Due to increasingly apparent toxicological concerns, the major PFOS manufacturer, 3M, phased out its production in 2002, thus PFOS production dropped to 175 metric tons by 2003. As a result, global PFOA production increased to 1200 metric tons per year by 2004, and presumably became the most common PFAA used industry.<sup>4,9</sup> The Federal government became involved in 2006, when eight major PFOA manufacturers pledged to reduce product contents and industrial facility emissions by 95% by 2010 under the EPA PFOA Stewardship program.<sup>10</sup> However, shorter carbon-chain PFAAs have been developed

to fill the void, and published findings suggest these chemicals still pose a significant threat to human health.<sup>9</sup>

### *Toxicity of PFAAs*

Currently, perfluorinated compounds (PFCs), including PFAAs, have been ubiquitously found in diverse environments globally including rivers, lakes, food products and air particles, on parts per billion (ppb) to parts per trillion (ppt) levels.<sup>11</sup> After over 50 years of manufacture, the global distribution of these PFCs is largely due to the extreme resistance to chemical (C-F bond dissociation is between 100-130 kcal/mol) and biological decomposition and high water solubility.<sup>11</sup> PFAAs bioaccumulate in the environment and tend to accumulate in the blood, liver and kidneys, opposed to adipose tissue, and human exposure occurs mainly through contaminated drinking water.<sup>8</sup> It has been shown that PFOS emitted in air from fluoropolymer manufacturing sites becomes deposited in surface soils and eventually migrates and precipitates into underlying groundwater aquifers; other PFC exposure pathways are outlined in Figure 3.<sup>12</sup>

PFAA exposure has been linked to changes in membrane function, peroxisome proliferation, as well as thyroid, testicular, and liver cancer, and thyroid disease, and in addition, PFOA has displayed endocrine disruptive activity.<sup>13-17</sup> Due to increasing public health concerns over contaminated drinking water, especially in areas close to manufacturing plants, in May 2016, the EPA set a lifetime health advisory limit for PFOA in drinking water at 70 ppt.<sup>18</sup>



**Figure 3.** Possible routes of PFCs into the environment and pathways to humans.<sup>37</sup>

### *Methods of PFAA Remediation*

PFASs (perfluoroalkyl substances) are not substantially removed during drinking water treatment plant processes, which include coagulation, flocculation, biofiltration, sedimentation, oxidation, UV irradiation, and low pressure membranes.<sup>19</sup> Therefore, more specifically targeted filtration methods are necessary. Due to the increased stability of PFAAs, conventional degradation and oxidation methods are insufficient. Some systems specifically designed for PFAA water remediation include degradation via photocatalysts,<sup>20,21</sup> sonochemical decomposition,<sup>22</sup> oxidation via periodate<sup>23</sup> or persulfate,<sup>24</sup> reduction with zero-valent iron,<sup>25</sup> iodide ion,<sup>26</sup> and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>,<sup>27</sup> electrochemical deposition via boron-doped

diamond electrode,<sup>28</sup> and photolysis in a specific reactor system.<sup>29</sup> Inherent weaknesses associated with these strategies include high energy consumption, expensive and specialized materials, harsh reaction conditions, and complicated operation, which deem these methods unfit for large-scale use.<sup>30</sup> When selecting a superior PFAA remediation system, cost, efficiency, energy-use, and simplicity of use must be considered. Taking this into account, adsorption is considered both a superior and effective technique for PFAA remediation from water.<sup>30</sup>

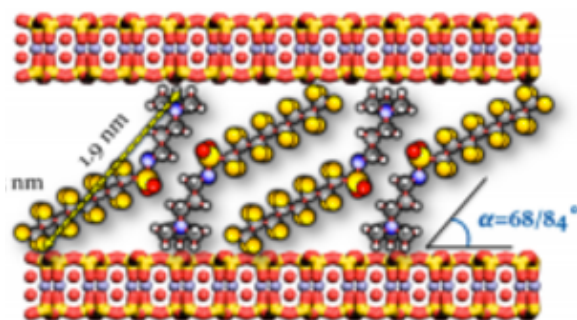
### *Adsorption Materials*

Filter materials such as granulated activated carbon (GAC), ion exchange resins, and clays have been used to filter PFAAs from water. Additionally, recently Zhou et al. showed that a silica-  $\text{Fe}_3\text{O}_4$  magnetic nanocomposite could successfully adsorb multiple chain length PFAAs from water.<sup>30</sup> GAC has shown successful adsorption of PFOA and PFOS, it is highly cost-effective and widely used.<sup>31</sup> However, a decreased removal efficiency was observed with increased loading and decreased C-F chain length of PFAA with GAC<sup>32</sup>, and additionally PFAAs cannot be regenerated from spent GAC, leaving PFAA-contaminated waste to be disposed of.<sup>31</sup> Compared to GAC, some ionic exchange resins display higher PFOA removal capabilities, and unlike GAC the resins can be reused and the resulting PFAAs can be recycled.<sup>33</sup> Ionic exchange resins are expensive and therefore not widely used. Testing with PFAAs of different chain lengths for either filter material is yet to be done; however, there is an example of a system that has worked for multiple carbon chain length PFAAs,<sup>27</sup> but it is not yet widely used. There exists a need for a filter material that is cost-effective, can be reused, and is successful at adsorbing multiple chain-length PFAAs.

Recently, a filter material system has been designed to more specifically adsorb PFAAs made from cheap and readily available, naturally occurring Montmorillonite clay.

