보건학석사 학위논문

Reductive decomposition of perfluorooctanoic acid (PFOA) during VUV-based processes

VUV 기반 공정에서의 perfluorooctanoic acid (PFOA)의 환원적 분해

2023 년 2 월

서울대학교 보건대학원

환경보건학과 환경보건학전공

박 홍 주

Reductive decomposition of perfluorooctanoic acid (PFOA) during VUV-based processes

VUV 기반 공정에서의 **perfluorooctanoic acid (PFOA)**의 환원적 분해

지도 교수 조 경 덕

이 논문을 보건학석사 학위논문으로 제출함
2022 년 11 월

서울대학교 보건대학원
환경보건학과 환경보건학전공
박 홍 주

박홍주의 석사 학위논문을 인준함
2022 년 12 월

위 원 장 _____ 최 경 호 _____ (인)

부위원장 _____ 김 화 진 _____ (인)

위   원 _____ 조 경 덕 _____ (인)

Contents

List of Tables

List of Figures

Abstract

Reductive decomposition of perfluorooctanoic acid (PFOA) during VUV/sulfite/iodide process

Heungjoo Park

Department of Environmental Health Sciences

Graduate School of Public Health

Seoul National University

Because of its high stability and persistence, PFOA is not easily degraded in the water. Hydrated electrons (e_{aq}^-) are known as strong reducing agents that can remove recalcitrant PFOA through reductive decomposition. In this study, the efficient removal and defluorination of PFOA were confirmed using e_{aq}^-, and the removal and defluorination rates were compared in the vacuum ultraviolet (VUV) photolysis, VUV/sulfite, VUV/sulfite/iodide processes. In the VUV photolysis process, 88.6 % of PFOA is removed within 6 hr, and the removal rate constant for this is 0.007 min^{-1}. In the VUV/sulfite process, PFOA is all removed within 90 minutes, and the removal rate constant is 0.083 min^{-1}. In the VUV/sulfite/iodide process, PFOA is all removed within 30 minutes, and the removal rate constant is 0.230 min^{-1}. The defluorination rate for PFOA removal in VUV photolysis, VUV/sulfite, and VUV/sulfite/iodide process was 34.6 %, 72.7 %, and 73.9 % in 6 hr, respectively. Adding tert-butanol, NO_2^-, and NO_3^- as scavengers confirmed that e_{aq}^- can degrade

PFOA most efficiently and can cause defluorination because it has strong reducing power.

In the VUV photolysis process, short-chain perfluoroalkyl carboxylic acids (PFCAs) were mainly produced as transformation products (TPs) by chain shortening mechanism. In the VUV/sulfite and VUV/sulfite/iodide processes, it was confirmed that 16 and 15 TPs were found respectively and were mainly generated through the mechanism of H-F exchange (e.g. TP377, TP395), $SO_3^{\cdot-}$-F exchange (e.g. TP474), generation of an unsaturated compound (e.g. TP392, TP410, TP436), or hydration (e.g. TP393). Based on the results and TPs found in UPLC-QTOF/MS, PFOA degradation pathways are proposed in the VUV-based processes.

Keywords : PFOA, vacuum ultraviolet, sulfite, iodide, hydrated electron, defluorination

Student Number : 2021-23994

1.Introduction

1.1. Background

Perfluoroalkyl substances (PFASs) are a class of artificial compounds comprised of a perfluoroalkyl main chain, which has many C-F bonds, and a terminal functional group. Since the C-F bond is very strongly bound, PFASs are not easily degraded from the environment (Deng et al., 2021; Xu et al., 2015). Perfluorooctanoic acid (PFOA), a representative material among PFASs, exhibits properties such as heat resistance, chemical stability, surfactant properties and has been used in textiles products, fire-fighting foams, paper and packaging, and semiconductors (Esfahani, 2022).

Emission pathways for PFOA can be divided into direct sources released to nature from industrial and domestic environments, and indirect sources resulting from the transformation of several PFAS precursors, such as fluorotelomer alcohols (FTOHs) (Podder et al., 2021). Therefore, PFOA is frequently detected in water environments, mainly in surface water, groundwater, drinking water, and soil leachate (Busch et al., 2010; Houtz et al., 2013; Mak et al., 2009; So et al., 2007). Table 1 summarizes the previous papers that investigated the concentration of PFOA in the water from different countries.

Table 1. PFOA concentrations in the water from different countries

Country	Sampling location	PFOA concentration (ng/L)	Reference
China	Yellow River Estuary	0.96 – 14.15	(Cai et al., 2018)
China	Pearl River	0.7 - 18.7	(Cai et al., 2018)
China	Yangtze River	6.81 – 15.61	(Pan et al., 2014)
Germany	Elbe River	0.8 - 5.1	(Zhao et al., 2015)
Australia	Brisbane River	1.2 – 1.4	(Gallen et al., 2014)
Korea	Youngsan River Estuaries	1.3 – 3.6	(Hong et al., 2013)
Korea	Nakdong River Estuaries	11 - 23	(Hong et al., 2013)
Korea	Asan Lake	5.4 - 44	(Lee et al., 2020)

Because of its high stability and persistence, PFOA has even been detected in significant quantities in animal and humans and has clear toxicity. PFOA has an average half-life of 3.8 years and accumulates mainly in the liver, kidney, and serum (EFSA, 2008). PFOA has been known to be highly associated with diseases such as kidney cancer, testicular cancer, ulcerative colitis, thyroid disease, hypercholesterolemia, and pregnancy-induced hypertension (Nicole, 2013). Due to positive association between exposure to PFOA and cancers of the testis and kidney, the International Agency for Research on Cancer (IARC) classifies PFOA as possibly carcinogenic to humans (Group 2B) (IARC, 2016). In 2019, PFOA was classified as new persistent organic pollutants (POPs) at the Stockholm Conference, and the production and use of PFOA was discontinued (UNEP, 2019). The United States environmental protection agency (USEPA) set the health advisory level of PFOA in drinking water to 0.4 μg/L in 2009, PFOS and PFOA mixed to 70 ng/L in 2016, and PFOA to 0.004 ng/L in 2022 (USEPA, 2016, 2022a).

Table 2. Physicochemical properties of perfluorooctanoic acid (PFOA)

Chemical structure	
Molecular formula	$C_8HF_{15}O_2$
Molecular weight (g mol^{-1})	414.07
pK$_a$	-0.2
Log Kow	5.3
Solubility (g L^{-1}, 25°C)	3.4

Table 2 shows the structural formula and physicochemical properties of PFOA (Podder et al., 2021). PFOA is a fluorinated organic compound with a carboxyl group. Defluorination is a necessary process because it reduces the toxicity of PFOA by degrading PFOA while reducing the F of the C-F bond. Due to the stable bond of C-F due to the high electronegativity of F, PFOA is difficult to remove with the conventional water treatment processes (filtration, UV photolysis, etc.) (Arias Espana et al., 2015; Boonya-atichart et al., 2018; Chen et al., 2007). Advanced oxidation processes (AOPs) using hydroxyl radical (OH·) or sulfate radical ($SO_4^{\bullet-}$) a are also not effective for the removal of PFOA and defluorination (Cao et al., 2010; Chen & Zhang, 2006). Instead, since the C-F bond can be removed by a nucleophilic reaction, the defluorination rate can be increased through a reductive reaction with a reductive species such as a hydrated electron (e_{aq}^-). In previous papers, PFOA has been studied to be removed by reductive reactions (Cao et al., 2010; Chen et al., 2007; Giri et al., 2014; Gu et al., 2017b).

Advanced reductive processes (ARPs) are one of the emerging options for dealing with recalcitrant PFAS. ARPs represent a chemical degradation process by activating reducing free radicals to decompose contaminants in water. As reducing radicals, hydrated electrons (e_{aq}^-), hydrogen radicals (H·), sulfite radical anions ($SO_3^{\bullet-}$), sulfur dioxide radical anions ($SO_2^{\bullet-}$), and iodide (I^-) are used as reductive species.

Substances used as reducing agents typically sulfite and iodide. These two reducing agents generate hydrated electrons with high quantum yield while absorbing wavelengths below 200 nm (Eq. (1) and (2)) (Esfahani, 2022).

$$SO_3^{2-} + h\nu \rightarrow SO_3^{\bullet-} + e_{aq}^- \qquad (\Phi_{254/185nm} = 0.85) \qquad (1)$$

$$I^{-} + h\nu \rightarrow (I^{\cdot} + e^{-}) \rightarrow I^{\cdot} + e_{aq}^{-} \qquad (\Phi_{185nm} = 0.97) \qquad (2)$$

The produced hydrated electron is a strong reducing agent and is effective in removing organic compounds with halogen atoms. PFOA is difficult to remove through the ultraviolet C (UV-C) photolysis process, but it can be removed through the vacuum ultraviolet (VUV) process (Esfahani, 2022). In previous studies, direct VUV, VUV/iodide, UV/sulfite, and UV/iodide systems were used to remove PFOA by advanced reduction processes (ARPs) (Gu et al., 2017b). Compared to other studies, this study is expected to show efficient degradation and defluorination of PFOA, and it will be possible to suggest a pathway for PFOA degradation through the identification of various transformation products (TPs) using LC-QTOF/MS.

