FINAL REPORT

Effective Destruction of PFAS in Water by Modified SiC-Based Photocatalysts

SERDP Project ER18-1513

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ACRONYMS AND ABBREVIATIONS

AFFF	aqueous film forming foam
APTMS	Aminopropyltrimethoxysilane
BNL	Brookhaven National Lab
C-F	carbon-fluorine
CA	Cellulose Acetate
EEO	electrical energy per order
GFC	Glass Microfiber Filter
HAADF-STEM	high-angle annular dark-field scanning TEM
kJ	kilojoule
mol	mole
NY	Nylon
PES	Polyethersulfone
PFAS	per- and polyfluoroalkyl substance
PFBA	Perfluorbutanoic acid
PFBS	perfluorobutane sulfonic acid
PFHpA	perfluoroheptanoic acid
PFHpS	perfluoroheptanesulfonate
PFHxA	Perfluorohexanoic acid
PFHxS	perfluorohexanesulfonate
PFNA	perfluorononanoic acid
PFA	perfluoroalkoxy alkane
PFOA	perfluorooctanoic acid
PFOS	perfluoroctane sulfonic
PFPeA	Perfluoropentanoic acid
PFPeS	Tetrafluoro-2-(heptafluoropropoxy)propanoic acid (GenX)
PFPpA	Perfluoropropionic acid
PFS	perfluorinated surfactant
Pt/SiC	platinum/silicon carbide
SAC Pt	single atom platinum catalyst
SFCA	Surfactant free Cellulose Acetate
Si-H	silicon-hydrogen
Si-OH	silicon-hydroxide
SiC	silicon carbide

TiO_2	titanium dioxide
TOF	total organic fluorinate
UHPLC-TOF MS	ultra-high-performance liquid chromatography with high resolution time-of-flight mass spectrometry
UV	ultraviolet
XPS	X-ray Photoelectron spectroscopy

ABSTRACT

The main objective of this study is to develop and demonstrate a novel catalyst material's ability to enhance the ultraviolet (UV) based carbon-fluorine (C-F) bond cleavage using a silicon carbide (SiC) catalyst composited with single atom platinum catalyst (SAC Pt). The team investigated both perfluorooctanoic acid (PFOA), perfluoroctane sulfonic acid (PFOS) and byproducts of the reaction. The research will seek to answer specific technical questions on catalyst performance that will be necessary for scale-up and deployment of this technology: (1) evaluating the catalyst performance as measured by reduced reaction time relative to titanium dioxide (TiO_2), (2) measuring the percent destruction of per- and polyfluoroalkyl substance (PFAS) molecules and monitoring daughter products, and (3) understanding catalyst degradation pathway and ultimate lifecycle of the material in order to assess potential for field deployment.

The platinum/silicon carbide (Pt/SiC) catalyst showed excellent destruction efficiency for PFOA. Analytical results demonstrated sequential stepwise destruction of PFOA as well as all daughter products. The initial degradation rate for Pt/SiC was ~30% faster than that for TiO_2 and equivalent reaction conditions. In addition, while PFOA destruction via TiO_2 decreased by >70% upon repeating dosing cycles, the PFOA destruction rate was maintained. This suggest the material has promise as a long-term option for site treatment. However, these results were not observed for PFOS, with only ~50% degradation observed. Additionally, catalyst surface characterization identified -F atoms on the surface, which supported degradation mechanism showing that the catalyst is the final sink, but the degradation capacity was not reached under test conditions and remains a key question for this material. Finally, results showed that UV185nm showed significantly higher degradation performance relative the UV254nm, with >90% reduction in electrical energy per order (EEO). This is a new finding and has implications for UV-based photocatalytic PFAS destruction.

Based on the experimental results and challenges identified, two research pathways envisioned:

1. **Extended Testing.** What is the ultimate mg PFOA destroyed/g Pt/SiC? Is the Pt/SiC regenerable? Does material lifecycle offset energy savings realized?

Project results showed that continued dosing of PFOA demonstrated a degradation capacity is maintained over the timeframe investigated, but F on surface suggests the material may be capacity limited. The key research questions we seek to answer next is the ultimate mg PFOA destroyed/g Pt/SiC.

2. **PFOS Destruction Potential.** Can Pt/SiC be combined with additional oxidative processes/ pH control, etc. to achieve PFOS degradation?

Although excellent PFOA destruction was observed, only ~50% PFOS destruction was achieved. Results from PFOA/PFOS co-testing indicate that the catalyst was not poisoned, suggesting there may still be a pathway to achieving efficient PFOS degradation via this catalyst material. Here we recommend a research pathway that investigates the PFOS degradation using Pt/SiC in combination with additional oxidative processes and/or pH control.

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1.0 INTRODUCTION

PFAS molecules are recalcitrant to degradation and/or transformation by redox schemes commonly employed in water treatment, because the C-F bond is one of the strongest chemical bonds in chemistry (485 kJ mol^{-1}).[i,ii] PFAS compounds can be removed from water via activated carbon adsorption or membrane filtration, but these removal approaches cannot destroy the compounds. Instead, the process regeneration/brine will create streams with higher concentrations that pose additional health risks and disposal challenges. Commercial approaches to PFAS groundwater treatment include (1) ion exchange resins, which tend to be costly and generate a highly concentrated difficult-to-treat byproduct stream; and (2) adsorption using activated carbon, which, although useful for PFOS removal (90% efficiency), is not as effective for PFOA and other smaller chain perfluorinated compound removal and produces a solid waste that requires incineration for final disposal.[iii] Early-stage destructive approaches show that the effectiveness of the technology is highly variable with different PFAS compounds and on the aqueous matrix composition.[iv,v,vi,vii] A process needs to be developed that can achieve both removal and degradation of a broad range of PFAS molecules without the need for transportation disposal of secondary waste products.

