Supplementary Information

Photo-chemical/catalytic Oxidative/Reductive Decomposition of Per- and Polyfluoroalkyl Substances (PFAS), Decomposition Mechanisms and Effects of Key Factors: A Review

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Extent of degradation and defluorination in this supplementary information are presented using the following abbreviations:

- deG: degradation efficiency (%)
- k_{deG}: degradation rate constant
- deF: defluorination efficiency (%)
- k_{deF}: defluorination rate constant

Table S1 Effect of operational parameters (i.e., pH, dissolved oxygen and temperature) on PFAS photodegradation

Method	Experimental conditions		pH	Decomposition & defluorination		Reference
Photo-oxidation	400 W LP lamp UV (254 nm) $NaHCO_3$: 40 mM H_2O_2: 0.075% PFOA (50 mg/L) 25 ℃		4.09 8.8 11	deF: 72.1% deF: 82.3% deF: 65%	12 h	(1)
	12 W LP-Hg lamp UV/VUV (254/185 nm) Fe^{3+}: 20 μM PFOA (14.9 mg/L) room temperature		2.5 3 4 5 7	deF: ~32% deF: ~34% deF: 43.4% deF: ~12% deF: ~3%	4 h	(2)
	9 W LP-Hg lamp UV (254 nm) Fe^{2+}: 1 mM $S_2O_8^{2-}$: 30 mM PFOA (20 mol/L) 25 ℃		2 3 4 5 5.8 6.4	deF: 23.7% deF: ~30% deF: ~47% deF: 63.3% deF: ~40% deF: 26%	5 h	(3)
	500 W Hg lamp UV (254 nm) 0.86% CeO_2/In_2O_3 PFOA (100 mg/L) 25 ℃		2.84 3.63 4.64 7.10 8.17 9.51	deG: ~92% deG: ~88% deG: ~72% deG: ~56% deG: ~52% deG: ~42%	0.5 h	(4)
	14 W LP-Hg lamp UV/VUV (254/185 nm) Sheaf-like Ga_2O_3 PFOA (500 μg/L) Sewage water 25 ℃	UV/Ga_2O_3	4.3 7.8	k_{deG} = 1.43 h^{-1} k_{deG} = 1.00 h^{-1}		(5)
		UV/VUV/Ga_2O_3	4.3 7.8	k_{deG} = 4.29 h^{-1} k_{deG} = 1.95 h^{-1}		
Photo-reduction	10 W LP-Hg lamp: 254 nm Sulfite: 10 mM PFOA (8.28 mg/L) N_2 atmosphere 25 ℃		6.0 8.1 9.3 10.3	deF: ~4% deF: ~44% deF: ~58% deF: ~62%	6 h	(6)
	250 W HP-Hg UV lamp: 200-400 nm Sulfite: 10 mM PFOA (16 mg/L) DO (5 mg/L) 25 ℃		7 8 9.2 10.2	deF: ~2% deF: ~24% deF: ~46% deF: ~50%	10 min	(7)
	HP-Hg UV lamp: 200 - 400 nm Sulfite: 10 mM PFOS (16 mg/L)		7 8 9.2	deF: ~0% deF: ~34% deF: ~56%	30 min	(8)

