Dependency of the photocatalytic and photochemical decomposition of per- and polyfluoroalkyl substances (PFAS) on their chain lengths, functional groups, and structural properties

Nusrat Chowdhury, Srinivas Prabakar and Hyeok Choi

Department of Civil Engineering, The University of Texas at Arlington, 416 Yates Street, Arlington, Texas 76019-0308, USA
*Corresponding author. E-mail: hchoi@uta.edu
NC, 0000-0003-2827-5113; HC, 0000-0002-6313-1361

ABSTRACT

This study reports the removal of per- and polyfluoroalkyl substances (PFAS) in water using various photocatalytic and photochemical processes. PFAS were chosen, based on chain lengths, functional groups, and structural properties: four perfluorocarboxylic acids (PFCAs), including perfluorooctanoic acid (PFOA), three perfluorosulfonic acids (PFSAs), including perfluorooctanesulfonic acid (PFOS), hexafluoropropylene oxide dimer (GenX), and 6:2 fluorotelomer sulfonate (6:2 FTS), and dependency of the photocatalytic decomposition of PFAS on their properties was investigated. Oxidants and reductants were introduced to study the photochemical decomposition of PFAS, and reactive species and reaction byproducts were identified to elucidate the decomposition mechanism of PFAS. Some notable findings include: long chain PFCAs (95% in 48 h) and 6:2 FTS (100%) were removed via chemical decomposition in TiO$_2$/UVC while GenX (37%), long chain PFSAs (60%), short chain PFSAs (0–10%) and short chain PFCAs (5–18%) were removed via physical adsorption. Sulfate radicals generated with persulfate (PS) played an important role in decomposing PFCAs (60–90%). Sulfite activated by UVC worked for defluorination of PFOA (75%) and PFOS (80%). PFOA was removed faster by UVC/sulfite $\Rightarrow$ UVC/TiO$_2$/sulfite $\approx$ UVC/TiO$_2$/PS $\approx$ UVC/PS $\Rightarrow$ UVC/TiO$_2$ while PFOS was removed faster by UVC/sulfite $\Rightarrow$ UVC/TiO$_2$/sulfite $\approx$ UVC/TiO$_2$/PS $\approx$ UVC/TiO$_2$ $\Rightarrow$ UVC/PS. Susceptibility of PFAS to the chemical reactions could be explained by their properties and the reactive species produced in each system.

Key words: chemical vulnerability, per- and polyfluoroalkyl substances, photochemical decomposition, structural property, TiO$_2$/UV photocatalysis

HIGHLIGHTS

- TiO$_2$ photocatalytic/photochemical decomposition of nine different PFAS was compared.
- TiO$_2$/UV removed PFAS via physical adsorption and/or chemical decomposition.
- Sulfate radicals generated with $S_2O_8^{2-}$ played a major role in decomposing PFCAs.
- Sulfite activated by UV worked significantly for defluorination of PFAS.
- Overall susceptibility of PFAS to the chemical reactions was explained.

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (http://creativecommons.org/licenses/by/4.0/).
INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) with chemically inert C-F bonds have been widely used in various industries thanks to their many useful properties such as both water and oil repelling property (Fujii et al. 2007). PFAS are designed to contain different functional groups and carbon chain lengths, which imparts unique physiochemical properties and affects their affinity and reactivity (Buck et al. 2011). Historically, two PFAS groups, namely perfluorocarboxylic acids (PFCAs; CₙF₂ₙ₊₁COOH) and perfluorosulfonic acids (PFSAs; CₙF₂ₙ₊₁SO₃H) are most known. In particular, long chain PFSAs containing ≥6 carbons, such as perfluorooctanesulfonic acid (PFOS), and PFCAs containing ≥8 carbons, such as perfluorooctanoic acid (PFOA), have been popularly used (US EPA 2017a; Trojanowicz et al. 2018).

The occurrence, fate, and transformation of long chain PFAS, mainly PFOA and PFOS, have been relatively well documented (Rahman et al. 2014). Exposure to PFOA and PFOS could cause serious health problems such as reduced birth weight, elevated infertility, thyroid diseases, and kidney cancer (Fei et al. 2007; Benford et al. 2008). Unfortunately, but as well expected, PFAS with extraordinarily stable C-F bonds (dissociation energy of 533 kJ/mol) are rarely decomposed in the environment, presenting a huge challenge for environmental remediation (Rayne & Forest 2009; Li et al. 2020). The challenge becomes serious especially for PFOA and PFOS as two presenting perfluoroalkyl substances due to their highly oxidized states and complete substitution of C-H bonds with C-F bonds. United States Environmental Protection Agency (US EPA) released a drinking water health advisory for PFOA and PFOS and limits their concentration to 70 parts per trillion in drinking water separately or in combination (US EPA 2017b).

Long chain PFAS have been phased out by manufacturers and end-users and switched to short chain surrogates, which have not been regulated yet. These short chain PFAS are characterized by the presence of hetero atoms and/or vulnerable C-H bonds along with shortened chain length, including perfluorobutane sulfonic acid (PFBS), hexafluoropropylene oxide dimer acid (HFPO-DA), and 6:2 fluorotelomer sulfonic acid (6:2 FTS) (note Table S1 and Figure S1 in Supplementary Information) (Renner 2006; Danish Ministry of the Environment 2015; Xiao 2017). For example, ammonium salt of HFPO-DA (also known as GenX) with a hetero atom O in the middle of an alkyl chain has replaced PFOA (DuPont Marketing 2010). The most common alternative to PFOS is 6:2 FTS with 4 C-H bonds as one of the polyfluoroalkyl substances (Ritter 2010). Such
alternatives and short chain PFAS recently started being detected in water (Cai et al. 2012). Short chain PFAS can spread faster in the environment due to their high mobility (Hoisaefer et al. 2019). Although less information is available regarding their adverse health impact, short chain PFAS are assumed to be as toxic as long chain PFAS (Wang et al. 2015).

Considering the chemical stability of PFAS, photocatalytic, photochemical, sonochemical, electrochemical, radiochemical, thermochemical, subcritical, and plasma treatment processes have been studied for destroying PFAS in water (Fujishima et al. 2000; Chen & Zhang 2006; Tang et al. 2012; Chen et al. 2015, 2016; Dong et al. 2015; Wang et al. 2017). Those advanced oxidation processes introduce powerful radicals such as hydroxyl (HRs; •OH) and sulfate radicals (SRs; SO4*-) to decompose PFAS, along with other decomposition mechanisms (Chen & Zhang 2006; Tang et al. 2012). Especially titanium dioxide (TiO2)-based photocatalysis has shown effective degradation and defluorination of PFAS and other halogenated chemicals under ultraviolet (UV) irradiation (Fujishima et al. 2000; Chen et al. 2015, 2016; Dong et al. 2015). PFOA (50 mg/L) was successfully decomposed by TiO2/UV (0.5 g/L), showing pseudo-first order reaction rate constant at 0.0158 h−1 (Chen et al. 2016). Long chain PFAS, especially PFCAs, have been the centre of the research (but limited information is still available) while the reactivity of emerging short chain PFAS and their treatability by TiO2 photocatalysis are less known (Wang et al. 2017). In general, short chain and polyfluoro ones are expected to be relatively easier to decompose than their counterparts, i.e., long chain and perfluoro ones, due to the presence of overall fewer C-F bonds and more C-H bonds. However, previous work reported that short chain PFAS are nearly as resistant to chemical oxidation as PFOA and PFOS (Park et al. 2009).