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2.0 OBJECTIVES

The main objective of this study is to assess the performance of Pt/SiC-based photocatalytic technologies to destroy the PFAS compounds in impaired water sources rather than concentrating them with adsorption-based treatment. The current state-of-the-art for PFAS compound removal from impaired waters is adsorption followed by incineration as there is not yet a commercially available approach that can pump and treat impaired waters to suitable quality for onsite discharge. Current catalytic degradation of PFOA/PFOS by UV and titanium dioxide (TiO_2) requires high temperature and/or pH change and has shown limited effectiveness (slow reaction, low destruction rate). Our work aims to demonstrate a more effective catalytic approach. The enabling technology we propose is to enhance the UV effectiveness for C-F bond cleavage using a novel Pt/SiC catalyst. With this Pt/SiC composite catalyst, the hypothesis tested was that PFOA/PFOS degradation can be done at low pressure, neutral pH, and ambient temperature, with the goal of reducing the energy consumption and safety risks, and increasing the potential for full-scale feasibility of this technology. The proposed effort will seek to answer specific research questions on catalyst performance that will be necessary for scale-up and deployment of this technology:

1. How significant are the reaction rate improvements of the Pt/SiC SAC catalyst relative to the current state of the (such as TiO_2 catalysts)?
2. How do different UV wavelengths impact the rate of destruction for both parent PFAS compounds as well as fluorinated daughter products?
3. What reaction times and conditions are required to achieve complete destruction of PFAS compounds and fluorinated daughter products?
4. What is the lifetime or capacity of the catalyst material to understand its potential lifecycle for field use?

All technology components were evaluated in lab scale to demonstrate proof of concept for this novel photocatalytic defluorination approach. Demonstration of this approach and lab scale data obtained will provide crucial understanding necessary for scale-up reactor design. Specific technical efforts will focus on (1) evaluating the catalyst performance as measured by reduced reaction time relative to TiO_2, (2) measuring the percent destruction of PFAS molecules and monitoring daughter products, and (3) understanding catalyst degradation pathway and ultimate lifecycle of the material in order to assess potential for field deployment.

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3.0 BACKGROUND

We propose to evaluate proof-of-concept performance of an advanced UV oxidation system enhanced with the newly developed Pt/SiC composite photocatalyst to achieve complete hydrodefluorination. The research efforts will be organized so that the data obtained can be used to evaluate two hypotheses:

Hypothesis 1: The combination of UV with Pt/SiC catalyst will result in the stepwise and complete hydrodefluorination of the H-F bonds within a PFAS molecule.

Hypothesis 2: Applying both 185 and 254 nm UV wavelengths in combination with Pt/SiC catalyst will result in more efficient PFAS degradation than either wavelength alone.

We envision the proposed catalyst method can be developed into a modular treatment process that can be incorporated into a comprehensive treatment train that includes reverse osmosis membrane system that will concentrate PFAS molecules, reduce the contamination water volume, and remove co-contaminants that may be present. The following discussion outlines the technical rationale and early-stage results for the proposed approach to PFAS molecule destruction.

The destruction mechanism of Pt/SiC is summarized in **Figure 1**. The catalytic process is conceptually different from previous PFAS decomposition approaches; the defluorination is based on nucleophilic substitution via redistribution of the silicon-hydrogen [Si-H]/C-F bonds. The chemically robust silicon carbide semiconductor dissociates surface-adsorbed water molecules and forms Si-H bonds under UV irradiation and acts as an electron donor to initiate PFAS decarboxylation/ desulfonation.[ix]

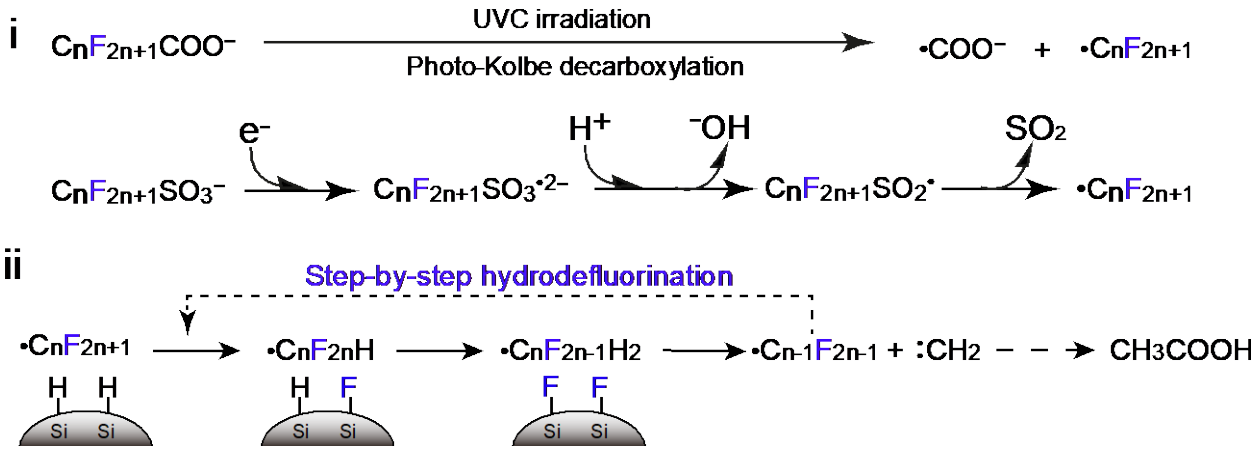

Figure 1. PFOA/PFOS Destruction Mechanism Using Pt/SiC Catalyst[9].