Unlike UV-C (254 nm), VUV process can generate hydrated electrons (e_{aq}^{-}) through the reaction of water ionization and homolysis at wavelengths below 200 nm (Eq. (3) and (4)) (Gu et al., 2017a).

$$H_2O + h\nu \ (185 \ nm) \rightarrow H\cdot + OH\cdot \qquad \text{Homolysis} \qquad (3)$$
$$H_2O + h\nu \ (185 \ nm) \rightarrow H^{+} + e_{aq}^{-} + OH\cdot \qquad \text{Ionization} \qquad (4)$$

The combined process of these two reducing agents (Eq. (1) and (2)) is expected to result in faster removal rate values.

1.2. Objectives

The purpose of this study is (1) to compare the removal rate, the kinetics constant, and defluorination of PFOA in the VUV photolysis and VUV/sulfite process, and VUV/sulfite/iodide process, (2) to examine the effects of change of various factors (pH, sulfite concentration, iodide concentration) on the removal rate of PFOA in VUV-based processes, (3) to confirm the contribution of reactive species (e_{aq}^-, OH·, H·) on the removal of PFOA by VUV-based processes, (4) to identify the transformation products (TPs) of PFOA and propose the degradation mechanism of the PFOA, (5) to evaluate the toxicity of PFOA and its TPs using the ecological structure activity relationships (ECOSAR) program.

2. Materials and methods

2.1. Chemicals

Ammonium acetate ($CH_3CO_2NH_4$, CAS No. 631-61-8), perfluorobutanoic acid ($C_4HF_7O_2$, PFBA, CAS No. 375-22-4), perfluoroheptanoic acid ($C_7HF_{13}O_2$, PFHpA, CAS No. 375-85-9), perfluorohexanoic acid ($C_6HF_{11}O_2$, PFHxA, CAS No. 307-24-4), perfluorooctanoic acid ($C_8HF_{15}O_2$, PFOA, CAS No. 335-67-1), perfluoropentanoic acid ($C_5HF_9O_2$, PFPeA, CAS No. 2706-90-3), perfluoropropionic acid ($C_3HF_5O_2$, PFPrA, CAS No. 422-64-0), potassium iodide (KI, CAS No. 7681-11-0), sodium acetate (CH_3COONa, CAS No. 127-09-3), sodium hydroxide (NaOH, CAS No. 1310-73-2), sodium nitrate ($NaNO_3$, CAS No. 7631-99-4), sodium nitrite ($NaNO_2$, CAS No. 7632-00-0), sodium phosphate dibasic (Na_2HPO_4, CAS No. 7558-79-4), sodium phosphate monobasic dihydrate ($NaH_2PO_4 \cdot 2H_2O$, CAS No. 13472-35-0), sodium sulfite (Na_2SO_3, CAS No. 7757-83-7), sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$, CAS No. 1303-96-4), sulfuric acid (H_2SO_4, CAS No. 7664-93-9), tert-butanol (($CH_3)_3COH$, tert-BuOH, CAS No. 75-65-0), and trifluoroacetic acid ($C_2HF_3O_2$, TFA, CAS No. 76-05-1) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Deionized water to prepare the solutions was generated by a Milli-Q Integral system (Merck & Co., Inc., Kenilworth, NJ, USA). Ultrapure nitrogen gas (N_2) was obtained from Daehangas (Gimpo, Korea) to purge oxygen in the reaction solution. LC-MS grade methanol was purchased from Thermo Fisher Scientific (Waltham, MA, USA), which was used as the mobile phase for liquid chromatography analysis.

2.2. Photo-degradation of PFOA

All experiments were conducted using a 2 L photoreactor equipped with three 6 W low-pressure VUV mercury lamp (185 nm/254 nm, Sankyo Electric Co., Tokyo, Japan) with a concentration of PFOA of 0.24 μM. Because the 2 L beaker did not have a water chilling system, the solution was gradually heated from about 20 to 36℃ in 180 min by the VUV lamp. A schematic diagram of the experiment was drawn in Fig. 1. The initial pH of the solution was adjusted to 10 with 5 mM tetraborate buffer and 1 M NaOH, 6 and 8 with 10 mM phosphate buffer and 1 M NaOH, and 4 with 10 mM with 10 Mm acetate buffer and 1 M H_2SO_4.

Fig. 1. Schematic diagram of the photochemical reactor

The solution was continuously purged with nitrogen with high purity of 99.99% during the reaction. Since hydrated electrons can be scavenged by oxygen present in water, oxygen is removed through nitrogen purging (Cao et al., 2022). The experiment was conducted for 180 min. Na_2SO_3 (0.8 ~ 12 mM) was used in the experiments to determine the concentration of sulfite. KI (0.04 ~ 1.6 mM) was used in the experiments to determine the concentration of iodide. To calculate the contribution rate of hydrated electrons, 1 mM tert-butanol, $NaNO_2$, and $NaNO_3$ as scavengers were used.

In the kinetic experiment comparing various conditions, the initial PFOA concentration was set to 0.24 µM. To confirm defluorination and clearly identifying TPs and the time-profile corresponding to each TP, the concentration of PFOA was increased to 24 µM.

2.3. Analytical methods

The concentration of PFOA and its TPs were analyzed by high-performance liquid chromatography (HPLC-MS/MS, Nexera, Shimadzu, Japan) - tandem mass spectrometer (API 4000, AB Sciex,USA) equipped with a Restek Raptor Polar X (2.1 mm x 50 mm, 2.7um) analytical column. The detailed analysis conditions were provided in Table 3.

To identify the organic transformation products (TPs) of PFOA during the VUV/sulfite/iodide reaction, ultra-performance liquid chromatography quadrupole time-of-flight mass spectrometry (UPLC-QTOF/MS) (Acquity UPLC Synapt G2-Si, Waters, USA) equipped with Waters Acquity UPLC C18 column (2.1 mm × 100 mm, 1.7 μm). The detailed analysis conditions were provided in Table 4. When analyzing by increasing the initial concentration of PFOA 100 times (24 μM), the analysis was performed by diluting 5 times.

An Orion Ionplus Sure-Flow Fluoride Electrode (Thermo Scientific, Waltham, MA, USA) was used for the analysis of fluoride ion (F⁻) concentration in the samples. Low-level total ionic strength adjustment buffer (Low-Level TISAB) is used for measurements on samples. When making a fluoride measurement, an equal amount of low-level TISAB is combined with the sample or standard. In this experiment, the fluoride measurement was conducted through low-level calibration using the millivolt (mV) mode. A low-level calibration curve was measured by setting the concentration of the fluoride standard to 0, 0.02, 0.04, 0.06, 0.1, 0.29, 0.48, 0.7, 0.91, 2, 3.33, 6.79, and 10 ppm. When making a fluoride measurement, a new calibration curve should be prepared with a new standard every day. The detection limit of fluoride electrode is 0.02 ppm.

Table 3. Analysis conditions of HPLC-MS/MS for the analysis of PFOA and short chain perfluoro carboxylic acids(PFCAs)

HPLC-MS/MS	HPLC	Column	Restek Raptor Polar X (2.1 mm x 50 mm, 2.7um)	
		Injection volume	10 μL	
		Flow rate	0.5 mL/min	
		Run time	8 min	
		Mobile phase	(A) 10 mM NH$_4$COOH, 0.05% formic acid in DIW	
			(B) 0.05% formic acid in 60:40 ACN:MeOH	
			Time (min)	%B
			0.00	85
			8.00	85
	MS/MS	Ionization mode	ESI negative	
		Curtain gas	20 psi	
		Collision gas	4 eV	
		IonSpray voltage	-4500 V	
		Source temperature	500 ℃	
		Ion source gas 1	50 psi	
		Ion source gas 2	50 psi	

Table 4. Analysis conditions of UPLC-QTOF/MS for the identification of TPs

UPLC-QTOF/MS	UPLC	Column	Waters, ACQUITY UPLC BEH C18 (2.1 × 100 mm, 1.7 μm)				
		Injection volume	10 μL				
		Flow rate	0.3 mL/min				
		Run time	10 min				
		Mobile phase	(A) 95:5 DIW:MeOH with 2 mM ammonium acetate (B) Methanol with 2 mM ammonium acetate				
			Time (min)	Flow (mL/min)	%A	%B	Curve
			0.0	0.3	100	0	-
			0.5	0.3	80	20	6
			3.0	0.3	55	45	6
			6.0	0.3	20	80	6
			7.0	0.3	5	95	6

			8.0	0.3	5	95	6
			9.0	0.3	100	0	1
			10.0	0.3	100	0	1
	MS/MS	Ionization mode	ESI negative				
		Acquisition range	50 – 1200 Da				
		Capillary voltage	1.5 kV				
		Cone voltage	40 V				
		Collision voltage	Low: 4 V / High: 20 – 70 V				
		Desolvation temperature	250 °C				
		Source temperature	100 °C				
		Desolvation gas flow	800 L/h				
		Cone gas	0 L/h				

2.4. Theoretical calculation methods for identifying reactive sites

Density functional theory (DFT) was calculated using the Gaussian 09 program (Frisch et al., 2016). Calculations were made for PFOA as well as for some TPs resulting from the removal of PFOA. Geometrical Optimization and vibrational frequency calculations of all compounds except for TP477 with iodide added was performed using B3LYP method by inputting the 6-311G+(d,p) basis set and the charge of each corresponding compound (Bao et al., 2018). In addition, empirical dispersion=gd3bj was additionally input to improve dispersion correction. Since TP477, which includes iodide, is outs of the orbital range of constituent atoms, the calculation was performed by changing to the basis set of LanL2DZ instead of the existing basis set of 6-311G. The solvent effect was also considered using the integral equation formalism polarizable continuum model (IEFPCM) in the water environment (Marenich et al., 2009).

