

Supporting Information for the Article:

Perfluorooctanoic Acid Degradation Using UV-Persulfate Process: Modeling of the Degradation and Chlorate Formation

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Text S1. Chemicals

Perfluorooctanoic acid (PFOA, 96.0%), perfluoroheptanoic acid (PFHpA, 99.9%), perfluorohexanoic acid (PFHxA, 97.0%), perfluoropentanoic acid (PFPeA, 97.0%), perfluorobutyric acid (PFBA, 98.0%) and pentafluoropropionic acid (PFPrA, 97.0%) were all purchased from Sigma-Aldrich (St. Louis, MO). HPLC-grade methanol (99.9%) and sodium persulfate (PS, 98.0%) were obtained from Sigma-Aldrich. Sodium chloride (NaCl, 99.0%), sodium bicarbonate (NaHCO₃, 99.7%) and sodium chlorate (NaClO₃, 99.0%) were supplied by Sigma-Aldrich. Ammonium acetate (CH₃COONH₄, 97.0%) and potassium iodide (KI, 99.0%) were purchased from Fisher Scientific (Pittsburgh, PA). All other reagents were of analytical grade and obtained from Sigma-Aldrich or Fisher Scientific. Milli-Q (deionized, DI) water was prepared from a nanopure Millipore system (D11911, Thermo Scientific) and had a conductance of 18.2 MΩ·cm at 25 ± 1 °C (here after called ultrapure water-UW). UW was used in all the experiments except those involving surface water (SW) and wastewater (WW) matrices.

Text S2. Water Sampling and Characterization

SW samples were collected from Lanier Lake in Atlanta. WW samples were collected from the secondary effluent at a local municipal wastewater treatment plant before disinfection. The water samples were further filtered through a 0.45 μm membrane to remove particles before use. The characteristics of the water samples are provided in Table S2. Dissolved organic matter (DOC) was measured using a Shimadzu TOC analyzer and pH was measured using a pH meter. Chloride, fluoride, nitrate, phosphate ions were measured using a Dionex DX-100 ion chromatography with a conductivity detector. Fe²⁺ and Mn²⁺ were measured by an Agilent inductively coupled plasma mass spectrometer (ICP-MS).

Text S3. Analytical Methods

PS concentration was determined using the spectrophotometric method described by Liang et al.¹ For the method, PS is reacted with KI in the presence of NaHCO₃ and forms an iodine yellow color which is quantified using UV-Vis spectrophotometer (DU520, Beckman) at a wavelength of 352 nm. Chloride and chlorate and the anions in real water samples were measured by an ion chromatography (ICS2500, Dionex) system with a conductivity detector. A medium capacity carbonate eluent column (AS9-HC, 4 mm × 250 mm, Thermo Scientific) and its guard column (AG9-HC, 4 mm × 50 mm, Thermo Scientific) were used for separation. The mobile phase contained 10 mM Na₂CO₃ and 1.2 mM NaHCO₃ and the flow rate was 1 mL·min⁻¹. Total organic carbon (TOC) was measured by a TOC analyzer (TOC-C CSH, Shimadzu). Iron and manganese were measured by IC-MS. A Dionex CG5A guard column was used to separate. The forward power was 1250 W with the 0.7 mL·min⁻¹ nebuliser gas.

PFOA was measured using an Agilent 1200 Series HPLC that was equipped with a C18 column (4.6 mm × 250 mm, 5μm). Isocratic elution was employed using 20 mM CH₃COONH₄ solution and HPLC-grade methanol (25:75, v/v) with a flow rate of 0.4 mL/min. PFOA was detected using UV absorbance at 210 nm. The intermediates of PFOA were measured using an Agilent 1100 Series high performance liquid chromatography mass spectrometry (HPLC/MS) system coupled with a C18 column (4.6 mm × 150 mm, 3.5 μm). The mobile phase consisted of (A) an aqueous solution containing 20 mM CH₃COONH₄ solution and (B) HPLC-grade methanol (25:75, v/v). The flow rate was 0.4 mL/min. An electrospray negative ionization mode was used to identify the products in the liquid phase. The pressure of sheath gas (N₂) was 0.4 MPa. The capillary potential was -3.0 kV. The source temperature was 120 °C, and the desolvation temperature was set to 350 °C.