While we aim to find solutions for PFAS in general, our focus will be on PFOA/PFOS and their daughter products, such as perfluoroheptanesulfonate (PFHpS), perfluorohexanesulfonate (PFHxS), and perfluorobutane sulfonic acid (PFBS), since PFOS is much more difficult to treat compared with PFOA. Also, aqueous film forming foam (AFFF) is a source of PFOS but not as much for PFOA or perfluoroheptanoic acid (PFHpA), which will be studied with perfluorononanoic acid (PFNA).[viii]

AFFF may contain may different types of PFAS that are still unidentified, and it is important to include other PFAS, such as PFNA. Our efforts will concentrate on two aspects of the compound degradation.

Team efforts in this proposed project will focus on further enhancing the catalytic efficiency of these composite catalysts, testing them in a real water matrix, and demonstrating their potential for complete degradation of the parent and subsequent breakdown products.

4.0 MATERIALS AND METHODS

Pt/SiC catalyst was prepared using the recipe summarized in the left picture in **Figure 2**. Aminopropyltrimethoxysilane (APTMS) reacted with silicon-hydroxide (Si-OH) groups on the SiC surface, leading to the SiC amination (SiC-NH_3^+). The negatively charged Pt precursor ($PtCl_6^{2-}$) attached to the positively charged ammonium group on SiC via electrostatic self-assembly. After photoreduction of $PtCl_6^{2-}$ under UVC light, chlorine atoms were completely removed from $PtCl_6^{2-}$, obtaining single-atom Pt on SiC. High resolution image of Pt_1/SiC using high-angle annular dark-field scanning TEM (HAADF-STEM) taken at Brookhaven National Lab (BNL), This technology lends itself to atomic-scale resolution by faster scanning the electron beam over the sample and collecting scattered electrons which otherwise do not pass through the aperture of the microscope. A preliminary test has been conducted on Pt_1/SiC, where the atomic dispersion of Pt on SiC support was confirmed, with the radius of Pt species estimated to be ~2 angstrom (Å). This provides visual confirmation that the synthetic scheme does not yield large metal nanoparticles.[ix]

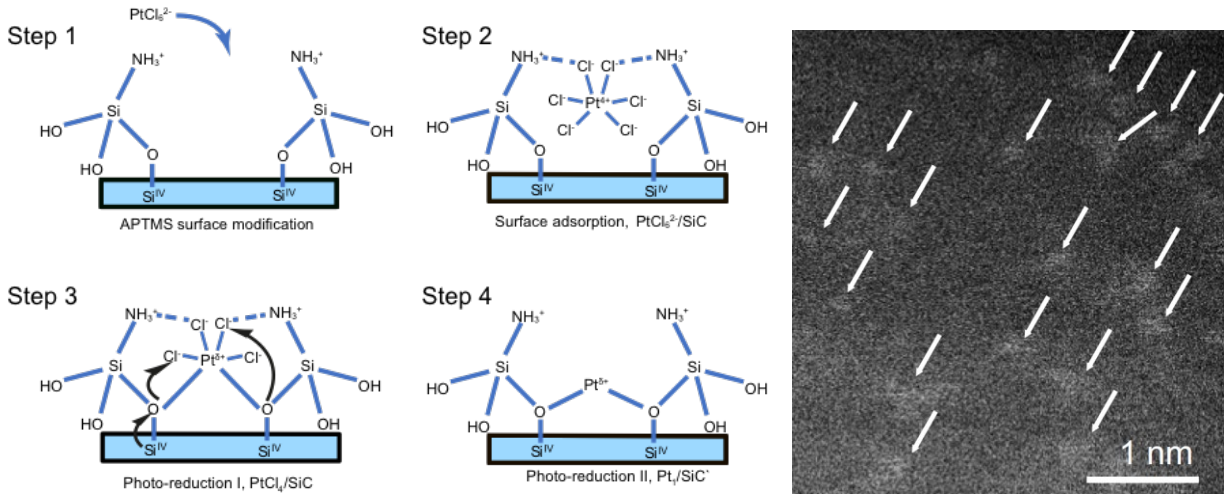

Figure 2. (Left) Schematic Diagram of Pt/SiC Preparation and (Right) TEM Image of the Pt/SiC Catalyst

Degradation experiments are performed in a setup that includes an external mixing vessel and recirculating line to the UV reaction chamber. TiO_2 and Pt/SiC were tested as catalysts. Oxalic acid was used to control pH. The catalyst as prepared remains suspended in the fluid. 3mL aliquots are periodically taken to determine target PFAS concentration. Sample volume was 250mL, sample flow rate was 0.5L/min, Two UV wavelengths (185nm and 254nm) were used in this experiment. The test set-up is presented in **Figure *3***. pH was monitored and recorded using the pH probe (Hach, PHC301) connected to the pH meter (Hach, HQ40D).