### *Modified Clay Materials*

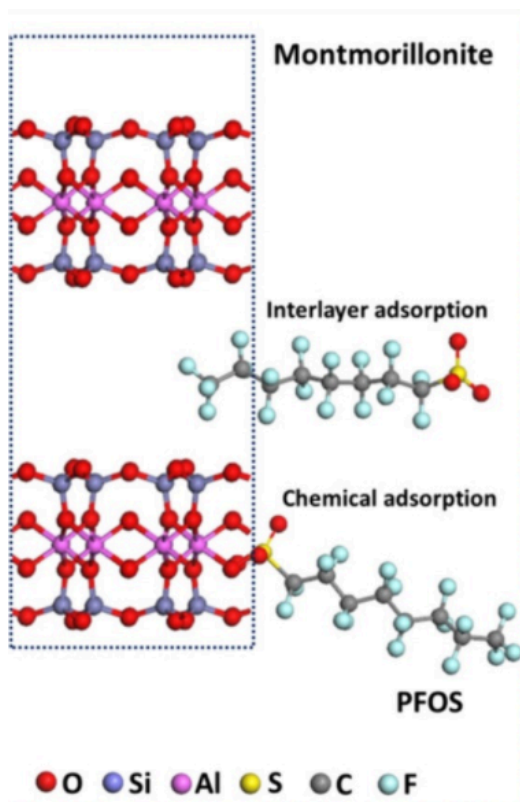
A modified clay material has been proven to selectively remove two different eight carbon chain PFAAs, perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA), (the deprotonated forms of perfluorinated carboxylic and sulfonic acid, shown in Figure 1) from water.<sup>34</sup> Specifically, an anionic clay material called montmorillonite was modified with a specialized fluorinated surfactant (Figure 4), which allowed the material to sequester PFAAs from water.<sup>34</sup> The amount of loaded perfluorinated surfactant was shown to affect the



**Figure 4.** Montmorillonite with loaded perfluorinated surfactant adopting paraffin structure.

clay structure and the ability of the material to bind to PFOA and PFOS.<sup>34</sup> The functionality of the clay is also affected by the extent of cationic exchange.<sup>9</sup> As shown in Figure 5, there are multiple ways PFAAs can bind to a layered smectite clay, interlayer adsorption, and chemical adsorption.<sup>35</sup> By loading a cationic surfactant into the anionic clay, the positive charge density in the clay is increased and the clay is able to bind more easily to anionic PFAAs in solution, and additionally, the surfactant size and length can affect the interlayer size.<sup>34</sup> A specific clay has an inherent cation exchange capacity (CEC) which dictates the

maximum amount of cation that can physically be exchanged. In this work a similar clay, Hectorite, was modified with common and widely available cationic surfactants of various chain lengths and shapes, and the removal ability of Hectorite and tetrabutylammonium bromide (HECT/TBAB) was tested on water spiked with known concentrations of PFOA.



**Figure 5.** Two different adsorption mechanisms of PFOS on montmorillonite clay.

## Materials and Methods:

### *A. Materials*

Tetrabutylammonium bromide (TBAB), cetyldimethylethylammonium bromide (CDMEAB), and hexyltrimethylammonium bromide (HTMAB) were purchased from Sigma Aldrich Chemical Co. Tetraethylhexylammonium bromide (TEHAB) and perfluorooctanoic acid (PFOA; 96%) were purchased from Acros Organics (Morris Plains, NJ). Polypropylene centrifuge tubes (50 mL) were obtained from Corning Incorporated (Corning, NY). Methanol (Optima UHPLC/LC-MS grade, 0.1- micron filtered), water (Optima UHPLC/LC-MS grade, 0.1-micron filtered), ammonium acetate (Optima HPLC) and 200 mesh <75  $\mu\text{m}$  sieves were obtained from Fisher Scientific (Fair Lawn, NJ). HPLC 2-mL clear autosampler vials with marking panel were obtained from Kinesis Incorporated (West Berlin, NJ). Blue screw caps (9-mm) for the autosampler vials were obtained from Agilent Technologies (Santa Clara, CA). A C<sub>18</sub> Targa Sprite column (40 x 2.1 mm x 5  $\mu\text{m}$ ) was obtained from Higgins Analytical (Mountain View, CA). Mass-labeled (<sup>13</sup>C<sub>4</sub>) PFOA internal standard (50  $\mu\text{g/mL}$ ) was obtained from Wellington Laboratories, Inc. (Ontario, Canada).

### *B. Methods*

#### *i. OMS Synthesis*

Cationic surfactants were loaded individually to 700 mg of hectorite at five times the CEC (72 mmol/mg) and vigorously mixed for six hours at 120°C. The mixtures were centrifuged at 10,000 rpm at 5°C with a Beckman Coulter Allegra X-22R centrifuge for one hour until minimal bromide was detected and then dried at 120°C. Resultant dried OMSs were sieved in a 200 mesh (< 75  $\mu\text{m}$ ) sieve.

### *ii. Characterization*

Infrared (IR) spectra of OMS samples were obtained on a Thermo Scientific Nicolet iS5 Infrared Spectrometer equipped with iD7 Attenuated Total Reflectance using 128 scans at 4 cm<sup>-1</sup> resolution. Powder X-Ray Diffraction (XRD) Spectra were taken from 2.0- 40.0° at 0.12 deg/min with 1.54 Å incident monochromatic X-Ray source on a Phillips PW-1840 Powder X-Ray Spectrometer. D-spacing values were calculated using Bragg's Law:  $n\lambda = 2d\sin\theta$  with  $n=1$  and  $\lambda= 1.54$  Å. To approximate surfactant lengths, surfactants were modeled using WebMo. Samples were imaged with a Ziess EVO50 Scanning electron microscope (SEM) at magnifications of 2, 10, 20, and 100 µm.

### *iii. PFOA Exposure*

Samples of 20 mg Hectorite OMS and unmodified Hectorite were exposed separately to 15-mL solutions of 10, 100 and 1000 nM PFOA in HPLC grade water and shook for 48 hours in 50-mL polypropylene centrifuge tubes at 170 rpm. The same volume of the same PFOA solutions were added to 50-mL polypropylene centrifuge tubes, which were also shaken to serve as controls. All samples were centrifuged for 10 minutes at 10,000 rpm. The resulting supernatant was analyzed via an Agilent 1200 series High Performance Liquid Chromatograph 6410 Triple Quad Liquid Chromatograph/ Mass Spectrometer (LC/MS).