Text S4. Experimental Procedures

UV photolysis experiments were conducted in two symmetrical 500 mL cylindrical quartz reactors (optically symmetric bottles) with a 16 W low pressure (LP) mercury UV lamp (GPH317T5L/4, Heraeus) in the middle. The caps were placed on the reactors to reduce the volatilization of PFOA and reduce the dissolution of atmospheric carbon dioxide during the experiments. The reactors were operated in batch mode with magnetic stirring in the bottom of the reactor.

In all cases, the initial concentration in the reactor was 150 μM PFOA and the pH was not adjusted. Then PS (15 mM) was added to the reactor and mixed immediately for a few minutes prior to exposure to UV irradiation. PFOA is difficult to degrade; consequently, a high dosage of PS (5 - 30 mM) was required. The PS concentration that was used in our work is consistent with the previous reports of PFOA degradation by activated PS.^{2, 3} Control experiments were conducted with just PS or just UV light. Experiments were also conducted for different concentrations of Cl^- and HCO_3^- to determine their impact on PFOA destruction. All experiments were conducted in duplicate or triplicate at the ambient temperature (25 ± 2 °C). Samples were taken at pre-selected time intervals and methanol was added to quench any radicals that may be formed by thermolysis of PS.

Text S5. Modeling Approach and Rate Constants Determination

We used literature reported rate constants when we could find reported values. For the literature reported rate constants, most of them had a wide range. Consequently, the rate constants involving $\text{SO}_4^{\cdot-}$ or PS were fitted. The model fits were within the literature reported range. For the reactions resulting from radicals or species that were generated from $\text{SO}_4^{\cdot-}$, we used the literature reported rate constants.

For model fits, we used the following objective function (OF) which was minimized using the genetic algorithm (GA).⁴

$$OF = \sqrt{\frac{1}{N-1} \sum_{i=1}^N [(C_{\text{exp}, i} - C_{\text{cal}, i}) / C_{\text{exp}, i}]^2} \quad (\text{S1})$$

where, $C_{\text{exp},i}$ and $C_{\text{cal},i}$ are the experimental and calculated concentrations of different species, respectively; N is the number of the experimental data for each compound; and the index i refers to the compounds ranging from 1 to N . Different species were used to determine the rate constants. Genetic algorithm was used to fit the data of PS and PFOA and PFOA byproducts. And the rate constants of reactions 2-8 in Table S1 were determined from these fits. Data for the destruction of PFOA in the presence of HCO_3^- were used to determine scavenging rate constants of HCO_3^- (i.e., reaction 79 in Table S1). Finally, the data of Cl^- decay, ClO_3^- formation and PFOA degradation were used to determine the rate constants that describe Cl^- scavenging (i.e., reactions 40, 57-58, 62-64 in Table S1).

The kinetic equations used in the model were derived from the mass balance for a species, A, in a completely mixed batch reactor (CMBR).

$$\frac{dC_a}{dt} = r_a, \quad C_a|_{t=0} = C_{a0} \quad (\text{S2})$$

where, C_{a0} is the initial concentration of species A at time 0, C_a is the concentration of A at time t , and r_a is the overall rate expression of the species A. The backward differentiation formula (BDF) method [i.e. Gear's method]⁵ was used to solve all the ordinary differential equations (ODEs) and obtain the concentration profiles of all species.⁶