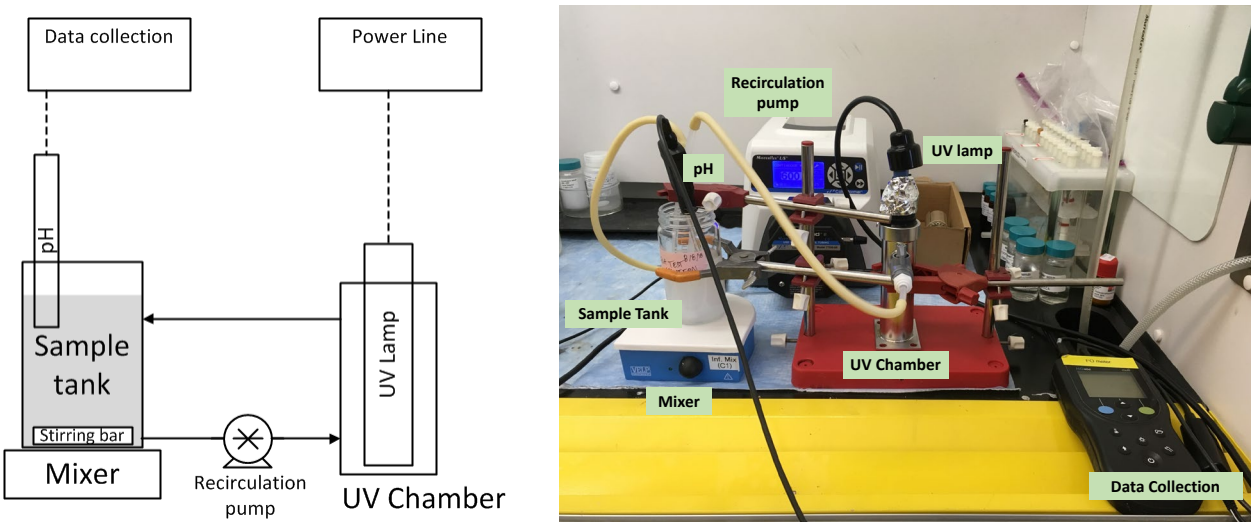

Figure 3. Photocatalytic Reaction Set-up

The catalyst was removed from sample to prevent any further reaction and to protect the analytical equipment. Since the absorbing affinity of PFAS to certain filter media was high, a preliminary test was conducted to minimize the loss of PFAS during the filtration and summarized in **Table 1**. Based on the results, the SFCA filter was used for the sample filtration.

Table 1. Recovery of PFOA and PFOS from Filtration

Membrane	PFOA (ppm)	Recovery	PFOS (ppm)	Recovery
Raw sample	0.91		1.18	
PES (Polyethersulfone)	0.11	12.5%	0.02	1.6%
SFCA (Surfactant free Cellulose Acetate)	0.93	102.4%	1.13	95.0%
CA (Cellulose Acetate)	0.92	101.6%	1.04	87.9%
GFC (Glass Microfiber Filter)	0.94	103.8%	1.06	89.2%
NY (Nylon)	0.01	0.8%	0.02	1.7%

The PFOA and PFOS concentration and their stepwise degraded components were analyzed using ultra-high-performance liquid chromatography with high resolution time-of-flight mass spectrometry (UHPLC-TOF MS, Agilent 1290 Infinity UHPLC/6230 TOF mass spectrometer). A UHPLC-TOF method was developed and optimized using PFOS, PFOA and other short-chain perfluorinated surfactant (PFS) standards. Calibration curves of each standard are prepared and analyzed at the beginning of each run to quantitate periodic aliquots of each PFAS molecule following UV-catalytic treatment. The short-chain perfluoroalkoxy alkane (PFA) ions being monitored are listed in **Table 2**.

Table 2. Analyte List for Project, Including PFOA/PFOS Daughter Products

Analyte Name	Acronym	Molecular Formula	Analytically measured?
Perfluorooctanoic acid	PFOA	$C_8F_{15}O_2H$	Yes
Perfluoroheptanoic acid	PFHpA	$C_7F_{13}O_2H$	Yes
Perfluorohexanoic acid	PFHxA	$C_6F_{11}O_2H$	Yes
Perfluoropentanoic acid	PFPeA	$C_5F_9O_2H$	Yes
Perfluorbutanoic acid	PFBA	$C_4F_7O_2H$	Yes
Perfluoropropionic acid	PFPpA	$C_3F_5O_2H$	Yes
C2F5 Breakdown project	-	C_2F_5	Yes – C2F5 species detected, but not quantitatively
Perfluoroctane sulfonic acid	PFOS	$C_8F_{17}SO_3H$	Yes
Perfluorobutane sulfonic acid	PFBS	$C_4F_9SO_3H$	No – not detected
Tetrafluoro-2-(heptafluoropropoxy)propanoic acid (GenX)	PFPeS	$C_6F_{11}O_3H$	No – not able test in project timeframe

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5.0 RESULTS AND DISCUSSION

A PFS degrading test was conducted using various conditions of PFOA/PFOS concentration, various catalyst (Pt/SiC and TiO_2), pH control using Oxalic acid, and various UV wavelengths (185nm and 254nm).