### *iv. LCMS Analysis*

To prepare LCMS samples, 100 µL of supernatant and 100 µL of a 70:30 solution of HPLC grade methanol and 0.01% ammonium hydroxide were pipetted into autosampler vials. A calibration curve was generated with PFOA standard solutions or (a mixture of equimolar PFOA, PFOS, PFBA, PFHxa, PFNA, PFPnA) in a linear concentration range of 0.8 - 25,000 nM which were prepared by nested dilutions of a solution of known



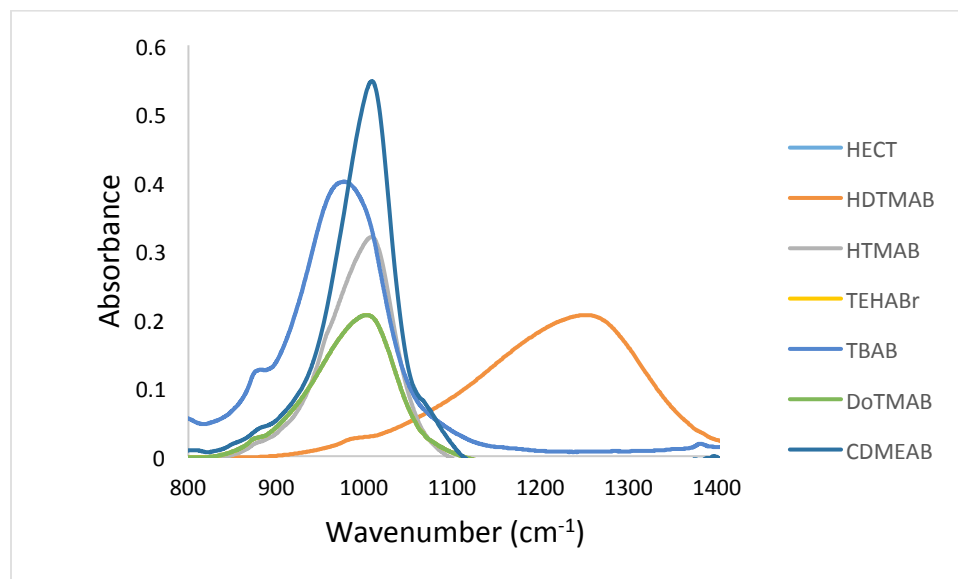
concentration of PFOA or the PFAA mixture in 70:30 HPLC grade methanol and 0.01% ammonium hydroxide. To autosampler vials, 100  $\mu\text{L}$  of standard solution was pipetted and diluted with 100  $\mu\text{L}$  of HPLC grade water. A 50- $\mu\text{L}$  aliquot of 250-nM mass-labeled ( $^{13}\text{C}_4$ ) PFOA internal standard in LCMS grade water was added to all autosampler vials (or equimolar 250 nM  $^{13}\text{C}_4$  PFOA, PFOS and PFBA), which resulted in a final volume of 250  $\mu\text{L}$  in each vial, and a final internal standard concentration of 50 nM. A 40  $\mu\text{L}$  injection volume and isocratic flow rate of 0.5 mL/min with 60% 2-mM ammonium acetate in methanol and 40% 2-mM ammonium acetate in water solvent program was used. Concentrations of PFOA in the supernatant were analyzed via an Agilent 1200 series High Performance Liquid Chromatograph 6410 Triple Quad Liquid Chromatograph/ Mass Spectrometer (LC/MS) (Fragmentor voltage set at 90 V, MS operated in scan mode (100-1000 m/z) with  $\text{N}_2$  pressure at 60 psi, flow rate of 12 L/min and temperature of 350°C) and compared to the concentrations of PFOA in control samples in order to calculate percent removal.

## Results

### A. Characterization

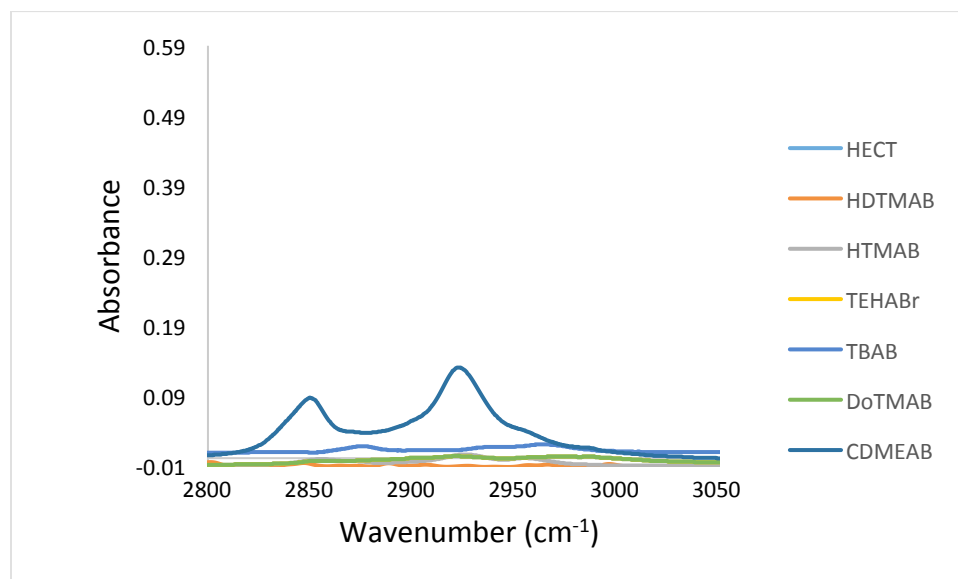
Once Hectorites were modified, “OMS’s” were characterized using IR and powder-XRD to determine if the synthesis was “clean.” The IR spectra of the surfactant, Hectorite, and each OMS were overlaid and compared. The IR spectra were used to qualitatively determine that surfactant was present in the OMS. Powder-XRD spectra were mainly used to calculate the increase in d-spacing value.