In the context that the photocatalytic decomposition of emerging short chain PFAS should be revealed and compared with that of conventional long chain PFAS, this present study reports the reactivity of nine PFAS, including four PFCAs, three PFSAs, GenX, and 6:2 FTS and specific chemical oxidants and reductants such as hydrogen peroxide, persulfate (PS), and sulfite, which can also be activated by UV to generate secondary reactive species, as shown in Equations (1)–(3) (Liao & Gurol 1995; Fischer & Warneck 1996; Chen & Zhang 2006), were introduced to induce the photochemical decomposition of PFAS and thus to combine it with the photocatalytic decomposition of PFAS, expecting a synergistic effect. Reactive species and reaction byproducts were identified to elucidate the decomposition mechanism of PFAS. As a result, this study would provide comprehensive information on the dependency of photocatalytic and photochemical decomposition of PFAS on their chain lengths, functional groups, and structural properties and thus help to establish powerful destructive chemical treatment approaches toward PFAS in water.

\[
\begin{align*}
H_2O_2 + \text{hv} & \rightarrow 2\text{OH}^- \\
S_2O_8^{2-} + \text{hv} & \rightarrow 2SO_4^* \\
SO_3^{2-} + \text{hv} & \rightarrow SO_4^* + e_{eq}
\end{align*}
\]

\( EQUATIONS (1) \)

\( EQUATIONS (2) \)

\( EQUATIONS (3) \)

**METHODS**

**Chemicals**

Perfluorooctanoic acid (PFOA; C8F18O2H; CAS 335-67-1; 95%), perfluorooctanesulfonic acid (PFOS; C9F17SO3H; CAS 2795-39-3; ≥98.0%), perfluorobutanesulfonic acid (PFBS; C4F9SO3H; CAS 2940-49-3; 98%), perfluorononanoic acid (PFNA; C9F19O2H; CAS 375-95-1; 97%), and perfluorobutanoic acid (PFBA; C3F7COOH; CAS 375-22-4; 98%) were obtained from Sigma-Aldrich (St. Louis, MO). Perfluorooctanoic acid (PFHxDA; C8F18O2H; CAS 375-85-9; ≥97.0%), 6:2 FTS (1H,1H,2H,2H-perfluoroocotane sulfonic acid; C8H5F13O3S; CAS 237619-97-2; 25%), and GenX (undecafluoro-2-methyl-3-oxa-hexanoic acid; C11F23O2H; CAS 13252-15-6; 97%) were purchased from Synquest Laboratories (Alachua, FL) while perfluorohexane sulfonic acid (PFHxS; C16F33SO3H; CAS 3871-99-6; ≥98.0%) was obtained from Frontier Scientific (Logan, UT). Sodium persulfate (PS; Na2S2O8; CAS 7775-27-1; ≥99%), sodium sulfate (Na2SO3; CAS 7757-83-7; ≥98%), sodium periodate (NaIO4; CAS 7799-28-5; 99%), sodium bromate (NaBrO3; CAS 7789-38-0; ≥99%), and sodium hydroxide (NaOH; CAS 1310-73-2; 1N) were purchased from Sigma-Aldrich while hydrogen peroxide (H2O2; CAS 7722-84-1; 30%), sodium hypochlorite (NaOCl; CAS 7681-52-9; 12%), potassium iodide (KI; CAS 7681-11-0; ≥95%), oxalic acid (OA; HO2CCO2H; CAS 144-62-7; ≥99%), formic acid (CH2O2; CAS 64-18-6; 99%), acetonitrile (ACN; C3H7N; CAS 75-05-8; ≥99%), and methanol (CH3O; CAS 67-56-1; 99.8%) were purchased from Thermo Fisher Scientific (Waltham, MA). TiO2...
(Degussa Aerioxide P25; CAS 13463-67-7; 99.5%) was obtained from Degussa Corp (Parsippany, NJ). Water used for all experiments was Milli-Q water produced by a Millipore Milli-Q filtration system (Billerica, Massachusetts).

Large molecule separation (LMS) solid phase extraction (SPE) cartridges (25 mg, 1 mL) were purchased from Agilent Technologies (Santa Clara, CA). Polyether sulfone syringe filters (0.22 μm pore size, 13 mm) manufactured by Foxx Life Sciences (Salem, NH) were purchased through Thermo Fisher Scientific. Isotopically marked standards for parent and byproduct PFAS were obtained as mixtures in methanol from Wellington Laboratories (Guelph, ON, Canada).

**Batch experiments**

All reactions were carried out in a Pyrex glass beaker with effective volume of 21 mL containing PFAS at 10 mg/L. The reason we used PFAS concentration at 10 mg/L, which is much higher than that found in the environment (7–50 μg/L) (Trojanowicz et al. 2018), is to reduce analytical burden for easy measurement of PFAS, intermediates, and fluoride ions, and also to quickly measure and compare the reactivity of the various systems. Concentration of TiO₂ was 0.66 g/L, which is typical for photocatalytic experiments (Wang & Zhang 2011; Sansotera et al. 2015). A 15 Watt 17-inch length lamp capable of producing wide 230–300 nm (UVC) was used as a UV source. Preliminary experiments showed that longer wavelengths such as UVA and UVB are not so effective for either photolytic or photocatalytic decomposition of PFAS. The lamp was placed on the top of the reactor, exhibiting around 6.0 mW/cm² UV intensity, which was measured by an Ophir starlite energy meter (P/N7Z01565).

No pH was adjusted. Initial pH was around 4.5, which ended at 2.5–7.0 depending on the reaction conditions. Buffer species were not used since they were expected to react easily with radicals produced and to interfere with the analysis of PFAS later. Temperature was kept at around 25 °C using cooling air flow around the reactor. A magnetic stirrer was used to agitate the reaction solution. The reactor was sealed using a clear ultra-thin plastic cover to prevent evaporation of PFAS solution during the experiment. UV lamp was located outside very close to the top of the sealed reactor. The reactor setup may have inhibited penetration of UV energy through the cover, in particular short wavelengths less than 260 nm, while some longer wavelengths penetrated well, which was proven by measuring light intensity using Ophir starlite energy meter (North Logan, UT).

In most cases, dissolved oxygen (DO) was not controlled at around 3.0 mg/L. Then, in order to determine the effect of DO or electron acceptor, air or nitrogen gas was purged into water to achieve oxygen-rich and oxygen-poor conditions at above 5.0 mg/L and below 1.0 mg/L, respectively. For experiments using 4.0 mM of OA as a hole scavenger, reaction solution was purged with nitrogen gas for 30 min to achieve oxygen-poor conditions in advance. Oxidants such as PS, bromate, hypochlorite, iodate, hydrogen peroxide, and reductants such as sulfite and iodide were added at 4.0 mM to investigate their effects on the photochemical decomposition of PFAS (Hori et al. 2004; Gu et al. 2017). Consequently, many combinatorial experiments were conducted with/without UV, TiO₂, DO, oxidant, reductant, and scavenger. At each time interval of 2, 6, 10, 24, and 48 h, aqueous sample of 800 μL was collected and filtered with 0.22 μm syringe. For some selected cases, especially with PFOA and PFOS, experiments were triplicated.