The formation rate of $\text{SO}_4^{\cdot-}$ can be described as follows (reaction 1 in Table S1):

$$r_{\text{SO}_4^{\cdot-}} = 2\phi_{\text{PS}} P_{\text{U-V}} f_{\text{PS}} (1 - e^{-2.303(\alpha(\lambda) + \varepsilon(\lambda)C)l}) \quad (\text{S3})$$

where, $r_{\text{SO}_4^{\cdot-}}$ is net formation rate of $\text{SO}_4^{\cdot-}$, $\text{M}\cdot\text{s}^{-1}$; ϕ_{PS} is quantum yield of PS; $P_{\text{U-V}}$ is UV intensity at 254 nm ($2.88 \times 10^{-7} \text{ Einstein}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$); f_{PS} is the fraction of light absorbed by PS, dimensionless; $\varepsilon(\lambda)$ is the molar extinction coefficient of PS at 254 nm ($20.07 \text{ M}^{-1}\cdot\text{cm}^{-1}$, determined in this work); C is the concentration of PS, M ; $\alpha(\lambda)$ is the light absorption of all other solution components at 254 nm, cm^{-1} (0.011 cm^{-1} for surface water and 0.085 cm^{-1} for wastewater); l is the path length of reaction reactor (5.97 cm). It should be noted that ϕ_{PS} in acidic condition is lower than that reported at neutral pH. According to Heidt's work,⁷ 0.5 is a reasonable value and was used in our study. The term $e^{-2.303(\alpha(\lambda) + \varepsilon(\lambda)C)l}$ was equal to $e^{-4139.22}$, $e^{-4139.26}$ and $e^{-4140.28}$ for UW, SW and WW, respectively. All of them were approximately zero;

consequently, all the light in the reactor was absorbed and an exact value for the path length is not needed.

Text S6. Quenching of the Reaction Rate (Q_R) Analysis

Impact of Carbonate Species Calculation. The scavenger of $\text{SO}_4^{\cdot-}$ caused by carbonate species can be expressed as the equation:

$$Q_R = \frac{k_R C_R}{k_{\text{HCO}_3^-} C_{\text{HCO}_3^-} + k_{\text{CO}_3^{2-}} C_{\text{CO}_3^{2-}} + k_R C_R} \quad (\text{S10})$$

In the open system, the calculated concentrations of HCO_3^- and CO_3^{2-} were 6.6×10^{-8} M and 4.2×10^{-14} M in equilibrium with atmospheric CO_2 . The concentration of PFOA is 1.5×10^{-4} M. Substituting the rate constants of $k_{\text{HCO}_3^-} = 3.6 \times 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$, $k_{\text{CO}_3^{2-}} = 6.5 \times 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$ and $k_R = 2.59 \times 10^5 \text{ M}^{-1} \cdot \text{s}^{-1}$ into the above Q_R equation, the calculated Q_R is 0.9939.

Q_R analysis for contaminant degradation under different concentrations of HCO_3^- impact (i.e., 5 mM, 10 mM and 15 mM) was also performed. Table S7 provided the calculated Q_R for a variety of k_R .

Impact of Cl^- Calculation. The scavenger of $\text{SO}_4^{\cdot-}$ caused by Cl^- can be expressed as the equation: $Q_R = \frac{k_R C_R}{k_{\text{Cl}^-} C_{\text{Cl}^-} + k_R C_R}$. Table S6 listed the calculated Q_R under different concentrations of Cl^- impact.

Text S7. Mass Balance of Carbon and Fluorine for PFOA and Its Products

Total carbon and fluorine of PFOA and its products were calculated using their concentration

measurements according to the following equations.

$$[\text{PFOA}]_C = n_{C(\text{PFOA})} \cdot C_{\text{PFOA}} \quad (\text{S4})$$

$$[\text{Products}]_C = n_{C(\text{PFHpA})} \cdot C_{\text{PFHpA}} + n_{C(\text{PFHeA})} \cdot C_{\text{PFHeA}} + n_{C(\text{PFPeA})} \cdot C_{\text{PFPeA}} + n_{C(\text{PFBA})} \cdot C_{\text{PFBA}} + n_{C(\text{PFPrA})} \cdot C_{\text{PFPrA}} \quad (\text{S5})$$