i. IR Spectra



**Figure 6.** Overlaid FT-IR spectra of all OMS's from 800-1400  $\text{cm}^{-1}$ .

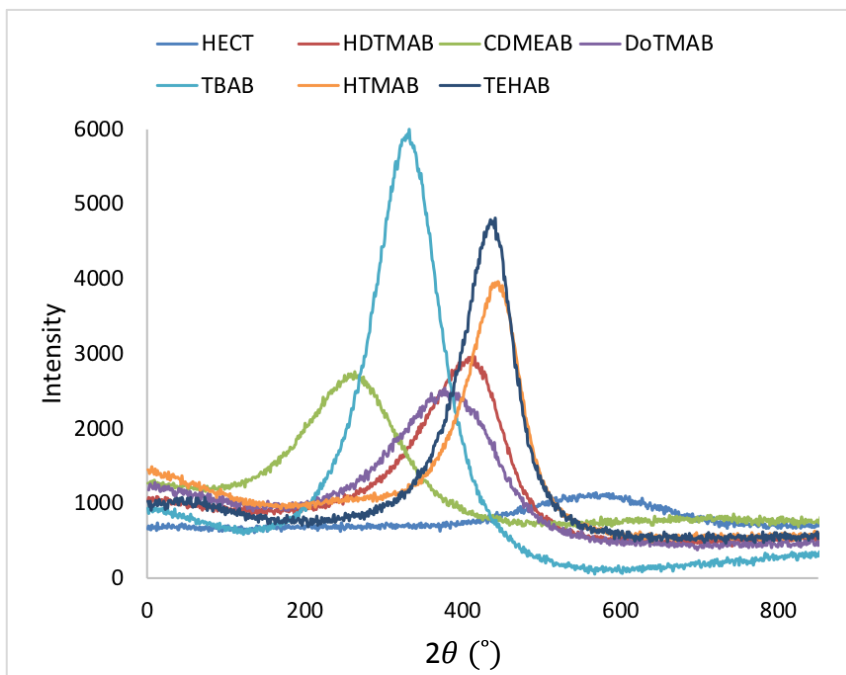
The IR spectra from 800-1400  $\text{cm}^{-1}$  shown in Figure 6, represents the Si-O stretching mode. The peaks present for five OMS's, excluding TEHABr and including Hectorite indicates that Si-O bonds are present in the OMSs, as expected.



**Figure 7.** Overlaid FT-IR Spectra of all OMS's from 2800 to 3050  $\text{cm}^{-1}$ .

The FT-IR spectra shown in Figure 7 show two C-H stretching modes. There is little to no absorbance for the two C-H stretching modes located between 2800 and 3500  $\text{cm}^{-1}$  for all OMS's. However, there are two low-intensity peaks present in the TBAB OMS.

ii. Powder-XRD Spectra



**Figure 8:** Overlaid XRD spectra of all OMS's from 0-800 °.

The XRD spectra of the OMS's (shown in Figure 8) with increased surfactant chain-length, listed here in-order (HTMAB, TEHAB, TBAB, DoTMAB, CDMEAB, and HDTMAB) show that the 001 peak ( $\sim 200$ - $400^\circ$ ) increased in intensity compared to the Hectorite 001 peak (around  $600^\circ$ ) for each OMS. The  $2\theta$  values of these 001 OMS peaks was used to calculate the d-spacing with Bragg's Law.

### iii. D-Spacing Calculations

**Table 1.** The effect of varied surfactant size on OMS d-spacing.

Surfactant	Chain Length	d-spacing (Å)	Length (Å)	Head Group Size (Å)
<b>HTMAB</b>	6	13.6	7.51	3.71
<b>TEHAB</b>	6	13.8	16.84	8.99
<b>TBAB</b>	4	16.7	11.81	5.93
<b>DoTMAB</b>	12	14.9	16.34	3.71
<b>CDMEAB</b>	16	18.9	21.45	5.07
<b>HDTMAB</b>	16	19.1	21.36	3.71

Table 1 shows that generally, with increased surfactant chain length, d-spacing increases as a result. The lengths estimated with WebMo do not exactly correlate with surfactant “chain length” since there are multiple possible configurations that the surfactants can take when they assemble in the inner-spacing of the clay. Computer modeling of the possible configurations the surfactants could take within the clay is far too complicated to attempt and lengths from WebMo are very rough estimates.

### B. Exposure Results

**Table 2.** Percent removal ability of TBAB OMS at 10, 100 and 1000 nM [PFOA].

[PFOA] (nM)	1000	100	10
<b>Average Blank (nM)</b>	751.1	81.1	6.8
<b>Average OMS (nM)</b>	656.7	55.2	3.1
<b>Removal</b>	12 %	31 %	54 %

The preliminary results from TBAB OMS exposure with 10, 100 and 1000 nM [PFOA] (summarized in table 2) show that percent removal decreases with increased concentration of [PFOA]. Removal ability is only about 50% at 10 nM (54%) and is negligible at 100 and 1000 nM [PFOA] (12 and 31%). It should be noted that blank concentrations are consistently around two times as concentrated as they should be, in vial

concentrations should be 400, 40, and 4 nM for 1000, 100 and 10 blank samples, respectively.

**Table 3:** Percent removal ability of DoTMAB OMS at 10, 100 and 1000 nM [PFOA].

<b>[PFOA] (nM)</b>	<b>1000</b>	<b>100</b>	<b>10</b>
<b>Average Blank (nM)</b>	454.8	38.7	3.6
<b>Average OMS (nM)</b>	31.9	18.9	2.3
<b>Removal</b>	92 %	53 %	26 %

The preliminary results from DoTMAB exposure with PFOA shown in Table 3 indicate that percent removal ability increases with increased [PFOA]. Blank [PFOA] concentrations were consistent with what was expected.