One of the PFS degrading tests can be summarized as following: PFOA and PFOS stock solution and Pt/SiC catalyst were added to the 250mL of deionized water to make 0.5ppm of PFOA and PFOS and 5ppm of Pt/SiC catalyst. Two UV lamps were installed in series (185nm → 254nm) and sample water passes through the UV lamps at the flow rate of 0.5L/min. 3mL of samples were taken every 15min for 1hour and every 1hour for 5hours. One final sample was taken 20hours later to monitor the leftover concentration after 20hours of UV irradiation. The concentration of PFOA, PFOS, and other short-chained PFS was analyzed using the developed high performance liquid chromatography–mass spectrometry method and pH was also monitored. Both results are presented in **Figure 4**. There was a short-time pH increase for 30min followed by constant decreases after 30min for 20hours. The main reason for the short increase can be the absorption of PFOA on the surface of Pt/SiC. The depletion of PFOA can increase the pH of the sample solution. After 30min, pH started decreasing as the PFOA degradation increases the concentration of acetic acid. The degradation of PFOA and PFOS was plotted on the left side of the figure, and regression lines (first-order reaction) were added for each degradation trend of PFOA and PFOS. The rate constant of each PFOA and PFOS degradation trends are added in the figure. The short-chain PFSs as a result of the PFOA/PFOS degradation were monitored as well and presented in **Figure 4**. The developed analysis method could find all breakdown components of PFS. The results showed the area in the resulting peak because the standard peak was not included. The results showed that the quantification of each breakdown components is possible with a proper standard. Based on the PFOA concentration, most of PFOA was degraded in 5–6 hours but a decent amount of PFS breakdown components was still detected. Therefore, the analysis of all PFS breakdown components and the tracking of the overall concentration of PFS and its breakdown are important for the assessment of any treatment technology. One interesting thing in this breakdown data is that the concentration of C_6F_{13} is more dominant than the concentration of $C_7F_{13}O_2H$. The possible reason for this result is that the reaction of Pt/SiC catalyst is fast enough to skip the step of PFS degradation mechanism.

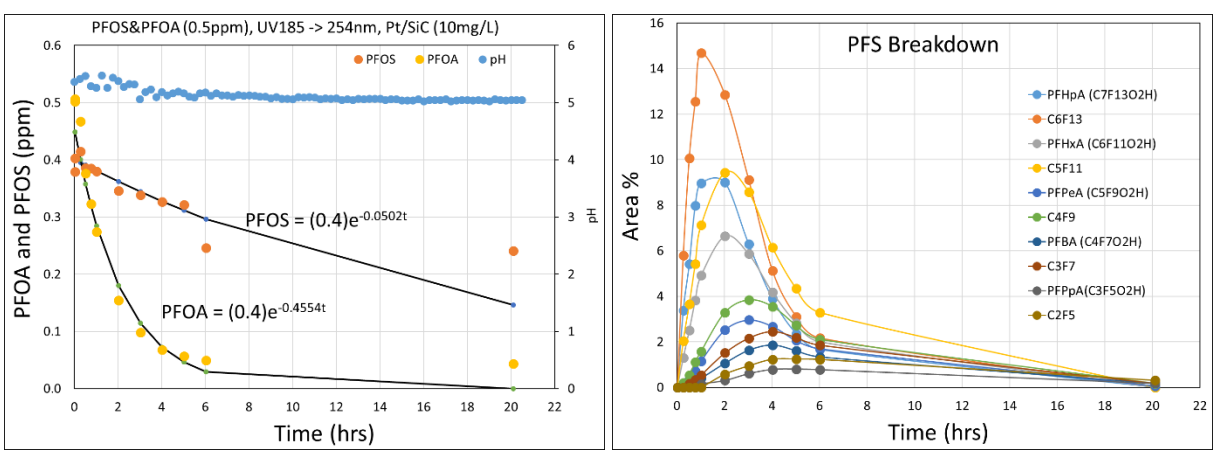

Figure 4. PFOA/PFOA Breakdown with Pt/SiC and Two UVs in Series (185nm→254nm)

Various test conditions, such as PFS species, catalyst, pH, and UV wavelength were tested and the reaction constant of each condition was calculated using the same method shown in **Figure 4**. The results are summarized and presented in **Figure 5**. The overall degradation rate of PFOA was higher than that of PFOS. On the contrary to our expectation, the PFOA degradation was the highest with TiO_2 catalyst under UV185nm irradiation. When the oxalic acid was added with TiO_2 catalyst, the degradation of PFOS was the highest. Since the desulfonation process requires hydrogen ion, the low pH is needed to accomplish the proper desulfonation.[ix] Another type of acid should be tested to see the effect of pH on these results.

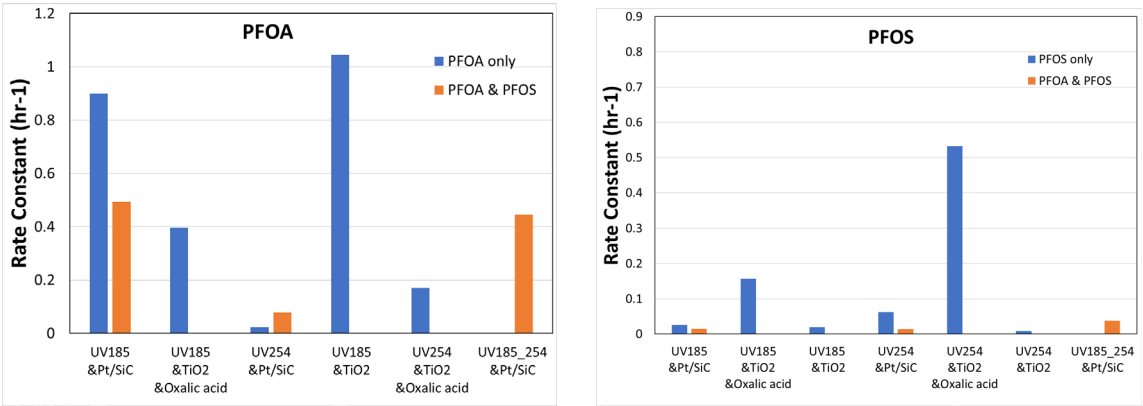

Figure 5. Rate Constants of PFOA/PFOS Degradation

The capacity of the catalyst lifetime was measured by injecting the PFOA/PFOS multiple times. The concentration of the initial PFOA/PFOS concentration increased to 5 ppm to monitor the fate of breakdown products (short-chain PFOA/PFOS). Since the performance of TiO_2 at UV185nm was effective, the TiO_2 and Pt/SiC were tested with UV185 irradiation in parallel. The PFOA/PFOS concentration and pH are presented in **Figure 6**. The degradation rate of PFOA was higher than that of PFOS. PFOS was hardly removed during the test so the concentration increased when the PFOA and PFOS were injected two more times. The PFOA degraded sharply in both TiO_2 and Pt/SiC catalyst. There was no degradation of Pt/SiC's reaction rate (0.1311 → 0.1374 → 0.1406 hr^{-1}) during the additional injection while there was decrease in reaction rate in TiO_2 catalyst setup (0.1024 → 0.0434 → 0.0296 hr^{-1}). The capacity of Pt/SiC could not be reached during this test and further testing would be required to check the capacity of catalysts.