$$[\text{Total}]_C = [\text{PFOA}]_C + [\text{Products}]_C \quad (\text{S6})$$

$$[\text{PFOA}]_F = n_{F(\text{PFOA})} \cdot C_{\text{PFOA}} \quad (\text{S7})$$

$$[\text{Products}]_F = n_{F(\text{PFHpA})} \cdot C_{\text{PFHpA}} + n_{F(\text{PFHeA})} \cdot C_{\text{PFHeA}} + n_{F(\text{PFPeA})} \cdot C_{\text{PFPeA}} + n_{F(\text{PFBA})} \cdot C_{\text{PFBA}} + n_{F(\text{PFPrA})} \cdot C_{\text{PFPrA}} \quad (\text{S8})$$

$$[\text{Total}]_F = [\text{PFOA}]_F + [\text{Products}]_F \quad (\text{S9})$$

where $[\text{PFOA}]_C$ (or $[\text{PFOA}]_F$) is the carbon (or fluorine) concentration in PFOA, mM; $[\text{Products}]_C$ (or $[\text{Products}]_F$) is the carbon (or fluorine) concentration in all the PFOA products; n_C (or n_F) is the number of carbon (or fluorine) in every compound; C is the concentration of every compound. Table S5 listed the results of carbon and fluorine mass balance for PFOA and its products. The initial measured TOC was 1.07 mM. The measured TOC and fluorine at 8 h were 0.67 mM and 0.89 mM, respectively. The theoretical TOC and fluorine concentration was based on the PFOA and PFOA byproduct measurements.

Text S8. EE/O Calculation

The electrical energy per order (EE/O) is defined as the electrical energy (in kWh/m³) required to reduce the concentration of a pollutant by one order of magnitude.⁸ EE/O can be expressed as the following equation:

$$\text{EE/O} = \frac{P \times t}{V \times \log(C_i / C_f)} \quad (\text{S11})$$

where EE/O is electrical efficiency per log order reduction, kWh/m³; P is energy input, including light intensity and PS doses in kW; t is irradiation time, h; V is the reactor volume, m³; C_i is the initial concentration of PFOA, mM; C_f is the final concentration of PFOA, mM.

We measure the light intensity using potassium tris(oxalato)ferrate(III) (See Section Materials and Methods) and it was 2.88×10^{-7} Einstein·L⁻¹·s⁻¹. One mole of photons (1 Einstein)

at 254 nm is equivalent to 0.1308 kWh of energy.⁹ We assumed that the energy efficiency for conversion of electricity to photons was 25%⁹; consequently, the energy input was 1.5×10^{-7} kWh/L·s. To the authors' best knowledge, the energy use for PS production was not available in the literature. Accordingly, the energy to produce PS was calculated from H₂O₂ production and the price of H₂O₂ and PS,. The reported energy use for H₂O₂ production is 10.80 kWh/kg and the price of H₂O₂ (30% wt) and PS are 314 \$·ton⁻¹ and 1048 \$·ton⁻¹, respectively. We assume that the energy use was proportion to the cost and the calculated energy of PS production was 10.81 kWh·kg⁻¹. The reactor volume was 3.5×10^{-4} m³. Using our model, the relationship between $\log(C_i/C_f)$ and different PS dosage was obtained. The results of EE/O values versus different dosage of PS are presented in Figure S12.