**Table 4.** Percent Removal abilities of various Hectorite OMSs at 100 nm [PFOA] only.

<b>Hectorite OMS</b>	<b>Average [PFOA] (nM)</b>	<b>Removal</b>
<b>Blank</b>	381.3	N/A
<b>Hectorite</b>	417.3	-9.4 % *
<b>CDMEAB</b>	8.2	98 %
<b>TBAB</b>	289.1	24 %
<b>TEHAB</b>	387.9	-1.7 % *
<b>HDTAB</b>	92.2	76 %
<b>HTAB</b>	267.1	30 %
<b>DoTMAB</b>	25.6	93 %

\*Negative percent removals result from slightly higher average detected [PFOA] in sample compared to the average. It is not meaningful or probable that exposing the stock solution of known PFOA concentration to the clay could result in a greater PFOA concentration.

Table 4 shows preliminary exposure results for all synthesized OMSs exposed to 100 nM PFOA in triplicate. The blank samples gave concentrations close to the expected in-vial concentration of 400 nM [PFOA], and average concentrations for samples below ~400 nM

indicate some removal of PFOA. Three OMSs showed removal abilities above 50%, CDMEAB (98%), HDTAB (76%), and DoTMAB (93%). All others gave percent removal values below 50%.

## **Discussion**

Six Hectorite OMS's were synthesized and characterized via FT-IR and Powder XRD Spectroscopy. Preliminary exposure data for two OMS's (DoTMAB and TBAB) with PFOA at 10, 100, 1000 nM were obtained. Preliminary exposure data was also found for a DoTMAB OMS exposure with equimolar solutions of 6 PFAAs at 10, 100 and 1000 nM. Lastly, each OMS was exposed to 100 nM PFOA in triplicate to test general adsorption capabilities for further work.

The preliminary data for the Hectorite TBAB exposure show consistently lower percent adsorption for Hectorite compared to the same surfactant with Montmorillonite.<sup>37</sup> It is important to note that the blank concentrations for the TBAB OMS exposure, listed in Table 2, were all about two times the target concentration. The concentrations of PFOA were 751.1, 81.1, and 6.8 nM compared to target concentrations of 400, 40 and 4 nM. The most probable explanation for this is in-vial evaporation before LCMS analysis, since if some solvent evaporated in the LCMS vials, then the PFOA concentration would increase. It is important that the concentrations of the control samples are reliable in order to obtain accurate results. Therefore, the TBAB OMS exposure with PFOA must be repeated in until consistent results are achieved.

For the TBAB OMS, preliminary data from the Montmorillonite OMS<sup>37</sup> showed greater adsorption ability for PFOA than the Hectorite OMS (shown in Table 2). It is possible

that Hectorite shows lower PFOA adsorption capabilities since it has a larger microcrystalline size and a more rigid structure. This can be explained using previous work by Hagerman et al.<sup>38</sup> In this work, it was demonstrated that  $[\text{Ru}(\text{bpy})_3]^{2+}$  guest species within Hectorite host are influenced by the environment of the inner space of the clay host and  $[\text{Ru}(\text{bpy})_3]^{2+}$  served as photoprobe of clay microcrystalline structure. The luminescence of the photo probe with a clay of smaller microcrystalline structure, laponite, was compared with that of the much larger clay, Hectorite. Hectorite was found to contain a more rigid inner spacing or “microenvironment”. It was concluded that solvent interaction with  $[\text{Ru}(\text{bpy})_3]^{2+}$  inside the Hectorite microenvironment is more limited due to the rigid hectorite structure. Therefore, access to the surfactant in the inner-spacing of Hectorite might be limited for the PFAAs compared to smaller clays such as Monmorillonite. This could explain lower absorption capacities for Hectorite compared to smectites of smaller microcrystalline size.<sup>37</sup>

The preliminarily DoTMAB OMS PFOA exposure results shown in Table 3 demonstrate that with increased concentration, percent removal increased; the percent removal values were 26, 53, and 92% for exposure concentrations of 10, 100 and 1000 nM [PFOA], respectively. A possible explanation for this could be a co-adsorption mechanism. As was illustrated in Figure 5 and previously discussed (page 10), the adsorbent could attach to the clay in more than one way. The main mode which has been discussed is “interlayer adsorption”. However, the adsorbent can chemically adsorb to the side of the clay microcrystal. It is possible, that if multiple PFOA molecules chemically attach in this way, that more PFOA will be attracted to the PFOA already adsorbed to the outsides of the Hectorite microcrystal. Therefore, as was previously discussed, it is possible that the large

and rigid nature of Hectorite limits the interlayer adsorption of PFOA, increasing the chemical adsorption at increased exposed PFOA concentration. This phenomenon would lead to increased percent removal of PFOA at larger exposure concentrations. It must be noted that the Hectorite TBAB OMS exposure results (Table 2) show the opposite effect, percent removal decreased with increased PFOA exposure concentration. These results were preliminary and must be repeated and investigated further before any conclusion is made.

The preliminary PFOA exposure test with each OMS (CDMEAB, TBAB, TEHAB, HDTAB, HTAB and DoTMAB) at 100 nM [PFOA] only, (the data is listed in Table 4) showed which OMS's have the most promising removal capacities for PFOA. The two larger (12 and 16-carbon) chain surfactants performed the best (DoTMAB and CDMEAB) with removal capacities close to 100%. The other 16-carbon chain surfactant, HTAB also showed a large removal capacity. Based on this evidence it is possible that for Hectorite, OMSs made with larger surfactants could work better to adsorb PFOA, perhaps due to increased d-spacing and thus increased area for PFOA adsorption compared to the shorter surfactants.