To predict the reactive sites of PFOA and its TPs, the condensed Fukui function (f^+) was calculated and visualized using Multiwfn 3.8 software (Lu & Chen, 2012). At this time, Hirshfeld atomic charge, which was atomic population method based on deformation density partition, was applied.

2.5. Toxicity assessment

The acute and chronic toxicities of PFOA and its TPs on the fish, *daphnia*, and green algae were predicted through the ecological structure activity relationships (ECOSAR ver2.2) simulation program provided by US EPA. To evaluate the acute toxicity, lethal concentration 50 (LC_{50}) and effective concentration 50 (EC_{50}) values were used (LC_{50} at 96 hr for fish, LC_{50} at 48 hr for *daphnia*, and EC_{50} at 96 hr for green algae). And to evaluate the chronic toxicity, chronic value (ChV), which was defined as the geometric mean of the no observed effect concentration (NOEC) and lowest observed effect concentration (LOEC), was used (USEPA, 2022b).

3. Results and discussion

3.1. Degradation of PFOA in VUV-based processes

There have been several researches that conducted the experiments under VUV photolysis conditions to remove PFOA with hydrated electrons generated from VUV (Chen et al., 2007; Cheng et al., 2014; Liang et al., 2016; Wang & Zhang, 2014). However, there is a disadvantage that the removal time of PFOA is long. Therefore, in order to increase the efficiency of PFOA removal, an attempt was made to increase the generation of hydrated electrons by adding reducing agents (e.g. sulfite (SO_3^{2-}), iodide (I^-)).

Fig. 2. (a) Degradation of PFOA during UV photolysis, VUV photolysis, VUV/sulfite, VUV/sulfite/iodide treatment and (b) defluorination of PFOA during VUV photolysis, VUV/sulfite, VUV/sulfite/iodide treatment

([PFOA]$_0$ = 24 μM; [SO$_3^{2-}$]$_0$ = 2.4 mM; [I$^-$]$_0$ = 0.48 mM; pH 10 without buffer; VUV intensity$_{(254\ nm)}$ = 0.65 mW cm^2; N$_2$ purging; n = 2).

Table 5. Degradation rate constants and defluorination during VUV-based processes ([PFOA]$_0$ = 24 μM; [SO$_3^{2-}$]$_0$ = 2.4 mM; [I$^-$]$_0$ = 0.48 mM; pH 10 without buffer; VUV intensity$_{(254 \text{ nm})}$ = 0.65 mW cm^2; N$_2$ purging; n = 2)

Process	rate constant (k_{obs}, min^{-1})	Defluorination (%)
VUV photolysis process	0.007	34.61
VUV/sulfite process	0.083	72.73
VUV/sulfite/iodide process	0.230	73.90

Fig. 2. shows the degradation and defluorination rates of PFOA in the different processes at pH 10. PFOA was hardly removed under UV photolysis process (Fig. 2(a)). Approximately 88.6 % of PFOA was removed within 6 hours under VUV photolysis process. During VUV/sulfite process, while PFOA was completely removed within 90 min, it was completely removed within 30 min in VUV/sulfite/iodide process. The removal rate of PFOA significantly increased by approximately 2.75 times when a reducing agent was added (Table 6). In addition, while the defluorination rate for PFOA removal was only about 34.6 % in 6 hours in the VUV photolysis, about 72.7 % was defluorinated in 6 hours in VUV/sulfite process and 73.9 % of the defluorination in 6 hours in VUV/sulfite/iodide process were observed. The removal rate of PFOA was greatly improved in the VUV/sulfite/iodide process compared to the VUV/sulfite process, but the defluorination rate of PFOA did not significantly change. Through the results of the defluorination rate in Fig. 2(b), there is only steadily increasing defluorination in VUV photolysis process. However, in the VUV/sulfite and VUV/sulfite/iodide processes, it proceeds in two stages : rapid defluorination at the beginning, followed by formation of a saturation curve. This is expected because it exists in the form of other transformation products (TPs) and defluorination of other TPs does not occur or proceeds very slowly.

3.2. Effect of sulfite, iodide concentration on degradation of PFOA

Fig. 3. shows the data from experiments to determine the concentrations of sulfite and iodide added as reducing agents. As shown in Fig. 3(a), when the sulfite concentration was 2.4 mM, the removal rate constants of PFOA was the largest. As increasing sulfite concentration, the rate constant kept decreasing to 0.072 min^{-1} at 12 mM sulfite concentration because the sulfite self-quenching reaction can occur according to Eq. (5) and (6) (Fischer & Warneck, 1996).

$$SO_3^- + SO_3^- \rightarrow S_2O_6^{2-} \qquad (2k = 6.2 \times 10^8) \qquad (5)$$

$$e_{aq}^- + S_2O_6^{2-} \rightarrow SO_3^{2-} + SO_3^- \qquad (k \approx 2 \times 10^5) \qquad (6)$$

(a)

(b)

Fig. 3. (a) Effect of sulfite concentration on PFOA degradation in the VUV/sulfite treatment, (b) Effect of iodide concentration on PFOA degradation in the VUV/sulfite/iodide treatment

([PFOA]$_0$ = 0.24 μM; (b) [SO$_3^{2-}$]$_0$ = 2.4 mM; pH 10 with tetraborate buffer; VUV intensity$_{(254nm)}$ = 0.65 mW cm^2; N$_2$ purging; n = 2).

Iodide can generate e_{aq}^- and at the same time it can generate reactive iodine species (RIS) (e.g., $I\cdot$, I_2, $I_2^{\cdot-}$, and I_3^-) (Eq. (1),(7)-(10)) (Qu et al., 2010).

$$I\cdot + I^- \rightarrow I_2^{\cdot-} \tag{7}$$

$$I\cdot + I\cdot \rightarrow I_2 \tag{8}$$

$$2I_2^{\cdot-} \rightarrow I^- + I_3^- \tag{9}$$

$$I^- + I_2 \rightarrow I_3^- \tag{10}$$

$$e_{aq}^- + I_2 \rightarrow I_2^{\cdot-} \qquad (k = 5.3 \times 10^{10}\ M^{-1}\ s^{-1}) \tag{11}$$

$$e_{aq}^- + I_2^{\cdot-} \rightarrow 2I^- \qquad (k = 9.0 \times 10^{10}\ M^{-1}\ s^{-1}) \tag{12}$$

$$e_{aq}^- + I_3^- \rightarrow I^- + I_2^{\cdot-} \qquad (k = 3.5 \times 10^{10}\ M^{-1}\ s^{-1}) \tag{13}$$

Since RIS scavenges e_{aq}^-, the removal efficiency of PFOA is expected to be reduced (Eq. (11)-(13)).

Fig. 4. Degradation of PFOA in the VUV/sulfite, VUV/iodide, VUV/sulfite/iodide processes

([PFOA]$_0$ = 0.24 μM; [SO$_3^{2-}$]$_0$ = 2.4 mM; [I$^-$]$_0$ = 0.48 mM; pH 10 with tetraborate buffer; VUV intensity$_{(254nm)}$ = 0.65 mW cm^2; N$_2$ purging; n = 2)

Fig. 4 presents the degradation of PFOA during VUV/sulfite, VUV/iodide, and VUV/sulfite/iodide processes. It was confirmed that the VUV/sulfite/iodide process showed a synergistic effect. The removal of PFOA was much faster than the VUV/sulfite and VUV/iodide processes.

To improve the disadvantage of iodide, if sulfite, another reducing agent, is added together, RIS can be scavenged by sulfite, thus the generation efficiency of e_{aq}^- can be increased (Eq. (14)-(22)) (Yu et al., 2018).

$$I\cdot + SO_3^{2-} \rightarrow I^- + SO_3^{\cdot-} \qquad (k = 1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}) \qquad (14)$$

$$I\cdot + HSO_3^- \rightarrow I^- + H^+ + SO_3^{\cdot-} \qquad (k = 6.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}) \qquad (15)$$

$$I_2^{\cdot-} + SO_3^{2-} \rightarrow 2I^- + SO_3^{\cdot-} \qquad (k = 1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}) \qquad (16)$$

$$I_2^{\cdot-} + HSO_3^- \rightarrow 2I^- + H^+ + SO_3^{\cdot-} \qquad (k = 1.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}) \qquad (17)$$

$$I_3^- + SO_3^{2-} \rightarrow 2I^- + ISO_3^{\cdot-} \qquad (k = 2.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}) \qquad (18)$$

$$I_3^- + HSO_3^- \rightarrow 2I^- + H^+ + SO_3^{\cdot-} \qquad (k = 1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}) \qquad (19)$$

$$I_2 + SO_3^{2-} \rightarrow ISO_3^- + I^- \qquad (k = 3.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}) \qquad (20)$$

$$I_2 + HSO_3^- \rightarrow ISO_3^- + I^- + H^+ \qquad (k = 1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}) \qquad (21)$$

$$ISO_3^- + H_2O \rightarrow SO_4^{2-} + I^- + 2H^+ \qquad (k = 8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}) \qquad (22)$$

As with sulfite, Fig. 3(b). showed that the concentration of iodide with the greatest increased in the rate constant when the iodide concentration is 0.48 mM during VUV/sulfite/iodide process. When the iodide was 0.48 mM or more, there was no significant difference in the PFOA removal rate constant. Therefore, the experiment was conducted at 0.48 mM iodide.