	DO (5 mg/L), 25 ℃	10.2	deF: ~70%		
	10 W LP-Hg lamp 254 nm and 185 nm Sulfite: 20 mM PFOS (18.6 mg/L) 25 ℃	6 7 8 9 10	deF: ~9% deF: ~20% deF: ~40% deF: ~55% deF: ~62%	4 h	(9)
	10 W UV/VUV lamp (254/185 nm) Emission intensity of 0.73 mW.cm^{-2} 254 nm 0.09 mW.cm^{-2} 185 nm PFOS (0.1 mg/L) Sulfite: 10 mM 22 ± 2 ℃ – DO 0.14 mg/L	3.3 4.6 7.0 9.1 11.1 12.0 12.4	deG: ~7% deG: ~11% deG: ~17% deG: ~54% deG: ~63% deG: ~65% deG: ~58%	6 h	(10)
	450 W MP-Hg lamp (200-400 nm) PFOA (2 mg/L) Sulfite: 10 mM 20 ℃ – DO 0.8 mg/L	2 7 9 12	deF: ~14% deF: ~38% deF: ~70% deF: ~82%	0.5 h	(11)
	15 W LP-Hg lamp: 254 nm Fe^{II}: 0.3 mM NTA: 2 mM PFOS: 0.01 mM Nitrogen saturated	5 6 7 8 9 10	deG: ~33% deG: ~40% deG: ~40% deG: ~60% deG: ~60% deG: ~48%	10 h	(24)
	15 W LP-Hg lamp: 254 nm Iodide: 0.3 mM PFOA (10.35 mg/L) N_2 atmosphere	5 7 8 9 10	deF: ~8% deF: ~22% deF: ~45% deF: ~64% deF: ~70%	6 h	(12)
	36 W LP-Hg lamp: 254 nm IAA: 1 mM PFOA (10 mg/L) 25 ℃	3 4 6 8 10 11	deF: ~74% deF: ~78% deF: ~88% deF: ~78% deF: ~82% deF: ~85%	10 h	(13)
	14 W LP-Hg lamp: 254 nm Iodide: 0.3 mM PFOS (15 mg/L) N_2 atmosphere 25 ℃	7 8 9 10	deF: ~3% deF: ~16% deF: ~34% deF: ~56%	1.5 h	(14)

Method	Experimental Conditions	Atmosphere	Decomposition & defluorination		Reference
Photo-oxidation	200 W UV-visible Xenon-mercury lamp Fe^{3+}: 5 mM PFPeA (17.8 g/L) pH 1.5	Oxygen Argon	deG: 64.5% deG: 35.6%	24 h	(15)

	25 ℃				
	500 W HP-Hg lamp 260-600 nm $PW_{12}O_{40}^{3-}$: 6.7 mM PFPeA (0.41 g/L) pH 0.8 25 ℃	Oxygen Argon	deG: 24% deG: 0.8%	48 h	(16)
	500 W UV lamp 315 – 400 nm TiO_2: 0.66 g/L PFOA (1.66 g/L) 30 ℃	O_2 Air N_2 N_2 saturated	$k_{deG} = 0.335\ h^{-1}$ $k_{deG} = 0.172\ h^{-1}$ $k_{deG} = 0.056\ h^{-1}$ $k_{deG} = 0.008\ h^{-1}$		(17)
	23 W LP-Hg lamp UV (254 nm) and VUV (185 nm) $S_2O_8^{2-}$: 407 mg/L PFOA (25 mg/L) 25 ℃	Oxygen Nitrogen	deF: 42.8% deF: 24.5%	2 h	(18)
	5 W LP-Hg lamp UV/VUV (254/185 nm) Fe^{3+}: 20 μM PFOA (14.9 mg/L) pH ~4 room temperature	Air Oxygen Nitrogen	deF: 33% deF: 34% deF: 31%	2 h	(19)
	400 W UV lamp: 254 nm TiO_2: 0.5 g/L PFOA (50 mg/L) pH 3 25 ℃	No gas Air Nitrogen	deF: 23% deF: 29.6% deF: 0.9%	1 h	(20)
Photo-reduction	10 W LP-Hg lamp: 254 nm Sulfite: 10 mM PFOA (8.28 mg/L) pH 10.3 room temperature	Air Nitrogen	deF: 6.4% deF: 88.5%	24 h	(6)
	10 W UV/VUV lamp (254/185 nm) PFOS (0.1 mg/L) Sulfite: 10 mM pH 12.0 22 ± 2 ℃	Air No gas Nitrogen	deG: ~18% deG: ~30% deG: ~31%	3 h	(10)
	450 W MP-Hg lamp (200-400 nm) PFOA (2 mg/L) Sulfite: 10 mM 20 ℃	DO=1 mg/L DO=5 mg/L DO=8 mg/L	deF: ~82% deF: ~81% deF: ~80%	0.5 h	(11)