**Chemical analysis and TiO₂ characterization**

For liquid chromatography (LC) coupled with mass spectrophotometer (MS) analysis, samples were diluted 10 times. Potential interferences were removed by SPE techniques. Vacuum manifold was loaded with LMS Bond-Elut cartridges, which were conditioned by eluting 1 mL of methanol and then rinsed/equilibrated with 1 mL water. Then, 1 mL of the diluted sample was injected into the cartridge and passed through at a flow rate of 1 mL/min, which was needed to ensure that the target compound was completely adsorbed onto the cartridge. After loading the sample, the cartridge was rinsed with 1 mL water to remove any impurities that could interfere with analysis, and then PFAS were eluted from the sample matrix using 1 mL of methanol at a rate of 1 mL/min.

PFAS were analysed using a Shimadzu Nexera X2 LC (Nakagyo-ku, Kyoto, Japan) coupled with a Shimadzu 8040 triple quadrupole MS. Mobile phase was a mixture of LC/MS grade ACN with 0.1% formic acid and LC/MS grade water with 0.1% formic acid at a flow rate of 0.3 mL/min. Binary gradient was used where ACN contribution was increased from 30% to 90% over 6 min, held at 90% for 3 min, and ramped down back to 30% over 3 min. Separation was carried out using an Agilent Zorbax Eclipse C18 (50 mm × 3 mm × 1.8 μm particle size) column. Sample injection volume was 10 μL. Multiple reaction monitoring mode was used to identify and quantify PFAS and targeted byproducts formed during the reaction. Aquous fluoride ions detached from PFAS were measured by using a Hach (Loveland, CO) HQ 440D base combined with an Intellical ISE F121 electrode. Detection limit of fluoride ion measurement was at 0.002 mg/L.
A UV-visible light spectrophotometer (Shimadzu UV-1800, Kyoto, Japan) mounted with an integrating sphere attachment for diffuse reflectance measurement was used to investigate the optical bandgap of TiO$_2$. X-ray diffraction (XRD) analysis of TiO$_2$ using a Bruker D8 X-ray diffraction instrument (Billerica, MA) was employed to study the crystallographic properties of TiO$_2$. A Micromeritics Tristar 3,000 porosimeter analyser (Norcross, GA) was used to determine the structural characteristics of TiO$_2$. Particle size of TiO$_2$ (segregated particle size after extensive sonication) was measured using a Horiba SZ 100 nanosizer (Kyoto, Japan).

RESULTS AND DISCUSSION

In our preliminary experiments (note Figure S2), none of UVA, UVB, TiO$_2$/UVA, and TiO$_2$/UVB systems showed significant decomposition of PFAS (i.e., kinetically too slow) while only UVC and TiO$_2$/UVC exhibited certain decomposition of some PFAS, especially, long chain PFAS. According to the Planck-Einstein relation for photon energy, the photon energy is inversely proportional to wavelength. Use of UVC is beneficial to electron excitation and spatial charge separation, and most importantly, it can cause photolysis of organic chemicals to initiate their decomposition (Furube et al. 2001; Dong et al. 2015). This agrees with a previous study concluding that UVA and UVB absorption by PFOA in water was negligible, and thus UVC and vacuum UV were effective (Chen & Zhang 2006). Although TiO$_2$ under UVA, UVB, or UVC irradiation can generate various reactive species such as electrons, holes, and radicals, which might be potentially involved in PFAS decomposition, only TiO$_2$/UVC system worked. It can be explained by charge carrier dynamics and electron/hole recombination phenomena (Qian et al. 2019). As shown in Figure S2, TiO$_2$/UVC generally showed better performance (around 18% removal) than UVC alone (around 5% removal). Initial UVC photolysis of PFOA might have enhanced subsequent TiO$_2$ photocatalysis to synergistically decompose PFAS. As a result, UVC was used for the photolytic and photocatalytic decomposition of PFAS in this present study. Some selected experiments especially with PFOA and PFOS were triplicated to notice the reproducibility of experimental results.

Since the properties of P25 TiO$_2$ have been well documented, we briefly characterized it for confirmation purposes (Figure S3). It was a mixture of anatase (note the diffraction peaks at 25.2 and 48.1°) and rutile (27.4, 55.0, 62.6, and 68.8°) at around 7:3 ratio and its crystal size was around 27 nm, which are consistent with those reported elsewhere (Chen et al. 2016). Its UV absorption spectra spanned up to 379 nm, which is equivalent to bandgap energy of 3.27 eV (Yin et al. 2003). The surface area and pore volume of TiO$_2$ were 54 m$^2$/g and 0.173 cm$^3$/g, respectively. Mean size of completely segregated TiO$_2$ particles after use was measured at 47 $\pm$ 11 nm.

Adsorptive, photolytic, and photocatalytic removal of PFAS

Removal of PFAS via adsorption to TiO$_2$ and photolysis by UVC in comparison is shown in Figure 1(a) and 1(b), respectively (please also note Figure S4 for individual PFAS). Unlike typical adsorption behaviour of organic chemicals onto adsorbents, which is initial significant removal followed by quick equilibrium within several hours, adsorption of PFAS onto TiO$_2$ proceeded gradually even after 24 h (Figure 1(a)). The structural and electrical properties of TiO$_2$ may change over the time due to water absorption (Bredow & Jug 1995) and PFAS adsorption increases due to electrostatic interaction of anionic...
PFAS to positively charged TiO₂ surface under the tested pH condition (Qian et al. 2019). However, PFAS adsorption behaviour seems much more complex, involving initial covalent interactions and then hydrophobic attractions to form PFAS monolayer clusters followed by PFAS surfactant bilayers as reported elsewhere (Lawal & Choi 2018). PFAS removal by adsorption was 9–50% for PFCAs, 23–45% for PFSAs, 5% for 6:2 FTS, and 50% for GenX after 48 h. It should be noted that the reaction time can be significantly shortened when PFAS in real water samples is treated, since the concentration of PFAS used in this experiment was roughly 1,000 times higher than that found in the environment.

Adsorption tendency was in order of PFOS > PFHxS > PFBS > 6:2 FTS within sulfonic group and GenX > PFOA ≈ PFNA > PFHxS > PFBA within carboxylic group. Within similar alkyl chain length, PFSAs were removed faster than PFCAs (Zhao et al. 2014; Maimaiti et al. 2018). In general, adsorption process is driven by hydrophobic interaction between nonpolar tail of PFAS and hydrophobic site of adsorbents, implying that hydrophobic PFAS are beneficial to adsorption (Senevirathna 2010). The finding that long chain PFAS, except for PFNA, were removed better is supported by the fact that alkyl chains of typical PFAS are hydrophobic while their functional groups are hydrophilic, which makes long chain PFAS relatively more hydrophobic and less water-soluble than short chain PFAS (Deng et al. 2012).