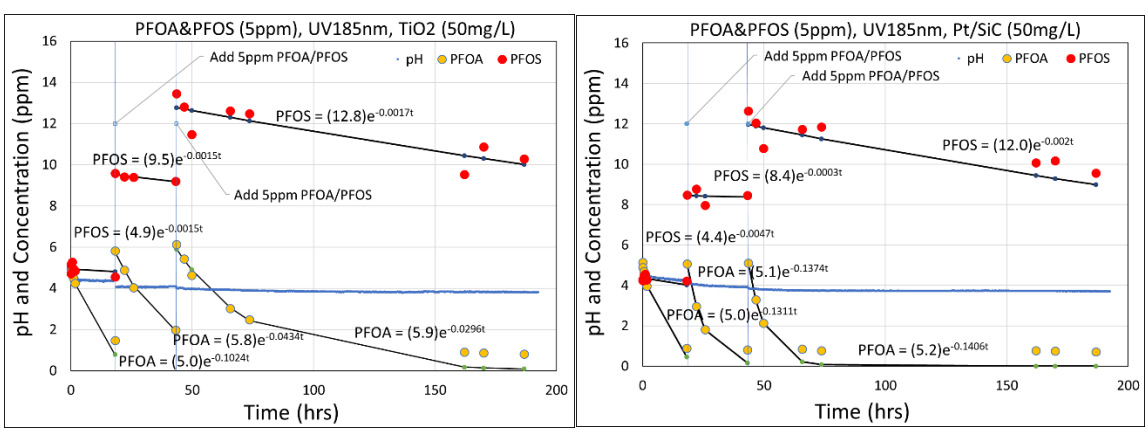

Figure 6. Long Term Destruction of PFOA/PFOS with Pt/SiC at UV 185nm

During the breakdown of PFOA/PFOS, short-chain PFS could be generated. The monitoring of this kind of short-chain PFS was not easy since the species of breakdown components are too many. In this experiment, the C7 to C3 short-chain PFS were monitored and presented in **Figure 7**. At this test, perfluorohexanoic acid (PFHxA), perfluoropentanoic acid (PFPeA) and perfluorbutanoic acid (PFBA) can be quantified using standard solution. Since there was no standard solution for PFHpA and perfluoropropionic acid (PFPpA) , only area in the peak was used in the graph. The ratio of area to concentration was about 20 to 1, so the graph was prepared using the ratio. Based on the PFOA/PFOS destruction mechanism, the PFAS will be degraded into smaller carbon number, such as C8 (PFOA/PFOS) → C7 → C6, etc. .[ix] The analyzed short-chain PFAS showed similar degradation pattern with TiO_2 as shown in the left graph of **Figure 7**. For the test with Pt/SiC, the pattern looks different. The PFHxA (C6) showed more than PFHpA (C7). The single atom Pt expedite the reaction of Pt/SiC catalyst so there could exist reactions that degrade the C8 to C6 or C8 to C5 directly. Even though the concentration of PFOA decreased to around 1 ppm with TiO_2 catalyst, the concentration of breakdown PFAS is still high in TiO_2 catalyst, while it significantly decreases and becomes almost zero in Pt/SiC catalyst.

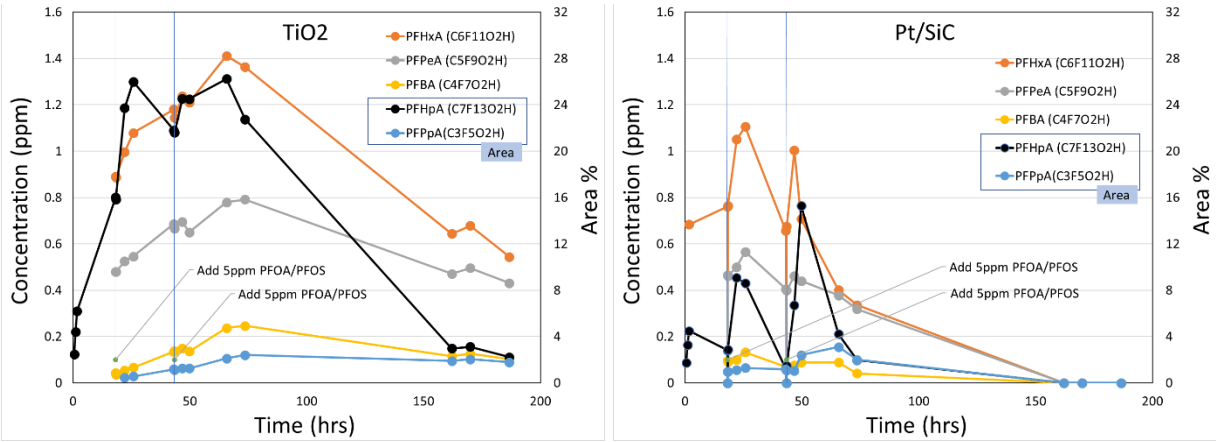

Figure 7. Breakdown of PFA During Long Term Test with Pt/SiC at UV 185nm

The surface of the Pt/SiC catalyst was analyzed using XPS (X-ray Photoelectron spectroscopy) to check the attachment of PFAs on the surface of Pt/SiC. The scanning result data are summarized in **Figure 8**. The left graph shows the raw Pt/SiC catalyst with Pt on the surface. The right graph shows Fluoride ion on the surface of the used catalyst, which can be proof of the Si-F bond on the catalyst. The Pt ion was not detected by the used catalyst. The blockage of Pt ion by other components can be the main reason since there was no degradation of the catalyst performance during the long-term test.