	15 W LP-Hg lamp: 254 nm Iodide: 0.3 mM PFOA (10.35 mg/L) pH 9 room temperature	Oxygen Nitrogen	deF: ~6% 14 h deF: 98.8%	(21)
	8 W UV lamp 254 nm Iodide: 10 mM PFOA & PFOS (0.1 mg/L)	Air	$k_{deG,\,PFOA} = 0\ min^{-1}$ $k_{deG,\,PFOS} = 0\ min^{-1}$	(22)
		Argon	$k_{deG,\,PFOA} = 2.9 \times 10^{-3}\ min^{-1}$ $k_{deG,\,PFOS} = 6.5\ \times 10^{-3}\ min^{-1}$	
	36 W LP-Hg lamp: 254 nm IAA: 1 mM HDTMA clay: 2.2 g/L PFOA (10 mg/L) pH 6 25 ℃	Oxygen Nitrogen	deF: 90% 10 h deF: 90%	(13)

Method	Experimental Conditions	Temperature	Decomposition & defluorination	Reference
Photo-reduction	15 W LP-Hg lamp: 254 nm Iodide: 0.6 mM	20	$k_{deG} = 0.302\ h^{-1}$	(23)
	PFOA (8.28 mg/L)	25	$k_{deG} = 0.564\ h^{-1}$	
	N_2 atmosphere pH 9	40	$k_{deG} = 1.526\ h^{-1}$	
	10 W UV/VUV lamp (254/185 nm)	5	deG: ~34% 6 h	(10)
	Emission intensity of 0.4 $mW.cm^{-2}$ 254 nm	15	deG: ~42%	
	0.05 $mW.cm^{-2}$ 185 nm PFOS (0.1 mg/L)	25	deG: ~50%	
	Sulfite: 10 mM DO 0.14 mg/L	35	deG: ~59%	
	15 W LP-Hg lamp: 254 nm Fe^{II}: 0.3 mM	30	$k_{deG} = 0.081\ h^{-1}$	(24)
	NTA: 2 mM PFOS: 0.01 mM	40	$k_{deG} = 0.086\ h^{-1}$	
	Nitrogen saturated pH 8.0	50	$k_{deG} = 0.091\ h^{-1}$	

Table S2 Effect of photon parameters (i.e. wavelength and intensity) on PFAS photodegradation

Method	Experimental conditions	Wavelength	Decomposition & defluorination		Reference
Photo-Oxidation	23 W LP-Hg lamp UV/VUV (254/185 nm) $S_2O_8^{2-}$: 1.5 mM PFOA (25 mg/L) O_2 atmosphere, 25 ℃	254 nm 254 nm & 185 nm	k_{deG} = 0.81 min^{-1} k_{deG} = 1.44 min^{-1}		(18)
	200 W UV-visible Xenon-mercury lamp Fe^{3+} : 5 mM TFA (7.65 g/L) O_2 atmosphere, 25 ℃	220-460 nm > 290 nm	deG: 64.7% deG: 14.7%	24 h	(15)
	23 W LP lamp UV/VUV (254/185 nm) IO_4^-: 0.5 mM PFOA: 4.14 mg/L	254 nm 254 nm & 185 nm	deG: 70% deG: 60%	2 h	(25)
Photo-Reduction	10 W LP-Hg lamp UV/VUV (254/185 nm) Sulfite: 20 mM PFOS (37.2 μM: 18.6 mg/L) pH 10, 25 ℃	254 nm 254 nm & 185 nm	deG: 85.8% deG: 97.3%	4 h	(9)
	20 W LP-Hg lamp UV/VUV (254/185 nm) Iodide: 0.3 mM PFOA (0.81-1.27 mg/L) N_2 atmosphere	254 nm 254 nm & 185 nm	deG: 39% deG: 72%	3 h	(26)
	10 W UV/VUV lamp (254/185 nm) PFOS (0.1 mg/L) Sulfite: 10 mM DO 0.14 mg/L	254 nm 254 nm & 185 nm	deG: ~44% deG: ~64%	6 h	(10)