Other adsorption materials have been tested previously for PFOA and PFOS. Even though only preliminary data was obtained for Hectorite OMSs, and adsorption capacities were not yet obtained, it is possible to loosely compare the adsorption capacities of other materials for future consideration. The adsorption capacities of other materials are shown in Table 4.



**Table 4.** Comparison of other PFOA/PFOS adsorption on various adsorption materials

Adsorbent	Adsorbate	Adsorption Capacity (mg/L)	Reference
Powdered activated carbons	PFOA	200-300	39
Granulated activated carbons	PFOA	15-250	39
Anion-exchange resins	PFOA	20-400	39
Montmorillonite	PFOS	50-500	40
HDTMAB-Mt OMS	PFOS	50-500	40

Table 4 shows that, on average, powdered activated carbons show the greatest adsorption capacity for PFOA. However, a Zhou et al. showed that cation-exchanged HDTMAB-Montmorillonite can be capable of a higher adsorption capacity than powdered or granulated activated carbons.<sup>40</sup>

## Conclusions

Modified smectite clays, including montmorillonites modified with specialized fluorinated surfactants,<sup>34</sup> common surfactants,<sup>37</sup> along with the modified hectorites reported in this work show promising adsorption capabilities for PFOA and PFOS.<sup>39</sup> These modified smectite clays have the potential to eventually replace GAC as the superior point-of-use remediation method for PFAS-contaminated drinking water. In this work, six Hectorite OMS's were synthesized and confirmed clean via FT-IR and Powder-XRD spectroscopy. Anticipated Hectorite d-spacing increase as a result of increased surfactant size was confirmed with Powder-XRD spectra of six Hectorite OMS's made with different quaternary ammonium salt surfactants. Hectorite TBAB OMS showed decreased PFOA removal capability compared to DoTMAB OMS, and the TBAB OMS showed decreased removal ability with increased PFOA exposure concentration and DoTMAB displayed the opposite effect. Larger carbon chain-length surfactants (CDMEAB, DoTMAB, and HDTAB) outperformed shorter chain surfactants (TEHAB, TBAB and HTAB) when exposed to 100 nM PFOA, showing that for Hectorite and PFOA, larger surfactants may work better.

## Future Work

There is an appreciable amount of work to be done in order to completely assess the PFAA adsorption capabilities and future applications of organically modified Hectorites. First, the PFOA exposures with both TBAB OMS and DoTMAB OMS need to be repeated until consistent results are achieved. Additionally, the test of all OMS's with 100 nM PFOA should be repeated. Once this is repeated it can serve as a guide to see which OMSs may work the best to see which should be further tested.

Once the adsorption abilities of promising OMS's are found, the next step would be to expose the OMSs to equimolar mixtures of different chain length PFAAs to simulate contaminated water that could contain more than just PFOA or PFOS. In the 2017 paper by Du et al., the adsorption capacity of multiple carbon-chain length PFAAs was tested on a modified montmorillonite containing only one 8 carbon chain length (fluorinated) surfactant.<sup>34</sup> The adsorption capacity increased with increasing PFAA chain length, in the order: PFBA<PFBS<PFHxA<PFHxS<PFOA<PFOS.<sup>34</sup> Since the modified montmorillonite showed the greatest adsorption ability for the C8 PFAAS, PFOA and PFOS, it is probable that a clay modified with 4 or 6 carbon chain length surfactants could work better for the smaller chain PFAAs. OMS's with surfactants of these of these sizes (TBAB (4C), TEHAB (6C) and HTMAB (6C)) were synthesized in this work. These OMS's could be exposed to solutions of single PFAAs of the same size as the surfactant to see if matching the surfactant size with the PFAA enhances adsorption. This does suggest that a single OMS can't achieve high adsorption for PFAAs of all sizes, however this opens the door to further investigate exposing PFAA mixtures to mixtures of different OMSs in the future.

There are other parameters that can be varied to enhance and optimize clay performance. The loaded surfactant amount must also be considered. For example, Du et al. found that surfactant loaded at about 1:1 molar ratio to the cation exchange capacity (CEC) of Montmorillonite resulted in the most adsorbed PFOA compared to lower surfactant loadings.<sup>34</sup> Also, since it is difficult to ensure to what extent loaded surfactant actually intercalated into the clay inner-gallery, thermogravimetric analysis was used and should be utilized in the future. For comparison purposes, in this work all OMS's were synthesized at 5x the CEC of Hectorite. This effect should be further researched for Hectorite to ensure that OMS materials are synthesized at the surfactant loading which is optimal for adsorption. As an ultimate goal of the project, using real contaminated well samples from Bennington, VT or Hoosick Falls, NY to expose OMS materials would be desirable to demonstrate the feasibility of these filter materials in a real-life setting.

If an OMS material is found which shows promising PFAS removal abilities, there are still many tests that need to be done to ensure that the materials can be used safely. For example, a common issue encountered with point-of-use water filters involves not knowing when the filter is spent and must be replaced. Tests must be done in order to see how many times the material can be recycled with little decrease in adsorption capacity. In the work done by Du et al., it was found that the modified Montmorillonite materials could be recycled five times when shaken with ethanol. It is probably unlikely that this could be done in practice, so other ways to recycle modified clay materials must be further assessed.

A next step to further assess OMS adsorption abilities is to analyze the adsorption kinetics by generating a sorption isotherm. This allows for better further comparison with other types of previously discussed adsorption materials. This is done by taking timed

samples during an exposure over a several hour period to determine the adsorbed PFAA amount over time. In Du et al., it was found that sorption equilibria of PFOA and PFOS on the modified Montmorillonite were around 21 hours, and that the initial sorption rates of PFOS and PFOA were 263.2 and 225.7  $\mu\text{mol/g/h}$ , respectively, which are much higher than reported values of activated carbon and anion-exchange resin (8.1  $\mu\text{mol/g/h}$  for PFOA and 6.2  $\mu\text{mol/g/h}$  for PFOS). It would also be advantageous to study the effect of PFAA exposure concentration on adsorption by varying concentration and measuring adsorption. It could be determined if there is an effect of increased PFAA concentration on adsorption as mentioned previously in the discussion.