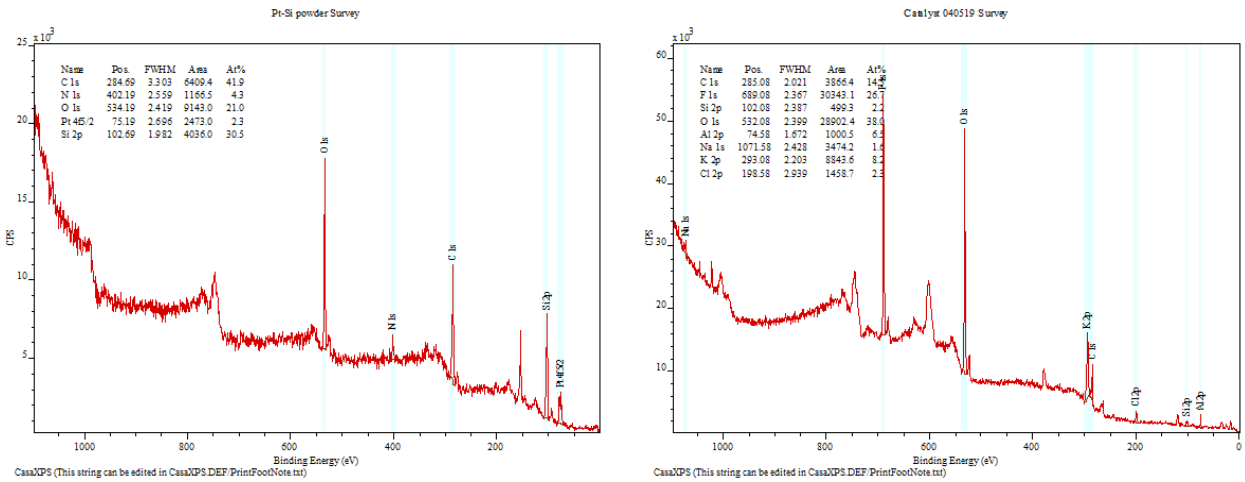

Figure 8. Pt/SiC Catalyst XPS Analysis (left) Before Test, (right) After Test (PFOA/PFOS at UV 185nm)

Using the rate constant calculated in this work, the EEO (Electrical Energy per Order) was calculated to compare the specific energy consumption of various conditions. The results are summarized in **Figure 9**. EEO is the normalized measure of energy consumption to achieve a 90% reduction of a pollutant. From the previous study, the Pt/SiC showed 73 kWh/m^3 of EEO was observed, which costs $202,500/year to reduce PFAS concentration to 99% for 10,000 gal/day plant ($0.10/kWh). [ix] Results show that 185nm requires significantly less energy to achieve destruction as 254nm and oxalic acid also significantly increases the PFOS reaction rate.

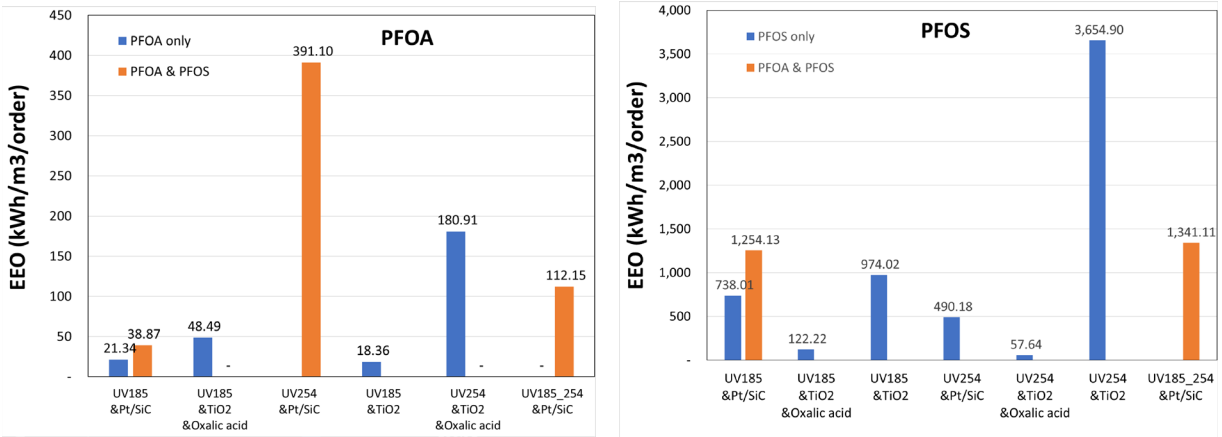

Figure 9. Energy Consumption by EEO.