Method	Experimental conditions	Intensity	Decomposition & defluorination		Reference
Photo-Oxidation	LP-Hg UV lamp: 310-400 nm TiO_2: 0.66 g/L PFOA (1.656 g/L) 30 $\pm$ 5 ℃	7.5 $mW.cm^{-2}$ 9.5 $mW.cm^{-2}$	deG: 21% deG: 32%	4 h	(27)
Photo-	250 W HP-Hg UV lamp:	6.6×10^{-7} $einstein\ cm^{-2}s^{-1}$	k_{deG} = 0.455 min^{-1}		(7)

Reduction	200-400 nm				
	Sulfite: 10 mM	5×10^{-7} $einstein\ cm^{-2} s^{-1}$	$k_{deG} = 0.295\ min^{-1}$		
	PFOA (16 mg/L)	3.3×10^{-7} $einstein\ cm^{-2} s^{-1}$	$k_{deG} = 0.198\ min^{-1}$		
	pH 9.2	2×10^{-7} $einstein\ cm^{-2} s^{-1}$	$k_{deG} = 0.098\ min^{-1}$		
	DO 5 mg/L	9.9×10^{-8} $einstein\ cm^{-2} s^{-1}$	$k_{deG} = 0.032\ min^{-1}$		
	25 ℃				
	HP-Hg UV lamp	6.6×10^{-7} $einstein\ cm^{-2} s^{-1}$	$k_{deG} = 0.118\ min^{-1}$		(8)
	200 – 400 nm	5×10^{-7} $einstein\ cm^{-2} s^{-1}$	$k_{deG} = 0.059\ min^{-1}$		
	Sulfite: 10 mM	3.3×10^{-7} $einstein\ cm^{-2} s^{-1}$	$k_{deG} = 0.036\ min^{-1}$		
	PFOS (16 mg/L)	2×10^{-7} $einstein\ cm^{-2} s^{-1}$	$k_{deG} = 0.020\ min^{-1}$		
	pH 9.2				
	25 ± 3 ℃				
	10 W UV/VUV lamp (254/185 nm)	254 nm, 0.39 mW.cm^{-2}	deG: 47%	6 h	(10)
	185: 254 nm = 0.12:1.0	254 nm, 0.46 mW.cm^{-2}	deG: 52%		
	PFOS (0.1 mg/L)				
	Sulfite: 10 mM	254 nm, 0.73 mW.cm^{-2}	deG 65%		
	DO 0.14 mg/L	254 nm, 0.39 mW.cm^{-2}	deG: 63.7%	15.7 J cm^{-2}	
		254 nm, 0.46 mW.cm^{-2}	deG: 64.2%		
		254 nm, 0.73 mW.cm^{-2}	deG: 65.2%		

Table S3 Effect of PFAS characteristics (i.e. initial concentration and structure) on PFAS photodegradation

Method	Experimental conditions	Initial concentration	Decomposition & defluorination	Reference
Photo-Oxidation	12 W LP-Hg lamp UV (254 nm) and VUV (185 nm) PFOA Fe^{3+}: 10 μM pH 3.8-4.1 room temperature	5 mg/L	$k_{deF} = 3.08 \times 10^{-3}\ min^{-1}$	(2)
		15 mg/L	$k_{deF} = 1.86 \times 10^{-3}\ min^{-1}$	
		30 mg/L	$k_{deF} = 1.51 \times 10^{-3}\ min^{-1}$	
		60 mg/L	$k_{deF} = 1.11 \times 10^{-3}\ min^{-1}$	
	LP-Hg UV lamp 310-400 nm PFOA TiO_2: 0.66 g/L 30 ± 5 ℃	1.66 g/L	deG: 30% (6 h)	(27)
		3.23 g/L	deG: 24% (6 h)	
		5 g/L	deG: 17% (6 h)	
Photo-Reduction	8 W UV lamp: 254 nm Iodide: 10 mM Argon	PFOS = 0.05 mg/L	$k_{deG} = 0.04\ min^{-1}$	(28)
		PFOS = 0.1 mg/L	$k_{deG} = 0.005\ min^{-1}$	
		PFOS = 0.25 mg/L	$k_{deG} = 0.004\ min^{-1}$	
		PFOS = 0.5 mg/L	$k_{deG} = 0.0028\ min^{-1}$	
		PFOS = 1 mg/L	$k_{deG} = 0.0025\ min^{-1}$	
		PFOS = 5 mg/L	$k_{deG} = 0.003\ min^{-1}$	
		PFOS = 10 mg/L	$k_{deG} = 0.003\ min^{-1}$	
		PFOA = 0.05 mg/L	$k_{deG} = 0.0075\ min^{-1}$	
		PFOA = 0.1 mg/L	$k_{deG} = 0.0028\ min^{-1}$	
		PFOA = 0.25 mg/L	$k_{deG} = 0.0022\ min^{-1}$	
		PFOA = 0.5 mg/L	$k_{deG} = 0.0016\ min^{-1}$	
		PFOA = 1 mg/L	$k_{deG} = 0.0017\ min^{-1}$	
		PFOA = 5 mg/L	$k_{deG} = 0.0015\ min^{-1}$	
		PFOA = 10 mg/L	$k_{deG} = 0.0015\ min^{-1}$	