## References

1. Olsen, G. W.; Burris, J. M.; Ehresman, D. J.; Froehlich, J. W.; Seacat, A. M.; Butenhoff, J. L.; Zobel, L. R. Half-life of serum elimination of perfluorooctanesulfonate, perfluorohexanesulfonate, and perfluorooctanoate in retired fluorochemical production workers. *Environ. Health Perspect.* **2007**, *115*, 1298.
2. Renner, R. Growing concern over perfluorinated chemicals. *Environ. Sci. Toxicol.* **2001**.
3. Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H. Sources, fate and transport of perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40*, 32-44.
4. Lau, C.; Anitole, K.; Hodes, C.; Lai, D.; Pfahles-Hutchens, A.; Seed, J. Perfluoroalkyl acids: a review of monitoring and toxicological findings. *Toxicol. Sci.* **2007**, *99*, 366-394.
5. Land, M.; de Wit, C. A.; Cousins, I. T.; Herzke, D.; Johansson, J.; Martin, J. W. What is the effect of phasing out long-chain per-and polyfluoroalkyl substances on the concentrations of perfluoroalkyl acids and their precursors in the environment? A systematic review protocol. *Environmental Evidence* **2015**, *4*, 3.
6. Calafat, A. M.; Kuklenyik, Z.; Reidy, J. A.; Caudill, S. P.; Tully, J. S.; Needham, L. L. Serum concentrations of 11 polyfluoroalkyl compounds in the US population: data from the National Health and Nutrition Examination Survey (NHANES) 1999– 2000. *Environ. Sci. Technol.* **2007**, *41*, 2237-2242.
7. Gao, Y.; Fu, J.; Cao, H.; Wang, Y.; Zhang, A.; Liang, Y.; Wang, T.; Zhao, C.; Jiang, G. Differential accumulation and elimination behavior of perfluoroalkyl acid isomers in occupational workers in a manufactory in China. *Environ. Sci. Technol.* **2015**, *49*, 6953-6962.

8. D'eon, J. C.; Mabury, S. A. Exploring indirect sources of human exposure to perfluoroalkyl carboxylates (PFCAs): evaluating uptake, elimination, and biotransformation of polyfluoroalkyl phosphate esters (PAPs) in the rat. *Environ. Health Perspect.* **2011**, *119*, 344.
9. Environmental and Health Assessment of Perfluorooctane Sulfonic Acid and its Salts; *3M Company*, Technical Report. **2003**.
10. U.S. Environmental Protection Agency (U.S. EPA) Announcement of Stewardship Program by Administrator Stephen L. Johnson.  
<http://www.epa.gov/opptintr/pfoa/pubs/pfoastewardship.htm>. (accessed November 7, 2017).
11. Post, G. B.; Louis, J. B.; Lippincott, R. L.; Procopio, N. A. Occurrence of perfluorinated compounds in raw water from New Jersey public drinking water systems. *Environ. Sci. Technol.* **2013**, *47*, 13266-13275.
12. Davis, K. L.; Aucoin, M. D.; Larsen, B. S.; Kaiser, M. A.; Hartten, A. S. Transport of ammonium perfluorooctanoate in environmental media near a fluoropolymer manufacturing facility. *Chemosphere* **2007**, *67*, 2011-2019.
13. Vieira, V. M.; Hoffman, K.; Shin, H.; Weinberg, J. M.; Webster, T. F.; Fletcher, T. Perfluorooctanoic acid exposure and cancer outcomes in a contaminated community: a geographic analysis. *Environ. Health Perspect.* **2013**, *121*, 318.
14. Lam, J. C.; Lyu, J.; Kwok, K. Y.; Lam, P. K. Perfluoroalkyl Substances (PFASs) in Marine Mammals from the South China Sea and Their Temporal Changes 2002–2014: Concern for Alternatives of PFOS? *Environ. Sci. Technol.* **2016**, *50*, 6728-6736.

15. Falk, S.; Failing, K.; Georgii, S.; Brunn, H.; Stahl, T. Tissue specific uptake and elimination of perfluoroalkyl acids (PFAAs) in adult rainbow trout (*Oncorhynchus mykiss*) after dietary exposure. *Chemosphere* **2015**, *129*, 150-156.
16. White, S. S.; Fenton, S. E.; Hines, E. P. Endocrine disrupting properties of perfluorooctanoic acid. *J. Steroid Biochem. Mol. Biol.* **2011**, *127*, 16-26.
17. Melzer, D.; Rice, N.; Depledge, M. H.; Henley, W. E.; Galloway, T. S. Association between serum perfluorooctanoic acid (PFOA) and thyroid disease in the US National Health and Nutrition Examination Survey. *Environ. Health Perspect.* **2010**, *118*, 686.
18. EPA Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA).  
[https://www.epa.gov/sites/production/files/2016-05/documents/pfoa\\_health\\_advisory\\_final\\_508.pdf](https://www.epa.gov/sites/production/files/2016-05/documents/pfoa_health_advisory_final_508.pdf) (accessed November 7, 2017).
19. Rahman, M. F.; Peldszus, S.; Anderson, W. B. Behaviour and fate of perfluoroalkyl and polyfluoroalkyl substances (PFASs) in drinking water treatment: a review. *Water Res.* **2014**, *50*, 318-340.
20. Dillert, R.; Bahnemann, D.; Hidaka, H. Light-induced degradation of perfluorocarboxylic acids in the presence of titanium dioxide. *Chemosphere* **2007**, *67*, 785-792.
21. Tang, H.; Xiang, Q.; Lei, M.; Yan, J.; Zhu, L.; Zou, J. Efficient degradation of perfluorooctanoic acid by UV–Fenton process. *Chem. Eng. J.* **2012**, *184*, 156-162.
22. Moriwaki, H.; Takagi, Y.; Tanaka, M.; Tsuruho, K.; Okitsu, K.; Maeda, Y. Sonochemical decomposition of perfluorooctane sulfonate and perfluorooctanoic acid. *Environ. Sci. Technol.* **2005**, *39*, 3388-3392.