Table S1. Reactions and Rate Constants of the Kinetic Model

#	Reaction	k (M ⁻¹ s ⁻¹)	Ref.
1	$\text{S}_2\text{O}_8^{2-} + h\nu \longrightarrow 2\text{SO}_4^{\cdot-}$	$\phi^{254} = 0.50 \text{ mol/Einstein};$ $\epsilon_{\text{S}_2\text{O}_8^{2-}}^{254} = 22.07 \text{ M}^{-1}\text{cm}^{-1}$	10, 11
2	$\text{SO}_4^{\cdot-} + \text{S}_2\text{O}_8^{2-} \longrightarrow \text{S}_2\text{O}_8^{\cdot-} + \text{SO}_4^{2-}$	$k_2 = 1.80 \times 10^5 \text{ (fitted)}$	12
3	$\text{S}_2\text{O}_8^{\cdot-} + \text{SO}_4^{2-} \longrightarrow \text{S}_2\text{O}_8^{2-} + \text{SO}_4^{\cdot-}$	$k_3 = 0.095 \text{ (fitted)}$	12
4	$\text{SO}_4^{\cdot-} + \text{H}_2\text{O} \longrightarrow \text{HO}\cdot + \text{HSO}_4^-$	$k_4[\text{H}_2\text{O}] = 1.817 \times 10^3 \text{ s}^{-1} \text{ (fitted)}$	13
5	$\text{S}_2\text{O}_8^{\cdot-} + \text{H}_2\text{O} \longrightarrow \text{HO}\cdot + \text{H}^+ + \text{S}_2\text{O}_8^{2-}$	$k_5[\text{H}_2\text{O}] = 8.30 \times 10^{-4} \text{ s}^{-1} \text{ (fitted)}$	Fitted
6	$\text{HO}\cdot + \text{HSO}_4^- \longrightarrow \text{SO}_4^{\cdot-} + \text{H}_2\text{O}$	$k_6 = 3.74 \times 10^5 \text{ (fitted)}$	12
7	$\text{SO}_4^{\cdot-} + \text{SO}_4^{\cdot-} \longrightarrow \text{S}_2\text{O}_8^{2-}$	$k_7 = 8.20 \times 10^9 \text{ (fitted)}$	14
8	$\text{SO}_4^{\cdot-} + \text{S}_2\text{O}_8^{\cdot-} \longrightarrow \text{S}_2\text{O}_8^{2-} + \text{SO}_2 + \text{O}_2$	$k_8 = 9.92 \times 10^5 \text{ (fitted)}$	Fitted
9	$\text{HO}\cdot + \text{HO}\cdot \longrightarrow \text{H}_2\text{O}_2$	$k_9 = 5.0 \times 10^9$	15
10	$\text{HO}\cdot + \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{HO}_2\cdot$	$k_{10} = 2.7 \times 10^7$	16
11	$\text{HO}\cdot + \text{HO}_2\cdot \longrightarrow \text{H}_2\text{O} + \text{O}_2$	$k_{11} = 6.6 \times 10^9$	17
12	$\text{HO}_2\cdot + \text{HO}_2\cdot \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k_{12} = 8.3 \times 10^5$	18
13	$\text{SO}_4^{\cdot-} + \text{H}_2\text{O}_2 \longrightarrow \text{HSO}_4^- + \text{HO}_2\cdot$	$k_{13} = 1.2 \times 10^7$	19