Since the amount of RIS increases as the iodide concentration increases, it can be confirmed that there is no significant change in the rate constant. Therefore,

according to the above results, sulfite not only generates hydrated electrons through VUV, but also can efficiently increase hydrated electrons generated from iodide by reducing RIS.

3.3. Effect of pH

Fig. 5 showed the removal rate constant of PFOA under different pH conditions for each VUV-based process. In the VUV photolysis process, the rate constants are not significantly different except for pH 4, which is a strong acid condition. In Eq. (23) (Gu et al., 2017a), the removal rate constant of PFOA in the VUV photolysis was lower because H^+ can quench the produced hydrated electrons in acidic conditions.

$$H^+ + e_{aq}^- \rightarrow H\cdot \qquad (k = 2.3 \text{ x } 10^{10} \text{ M}^{-1} \text{ s}^{-1}) \qquad (23)$$

Fig. 5. The effect of different pH on degradation of PFOA in the VUV photolysis, VUV/sulfite, VUV/sulfite/iodide treatment

([PFOA]$_0$ = 0.24 μM; pH 4 with acetate buffer, pH 6 and 8 with phosphate buffer, pH 10 with tetraborate buffer; VUV intensity$_{(254nm)}$ = 0.65 mW cm^2; N$_2$ purging; n = 2).

In the VUV/sulfite process, it can be confirmed that the rate constant is the largest in alkaline conditions. Referring to the previous paper (Esfahani, 2022), since the mole fraction of sulfur species in the sulfur distribution is different for each pH, hydrogen sulfite (HSO_3^-), which exists as the largest mole fraction under acidic conditions, does not generate hydrated electrons even when photodecomposed. HSO_3^- undergoes photodecomposition to generate SO_3^- radical ($SO_3^{\cdot-}$) (Fig. 6) (Eq. (24)) (Fischer & Warneck, 1996).

$$HSO_3^- + h\nu \rightarrow SO_3^{\cdot-} + H\cdot \qquad (24)$$

Therefore, the experiments during VUV/sulfite process were conducted under alkaline conditions with the maximum mole fraction of sulfite to improve the generation of hydrated electrons (Eq. (1)) (Fig. 6).

PFOA removal was larger in alkaline conditions than acidic or neutral conditions probably because the generation of hydrated electrons increased through the reaction of H· and OH^- in alkaline conditions by Eq. (25) (Gu et al., 2017a),.

$$H\cdot + OH^- \rightarrow e_{aq}^- + H_2O \qquad (k = 2.2 \times 10^7 \ M^{-1} \ s^{-1}) \qquad (25)$$

Fig. 6. The mole fraction of S(IV) species distribution in a solution as a function of pH

3.4. The roles of reactive species in PFOA degradation

As mentioned previously, PFOA is better removed by ARPs than AOPs. Through experiments with the addition of radical scavengers, the contribution of the reductive species was confirmed by comparing the PFOA removal rates of hydrated electrons and hydrogen radicals, which are generated in VUV-based processes.

Fig. 7. The inhibitory effects of different radical scavengers on the degradation of PFOA in the VUV photolysis, VUV/sulfite, VUV/sulfite/iodide treatment ($[PFOA]_0 = 0.24$ μM; $[SO_3^{2-}]_0 = 2.4$ mM; $[I^-]_0 = 0.48$ mM; pH 10 with tetraborate buffer; VUV intensity$_{(254nm)} = 0.65$ mW cm^2; N$_2$ purging; n = 2).

As shown in Fig. 7. an experiment was conducted to confirm the roles of reactive species when PFOA was removed by each process by adding radical scavengers such as tert-butanol (t-BuOH), NO_2^-, and NO_3^-.

t-BuOH is known as a strong scavenger for hydroxyl radical (HO·) (Eq. (26)). At the same time, t-BuOH can also scavenge e_{aq}^- or H·, but the effect is negligible because the k value is very small (Eq. (27) and (28)) (Wu et al., 2020).

$$(CH_3)_3COH + \cdot OH \rightarrow H_2O + \cdot CH_2(CH_3)_2COH$$

$(k = 6.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})$ \hfill (26)

$$(CH_3)_3COH + H\cdot \rightarrow H_2 + \cdot CH_2(CH_3)_2COH$$

$(k = 1.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1})$ \hfill (27)

$$(CH_3)_3COH + e_{aq}^- \rightarrow [(CH_3)_3COH]^-$$

$(k = 4.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1})$ \hfill (28)

Since the quantum yield of ·OH generated through the ionization of H_2O is low (Esfahani, 2022), there is no significant difference in the rate constant even when t-BuOH was added in the VUV photolysis, VUV/sulfite, VUV/sulfite/iodide processes.

On the other hand, since NO_2^- and NO_3^- ions can effectively scavenge e_{aq}^-, the degradation rate constants of PFOA with NO_2^- or NO_3^- showed a remarkably lower value than that of PFOA without NO_2^- or NO_3^- (Eq. (29) and (32)). Especially, NO_3^- can more effectively inhibit the removal of PFOA by hydrated electrons more than NO_2^- because the k value on the reaction between NO_3^- and e_{aq}^- is twice as fast as that between NO_2^- and e_{aq}^-.

$NO_2^- + e_{aq}^- \rightarrow (\cdot NO_2)^{2-}$ \qquad $(k = 4.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ \hfill (29)

$NO_2^- + H\cdot \rightarrow NO\cdot + OH^-$ \qquad $(k = 7.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})$ \hfill (30)

$NO_2^- + HO\cdot \rightarrow NO_2\cdot + OH^-$ $(k = 0.6\text{-}1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})$ (31)

$NO_3^- + e_{aq}^- \rightarrow (\cdot NO_3)^{2-}$ $(k = 9.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$ (32)

$NO_3^- + H\cdot \rightarrow (NO_3H\cdot)^-$ $(k = 1.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1})$ (33)

3.5. Degradation pathways and mechanism in VUV-based processes

Prior to the experiment, the condensed Fukui function of PFOA was calculated using Gaussian 09 and Multiwfn 3.8 program to find theoretical reactive sites and to predict how TPs would be produced. Among the calculated values, the f^+ value indicates the position of an atom capable of undergoing a nucleophilic reaction based on the calculated electron density. The higher the f^+ value, the better the nucleophilic reaction, which means that ARPs can easily occur through hydrated electrons or hydrogen radicals (Oláh et al., 2002). Comparing the visualized data and data of the condensed Fukui function of TP392 as a representative of TPs with PFOA (Fig. 8, Table 7.), it can be confirmed that PFOA has more sites for nucleophilic reactions and ARPs occur more easily. On the other hand, TP392 is a TP with a sulfite group and a double bond. The nucleophilic reaction of TP392 does not occur well except for the carbons of the double bond, which are a position where a nucleophilic reaction can occur, so the removal of TP392 in VUV/sulfite and VUV/sulfite/iodide processes is expected to be slow.

Fig. 8. The prediction of the most reactive reaction site by calculating the condensed Fukui function of (a) PFOA (b) TP392

Table 6. Hirshfeld charge and condensed Fukui function of (a) PFOA, (b) TP392

(a) PFOA

Atom	q(N+1)	q(N)	q(N-1)	f^+	f^-	f^0	Δf
C(1)	0.2387	0.2674	0.2678	0.0288	0.0004	0.0146	0.0283
C(2)	0.1221	0.1686	0.1692	0.0465	0.0006	0.0235	0.0459
C(3)	0.1166	0.1713	0.1724	0.0547	0.0011	0.0279	0.0536
C(4)	0.1134	0.1703	0.1724	0.0569	0.0021	0.0295	0.0548
C(5)	0.1186	0.1687	0.1727	0.0501	0.0040	0.0270	0.0461
C(6)	0.1319	0.1663	0.1726	0.0344	0.0063	0.0203	0.0281
C(7)	0.1238	0.1513	0.1760	0.0275	0.0247	0.0261	0.0028
C(8)	0.0545	0.0842	0.2144	0.0297	0.1302	0.0799	-0.1005
O(9)	-0.4762	-0.4427	-0.1084	0.0335	0.3343	0.1839	-0.3008
O(10)	-0.4773	-0.4398	-0.0749	0.0375	0.3649	0.2012	-0.3275
F(11)	-0.1098	-0.0881	-0.0877	0.0217	0.0004	0.0111	0.0213
F(12)	-0.1222	-0.0879	-0.0872	0.0343	0.0007	0.0175	0.0336
F(13)	-0.1140	-0.0881	-0.0877	0.0259	0.0004	0.0132	0.0255
F(14)	-0.1527	-0.0881	-0.0874	0.0645	0.0008	0.0326	0.0638
F(15)	-0.1220	-0.0890	-0.0882	0.0330	0.0009	0.0169	0.0321
F(16)	-0.1286	-0.0887	-0.0871	0.0400	0.0016	0.0208	0.0384
F(17)	-0.1527	-0.0888	-0.0873	0.0639	0.0015	0.0327	0.0624