23. Cao, M. H.; Wang, B. B.; Yu, H. S.; Wang, L. L.; Yuan, S. H.; Chen, J. Photochemical decomposition of perfluorooctanoic acid in aqueous periodate with VUV and UV light irradiation. *J. Hazard. Mater.* **2010**, *179*, 1143-1146.
24. Hori, H.; Yamamoto, A.; Hayakawa, E.; Taniyasu, S.; Yamashita, N.; Kutsuna, S.; Kiatagawa, H.; Arakawa, R. Efficient decomposition of environmentally persistent perfluorocarboxylic acids by use of persulfate as a photochemical oxidant. *Environ. Sci. Technol.* **2005**, *39*, 2383-2388.
25. Hori, H.; Nagaoka, Y.; Yamamoto, A.; Sano, T.; Yamashita, N.; Taniyasu, S.; Kutsuna, S.; Osaka, I.; Arakawa, R. Efficient decomposition of environmentally persistent perfluorooctanesulfonate and related fluorochemicals using zerovalent iron in subcritical water. *Environ. Sci. Technol.* **2006**, *40*, 1049-1054.
26. Qu, Y.; Zhang, C.; Li, F.; Chen, J.; Zhou, Q. Photo-reductive defluorination of perfluorooctanoic acid in water. *Water Res.* **2010**, *44*, 2939-2947.
27. Zhao, B.; Zhang, P. Photocatalytic decomposition of perfluorooctanoic acid with  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> wide bandgap photocatalyst. *Catal. Commun.* **2009**, *10*, 1184-1187.
28. Ochiai, T.; Iizuka, Y.; Nakata, K.; Murakami, T.; Tryk, D. A.; Fujishima, A.; Koide, Y.; Morito, Y. Efficient electrochemical decomposition of perfluorocarboxylic acids by the use of a boron-doped diamond electrode. *Diamond and Relat. Mater.* **2011**, *20*, 64-67.
29. Giri, R. R.; Ozaki, H.; Morigaki, T.; Taniguchi, S.; Takanami, R. UV photolysis of perfluorooctanoic acid (PFOA) in dilute aqueous solution. *Water Sci. and Technol.* **2011**, *63*, 276-282.
30. Zhou, Y.; He, Z.; Tao, Y.; Xiao, Y.; Zhou, T.; Jing, T.; Zhou, Y.; Mei, S. Preparation of a functional silica membrane coated on Fe<sub>3</sub>O<sub>4</sub> nanoparticle for rapid and selective removal

- of perfluorinated compounds from surface water sample. *Chem. Eng. J.* **2016**, *303*, 156-166.
31. Du, Z.; Deng, S.; Bei, Y.; Huang, Q.; Wang, B.; Huang, J.; Yu, G. Adsorption behavior and mechanism of perfluorinated compounds on various adsorbents—a review. *J. Hazard. Mater.* **2014**, *274*, 443-454.
  32. Eschauzier, C.; Beerendonk, E.; Scholte-Veenendaal, P.; De Voogt, P. Impact of treatment processes on the removal of perfluoroalkyl acids from the drinking water production chain. *Environ. Sci. Technol.* **2012**, *46*, 1708-1715.
  33. Chularueangaksorn, P.; Tanaka, S.; Fujii, S.; Kunacheva, C. Adsorption of perfluorooctanoic acid (PFOA) onto anion exchange resin, non-ion exchange resin, and granular-activated carbon by batch and column. *Desalin. Water Treat.* **2014**, *52*, 6542-6548.
  34. Du, Z.; Deng, S.; Zhang, S.; Wang, B.; Huang, J.; Wang, Y.; Yu, G.; Xing, B. Selective and High Sorption of Perfluorooctanesulfonate and Perfluorooctanoate by Fluorinated Alkyl Chain Modified Montmorillonite. *J. Phys. Chem. C* **2016**, *120*, 16782-16790.
  35. Van den Hoop, M.; Benegas, J. C. Colloids and surfaces a: physicochemical and engineering aspects. *Colloids Surf. Physicochem. Eng. Aspects* **2000**, *170*, 151-160.
  36. Oliaei, F.; Kriens, D.; Weber, R.; Watson, A. PFOS and PFC releases and associated pollution from a PFC production plant in Minnesota (USA). *Environ. Sci. Pollut Res.* **2013**, *20*, 1977-1992.
  37. Cooley, K. Synthesis and Characterization of Modified Montmorillonites for Sequestration of PFAAs from Contaminated Drinking Water. Senior Thesis, Union College, **2018**.

38. Hagerman, M. E.; Salamone, S. J.; Herbst, R. W.; Payeur, A. L. Tris (2, 2'-bipyridine) ruthenium (II) cations as photoprobes of clay tactoid architecture within hectorite and laponite films. *Chemistry of materials* **2003**, *15*, 443-450.
39. Yu, Q.; Zhang, R.; Deng, S.; Huang, J.; Yu, G. Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated carbons and resin: kinetic and isotherm study. *Water Res.* **2009**, *43*, 1150-1158.
40. Zhou, Q.; Deng, S.; Yu, Q.; Zhang, Q.; Yu, G.; Huang, J.; He, H. Sorption of perfluorooctane sulfonate on organo-montmorillonites. *Chemosphere* **2010**, *78*, 688-694.