Method	Experimental Conditions		PFAS structure (Branched – Linear)	Decomposition & defluorination	Reference
Photo-Reduction	18 W LP-Hg lamp: 254 nm Sulfite: 10 mM PFECAs (25 μM) pH 9.5 20 ℃	Branched	$C_2F_5(CF_2OC_2F_4)_nCOOH$	n = 1, deF: 44.9% n = 2, deF: 36.5% n = 3, deF: 30.8% (48 h)	(29)
		Linear	$CF_3O(CF_2)_nCOOH$	n = 1, deF: 90.5% n = 2, deF: 61.2% n = 3, deF: 52.3% (48 h)	
			$CF_3O(C_2F_4O)_nCF_2COOH$	n = 1, deF: 82.3% n = 2, deF: 75.0% (48 h)	
			$C_4F_9O(C_2F_4O)_nCF_2COOH$	n = 1, deF: 58.0% (48 h)	

				n = 2, deF: 65.4%		
	10 W UV/VUV lamp (254/185 nm) Emission intensity of 0.73 mW.cm^{-2} 254 nm 0.09 mW.cm^{-2} 185 nm PFOS (0.1 mg/L) Sulfite: 10 mM 22 ± 2 ℃ – DO 0.14 mg/L	Branched-PFOS Linear-PFOS		$k_{deG} = 2.044\ J^{-1}cm^2$ $k_{deG} = 0.053\ J^{-1}cm^2$		(10)

Method	Experimental conditions	PFAS structure (Chain length)		Decomposition & defluorination		Reference
Photo-Oxidation	200 W UV-visible Xenon-mercury lamp Fe^{3+}: 5 mM PFCAs (67.3 mM) O_2 atmosphere 25 ℃	$C_nF_{2n+1}COOH$	n = 2 n = 3 n = 4	$k_{deG} = 3.83 \times 10^{-2}\ h^{-1}$ $k_{deG} = 2.78 \times 10^{-2}\ h^{-1}$ $k_{deG} = 4.26 \times 10^{-2}\ h^{-1}$		(15)
	16 W LP-Hg lamp 254 nm TiO_2: 0.66 g/L $HClO_4$: 0.075 mM PFOA (50 mg/L) pH < 3 25 ± 1 ℃	$C_nF_{2n+1}COOH$	n = 7 n = 8 n = 9	deG: 86% deG: 99% deG: 100%	7 h	(30)
Photo-Reduction	Laser flash photolysis $Fe(CN)_6^{4-}$ PFCAs	$C_nF_{2n+1}COOH$	n = 1 n = 3 n = 7	k = $1.9 \times 10^6\ M^{-1}s^{-1}$ k = $7.1 \times 10^6\ M^{-1}s^{-1}$ k = $1.7 \times 10^7\ M^{-1}s^{-1}$		(31)
	36 W LP-Hg lamp UV (254 nm) IAA: 1 mM HDTMA: 2.2 g/L PFCAs (0.0241 mM) pH 6	$C_nF_{2n+1}COOH$	n = 4 n = 5 n = 6 n = 7	deF: ~40% deF: ~50% deF: ~65% deF: ~90%	10 h	(32)
	8 W UV lamp 254 nm Iodide: 10 mM	$C_nF_{2n+1}COOH$	n = 3 n = 5 n = 7	$k_{deG} \approx 1.3 \times 10^{-3}\ min^{-1}$ $k_{deG} \approx 1.3 \times 10^{-3}\ min^{-1}$ $k_{deG} \approx 1.3 \times 10^{-3}\ min^{-1}$		(22)
		$C_nF_{2n+1}SO_3H$	n = 4 n = 6 n = 8	$k_{deG} = 0.4 \times 10^{-3}\ min^{-1}$ $k_{deG} = 1.2 \times 10^{-3}\ min^{-1}$ $k_{deG} = 3.0 \times 10^{-3}\ min^{-1}$		
	18 W LP-Hg lamp UV (254 nm)	$C_nF_{2n+1}COOH$	n: 2-10	deF: ~55%	48 h	(33)