F(18)	-0.1367	-0.0906	-0.0874	0.0461	0.0032	0.0247	0.0429
F(19)	-0.1497	-0.0903	-0.0874	0.0594	0.0029	0.0311	0.0565
F(20)	-0.1408	-0.0946	-0.0885	0.0462	0.0061	0.0261	0.0402
F(21)	-0.1430	-0.0952	-0.0888	0.0478	0.0064	0.0271	0.0414
F(22)	-0.1380	-0.1037	-0.0883	0.0343	0.0154	0.0248	0.0190
F(23)	-0.1314	-0.1026	-0.0892	0.0289	0.0134	0.0211	0.0155
F(24)	-0.1597	-0.1356	-0.0978	0.0242	0.0378	0.0310	-0.0136
F(25)	-0.1647	-0.1344	-0.0943	0.0304	0.0400	0.0352	-0.0097

(b) TP392

Atom	q(N+1)	q(N)	q(N-1)	f^+	f^-	f^0	Δf
C(1)	0.2592	0.2673	0.2678	0.0081	0.0004	0.0043	0.0077
C(2)	0.1548	0.1682	0.1688	0.0134	0.0006	0.0070	0.0128
C(3)	0.1493	0.1716	0.1728	0.0222	0.0012	0.0117	0.0210
C(4)	0.1403	0.1707	0.1730	0.0305	0.0023	0.0164	0.0282
F(5)	-0.1237	-0.0854	-0.0780	0.0383	0.0074	0.0229	0.0309
F(6)	-0.1696	-0.1081	-0.0984	0.0614	0.0097	0.0356	0.0517
F(7)	-0.1214	-0.0915	-0.0881	0.0299	0.0035	0.0167	0.0264
F(8)	-0.1169	-0.0924	-0.0890	0.0245	0.0034	0.0139	0.0211
F(9)	-0.1087	-0.0902	-0.0886	0.0185	0.0017	0.0101	0.0168
F(10)	-0.1037	-0.0887	-0.0879	0.0150	0.0008	0.0079	0.0143
F(11)	-0.1013	-0.0896	-0.0887	0.0117	0.0009	0.0063	0.0108
F(12)	-0.0952	-0.0885	-0.0880	0.0068	0.0004	0.0036	0.0063
F(13)	-0.0957	-0.0884	-0.0879	0.0074	0.0005	0.0039	0.0069
F(14)	-0.0990	-0.0884	-0.0877	0.0105	0.0007	0.0056	0.0098
F(15)	-0.1144	-0.0898	-0.0882	0.0245	0.0017	0.0131	0.0229
C(16)	0.1280	0.1797	0.1868	0.0517	0.0070	0.0294	0.0446
C(17)	-0.0607	0.0643	0.0963	0.1250	0.0320	0.0785	0.0931
C(18)	-0.2285	-0.0708	-0.0536	0.1577	0.0173	0.0875	0.1404

H(19)	-0.0008	0.0624	0.0825	0.0632	0.0201	0.0416	0.0431
S(20)	0.3571	0.4156	0.5463	0.0585	0.1307	0.0946	-0.0722
O(21)	-0.5014	-0.4470	-0.1961	0.0544	0.2509	0.1527	-0.1966
O(22)	-0.4799	-0.4390	-0.2037	0.0408	0.2354	0.1381	-0.1945
O(23)	-0.5081	-0.4469	-0.1972	0.0613	0.2496	0.1555	-0.1884
F(24)	-0.1598	-0.0951	-0.0733	0.0647	0.0218	0.0432	0.0429

Fig. 9 showed the changes in F species during VUV photolysis, VUV/sulfite, and VUV/sulfite/iodide processes. During VUV photolysis, short chain perfluoro carboxylic acids (PFCAs) such as PFHpA, PFHxA, and PFPeA were produced as TPs by LC-QTOF/MS (Fig. 10). As described in Chapter 3.1., defluorination in the VUV/sulfite and VUV/sulfite/iodide processes showed an initial rapid defluorination, followed by formation of a saturation curve.

Through the results in Fig. 9, in the VUV photolysis process, short chain PFCAs were generated as TPs of PFOA removal. In the VUV/sulfite and VUV/sulfite/iodide processes, other TPs were generated more than short chain PFCAs. Hydrated electrons are generated more and faster in the VUV/sulfite and VUV/sulfite/iodide processes than in the VUV photolysis process, and it can be expected that short chain PFCAs are quickly generated and removed and various TPs including sulfite and iodide are generated. In addition, in the defluorination of the VUV/sulfite and VUV/sulfite/iodide processes, others increase and then decrease, indicating that defluorination increases as various TPs including sulfite and iodide are removed again.

Fig. 9. Mass balance of fluorine on degradation of PFOA during (a) VUV photolysis (b) VUV/sulfite (c)VUV/sulfite/iodide treatment

([PFOA]$_0$ = 24 μM; [SO$_3^{2-}$]$_0$ = 2.4 mM; [I$^-$]$_0$ = 0.48 mM; pH 10 without buffer; VUV intensity$_{(254nm)}$ = 0.65 mW cm^2; N$_2$ purging; n = 2).

Fig. 10. Time-profiles of TPs on the degradation of PFOA during VUV photolysis treatment using LC-QTOF/MS

([PFOA]$_0$ = 24 μM; pH 10 without buffer; VUV intensity$_{(254nm)}$ = 0.65 mW cm^2; N$_2$ purging; n=2).

As a result, based on the above data and TPs detected by UPLC-QTOF/MS, the pathways of PFOA reductive decomposition in the VUV photolysis, VUV/sulfite, and VUV/sulfite/iodide processes were proposed in Fig. 12.

Two mechanisms during VUV-based process have been reported: decarboxylation-hydroxylation-elimination-hydrolysis (DHEH, chain shortening) and H/F exchange (Bentel et al., 2019; Cui et al., 2020; Fennell et al., 2022). Existing TPs pathways by degradation of PFOA have been extensively studied (Deng et al., 2021; Qu et al., 2010). In addition to the TPs generated through the above two mechanisms, there were also papers that presented TPs generated by the reaction between PFOA and sulfite radicals (Ren et al., 2021; Song et al., 2013).

First, defluorination occurred as sequential chain-shortening (DHEH) occurred, as short-chain PFCAs increased over time in the VUV photolysis process (Fig. 9(a), Fig. 10). Considering only about 35 % defluorination, the result indicates that the short chain PFCAs produced through the removal of PFOA are predicted to be less likely to be removed than PFOA during VUV-based processes.

Next, unlike in the VUV photolysis process, in the VUV/sulfite and VUV/sulfite/iodide processes, the production of other TPs accounts for a larger proportion than short-chain PFCAs. These two processes have in common that hydrated electrons are effectively generated and the degradation reaction of PFOA proceeds quickly. Fig. 11 presented the time-profile of TPs generated by the removal of PFOA in the VUV/sulfite and VUV/sulfite/iodide processes. In Fig. 11(a) and (b), various TPs were observed, indicating that the reaction of H-F exchange, $SO_3^{\cdot-}$-F exchange, generation of an unsaturated compound by defluorination, or the formation of hydrogen and hydroxyl group by hydration reaction. Through these mechanisms, four TPs (TP438, TP470, TP477, and TP497), which were not

44

identified in previous papers, were newly identified in this study. Fig. 11 also showed that the decomposition of not only PFOA, but also its TPs proceeded. In addition, approximately 73 and 74% of defluorination occurred in the VUV/sulfite and VUV/sulfite/iodide processes, respectively (Fig. 9(b) and 9(c)). These results imply that H-F exchange, SO_3^--F exchange, generation of unsaturated compounds, and hydration are considered to be major reactions in the VUV/sulfite and VUV/sulfite/iodide processes. In addition, we expect that other TPs are more effectively degraded than short-chain PFCAs, with higher defluorination rates in the VUV/sulfite and VUV/sulfite/iodide processes.

(a)

Fig. 11. Time-profiles of TPs on the degradation of PFOA during (a) VUV/sulfite treatment (b)VUV/sulfite/iodide treatment using LC-QTOF/MS ((a) $[PFOA]_0$ = 24 μM; $[SO_3^{2-}]_0$ = 2.4 mM / (b) $[PFOA]_0$ = 24 μM; $[SO_3^{2-}]_0$ = 2.4 mM; $[I^-]_0$ = 0.48 mM; pH 10 without buffer; VUV intensity$_{(254nm)}$ = 0.65 mW cm^2; N_2 purging; n=2).

47

Fig. 12. Proposed major pathways on the degradation of PFOA in the VUV photolysis, VUV/sulfite, VUV/sulfite/iodide treatment ([PFOA]$_0$ = 24 μM; [SO$_3^{2-}$]$_0$ = 2.4 mM; [I$^-$]$_0$ = 0.48 mM; pH 10 without buffer; VUV intensity$_{(254nm)}$ = 0.65 mW cm^2; N$_2$ purging; n = 2).

3.6. Toxicity evaluation of PFOA and its TPs

The predicted toxicity of PFOA and its TPs was evaluated using ECOSAR (Table 8). ECOSAR is a computerized predictive system that estimates aquatic toxicity. According to the classification of toxicity classes (Table S2), PFOA was classified as toxic for *daphnia* and harmful for fish and green algae for acute toxicity. For chronic toxicity, fish, *daphnia*, and green algae were classified as toxic. The toxicity of all TPs generated from the degradation of PFOA through VUV-based processes was also confirmed through ECOSAR. The toxicity of all TPs except for TP477 was lower than that of PFOA, and most of the TPs were classified as not harmful. However, TP477 is the only TP containing iodide, and it was confirmed that it exhibits higher toxicity than PFOA because of the toxicity of iodide.