Meanwhile, PFCAs exhibited photolysis under UVC to a certain extent (Figure 1(b)). Decomposition of PFOA and PFNA was achieved at around 15 and 68%, respectively, in 48 h. However, photolysis of PFSAs was negligible for 48 h. Typically, light energy can break down PFAS via direct photolysis if the photon energy (hν) provided is greater than the bond dissociation energy (BDE) of target PFAS. PFNA (C₈F₁₇COOH) as one of the long chain PFCAs was successfully photolysed into perfluoroalkyl (C₈F₁₇⁺) and carboxyl (−COOH) radicals (Equation (4)) under UVC. Then, C₈F₁₇⁺ radicals immediately react with water, transforming to shorter chain perfluorinated carboxylic acids (C₇F₁₅COOH) by losing one CF₂ unit in the chain (Equation (5)) (Jing et al. 2007).

\[
\text{C}_8\text{F}_{17}\text{COOH} + h\nu \rightarrow \text{C}_8\text{F}_{17}^+ + \text{COOH} \quad (4)
\]
\[
\text{C}_8\text{F}_{17}^+ + 2\text{H}_2\text{O} \rightarrow \text{C}_7\text{F}_{15}\text{COOH} + 2\text{F}^- + 3\text{H}^+ \quad (5)
\]

However, photolysis of PFSAs was negligible for 48 h. Photon energy required to break C-S bond between alkyl chain and head group in PFSAs is comparatively higher than that to break C-C bond in PFCAs (Rayne & Forest 2009). Thus, direct photolysis is ineffective for the decomposition of PFSAs under UVC to perfluoroalkyl radicals since PFSAs do not absorb wavelengths above 220 nm (Hori et al. 2004; Taniyasu et al. 2012). It was also reported that α-position C-F BDE of PFCAs are lower compared to that of PFSAs (Bentel et al. 2019). All 6:2 FTS, as a representative of polyfluoroalkyl substances with four C-H bonds vulnerable to chemical reactions, was removed, confirming that polyfluoroalkyl substances are more susceptible to photolysis than perfluoroalkyl substances (note that 6:2 FTS also contains sulfonic group). Consequently, photolytic decomposition of PFAS under UVC was found to rely on their alkyl chain length and functional group and the presence of C-H bonds.

Results of main photocatalytic experiments with TiO₂/UVC are shown in Figure 2(a). The observed removal of PFAS can be ascribed to adsorption, photolysis, and/or photocatalysis. Removal of PFAS by TiO₂/UVC, in particular long chain PFCAs and 6:2 FTS, was much enhanced compared to their removal by TiO₂ or UVC alone. Assuming first order removal kinetics, rate constants (k) were calculated and summarized in Table 1. For PFCAs, k was 0.0021–0.144 h⁻¹; for PFSAs, k was 0.0002–0.025 h⁻¹; for Gen X, k was 0.0105 h⁻¹; and for 6:2 FTS, k was 2.25 h⁻¹. Based on the removal rates observed in Figure 2(a), PFNA and 6:2 FTS removal does not seem to follow first order reaction kinetics.

In general, the polyfluoro one, 6:2 FTS, was removed much faster than perfluoro ones; longer chain PFAS were removed faster, e.g., PFNA > PFOA > PFHxA within PFCAs and PFOS > PFHxS > PFBS within PFSAs (Park et al. 2009; Qu et al. 2016); and PFOA as C₈ was removed faster than PFOS. Although poor adsorption of 6:2 FTS and PFNA to TiO₂ was observed, they were significantly removed by TiO₂/UVC in comparison to UVC only (note Figure S4) and LC/MS analysis proved significant chemical decomposition of those PFAS. Unlike a general expectation that adsorption-mediated decomposition of PFAS is beneficial to fast removal of PFAS, removal of GenX (50%) and short chain PFSAs (28–30%) by adsorption onto TiO₂ was slightly higher than photocatalysis for GenX (37%) and short chain PFSAs (2–10%) under TiO₂/UVC. 6:2 FTS and long chain PFCAs such as PFNA were removed mostly via chemical decomposition mechanism while GenX and PFSAs were removed mostly via physical adsorption mechanism. Short chain PFCAs could not be removed by TiO₂/UVC via either chemical decomposition or physical adsorption mechanism.
Effects of chain length and functional group

As shown in Figure 2(a), overall removal decreased in order of 6:2 FTS > PFNA > PFOS > GenX > PFHxS ≈ PFBA > PFBS. In general, PFSAs and short chain PFAS were removed much less. It can also be explained by Bentel and co-workers, who calculated BDE using density functional theory, proposing that the α-position C-F BDE for PFCAs and the primary and secondary C-F BDE for long chain PFAS are generally lower than their counterparts (Bentel et al. 2019). Even though both GenX and PFOA contain the same carboxylic head group, GenX (37% removal) was much more refractory than PFOA (95% removal) under the experimental conditions, most probably due to the presence of a hetero-atom in the middle of the alkyl chain of GenX (Bao et al. 2018). For similar chain length of PFNA vs. PFOS or PFOA vs. PFOS, removal rates were different because of the different functional groups. Carboxylic group was more vulnerable to attack by holes and HRs than sulfonic group. 6:2 FTS, a non-fully fluorinated one with 4 C-H bonds, was removed much faster than its homologue PFOS, a fully fluorinated one.

Figure 2(b) shows defluorination of PFAS by TiO2/UVC. Defluorination here describes detachment of fluorines caused by various reactions in a wide concept. Previous studies concluded that adsorption of fluoride ion onto TiO2 surface is not significant (Park & Choi 2004). As expected, defluorination of PFAS was much slower than their removal. Defluorination ranged at around 3.1–25.3% for PFCAs, 0–5.4% for PFSAs, 2.8% for GenX, and 10.8% for 6:2 FTS. PFCAs were defluorinated faster than PFSAs and defluorination increased with increase in their carbon chain length.

Evolution of reaction byproducts

Only in the cases showing significant defluorination, apparent reaction byproducts were observed. Figure 3 shows evolution of reaction byproducts simply found in the aqueous phase (also note Table S2). Shorter chain PFAS were formed as identifiable PFAS through the targeted LC/MS analysis. Under the tested conditions, short chain PFCAs with carbon number less than 5 were rarely identified. The longest PFNA (C9) was decomposed to PFOA (C8), PFHpA (C7), PFHxS (C6), and PFPeA (C5), which are all PFCAs. Similarly, decomposition of PFOA led to the formation of subsequent short chain PFCAs. Meanwhile, PFOS (C8) was decomposed to PFOA (C8) and other short chain PFCAs such as PFHpA (C7) (i.e., no short chain PFSAs), and 6:2 FTS (another sulfonic PFAS) was also decomposed to short chain PFCAs.

**Effects of chain length and functional group**

As shown in Figure 2(a), overall removal decreased in order of 6:2 FTS > PFNA > PFOA > PFOS > GenX > PFHxS ≈ PFBA > PFBS. In general, PFSAs and short chain PFAS were removed much less. It can also be explained by Bentel and co-workers, who calculated BDE using density functional theory, proposing that the α-position C-F BDE for PFCAs and the primary and secondary C-F BDE for long chain PFAS are generally lower than their counterparts (Bentel et al. 2019). Even though both GenX and PFOA contain the same carboxylic head group, GenX (37% removal) was much more refractory than PFOA (95% removal) under the experimental conditions, most probably due to the presence of a hetero-atom in the middle of the alkyl chain of GenX (Bao et al. 2018). For similar chain length of PFNA vs. PFOS or PFOA vs. PFOS, removal rates were different because of the different functional groups. Carboxylic group was more vulnerable to attack by holes and HRs than sulfonic group. 6:2 FTS, a non-fully fluorinated one with 4 C-H bonds, was removed much faster than its homologue PFOS, a fully fluorinated one.

Figure 2(b) shows defluorination of PFAS by TiO2/UVC. Defluorination here describes detachment of fluorines caused by various reactions in a wide concept. Previous studies concluded that adsorption of fluoride ion onto TiO2 surface is not significant (Park & Choi 2004). As expected, defluorination of PFAS was much slower than their removal. Defluorination ranged at around 3.1–25.3% for PFCAs, 0–5.4% for PFSAs, 2.8% for GenX, and 10.8% for 6:2 FTS. PFCAs were defluorinated faster than PFSAs and defluorination increased with increase in their carbon chain length.