	Sulfite: 10 mM pH 9.5 20 ℃	$HOOCC_nF_{2n+1}COOH$ n: 2-10	deF: ~67%	
		$C_nF_{2n+1}SO_3H$ n = 1	deF: ~0.94%	
		n = 4	deF: ~4.6%	
		n = 6	deF: ~31.8%	
		n = 8	deF: ~57%	
		$C_nF_{2n+1}C_2H_4COOH$ n = 5	deF: ~4.1%	
		n = 6	deF: ~7.4%	
		n = 7	deF: ~17.1%	
		n = 8	deF: ~33.4%	

Method	Experimental conditions	PFAS structure (Functional group)	Decomposition & defluorination	Reference
Photo-Reduction	16 lamps (254 nm) with emission intensity of 8.0 $mW.cm^{-2}$ for each lamp Sulfite: 20 mM pH 10	PFOA GenX	k_{deG} = 0.0410 min^{-1} k_{deG} = 0.0338 min^{-1}	(34)
	16 lamps (254 nm) with emission intensity of 8.0 $mW.cm^{-2}$ for each lamp Sulfite: 20 mM pH 10	F-53 PFOS F-53B	deG: ~99% 3 h deG: ~99% 2 h deG: ~99% 1 min	(35)
	18 W LP-Hg lamp UV (254 nm) Sulfite: 10 mM pH 9.5 20 ℃	$C_nF_{2n+1}COOH$ n = 8 $HOOCC_nF_{2n+1}COOH$ n = 8 $C_nF_{2n+1}SO_3H$ n = 8 $C_nF_{2n+1}C_2H_4COOH$ n = 8	deF: ~58.2% deF: ~63.6% deF: ~57.0% deF: ~33.4% 48 h	(33)