The iodine bound to the TP can react with the hydrated electrons to form a perfluoroalkyl radical and iodide (Park et al., 2009). Although the toxicity of TP477 is higher than that of PFOA, TP477 can be decomposed into iodide and perfluoroalkyl radical by hydrated electrons. The iodide remaining after the reaction can be removed through adsorption or ion exchange in post-treatment (Cao et al., 2022).

Table 7. Predictive toxicity of PFOA and its TPs using ECOSAR simulation software

	Fish	*Daphnia*	Green algae	Fish	*Daphnia*	Green algae
	LC50 (96hr) (mg/L)	LC50 (48hr) (mg/L)	EC50 (96hr) (mg/L)	ChV	ChV	ChV
PFOA	10.10	7.44	16.22	1.34	1.49	7.58
TP363 (PFHpA)	35.43	24.52	41.43	4.37	4.15	16.86
TP313 (PFHxA)	121.93	79.34	103.82	14.00	11.31	36.83
TP263 (PFPeA)	408.97	250.18	253.58	43.65	30.02	78.39
PFBA	1322.59	760.59	597.14	131.23	76.84	160.87
PFPrA	4043.70	2186.10	1329.43	373.03	185.98	312.11
TFA	20725.35	10248.30	4309.89	1720.96	680.19	829.54
TP448 (PFHpS)	84.97	57.10	85.36	10.13	8.90	32.53
TP398 (PFHxS)	301.32	190.35	220.42	33.40	24.98	73.20
TP348 (PFPeS)	1051.87	624.69	560.29	108.41	69.03	162.16

TP377	13.33	9.65	19.67	1.74	1.85	8.86
TP392	4610.29	2576.76	1798.21	442.33	240.49	454.65
TP393	180.94	116.86	148.26	20.59	16.31	51.72
TP395	18.37	13.14	25.46	2.36	2.44	11.16
TP410	4306.91	2419.35	1723.85	415.68	228.99	440.76
TP412	2405.61	1387.22	1101.62	239.47	141.24	298.61
TP430	1704.39	999.99	852.95	173.16	106.83	240.27
TP436	203.34	131.26	166.20	23.12	18.29	57.92
TP438	252.24	161.31	196.44	28.37	21.90	67.04
TP456	4042.79	2288.20	1682.12	393.68	221.17	437.39
TP470	138.91	91.52	126.05	16.18	13.50	45.96
TP474	21.06	15.10	29.51	2.71	2.82	12.99
TP477	**0.10**	**0.08**	**0.28**	**0.01**	**0.02**	**0.17**
TP497	7159.05	3965.42	2666.07	679.60	360.93	660.68

4. Conclusions

In this study, the efficient removal of PFOA and the defluorination rate were confirmed through a reductive degradation reaction using hydrated electrons. To apply conditions to generate as many hydrated electrons as possible, VUV mercury lamps were used and the experiment maximized the generation of hydrated electrons by adding sulfite and iodide together. More efficient removal and defluorination rates of PFOA were confirmed in the VUV/sulfite and VUV/sulfite/iodide processes than in the VUV photolysis process. The removal rate was greatly improved in the VUV/sulfite/iodide process compared to the VUV/sulfite process, but there was no significant difference in the defluorination rate. pH 10 is the condition for maximally generating hydrated electrons. And the concentrations of sulfite and iodide are set to 2.4 and 0.48 mM, respectively, at concentrations where self-quenching is minimized. PFOA is mainly degraded by hydrated electrons generated from sulfite and iodide.

In the VUV photolysis process, the degradation and defluorination of PFOA proceeded slowly, and short-chain PFCAs are mainly produced as TPs through the mechanism of DHEH. In the VUV/sulfite and VUV/sulfite/iodide processes, the degradation and defluorination of PFOA proceeded rapidly, and it was confirmed that various types of TPs were mainly generated through the mechanism of H-F exchange, SO_3^--F exchange, generation of an unsaturated compound, hydration. Based on previous research papers, different main degradation pathways for each process were proposed using the defluorination rate and TPs found in LC-QTOF/MS. This study would provide mechanistic insights and scientific information into the potential TPs of PFOA degradation during VUV-based processes.

5. References

Arias Espana, V. A., Mallavarapu, M., & Naidu, R. (2015). Treatment technologies for aqueous perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA): A critical review with an emphasis on field testing. *Environmental Technology & Innovation*, *4*, 168-181. https://doi.org/https://doi.org/10.1016/j.eti.2015.06.001

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? *Environmental Science & Technology*, *52*(20), 11728-11734. https://doi.org/10.1021/acs.est.8b02172

Bentel, M. J., Yu, Y., Xu, L., Li, Z., Wong, B. M., Men, Y., & Liu, J. (2019). Defluorination of Per- and Polyfluoroalkyl Substances (PFASs) with Hydrated Electrons: Structural Dependence and Implications to PFAS Remediation and Management. *Environmental Science & Technology*, *53*(7), 3718-3728. https://doi.org/10.1021/acs.est.8b06648

Boonya-atichart, A., Boontanon, S. K., & Boontanon, N. (2018). Study of hybrid membrane filtration and photocatalysis for removal of perfluorooctanoic acid (PFOA) in groundwater. *Water Science and Technology*, *2017*(2), 561-569. https://doi.org/10.2166/wst.2018.178

Busch, J., Ahrens, L., Sturm, R., & Ebinghaus, R. (2010). Polyfluoroalkyl compounds in landfill leachates. *Environmental Pollution*, *158*(5), 1467-1471. https://doi.org/https://doi.org/10.1016/j.envpol.2009.12.031

Cai, Y., Wang, X., Wu, Y., Zhao, S., Li, Y., Ma, L., Chen, C., Huang, J., & Yu, G. (2018). Temporal trends and transport of perfluoroalkyl substances (PFASs) in a subtropical estuary: Jiulong River Estuary, Fujian, China. *Science of The Total Environment*, *639*, 263-270. https://doi.org/https://doi.org/10.1016/j.scitotenv.2018.05.042

Cao, H., Zhang, W., Wang, C., Liang, Y., & Sun, H. (2022). Photodegradation of F–53B in aqueous solutions through an UV/Iodide system. *Chemosphere*, *292*, 133436. https://doi.org/https://doi.org/10.1016/j.chemosphere.2021.133436

Cao, M. H., Wang, B. B., Yu, H. S., Wang, L. L., Yuan, S. H., & Chen, J. (2010). Photochemical decomposition of perfluorooctanoic acid in aqueous periodate with VUV and UV light irradiation. *Journal of Hazardous Materials*, *179*(1), 1143-1146. https://doi.org/https://doi.org/10.1016/j.jhazmat.2010.02.030

Chen, J., Zhang, P.-y., & Liu, J. (2007). Photodegradation of perfluorooctanoic acid by 185 nm vacuum ultraviolet light. *Journal of Environmental Sciences*, *19*(4), 387-390. https://doi.org/https://doi.org/10.1016/S1001-0742(07)60064-3

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

Cheng, J.-h., Liang, X.-y., Yang, S.-w., & Hu, Y.-y. (2014). Photochemical defluorination of aqueous perfluorooctanoic acid (PFOA) by VUV/Fe3+ system. *Chemical Engineering Journal*, *239*, 242-249. https://doi.org/https://doi.org/10.1016/j.cej.2013.11.023

Cui, J., Gao, P., & Deng, Y. (2020). Destruction of Per- and Polyfluoroalkyl Substances (PFAS) with Advanced Reduction Processes (ARPs): A Critical Review. *Environmental Science & Technology*, *54*(7), 3752-3766. https://doi.org/10.1021/acs.est.9b05565

Deng, Y., Liang, Z., Lu, X., Chen, D., Li, Z., & Wang, F. (2021). The degradation mechanisms of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) by different chemical methods: A critical review. *Chemosphere*, *283*, 131168. https://doi.org/https://doi.org/10.1016/j.chemosphere.2021.131168

EFSA. (2008). Opinion of the Scientific panel on contaminants in the food chain on perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts. https://doi.org/https://pure.uva.nl/ws/files/4299097/62823_EFSA_J_2008_653_PFOS_PFOA.pdf

Esfahani, E. B., & Mohseni, M. (2022). Fluence-based photo-reductive decomposition of PFAS using vacuum UV (VUV) irradiation: Effects of key parameters and decomposition mechanism. *Journal of Environmental Chemical Engineering*, *10*(1), 107050. https://doi.org/https://doi.org/10.1016/j.jece.2021.107050

Fennell, B. D., Mezyk, S. P., & McKay, G. (2022). Critical Review of UV-Advanced Reduction Processes for the Treatment of Chemical Contaminants in Water. *ACS Environmental Au*, *2*(3), 178-205. https://doi.org/10.1021/acsenvironau.1c00042

Fischer, M., & Warneck, P. (1996). Photodecomposition and Photooxidation of Hydrogen Sulfite in Aqueous Solution. *The Journal of Physical Chemistry*, *100*(37), 15111-15117. https://doi.org/10.1021/jp953236b