**Table 1** First order removal rate constant (k) of PFAS by TiO2/UVC

| Group | PFCAs | PFSAs | Others |
|-------|-------|-------|--------|
| PFAS  | k(1/hr)|       |        |
| PFBA  | 0.0027 | 0.0002 | 0.0105 |
| PFHpA | 0.0021 | 0.0045 | 0.0252 |
| PFOA  | 0.063  | 0.0252 | 2.25   |
| PFNA  | 0.144  |        |        |
| PFBS  | 0.0045 |        |        |
| PFHxS | 0.0252 |        |        |
| PFOS  | 2.25   |        |        |

&nbnbspc=C0e−kt, where C0 is initial concentration (mg/L) at t=0, k is first order rate constant (1/h), and t is reaction time (h).
Previous studies also reported the formation of shorter chain PFCAs during decomposition of both PFCAs and PFSAs (Park et al. 2016; Gu et al. 2017).

Primary reactive species such as electrons, holes, and HRs are generated by TiO2/UVC (Equations (6) and (7)). Then, photocatalysis of PFAS, in particular PFCAs here, starts with ionization and formation of perfluoroalkyl anions (Equation (8)) which are oxidized to perfluoroperoxy radicals by holes (Equation (9)) (Dillert et al. 2007). The unstable perfluoroperoxy radicals undergo photo-Kolbe decarboxylation to form perfluoroalkyl radicals (Equation (10)) which are further oxidized to form one-CF2-shortened PFCA (Equation (11)) (Kutsuna & Hori 2007; Panchangam et al. 2009). This cycle repeats to form shorter chain PFCAs, and presumably, radicals generated such as HRs are also involved in the decomposition of PFCAs.

\[
\begin{align*}
\text{TiO}_2 + \text{hv} & \rightarrow e^- + h^+ \\
\text{h}^+ + \text{OH}^- & \rightarrow \text{HO}^* \\
\text{F(CF}_2\text{)_nCOOH} & \rightarrow \text{F(CF}_2\text{)_nCOO}^- + \text{H}^+ \\
\text{F(CF}_2\text{)_nCOO}^- + \text{h}^+ & \rightarrow \text{F(CF}_2\text{)_nCOO}^* \\
\text{F(CF}_2\text{)_nCOO}^* & \rightarrow \text{F(CF}_2\text{)_n}^* + \text{CO}_2 \\
\text{F(CF}_2\text{)_n}^* + \text{O}_2 & \rightarrow \text{F(CF}_2\text{)}_{n-1}\text{COO}^- + 2\text{F}^-
\end{align*}
\]

In Figure 3, the discrepancy between parent PFAS removed from the aqueous phase (10 mg/L of PFAS0 – PFASn) and total identifiable aqueous byproducts can be explained by various factors including mainly adsorption of PFAS and byproducts to TiO2 surface and partially and possibly presence of non-identifiable byproducts, complete mineralization, and loss due to formation of volatile byproducts (Parenky et al. 2020). Total identifiable byproducts explained nearly 40–50% of PFNA and 6:2 FTS completely removed in 48 h. Similarly, around 42% (4.2 mg/L) of removed PFOA in 48 h was turned into total identifiable byproducts and around 16% defluorination was observed. All these results implied significant photocatalytic decomposition of PFNA, 6:2 FTS, and PFOA. Meanwhile, significant removal of PFOS at 62% (from 10 mg/L to around
3.8 mg/L) was observed in 48 h while total identifiable aqueous byproducts (i.e., sum of C7–C8) accounted for only 2.7%. Among several reasons mentioned above, adsorption of PFOS to TiO2 surface was thus proposed to explain the observed PFOS removal, which was also supported by low defluorination at around 5.4%. Long chain byproducts were present at higher levels for the tested time frame, which confirms the stepwise decomposition of PFAS, in particular PFCAs and PFSAs, via the photo-Kolbe decarboxylation proposed in Equations (6) and (8)–(11), while decomposition of 6:2 FTS might have started at C-H bonds via hydrogen abstraction reaction. Definitely, however, accumulation of shorter chain byproducts, which are harder to decompose, is possible, requiring confirmation through further long-term experiments beyond 48 h.

Effects of electron and hole scavengers
In order to study the removal mechanisms of PFAS by TiO2/UVC, DO was controlled and OA was added as scavengers of photogenerated electrons and holes, respectively, as shown in Figure 4. DO levels were measured at above 5.0 mg/L for air purging and below 1.0 mg/L for N2 purging. DO significantly affected decomposition and defluorination of PFOA and PFOS. PFOA was removed at 99% in DO-rich condition in 48 h while it was removed only at around 60% in DO-poor condition. Similarly, 99% of PFOS removal was decreased to around 27%. In general, oxygen prevents recombination of photogenerated electrons and holes and accepts electrons in the conduction band of TiO2 to generate superoxide radical anions (O2–), which are strong reducing species and can be further protonated to form hydroperoxyl radical (HO2•) and subsequently H2O2 (Equation (12)) (Sansotera et al. 2015). Previous studies reported that reactive species such as O2– (redox potential E° = 0.53 V) and ‘OH (E° = 2.4 V) radicals are not so effective in decomposing PFAS (Maruthamuthu et al. 1995; Fujishima et al. 2000; Qiuying et al. 2019), and PFAS, in particular PFOA and PFOS, are present as fully oxidized. PFAS generally stay in an anionic form in water. Removal of PFAS via adsorption and/or decomposition was enhanced in DO-rich condition presumably because TiO2 surface becomes more positively charged when electrons are trapped by oxygen. Higher removal of PFOA and PFOS in DO-rich condition demonstrated greater defluorination. As expected, defluorination of PFOS was not significant at 5.8% and 2.6% in DO-rich and DO-poor conditions, respectively, proposing that adsorption of PFOS to TiO2 was the main mechanism for its removal, which was significantly influenced by DO level. High electron and hole

![Image](image.png)
recombination in DO-poor condition reduces net positive charge of TiO₂ surface, which may substantially reduce PFOS removal via adsorption mechanism.

\[
\begin{align*}
O_2 + e^- & \rightarrow O_2^- + \text{HO}_2^- + H_2O_2 \\
C_2O_2^- + h^+ & \rightarrow CO_2 + CO_2^-
\end{align*}
\]

(12) (13)

Meanwhile, holes in the valence band of TiO₂ were assumed to be one of the main oxidizing species. OA was added as a hole scavenger in DO-poor condition. OA significantly enhanced PFOA removal from 60% to 100% while it did not affect PFOS removal at around 26%. In general, OA quickly donates electrons to photogenerated holes, resulting in formation of CO₂ and carbonyl radical (CO₂⁺) in DO-poor condition (Equation (13)). This makes photogenerated electrons readily available for reaction with PFAS via reduction pathways. Previous work also indicated that carbonyl radicals, along with photogenerated electrons, induce quick PFOA decomposition (Wang & Zhang 2011).