14	$\text{SO}_4^{\cdot-} + \text{HO}_2\cdot \longrightarrow \text{HSO}_4^- + \text{O}_2$	$k_{14} = 3.5 \times 10^9$	19
15	$\text{S}_2\text{O}_8^{2-} + \text{HO}\cdot \longrightarrow \text{HSO}_4^- + \text{SO}_4^{\cdot-} + 0.5\text{O}_2$	$k_{15} = 1.2 \times 10^7$	11
16	$\text{SO}_4^{\cdot-} + \text{HO}\cdot \longrightarrow \text{HSO}_5^-$	$k_{16} = 1.0 \times 10^{10}$	20
17	$\text{SO}_4^{\cdot-} + \text{HSO}_5^- \longrightarrow \text{SO}_5^{\cdot-} + \text{HSO}_4^-$	$k_{17} = 1.0 \times 10^6$	20
18	$\text{SO}_5^{\cdot-} + \text{SO}_5^{\cdot-} \longrightarrow \text{SO}_4^{\cdot-} + \text{SO}_4^{\cdot-} + \text{O}_2$	$k_{18} = 2.1 \times 10^8$	20
19	$\text{SO}_5^{\cdot-} + \text{SO}_5^{\cdot-} \longrightarrow \text{S}_2\text{O}_8^{2-} + \text{O}_2$	$k_{19} = 2.2 \times 10^8$	20
20	$\text{SO}_4^{\cdot-} + \text{SO}_5^{\cdot-} \longrightarrow \text{S}_2\text{O}_8^{2-} + 0.5\text{O}_2$	$k_{20} = 8.96 \times 10^9 \text{ (fitted)}$	Fitted
21	$\text{SO}_4^{\cdot-} + \text{C}_7\text{F}_{15}\text{COOH} \longrightarrow \text{C}_6\text{F}_{13}\text{COOH} + \text{byproducts}$	$k_{21} = 2.59 \times 10^5 \text{ (fitted)}$	Fitted
22	$\text{SO}_4^{\cdot-} + \text{C}_6\text{F}_{13}\text{COOH} \longrightarrow \text{C}_5\text{F}_{11}\text{COOH} + \text{byproducts}$	$k_{22} = 2.68 \times 10^5 \text{ (fitted)}$	Fitted
23	$\text{SO}_4^{\cdot-} + \text{C}_5\text{F}_{11}\text{COOH} \longrightarrow \text{C}_4\text{F}_9\text{COOH} + \text{byproducts}$	$k_{23} = 7.02 \times 10^5 \text{ (fitted)}$	Fitted
24	$\text{SO}_4^{\cdot-} + \text{C}_4\text{F}_9\text{COOH} \longrightarrow \text{C}_3\text{F}_7\text{COOH} + \text{byproducts}$	$k_{24} = 1.26 \times 10^6 \text{ (fitted)}$	Fitted
25	$\text{SO}_4^{\cdot-} + \text{C}_3\text{F}_7\text{COOH} \longrightarrow \text{C}_2\text{F}_5\text{COOH} + \text{byproducts}$	$k_{25} = 1.05 \times 10^7 \text{ (fitted)}$	Fitted
26	$\text{SO}_4^{\cdot-} + \text{C}_2\text{F}_5\text{COOH} \longrightarrow \text{CF}_3\text{COOH} + \text{byproducts}$	$k_{26} = 9.31 \times 10^7 \text{ (fitted)}$	Fitted
27	$\text{HSO}_4^- \longleftrightarrow \text{SO}_4^{2-} + \text{H}^+$	$\text{pKa}_2 = 1.9$	21