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Petersson, G. A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A., Bloino, J., Janesko, B. G., Gomperts, R., Mennucci, B., Hratchian, H. P., Ortiz, J. V., . . . Fox, D. J. (2016). Gaussian 09, Revision A.02. https://doi.org/https://gaussian.com/g09citation/

Gallen, C., Baduel, C., Lai, F. Y., Thompson, K., Thompson, J., Warne, M., & Mueller, J. F. (2014). Spatio-temporal assessment of perfluorinated compounds in the Brisbane River system, Australia: Impact of a major flood event. *Marine Pollution Bulletin*, *85*(2), 597-605. https://doi.org/https://doi.org/10.1016/j.marpolbul.2014.02.014

Giri, R. R., Ozaki, H., Guo, X., Takanami, R., & Taniguchi, S. (2014). Oxidative–reductive photodecomposition of perfluorooctanoic acid in water. *International Journal of Environmental Science and Technology*, *11*(5), 1277-1284. https://doi.org/10.1007/s13762-013-0312-2

Gu, Y., Liu, T., Wang, H., Han, H., & Dong, W. (2017a). Hydrated electron based decomposition of perfluorooctane sulfonate (PFOS) in the VUV/sulfite system. *Science of The Total Environment*, *607-608*, 541-548. https://doi.org/https://doi.org/10.1016/j.scitotenv.2017.06.197

Gu, Y., Liu, T., Zhang, Q., & Dong, W. (2017b). Efficient decomposition of perfluorooctanoic acid by a high photon flux UV/sulfite process: Kinetics and associated toxicity. *Chemical Engineering Journal*, *326*, 1125-1133. https://doi.org/https://doi.org/10.1016/j.cej.2017.05.156

Hong, S., Khim, J. S., Park, J., Kim, M., Kim, W.-K., Jung, J., Hyun, S., Kim, J.-G., Lee, H., Choi, H. J., Codling, G., & Giesy, J. P. (2013). In situ fate and partitioning of waterborne perfluoroalkyl acids (PFAAs) in the Youngsan and Nakdong River Estuaries of South Korea. *Science of The Total Environment*, *445-446*, 136-145. https://doi.org/https://doi.org/10.1016/j.scitotenv.2012.12.040

Houtz, E. F., Higgins, C. P., Field, J. A., & Sedlak, D. L. (2013). Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil. *Environmental Science & Technology*, *47*(15), 8187-8195. https://doi.org/10.1021/es4018877

IARC. (2016). Perfluorooctanoic Acid, Monographs-110. https://doi.org/https://monographs.iarc.who.int/wp-content/uploads/2018/06/mono110-01.pdf

Lee, Y.-M., Lee, J.-Y., Kim, M.-K., Yang, H., Lee, J.-E., Son, Y., Kho, Y., Choi, K., & Zoh, K.-D. (2020). Concentration and distribution of per- and polyfluoroalkyl substances (PFAS) in the Asan Lake area of South Korea. *Journal of Hazardous Materials*, *381*, 120909. https://doi.org/https://doi.org/10.1016/j.jhazmat.2019.120909

Liang, X., Cheng, J., Yang, C., & Yang, S. (2016). Factors influencing aqueous perfluorooctanoic acid (PFOA) photodecomposition by VUV irradiation in the presence of ferric ions. *Chemical Engineering Journal*, *298*, 291-299. https://doi.org/https://doi.org/10.1016/j.cej.2016.03.150

Lu, T., & Chen, F. (2012). Multiwfn: A multifunctional wavefunction analyzer [https://doi.org/10.1002/jcc.22885]. *Journal of Computational Chemistry*, *33*(5), 580-592. https://doi.org/https://doi.org/10.1002/jcc.22885

Mak, Y. L., Taniyasu, S., Yeung, L. W. Y., Lu, G., Jin, L., Yang, Y., Lam, P. K. S., Kannan, K., & Yamashita, N. (2009). Perfluorinated Compounds in Tap Water from China and Several Other Countries. *Environmental Science & Technology*, *43*(13), 4824-4829. https://doi.org/10.1021/es900637a

Marenich, A. V., Cramer, C. J., & Truhlar, D. G. (2009). Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *The Journal of Physical Chemistry B*, *113*(18), 6378-6396. https://doi.org/10.1021/jp810292n

Nicole, W. (2013). PFOA and Cancer in a Highly Exposed Community: New Findings from the C8 Science Panel. *Environmental Health Perspectives*, *121*(11-12), A340-A340. https://doi.org/10.1289/ehp.121-A340

Oláh, J., Van Alsenoy, C., & Sannigrahi, A. B. (2002). Condensed Fukui Functions Derived from Stockholder Charges: Assessment of Their Performance as Local Reactivity Descriptors. *The Journal of Physical Chemistry A*, *106*(15), 3885-3890. https://doi.org/10.1021/jp014039h

Pan, C.-G., Ying, G.-G., Zhao, J.-L., Liu, Y.-S., Jiang, Y.-X., & Zhang, Q.-Q. (2014). Spatiotemporal distribution and mass loadings of perfluoroalkyl substances in the Yangtze River of China. *Science of The Total Environment*, *493*, 580-587. https://doi.org/https://doi.org/10.1016/j.scitotenv.2014.06.033

Park, H., Vecitis, C. D., Cheng, J., Choi, W., Mader, B. T., & Hoffmann, M. R. (2009). Reductive Defluorination of Aqueous Perfluorinated Alkyl Surfactants: Effects of Ionic Headgroup and Chain Length. *The Journal of Physical Chemistry A*, *113*(4), 690-696. https://doi.org/10.1021/jp807116q

Podder, A., Sadmani, A. H. M. A., Reinhart, D., Chang, N.-B., & Goel, R. (2021). Per and poly-fluoroalkyl substances (PFAS) as a contaminant of emerging concern in surface water: A transboundary review of their occurrences and toxicity effects. *Journal of Hazardous Materials*, *419*, 126361. https://doi.org/https://doi.org/10.1016/j.jhazmat.2021.126361

Qu, Y., Zhang, C., Li, F., Chen, J., & Zhou, Q. (2010). Photo-reductive defluorination of perfluorooctanoic acid in water. *Water Research*, *44*(9), 2939-2947. https://doi.org/https://doi.org/10.1016/j.watres.2010.02.019

Ren, Z., Bergmann, U., & Leiviskä, T. (2021). Reductive degradation of perfluorooctanoic acid in complex water matrices by using the UV/sulfite process. *Water Research*, *205*, 117676. https://doi.org/https://doi.org/10.1016/j.watres.2021.117676

So, M. K., Miyake, Y., Yeung, W. Y., Ho, Y. M., Taniyasu, S., Rostkowski, P., Yamashita, N., Zhou, B. S., Shi, X. J., Wang, J. X., Giesy, J. P., Yu, H., & Lam, P. K. S. (2007). Perfluorinated compounds in the Pearl River and Yangtze River of China. *Chemosphere*, *68*(11), 2085-2095. https://doi.org/https://doi.org/10.1016/j.chemosphere.2007.02.008

Song, Z., Tang, H., Wang, N., & Zhu, L. (2013). Reductive defluorination of perfluorooctanoic acid by hydrated electrons in a sulfite-mediated UV photochemical system. *Journal of Hazardous Materials*, *262*, 332-338. https://doi.org/https://doi.org/10.1016/j.jhazmat.2013.08.059

UNEP. (2019). Stockholm Convention 2019. https://doi.org/http://chm.pops.int/TheConvention/ThePOPs/AllPOPs/tabid/2509/Default.aspx

USEPA. (2016). FACT SHEET PFOA & PFOS Drinking Water Health Advisories. https://doi.org/https://www.epa.gov/sites/default/files/2016-06/documents/drinkingwaterhealthadvisories_pfoa_pfos_updated_5.31.16.pdf

USEPA. (2022a). Drinking Water Health Advisories for PFAS Fact Sheet for Communities. https://www.epa.gov/system/files/documents/2022-06/drinking-water-ha-pfas-factsheet-communities.pdf

USEPA. (2022b). Ecological Structure Activity Relationships (ECOSAR) Predictive Model. https://doi.org/https://www.epa.gov/tsca-screening-tools/ecological-structure-activity-relationships-ecosar-predictive-model

Wang, Y., & Zhang, P. (2014). Effects of pH on photochemical decomposition of perfluorooctanoic acid in different atmospheres by 185nm vacuum ultraviolet. *Journal of Environmental Sciences*, *26*(11), 2207-2214. https://doi.org/https://doi.org/10.1016/j.jes.2014.09.003

Wu, Z., Shang, C., Wang, D., Zheng, S., Wang, Y., & Fang, J. (2020). Rapid degradation of dichloroacetonitrile by hydrated electron (eaq–) produced in vacuum ultraviolet photolysis. *Chemosphere*, *256*, 126994. https://doi.org/https://doi.org/10.1016/j.chemosphere.2020.126994

Xu, C., Chen, H., & Jiang, F. (2015). Adsorption of perflourooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) on polyaniline nanotubes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *479*, 60-67. https://doi.org/https://doi.org/10.1016/j.colsurfa.2015.03.045

Yu, K., Li, X., Chen, L., Fang, J., Chen, H., Li, Q., Chi, N., & Ma, J. (2018). Mechanism and efficiency of contaminant reduction by hydrated electron in

the sulfite/iodide/UV process. *Water Research*, *129*, 357-364. https://doi.org/https://doi.org/10.1016/j.watres.2017.11.030

Zhao, Z., Xie, Z., Tang, J., Sturm, R., Chen, Y., Zhang, G., & Ebinghaus, R. (2015). Seasonal variations and spatial distributions of perfluoroalkyl substances in the rivers Elbe and lower Weser and the North Sea. *Chemosphere*, *129*, 118-125. https://doi.org/https://doi.org/10.1016/j.chemosphere.2014.03.050

국문 초록

진공 자외선 기반 공정에서의

과불화옥탄산의 환원적 분해

박 흥 주

서울대학교 보건대학원

환경보건학과 환경보건학 전공

수화 전자는 환원 분해를 통해 제거하기 어려운 과불화화합물을 제거할 수 있는 강력한 환원제로 알려져 있다. 본 연구에서는 수화 전자를 이용하여 대표적인 과불화화합물인 과불화옥탄산의 효율적인 제거 및 탈불화를 확인하였고, 진공 자외선 광분해, 진공 자외선 / 아황산염, 진공 자외선 / 아황산염 / 요오드화물 공정에서의 제거 및 탈불화율을 비교하였다.