From this study, the EEO was as low as 21.34 kWh/m^3 and annual electricity cost estimated to be $59,197. The energy cost of various treatment schemes to achieve 99% removal of PFOA in the plant of 10,000 gal/day capacity are summarized in **Table 3**. The increased degradation rate realized when switching from 185 nm to 254 nm decreases the energy cost for PFAS destruction by as much as ~95%. The Pt/SiC catalyst also provides the lowest cost to achieve 99% degradation relative to the baseline TiO_2 and TiO_2 + oxalic acid. However, those calculations don't include the destruction of short-chain PFAS, so the reaction rate should be recalculated using the total fluorinated compounds such as total organic fluorinate (TOF).

Table 3. Energy Cost for 99% Removal of PFOA @ 10,000 gal/day Scale

UV Wavelength	Catalyst Test Condition		
	TiO_2	TiO_2 + Oxalic Acid	Pt/SiC
254nm	N/A	$500,000*	$1,084,000
185nm	$51,000	$135,000*	$59,000

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6.0 CONCLUSIONS

A newly developed Pt/SiC catalyst was tested in this research using two UV wavelengths and the Pt/SiC showed excellent destruction efficiency for PFOA. Pt/SiC showed an initial rate of destruction that was ~30% faster than that for TiO_2. UV185nm showed significantly improved performance vs UV254 nm. The increased rate of reaction results in a more efficient degradation and potentially lower cost photocatalytic degradation process, even accounting for the higher energy of the 185 nm wavelength.

PFOA destruction via TiO_2 catalyst with UV 185nm wavelength showed the highest performance to remove PFOA, however, the PFOA destruction via TiO_2 decreased by more than 70% upon repeated dosing cycles and significant short-chain PFAS remains during the long-term removal test. Whereas the PFOA destruction rate actually increased slightly over time when the Pt/SiC was used as the catalyst at UV 185nm.

pH control can improve the degradation of PFOS, which showed poor degradation trends for both TiO_2 and Pt/SiC catalyst without pH adjustment.

Presence of F on the catalyst surface supports the mechanism that it is the final sink; degradation capacity is not reached. 185nm UV shows significant energy savings >90% reduction in EEO for Pt/SiC vs 254nm, 73% reduction in EEO for TiO_2/Oxalic acid. The tracking of all short-chain PFAS is needed to calculate actual cost to remove PFAS in the water.

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7.0 FUTURE RESEARCH GOALS AND NEXT STEPS/QUESTIONS

The Pt/SiC catalyst has shown promise as a material that achieves rapid degradation of PFOA, along with smaller chain daughter products and lower energy demand than existing commercial catalysts. Results suggest there this material may provide significant costs savings for PFS destruction if development continues. However, further research is needed to achieve a greater understanding of the long-term potential of the Pt/SiC catalyst material. Two research pathways are envisioned: (1) the first is to understand the lifecycle of Pt/SiC catalyst. This is necessary to put the energy cost savings in context with the material lifecycle (capital investment and/or any needed regeneration expenses); (2) the second area is to determine if there are operational conditions that would facilitate PFOS destruction.

1. **Extended Testing.** What is the ultimate mg PFOA destroyed/g Pt/SiC? Is the Pt/SiC regenerable? Does material lifecycle offset energy savings realized?

Project results showed that continued dosing of PFOA demonstrated that a degradation capacity is maintained over the timeframe investigated, but F on the surface suggests the material may be capacity-limited. The key research questions we seek to answer next is the ultimate mg PFOA destroyed/g Pt/SiC. This will feed into questions on the potential for the regeneration of the used Pt/SiC, and if the energy saved by the material lifecycle offsets this regeneration (or replacement) cost. Tests to date have reached 200hrs of PFS Pt/SiC exposure. We recommend long-term degradation testing of PFOA with Pt/SiC, at least four weeks of continuous PFOA dosing or until degradation capacity observed. Assuming that material degradation declines with time, different chemical/thermal treatments will be investigated to see if material reuse is possible or if disposal the most economic option.

2. **PFOS Destruction Potential.** Can Pt/SiC be combined with additional oxidative processes/ pH control, etc. to achieve PFOS degradation?

Although excellent PFOA destruction was observed, only ~50% PFOS destruction was achieved. Results from PFOA/PFOS co-testing indicate that the catalyst was not poisoned, suggesting there may still be a pathway to achieving efficient PFOS degradation via this catalyst material. Here we recommend a research pathway that investigates the PFOS degradation using Pt/SiC in combination with additional oxidative processes and/or pH control. For this line of investigation, the Pt/SiC catalyst should be tested at lower pH values (pH <4), with ozone, hydrogen peroxide, to determine of a synergist combination of conditions exists to achieve rapid molecule destruction.

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Table 1. UHPLC-TOF Parameters

UHPLC/MS	Agilent 1290 Infinity UHPLC/6230 TOF mass spectrometer
Column and Temperature	Waters Acquity HSS T3
Mobile Phases	**A**: 10 mM Ammonium Acetate **B**: Methanol
Flow	0.4 mL/min, 50/50 A/B
Gradient	**Time (min)** / **%B** 0 / 50 10 / 80 11 / 80 11.5 / 90 13 / 90 13.5 / 50 20 / 50 (Stop)
Injection Volume	1 µL
Ionization Mode	ESI - Agilent Jet Stream
Scan Type (Range)	Negative MS1 (65–1000 amu)
Drying Gas Temp, Flow	350 °C, 10 L/min
Nebulizer	50 psi
Sheath Gas Temp., Flow	350 °C, 11 L/min
Capillary Voltage	3500 V
Nozzle Voltage	1000 V
Fragmentor Voltage	120 V
Data System	Agilent MassHunter Workstation: LC/MS Data Acquisition (Version B.05.01)