Decomposition mechanism of PFOA by carbonyl radicals is possibly similar to that by SRs/hole in oxidation pathways, as shown in Equations (14)–(19), while PFOA is decomposed by photogenerated electrons (eaq) in reduction pathways, where α-position fluoride ions are eliminated, forming successively C₇F₁₄HCOOH (Equation (20)) and C₇F₁₃H₂COOH (Equation (21)). Then, C₆F₁₃ radicals, COOH radicals, and CH₂ carbene are generated from C₇F₁₃H₂COOH (Equation (22)). The reaction between C₆F₁₃ radicals and COOH radicals perhaps also occurs to form a shorter chain intermediate, C₆F₁₃COOH (Equation (23)), which is further degraded in the same manner. However, poor removal of PFOS in Figure 4(b) and its low defluorination in Figure 4(d) indicated that carbonyl radicals and conduction band electrons are not effective in decomposing PFOS. In addition, addition of OA can reduce net positive surface charge of TiO₂, resulting in less PFOS adsorption and thus rather less PFOS removal observed.

\[
\begin{align*}
F(CF_2)_n COO^- + SO_4^{2-} & \rightarrow F(CF_2)_n^* + CO_2 + SO_4^- \\
F(CF_2)_n^*COO^- + CO_2^- & \rightarrow F(CF_2)_nCOO^* + CO_2 \\
F(CF_2)_n COO^* & \rightarrow F(CF_2)_n^* + CO_2 \\
F(CF_2)_n^* + H_2O & \rightarrow F(CF_2)_n OH \\
F(CF_2)_n OH & \rightarrow F(CF_2)_n^-COF + H^+ + F^- \\
F(CF_2)_n^-COF + H_2O & \rightarrow F(CF_2)_n^-COOH + H^+ + F^- \\
C_7F_{15}COOH & \rightarrow C_6F_{13}^*COOH + H^+ + F^- \\
C_7F_{15}COOH & \rightarrow C_7F_{13}HCOOH + F^- \\
C_7F_{13}HCOOH & \rightarrow C_6F_{13}COOH + CH_2
\end{align*}
\]

(14) (15) (16) (17) (18) (19) (20) (21) (22) (23)

Holes also react with OH⁻ to yield HRs, which are strong oxidizing species. To confirm the effect of HRs on PFAS removal, HRs were generated by photolysis of H₂O₂ by UVC in the absence of TiO₂ (Equation (1)) (Liao & Gurol 1995). Removal of PFOA and PFOS under the condition was not different from that under only UVC, indicating that HRs alone generated from UVC/H₂O₂ were ineffective to decompose PFAS. Even UVC/TiO₂ was more effective than UVC/H₂O₂ (both systems commonly generate HRs), indicating that some photogenerated electrons and holes formed around TiO₂ surface may be directly involved in PFAS decomposition and TiO₂ surface-mediated reaction may exhibit better PFAS removal. All these results implied that prevention of the recombination of photogenerated electrons and holes is most important for PFAS removal and the secondary reactive species such as radicals work together with the primary reactive species such as electrons and holes.

**Effects of various oxidants and reductants**

Addition of oxidants can enhance PFAS decomposition by generating reactive species under UV radiation and later by preventing recombination of electrons and holes in TiO₂/UV system. As shown in Figure 5(a), PFOA was chosen as a
representative PFAS, and initially NaBrO₃, NaIO₄, H₂O₂, NaOCl, and Na₂S₂O₈ were selected as oxidants to produce bro-
mate, iodate, hydroxyl, hypochlorite, and sulfate radicals under UVC, respectively (Ravichandran et al. 2006). After 4 h,
PFOA removal was achieved at 0, 2, 5, 14, and 62% with NaBrO₃, NaIO₄, H₂O₂, NaOCl and Na₂S₂O₈, respectively, indicat-
ing that PS producing SRs was most ef
dicient. Meanwhile, previous studies on photolytic decomposition of PFAS reported
successful decomposition and defluorination of both PFCAs and PFSAs by using different reductants such as KI and
Na₂SO₃ (Park et al. 2009; Song et al. 2013). As shown in Figure 5(b), the presence of Na₂SO₃ under UVC greatly improved
PFOA removal, compared to KI.

Since PS was highly effective to remove PFOA, more detailed experiments were conducted to remove and de
fluorinate PFOA and PFOS, as shown in Figure 6. PS itself as an oxidant was not effective. In general, UV photolysis of PS produces
highly reactive SRs (Equation (2)). It is proposed that PFCAs are initially decomposed via decarboxylation reaction triggered
by SRs (Equation (14)) followed by HF elimination process as shown in Equations (17) and (18), which produces one-CF₂-
shortened perfluoroalkyl carboxylic acids (Equation (19)) in each step (Dogliotti & Hayon 1967). PS/UVC producing mostly
SRs was more effective to remove PFOA than TiO₂/UVC mostly producing HRs, and TiO₂/UVC/PS showed the best reac-
tivity for PFOA. TiO₂/UVC/PS is assumed to produce various radicals such as HRs and SRs. SRs are better species than HRs
for direct electron transfer reaction to decompose PFAS and reaction byproducts (Liang & Su 2009). Degree of PFOA
defluorination showed a very similar trend to that of PFOA removal. Continuous pH drop from 4.5 to 2.5 was observed in
case of TiO₂/UVC/PS, presumably resulting from formation of acidic byproducts. Meanwhile, PS/UVC was not effective
at all for PFOS removal while TiO₂/UVC showed comparable reactivity with PFOS to TiO₂/UVC/PS. The result indicated
that SRs are ineffective for PFOS. This finding obtained at pH 2.5–4.5 was not in agreement with a previous study reporting
that PFOS was decomposed faster than PFOA by PS/UV under adjusted pH 6–8 (Park et al. 2009). The result definitely
suggests a need of experiments under different and adjusted pH conditions. The presence of PS did not help PFOS
defluorination.

Then, removal of three PFCAs and three PFSAs with different chain lengths by TiO₂/UVC/PS was compared, as shown in
Figure 7. Removal of PFSAs was confirmed to be negligible while both long and short chain PFCAs were successfully
removed. Interestingly, short chain PFBA was removed faster than long chain PFOA and PFHpA in this TiO₂/UVC/PS case,
producing both HRs and SRs, while the opposite result was obtained in the previous experiment with TiO₂/UVC, pro-
ducing mainly HRs. Consequently, SRs (Equation (2)) along with HRs (Equation (7)) in TiO₂/UVC/PS seemed somehow to
play an important role in decomposing PFCAs, in particular short chain PFBA. Formation of short chain byproducts during
decomposition of PFOA by TiO₂/UVC/PS is shown in Figure 8. Decomposition mechanism of PFCAs by TiO₂/UVC/PS was
speculated to be very similar to that by TiO₂/UVC in Figure 3, i.e., gradual removal of CF₂ moieties and reformation of a
carboxylic functional group (Hori et al. 2004).

In comparison to addition of PS as an oxidant to TiO₂/UVC (Figure 8), sulfite as a reductant was introduced to TiO₂/UVC,
as shown in Figure 9. Sulfite itself was not effective to remove PFOA and PFOS. Sulfite/UVC was most effective, followed by
TiO₂/UVC/sulfite>TiO₂/UVC for PFOA and TiO₂/UVC>sulfite for PFOS. The observed decrease in the reactivity
of sulfite with PFAS in the presence of TiO₂ might be explained partially by quenching of sulfite-mediated hydrated

Figure 5 | Removal of PFOA by (a) oxidants and (b) reductants under UVC irradiation (10 mg/L PFOA, 4.0 mM oxidant or reductant, initial pH
4.5 to final pH 3.0–5.0 (no pH control), and temperature 25 °C). Please note the different time scales.
Figure 6 | Removal of (a) PFOA and (b) PFOS and defluorination of (c) PFOA and (d) PFOS by TiO₂/UVC in the presence of persulfate (PS) as sulfate radical generator (10 mg/L PFAS, 0.66 g/L TiO₂, 4.0 mM PS, initial pH 4.5 to final pH around 2.5 (no pH control), and temperature 25 °C).