Table S4 Effect of water solutes on PFAS photodegradation

Method	Experimental conditions	Water quality	Decomposition & defluorination		Reference
Photo-oxidation	16 W LP-Hg lamp UV (254 nm) Persulfate: 15 mM PFOA (62.11 mg/L) 25 ± 2 ℃ No pH adjustment	Cl^-: 0 mM	deG: ~70%	4 h	(36)
		Cl^-: 0.5 mM	deG: ~66%		
		Cl^-: 1 mM	deG: ~60%		
		Cl^-: 2 mM	deG: ~23%		
		Cl^-: 3 mM	deG: 0%		
		HCO_3^-: 0 mM	deG: ~70%		
		HCO_3^-: 5 mM	deG: ~48%		
		HCO_3^-: 10 mM	deG: ~40%		
		HCO_3^-: 15 mM	deG: ~21%		
		HCO_3^-: 25 mM	deG: ~8%		
	5 W LP-Hg lamp UV/VUV (254/185 nm) Ferric: 20 μM PFOA (14.9 mg/L)	ClO_4^-: 10 mM	$k_{deF}/k_{deF,0}$ = ~0.9		(19)
		Cl^-: 10 mM	$k_{deF}/k_{deF,0}$ = ~0.78		
		NO_3^-: 10 mM	$k_{deF}/k_{deF,0}$ = ~0.72		
		SO_4^{2-}: 10 mM	$k_{deF}/k_{deF,0}$ = ~0.4		
		HCO_3^-: 10 mM	$k_{deF}/k_{deF,0}$ = ~0.32		
		Methanol: 1 M	$k_{deF}/k_{deF,0}$ = ~0.5		
		Acetone: 1 M	$k_{deF}/k_{deF,0}$ = ~0.5		
		Isopropyl alcohol: 1 M	$k_{deF}/k_{deF,0}$ = ~0.24		
		Ethyl acetate: 1 M	$k_{deF}/k_{deF,0}$ = ~0.24		
		MTBE: 1 M	$k_{deF}/k_{deF,0}$ = ~0.18		
		HA: 15 mg/L	$k_{deF}/k_{deF,0}$ = ~0.63		
	23 W LP-Hg lamp 254 nm In_2O_3: 0.5 g/L PFOA (41.4 mg/L) 25 ℃ O_2 atmosphere	Secondary effluent of wastewater: Bicarbonate (4.76 mM) TOC (18.9 mg/L)	deG% = ~0%	4 h	(37)
		Pure water	deG% = ~85%		
	14 W LP-Hg lamp 254 nm Ga_2O_3: 0.5 g/L PFOA (500 μg/L) O_2 atmosphere pH 4.7 25 ℃	Secondary effluent of wastewater: Bicarbonate (4.76 mM) TOC (18.9 mg/L)	k_{deG}= 1.00 h^{-1}		(5)
		Pure water	k_{deG}= 4.85 h^{-1}		
Photo-reduction	10 W LP-Hg lamp 254 nm	DI water	deF: 88.5%		(6)

Sulfite:10 mM PFOA (8.28 mg/L) N_2 atmosphere pH 10.3 25 ℃	NO_3^-: 10 mM NO_2^-: 10 mM	deF: 4.1% deF: 5%	24 h	
10 W LP-Hg lamp UV/VUV (254/185 nm) Sulfite: 20 mM PFOS (18.6 mg/L) pH 10 25 ℃	HA: 0 mg/L HA: 2.64 mg/L HA: 5.43 mg/L	deG: ~83% deG: ~70% deG: ~58%	2 h	(9)
	NO_3^- : 0 mM NO_3^- : 0.1 mM NO_3^- : 0.5 mM NO_3^- : 1 mM	deG: ~83% deG: ~81.5% deG: ~58% deG: ~41.6%		
	HCO_3^- : 0 mM HCO_3^- : 0.1 mM	deG: ~83% deG: ~80%		
	HCO_3^-: 0.5 mM HCO_3^- : 1 mM	deG: ~74% deG: ~66%		
16 lamps (254 nm) with emission intensity of 8.0 $mW.cm^{-2}$ for each lamp Sulfite: 20 mM F-53B pH 10	DI water, F-53B$_0$ = 65.7 μg/L Chrome electroplating wastewater effluent F-53B$_0$ = 91.3 mg/L	deG: ~99% deG: 100%	1 min ~ 60 min	(35)
15 W LP-Hg lamp 254 nm Iodide: 0.3 mM PFOA (10.35 mg/L) N_2 atmosphere pH 9 room temperature	DI water, PFOA$_0$ = 10.35 mg/L Industrial wastewater, PFOA$_0$ = 6.04 mg/L	deG: 93.9% deG: 96%	6 h 12 h	(21)
14 W LP-Hg lamp 254 nm Iodide: 0.3 mM PFOS (15 mg/L) N_2 atmosphere pH 10 25 ℃	Without HA HA: MW < 5 kDa HA: MW = 5-10 kDa HA: MW = 10-30 kDa HA: MW = 30-100 kDa HA: MW > 100 kDa	deG: 51.7% deG: 27% deG: 20.4% deG: 31.3% deG: 59.8% deG: 91.3%	1.5 h	(14)
	[HA] = 0 mg/L [HA] = 0.1 mg/L [HA] = 1.0 mg/L [HA] = 10.0 mg/L [HA] = 30.0 mg/L	deG: 51.7% deG: 74.7% deG: 86% deG: 71.4% deG: 34.4%		
14 W LP-Hg lamp 254 nm Iodide: 0.3 mM	[HA] = 0 mg/L [HA] = 0.1 mg/L [HA] = 0.5 mg/L	deG: 9.23% deG: 10.1% deG: 37.2%	1.5 h	(38)