진공 자외선 광분해 공정에서는 6시간 이내에 약 88.6%의 과불화옥탄산이 제거된 반면, 진공 자외선 / 아황산염 공정에서는 과불화옥탄산이 90분 이내에, 진공 자외선 / 아황산염 / 요오드화물 공정에서는 30분 이내에 완전히 제거되었다. 진공 자외선 광분해, 진공

자외선 / 아황산염 및 진공 자외선 / 아황산염 / 요오드화물 공정에서 과불화옥탄산을 제거를 위한 탈불소화율은 6시간 동안 각각 약 34.6%, 72.7% 및 73.9%이다. 제거제로 삼차 뷰틸 알코올, 아질산염 및 질산염을 추가하여 수화 전자가 과불화옥탄산을 가장 효율적으로 분해할 수 있음이 확인되었다.

진공 자외선 광분해 공정에서 짧은 사슬의 과불화카르복실산은 주로 사슬 단축 메커니즘을 통해 부산물로 생성된다. 진공 자외선 / 아황산염 및 진공 자외선 / 아황산염 / 요오드화물 공정에서는 주로 수소-불소 치환(예: 부산물 377, 부산물 395), 아황산염 라디칼-불소 치환(예: 부산물 474), 불포화 화합물(예: 부산물 392, 부산물 410, 부산물 436)의 생성, 수화 반응(예: 부산물 393)의 메커니즘을 통해 다양한 유형의 부산물이 생성됨을 확인했다.

위의 결과들과 사중극자 비행시간형 액체크로마토그래피/질량분석기에서 발견된 부산물을 기반으로 진공 자외선 기반 공정에서 과불화옥탄산 분해 경로가 제안되었다.

주요어 : 과불화옥탄산, 진공 자외선, 아황산염, 요오드화물, 수화 전자, 탈불화

6. Supplementary materials

Table S1. Identified TPs on the degradation of PFOA during the VUV/sulfite and VUV/sulfite/iodide processes using UPLC-QTOF/MS

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
PFOA	$C_8HF_{15}O_2$	412.9651	6.70	-2.2

Item name: 221124_A_2PPM_S300_I048_0_1
Channel name: mz413_C7F15COOH(PFOA) [-H] : (50.0 PPM) 412.9661

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP497	$C_9H_2F_{12}O_8S^{2-}$	497.9261	8.41	-4.7

Item name: 221124_A_2PPM_S300_I048_360_2
Channel name: mz497_C9H2F12O8S_2-_3 [+e] : (50.0 PPM) 497.9261

mz497_C9H2F12O8S_2-_3
8.39

8.83

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP477	$C_7F_{14}HI$	476.8803	8.41	-4.7

Item name: 221124_A_2PPM_S300_I048_60_1
Channel name: mz477_C7F14HI(TP4) [-H] : (50.0 PPM) 474.8819

mz477_C7F14HI(TP4)
8.49

66

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP474	$C_7F_{14}SO_3HCOOH$	474.9323	7.77	-0.7

Item name: 221124_A_2PPM_S300_I048_15_2
Channel name: mz475_C7F14SO3HCOOH [-H] : (50.0 PPM) 474.9323

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP470	$C_8H_3F_{12}O_7S^-$	470.9392	3.24	-4.5

Item name: 221124_A_2PPM_S300_I048_60_2
Channel name: mz470_C8H3F12O7S− [+e] : (50.0 PPM) 470.9392

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP456	$C_7F_{13}HSO_3HCOOH$	456.9418	7.73	-0.7

Item name: 221124_A_2PPM_S300_I048_60_1
Channel name: mz457_C7F13HSO3HCOOH [-H] : (50.0 PPM) 456.9418

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP448 (PFHpS)	$C_7F_{15}HSO_3$	448.9315	8.57	-4.4

Item name: 221124_A_2PPM_S300_I0_60_2
Channel name: mz449_C7F15HSO3(PFHpS) [-H] : (50.0 PPM) 448.9315

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP438	$C_8H_3F_{12}O_5S^-$	438.9503	7.28	-2.7

Item name: 221124_A_2PPM_S300_I048_90_1
Channel name: mz438_C8H3F12O5S- [+e] : (50.0 PPM) 438.9503

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP436	$C_7F_{12}SO_3HCOOH$	436.9347	7.65	-2.6

Item name: 221124_A_2PPM_S300_I048_60_1
Channel name: mz437_C7F12SO3HCOOH [-H] : (50.0 PPM) 436.9347

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP430	$C_7F_{14}HSO_3H$	430.9407	7.79	-4.9

Item name: 221124_A_2PPM_S300_I048_10_1
Channel name: mz431_C7F14HSO3H [-H] : (50.0 PPM) 430.9407

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP412	$C_7F_{13}H_2SO_3H$	412.9518	8.45	-1.2

Item name: 221124_A_2PPM_S300_I048_360_1
Channel name: mz413_C7F13H2SO3H [-H] : (50.0 PPM) 412.9518

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP410	$C_7F_{13}SO_3^-$	410.9355	7.79	-2.7

Item name: 221124_A_2PPM_S300_I048_15_1
Channel name: mz410_C7F13SO3- [+e] : (50.0 PPM) 410.9355

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP398(PFHxS)	$C_6F_{13}HSO_3$	398.9340	8.42	-6.6

Item name: 221124_A_2PPM_S300_I0_240_2
Channel name: mz399_C6F13HSO3(PFHxS) [-H] : (50.0 PPM) 398.9340

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP395	$C_7F_{14}HCOOH$	394.9739	8.49	-5.0

Item name: 221124_A_2PPM_S300_I048_60_1
Channel name: mz395_C7F14HCOOH [-H] : (50.0 PPM) 392.9773

mz395_C7F14HCOOH
8.45

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP393	$C_7F_{13}HOHCOOH$	392.9773	8.46	-7.3

Item name: 221124_A_2PPM_S300_I048_60_1
Channel name: mz393_C7F13HOHCOOH [-H] : (50.0 PPM) 392.9773

mz393_C7F13HOHCOOH
8.45

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP392	$C_7F_{12}HSO_3H$	392.9455	7.74	-1.3

Item name: 221124_A_2PPM_S300_I048_60_1
Channel name: mz393_C7F12HSO3H [-H] : (50.0 PPM) 392.9455

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP377	$C_7F_{13}H_2COOH$	376.9838	8.50	-4.0

Item name: 221124_A_2PPM_S300_I048_180_1
Channel name: mz377_C7F13H2COOH [-H] : (50.0 PPM) 376.9838

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP363(PFHpA)	$C_6F_{13}COOH$	362.9750	8.44	-5.2

Item name: 221124_A_2PPM_S300_I0_15_2
Channel name: mz363_C6F13COOH(PFHpA) [-H] : (50.0 PPM) 362.9677

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP348(PFPeS)	$C_5F_{11}HSO3$	348.9378	8.26	-5.8

Item name: 221124_A_2PPM_S300_I048_240_1
Channel name: mz349_C5F11HSO3(PFPeS) [-H] : (50.0 PPM) 348.9378

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP313(PFHxA)	$C_5F_{11}COOH$	312.9713	8.25	-4.7

Item name: 221124_A_2PPM_S300_I0_0_2
Channel name: mz313_C5F11COOH(PFHxA) [-H] : (50.0 PPM) 312.9713

TPs	Formula	Observed m/z	Observed RT (min)	Mass error (ppm)
TP263(PFPeA)	C_4F_9COOH	262.9737	5.05	-8.6

Item name: A_S0_I0_300_2_221103
Channel name: mz263_C4F9COOH(PFPeA) [-H] : (50.0 PPM) 262.9737

Table S2. Classification into toxicity classes based on globally harmonized system of classification and labelling of chemicals (GHS)

Toxicity range (mg/L)	Class
$LC_{50} / EC_{50} / ChV \leq 1$	Very toxic
$1 < LC_{50} / EC_{50} / ChV \leq 10$	Toxic
$10 < LC_{50} / EC_{50} / ChV \leq 100$	Harmful
$LC_{50} / EC_{50} / ChV > 100$	Not harmful