Figure 7 | Removal of PFCAs and PFSAs by TiO₂/UVC/PS (10 mg/L PFAS, 0.66 g/L TiO₂, 4.0 mM PS, initial pH 4.5 to final pH around 2.5 (no pH control), and temperature 25 °C).

Figure 8 | Evolution of aqueous short chain byproducts formation during decomposition of PFOA by TiO₂/UVC/PS (10 mg/L PFAS, 0.66 g/L TiO₂, 4.0 mM PS, initial pH 4.5 to final pH around 2.5 (no pH control), and temperature 25 °C).
electrons by reactive species (h⁺) generated from TiO₂/UVC (Equation (24)). The reaction might lower the overall number of reactive species available for reaction with PFAS.

\[ h^+ + e^- \rightarrow \text{Heat} \]  

Interestingly, defluorination of both PFOA and PFOS was much more significant in cases of UVC/sulfite and TiO₂/UVC/sulfite, compared to TiO₂/UVC. Although PFOA was removed faster by UVC/sulfite than PFOS, defluorination of PFOS was marginally more significant. A previous study confirmed that sulfite radicals and hydrated electrons are produced (Equation (3)) via UV photolysis of sulfite (Fischer & Warneck 1996). Considering the absence of adsorptive removal of PFOA and PFOS in the UVC/sulfite system, hydrated electrons generated from sulfite activated by UVC should have played a significant role in decomposing PFOA and PFOS (Song et al. 2013), and the decomposition mechanism is similar to that by photogenerated electrons shown in Equations (20)–(23). Important PFAS removal kinetics by PS system and sulfite system are extracted and summarized in Figure S5. Sulfite system, either UVC/sulfite or TiO₂/UVC/sulfite, was marginally better than PS system for PFOA removal, while sulfite system, especially UVC/sulfite, was much better than PS system for PFOS removal. SRs generated from activation of PS by UVC (Equation (2)) were ineffective to decompose PFOS while hydrated electrons (eₗaq) produced from activation of sulfite by UVC (Equation (3)) defluorinated both PFOA and PFOS significantly at a rate of around 75 and 80%, respectively. Based on our observation and the literature, the decomposition mechanisms of PFCAs by different photocatalytic and photochemical methods are summarized in Figure 10. When prolonged time is given, the sulfite systems will have a high potential to achieve mineralization of PFAS.

**CONCLUSIONS**

In the TiO₂/UVC system, overall PFAS removal rate constant decreased in order of 6:2 FTS (2.25 h⁻¹) > PFNA (0.144) > PFOA (0.063) > PFOS (0.0252) > GenX (0.0105) > PFHxS (0.0045) > PFBA (0.0027) > PFHpA (0.0021) > PFBS (0.0002). A polyfluoroalkyl substance (6:2 FTS) was removed faster than perfluoroalkyl ones (PFOS). Longer chain PFAS were removed faster, e.g., PFNA > PFOA > PFHpA within PFCAs and PFOS > PFHxS > PFBS within PFSAs. PFOA was removed faster than PFOS. PFNA and 6:2 FTS were removed mostly via chemical decomposition mechanism while GenX and PFSAs were removed...
mostly via physical adsorption mechanism. Scavenger tests implied that electrons and holes are most important reactive species for PFAS removal in the TiO2/UV system. SRs generated by PS seemed to play a significant role in decomposing both long and short chain PFCAs while they were ineffective towards PFSAs. Hydrated electrons generated by sulfite/UVC decomposed both PFOA (100%) and PFOS (98%) with a significant defluorination at around 75 and 80%, respectively. Sulfite system (100%) was marginally better than PS system (95%) for PFOA removal while it was much better for PFOS removal (98% by sulfite and <5% by PS). Although it is hard to explain some of the observed results, overall susceptibility of PFAS to the chemical reactions could be explained by their properties and the reactivity of reactive species produced in each system. With a best-working and affordable system, more in-depth chemistry aspects of this study as well as engineering inquiries such as TiO2 property changes should be addressed in the near future. Perhaps, TiO2 should also be modified such as by doping to accommodate also decomposition of PFSAs. This comprehensive study on the dependency of photocatalytic and photochemical decomposition of PFAS on their properties would help to establish powerful destructive chemical approaches toward PFAS in water.

ACKNOWLEDGEMENTS

This research was supported mainly by the University of Texas at Arlington through Interdisciplinary Research Program and partially by the Department of Defense through the Strategic Environmental Research and Development Program (ER18-1482).

DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information. The data that support the findings of this study are available from the corresponding author upon reasonable request.
REFERENCES

Bao, Y., Deng, S., Jiang, X., Qu, Y., He, Y., Liu, L., Chai, Q., Mumtaz, M., Huang, J., Cagnetta, G. & Yu, G. 2018 Degradation of PFOA substitute: GenX (HFPO – DA ammonium salt): oxidation with UV/persulfate or reduction with UV/sulfite. Environ. Sci. Technol. 52 (20), 11728–11734. https://doi.org/10.1021/acs.est.8b02172.

Benford, D., Boer, D., Carrere, A., Domenico, D., Johansson, N., Schrenk, D., Schoeters, G., Voogt, D. & Dellelste, E. 2008 Opinion of the scientific panel on contaminants in the food chain on perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts. EFSA Journal 653, 1–131. https://doi.org/10.2903/j.efsa.2008.653.

Bentel, M. J., Yu, Y., Xu, L., Li, Z., Wong, B. M., Men, Y. & Liu, J. 2019 De
termination of short chain perfluorinated compounds (PFAS) in sediment and water matrices using liquid chromatography coupled with tandem mass spectrometry. Environ. Sci. Technol. 53 (7), 3718–3728. https://doi.org/10.1021/acs.est.8b06648.

Bredow, T. & Jug, K. 1995 Theoretical investigation of water adsorption at rutile and anatase surfaces. Surf. Sci. 327 (3), 398–408. https://doi.org/10.1016/0039-6028(94)00851-5.

Buck, R. C., Franklin, J., Berger, U., Conder, J. M., Cousins, I. T., Voogt, P. D., Jensen, A. A., Kannan, K., Mabury, S. A. & Leeuwen, S. P. V. 2011 Perfluoralkyl and polyfluoralkyl substances in the environment: terminology, classification, and origins. Integr. Environ. Assess. Manage. 7 (4), 513–541. https://doi.org/10.1002/ieam.258.

Cai, M. H., Zhao, Z., Yin, Z. G., Ahrens, L., Huang, P., Cai, M. G., Yang, H. Z., He, J. F., Sturm, R., Ebinghaus, R. & Xie, Z. Y. 2012 Occurrence of perfluoralkyl compounds in surface waters from the North Pacific to the Arctic Ocean. Environ. Sci. Technol. 46 (2), 661–668. https://doi.org/10.1021/es2026278.

Chen, J. & Zhang, P. 2006 Photodegradation of perfluorooctanoic acid in water under irradiation of 254 and 185 nm light by use of persulfate. Water Sci. Technol. 54 (11–12), 317–325. doi:10.2166/wst.2006.731.

Chen, M. J., Lo, S. L., Lee, Y. C. & Huang, C. C. 2015 Photocatalytic decomposition of perfluorooctanoic acid by transition-metal modified titanium dioxide. J. Hazard. Mater. 288, 168–175. https://doi.org/10.1016/j.jhazmat.2015.02.004.

Chen, M. J., Lo, S. L., Lee, Y. C., Kuo, J. & Wu, C. H. 2016 Decomposition of perfluorooctanoic acid by ultraviolet light irradiation with Pb-modified titanium dioxide. J. Hazard. Mater. 303, 111–118. https://doi.org/10.1016/j.jhazmat.2015.10.011.