	PFOA (12.42 mg/L) Helium atmosphere pH 10 25 ℃	[HA] = 1 mg/L		deG: 67.5%		
		[HA] = 5 mg/L		deG: 55.3%		
		HA: MW < 10 kDa		deG: 45.4%		
		HA: MW = 10-30 kDa		deG: 78.8%		
		HA: MW = 30-100 kDa		deG: 52.2%		
		HA: MW > 100 kDa		deG: 4.8%		
	36 W LP-Hg lamp UV (254 nm) IAA: 1 mM HDTMA: 2.2 g/L PFCAs (0.0241 mM) pH 6	DI water		deG: 100%	5 h	(32)
		Suwannee river humic acid (SRHA): 10 mg C/L		deG: 100%	8 h	
	Laser flash photolysis $Fe(CN)_6^{4-}$ $NaClO_4$ to adjust ionic strength (IS)	CF_3COO^-	IS: 0.010 M	k = (2.3 $\pm$ 0.2) $\times 10^6 M^{-1}s^{-1}$		(31)
			IS: 0.015 M	k = (2.5 $\pm$ 0.2) $\times 10^6 M^{-1}s^{-1}$		
			IS: 0.035 M	k = (2.9 $\pm$ 0.1) $\times 10^6 M^{-1}s^{-1}$		
			IS: 0.065 M	k = (3.0 $\pm$ 0.2) $\times 10^6 M^{-1}s^{-1}$		
			IS: 0.10 M	k = (3.4 $\pm$ 0.3) $\times 10^6 M^{-1}s^{-1}$		
		$C_3F_7COO^-$	IS: 0.010 M	k = (8.8 $\pm$ 0.2) $\times 10^6 M^{-1}s^{-1}$		
			IS: 0.015 M	k = (9.0 $\pm$ 0.3) $\times 10^6 M^{-1}s^{-1}$		
			IS: 0.035 M	k = (9.6 $\pm$ 0.1) $\times 10^6 M^{-1}s^{-1}$		
			IS: 0.065 M	k = (1.2 $\pm$ 0.1) $\times 10^7 M^{-1}s^{-1}$		
			IS: 0.10 M	k = (1.3 $\pm$ 0.1) $\times 10^7 M^{-1}s^{-1}$		

Table S5 Integration of photodegradation methods with other treatment processes

Method	Experimental conditions	Processes	Decomposition & defluorination		Reference
VUV/ Ultrasonic (US)	VUV (185 nm, 12-15 % of total emission) and UV (254 nm) Average US power density: 2 $W.cm^{-2}$ PFOS (10 mg/L) 10 ℃	VUV alone VUV/US	deF: 5.74% deF: 88.47%	4 h	(39)
UV/US/TiO_2	UV (254 nm) US probe: 40 kHz, 500 W PFOA (49.68 mg/L) 25 ℃	UV/$RdH\ TiO_2$ UV/US/$RdH\ TiO_2$	deG: 22% deG: 45%	7 h	(40)
Thermal-assisted photolysis	Adjustable mercury lamp emitting at different UV region Light intensity: $72 \pm 10 \times 100\ \mu W.cm^{-2}$ PFOA (1 mg/L) pH 7	25 ℃ 60 ℃	deG: 40% deG: 70%	12 h	(41)
Fe^0/GAC micro-electrolysis assisted VUV-Fenton photolysis	VUV (185 nm, 12-15 % of total emission) and UV (254 nm) Fe: 7.5 g/L GAC: 12.5 g/L H_2O_2: 22.8 mM PFOA (10 mg/L)	VUV alone Fe^0/GAC micro-electrolysis assisted VUV-Fenton	deF: 39% deF: 47%	6 h	(42)

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