Danish Ministry of the Environment 2015 Occurrence of perfluorinated chemicals and fetal growth: a study within the Danish National Birth Cohort, Environmental Project No. 1707. Available from: https://bladenonline.com/exposure-to-perfluorooctanoic-acid-and-fetal-growth-a-study-within-the-danish-national-birth-cohort-environmental-project-no-1707/

Deng, S., Zhang, Q., Nie, Y., Wei, H., Wang, B., Huang, J., Yu, G. & Xing, B. 2012 Sorption mechanisms of perfluorinated compounds on carbon nanotubes. Environ. Pollut. 168, 138–144. https://doi.org/10.1016/j.envpol.2012.03.048.

Dillert, R., Bahrenemann, D. & Hidaka, H. 2007 Light-induced degradation of perfluorocarboxylic acids in the presence of titanium dioxide. Chemosphere 67 (4), 785–792. https://doi.org/10.1016/j.chemosphere.2006.10.023.

Dogliotti, L. & Hayon, E. 1967 Flash photolysis of persulfate ions in aqueous solutions. Study of the sulfate and ozonide radical anions. J. Phys. Chem. 71 (8), 2511–2516. https://doi.org/10.1021/j100867a019.

Dong, H., Zeng, G., Tang, L., Fan, C., Zhang, C., He, X. & He, Y. 2015 An overview on limitations of TiO2-based particles for photocatalytic degradation of organic pollutants and the corresponding countermeasures. Water Res. 79, 128–146. https://doi.org/10.1016/j.watres.2015.04.038.

DuPont Marketing 2010 DuPont GenX Processing Aid for Making Fluoropolymer Resins. Available from: https://bladenonline.com/wpcontent/uploads/2016/07/Chemours_GenX_Brochure_Final_07July2010.pdf.

Fei, C., McLaughlin, J. K., Tarone, R. E. & Olsen, J. 2007 Perfluorinated chemicals and fetal growth: a study within the Danish National Birth Cohort. Environ. Health Perspect. 115, 1677–1682. https://doi.org/10.1289/ehp.10506.

Fischer, M. & Warneck, P. 1996 Photodecomposition and photooxidation of hydrogen sulfite in aqueous solution. J. Phys. Chem. 100 (57), 15111–15117. https://doi.org/10.1021/jp953236b.

Fujii, S., Tanaka, S., Lien, N. P. H., Qiu, Y. & Polpraseri, C. 2007 New POPs in the water environment: distribution, bioaccumulation and treatment of perfluorinated compounds – a review paper. J. Water Supply Res. Technol. AQUA 56 (5), 313–326. https://doi.org/10.2166/aqua.2007.005.

Fujishima, A., Rao, T. N. & Tryk, D. A. 2000 Titanium dioxide photocatalysis. J. Photochem. Photobiol. C: Photochem. Rev. 1 (1), 1–21. https://doi.org/10.1016/S1389-5567(00)00002-2.

Furube, A., Asahi, T., Masuhara, H., Yamashita, H. & Anpo, M. 2001 Direct observation of a picosecond charge separation process in photoexcited platinum loaded TiO2 particles by femtosecond diffuse reflectance spectroscopy. Chem. Phys. Lett. 336 (5–6), 424–430. https://doi.org/10.1016/S0009-2614(01)00128-2.

Gu, Y., Liu, T., Wang, H., Han, H. & Dong, W. 2017 Hydrated electron based decomposition of perfluorocarboxylate sulfonate (PFOS) in the VUV/sulfite system. Sci. Total Environ. 607–608, 541–548. https://doi.org/10.1016/j.scitotenv.2017.06.197.

Hoisaeter, A., Pfaff, A. & Breedveld, G. D. 2019 Leaching and transport of PFAS from aqueous film-forming foam (AFFF) in the unsaturated soil at a firefighting training facility under cold climatic conditions. J. Contam. Hydrol. 222, 112–122. https://doi.org/10.1016/j.jconhyd.2019.02.010.

Hori, H., Hayakawa, E., Einaga, H., Kutsuna, S., Koike, K., Ibusuki, T., Kiatahara, H. & Arakawa, R. 2004 Decomposition of environmentally persistent perfluorooctanoic acid in water by photochemical approaches. Environ. Sci. Technol. 38 (22), 6118–6124. https://doi.org/10.1021/es049719m.
Taniyasu, S., Yamashita, N., Yamazaki, E., Petrick, G. & Kannan, K. 2012 The environmental photolysis of perfluorooctane sulfonate, perfluorooctanoate, and related fluorochemicals. *Chemosphere* 90, 1686–1692. https://doi.org/10.1016/j.chemosphere.2012.09.065.

Trojanowicz, M., Bojanowska-Czajka, A., Bartosiewicz, I. & Kulisa, K. 2018 Advanced oxidation/reduction processes treatment for aqueous perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS): a review of recent advances. *Chem. Eng. J.* 336, 170–199. https://doi.org/10.1016/j.cej.2017.10.153.

US EPA 2017a *Risk Management for Per- and Polyfluoroalkyl Substances (PFASs) Under TSCA*. Available from: https://www.epa.gov/assessing-and-managing-chemicals-under-tscra/risk-management-and-polyfluoroalkyl-substances-pfas.

US EPA 2017b *Drinking Water Health Advisories for PFOA and PFOS*. Available from: https://www.epa.gov/ground-water-and-drinking-water/drinking-water-healthadvisoriespfoa-and-pfos.

Wang, Y. & Zhang, P. 2011 Photocatalytic decomposition of perfluorooctanoic acid (PFOA) by TiO2 in the presence of oxalic acid. *J. Hazard. Mater.* 192 (3), 1869–1875. https://doi.org/10.1016/j.jhazmat.2011.07.026.

Wang, Z., Cousins, I. T., Scheringer, M. & Hungerbuehler, K. 2015 Hazard assessment of fluorinated alternatives to long chain perfluoroalkyl acids (PFAAs) and their precursors: status quo, ongoing challenges and possible solutions. *Environ. Int.* 75, 172–179. https://doi.org/10.1016/j.envint.2014.11.013.

Wang, S., Yang, Q., Chen, F., Sun, J., Luo, K., Yao, F., Wang, X., Wang, D., Lia, X. & Zeng, G. 2017 Photocatalytic degradation of perfluorooctanoic acid and perfluorooctane sulfonate in water: a critical review. *Chem. Eng. J.* 328, 927–942. https://doi.org/10.1016/j.cej.2017.07.076.

Xiao, F. 2017 Emerging poly- and perfluoroalkyl substances in the aquatic environment: a review of current literature. *Water Res.* 124, 482–495. https://doi.org/10.1016/j.watres.2017.07.024.

Yin, S., Zhang, Q., Saito, F. & Sato, T. 2003 Preparation of visible light-activated titania photocatalyst by mechanochemical method. *Chem. Lett.* 32 (4), 358–359. https://doi.org/10.1246/cl.2003.358.

Zhao, L., Bian, J., Zhang, Y., Zhu, L. & Liu, Z. 2014 Comparison of the sorption behaviors and mechanisms of perfluoro sulfonates and perfluorocarboxylic acids on three kinds of clay minerals. *Chemosphere* 114, 51–58. https://doi.org/10.1016/j.chemosphere.2014.03.098.

First received 23 August 2021; accepted in revised form 9 October 2021. Available online 21 October 2021