28	$\text{HSO}_5^- \rightleftharpoons \text{SO}_5^{2-} + \text{H}^+$	$\text{pKa}_3 = 9.4$	22
29	$\text{C}_7\text{F}_{15}\text{COOH} \rightleftharpoons \text{C}_7\text{F}_{15}\text{COO}^- + \text{H}^+$	$\text{pKa}_1 = 2.8$	23
In the presence of Cl^-			
30	$\text{SO}_4^{\cdot-} + \text{Cl}^- \longrightarrow \text{SO}_4^{2-} + \text{Cl}^{\cdot}$	$k_{30} = 4.7 \times 10^8$	24
31	$\text{SO}_4^{2-} + \text{Cl}^{\cdot} \longrightarrow \text{SO}_4^{\cdot-} + \text{Cl}^-$	$k_{31} = 2.5 \times 10^8$	12
32	$\text{Cl}^{\cdot} + \text{H}_2\text{O} \longrightarrow \text{ClOH}^{\cdot-} + \text{H}^+$	$k_{32}[\text{H}_2\text{O}] = 1.3 \times 10^3$	25
33	$\text{ClOH}^{\cdot-} + \text{H}^+ \longrightarrow \text{Cl}^{\cdot} + \text{H}_2\text{O}$	$k_{33} = 2.1 \times 10^{10}$	26
34	$\text{OH}^{\cdot} + \text{Cl}^- \longrightarrow \text{ClOH}^{\cdot-}$	$k_{34} = 4.3 \times 10^9$	26
35	$\text{ClOH}^{\cdot-} \longrightarrow \text{OH}^{\cdot} + \text{Cl}^-$	$k_{35} = 6.1 \times 10^9 \text{ s}^{-1}$	26
36	$\text{ClOH}^{\cdot-} + \text{Cl}^- \longrightarrow \text{Cl}_2^{\cdot-} + \text{OH}^-$	$k_{36} = 1.0 \times 10^4$	27
37	$\text{Cl}^{\cdot} + \text{Cl}^- \longrightarrow \text{Cl}_2^{\cdot-}$	$k_{37} = 8 \times 10^9$	12
38	$\text{Cl}_2^{\cdot-} \longrightarrow \text{Cl}^{\cdot} + \text{Cl}^-$	$k_{38} = 5.3 \times 10^4 \text{ s}^{-1}$	12
39	$\text{Cl}^{\cdot} + \text{Cl}^{\cdot} \longrightarrow \text{Cl}_2$	$k_{39} = 8.8 \times 10^7$	28
40	$\text{Cl}_2^{\cdot-} + \text{Cl}_2^{\cdot-} \longrightarrow \text{Cl}_2 + 2\text{Cl}^-$	$k_{40} = 6.41 \times 10^9$ (fitted)	29
41	$\text{Cl}^{\cdot} + \text{Cl}_2^{\cdot-} \longrightarrow \text{Cl}^- + \text{Cl}_2$	$k_{41} = 2.1 \times 10^9$	30
42	$\text{Cl}_2^{\cdot-} + \text{H}_2\text{O}_2 \longrightarrow \text{H}^+ + 2\text{Cl}^- + \text{HO}_2^{\cdot}$	$k_{42} = 1.4 \times 10^5$	29
43	$\text{Cl}_2^{\cdot-} + \text{HO}_2^{\cdot} \longrightarrow \text{H}^+ + \text{O}_2 + 2\text{Cl}^-$	$k_{43} = 3.0 \times 10^9$	29
44	$\text{Cl}_2^{\cdot-} + \text{H}_2\text{O} \longrightarrow \text{HClOH} + \text{Cl}^-$	$k_{44}[\text{H}_2\text{O}] = 1.3 \times 10^3$	31
45	$\text{HClOH} \longrightarrow \text{ClOH}^{\cdot-} + \text{H}^+$	$k_{45} = 1.0 \times 10^2$	31
46	$\text{HClOH} \longrightarrow \text{Cl}^{\cdot} + \text{H}_2\text{O}$	$k_{46} = 5.0 \times 10^9$	31
47	$\text{HClOH} + \text{Cl}^- \longrightarrow \text{Cl}_2^{\cdot-} + \text{H}_2\text{O}$	$k_{47} = 1.0 \times 10^8$	31
48	$\text{Cl}^{\cdot} + \text{H}_2\text{O}_2 \longrightarrow \text{HO}_2^{\cdot} + \text{Cl}^- + \text{H}^+$	$k_{48} = 2.0 \times 10^9$	30
49	$\text{HO}^{\cdot} + \text{Cl}_2^{\cdot-} \longrightarrow \text{HClO} + \text{Cl}^-$	$k_{49} = 1.0 \times 10^9$	32
50	$\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow \text{Cl}^{\cdot} + \text{HClO} + \text{H}^+$	$k_{50}[\text{H}_2\text{O}] = 15 \text{ s}^{-1}$	33
51	$\text{HO}^{\cdot} + \text{HClO} \longrightarrow \text{ClO}^{\cdot} + \text{H}_2\text{O}$	$k_{51} = 2.0 \times 10^9$	34
52	$\text{HO}^{\cdot} + \text{ClO}^- \longrightarrow \text{ClO}^{\cdot} + \text{OH}^-$	$k_{52} = 8.8 \times 10^9$	35
53	$\text{Cl}^{\cdot} + \text{HClO} \longrightarrow \text{ClO}^{\cdot} + \text{H}^+ + \text{Cl}^-$	$k_{53} = 3.0 \times 10^9$	29
54	$\text{Cl}^{\cdot} + \text{ClO}^- \longrightarrow \text{ClO}^{\cdot} + \text{Cl}^-$	$k_{54} = 8.2 \times 10^9$	29
55	$\text{HO}^{\cdot} + \text{ClO}_2^- \longrightarrow \text{ClO}_2^{\cdot} + \text{OH}^-$	$k_{55} = 1.0 \times 10^9$	29
56	$\text{HO}^{\cdot} + \text{ClO}_2^{\cdot} \longrightarrow \text{ClO}_3^- + \text{H}^+$	$k_{56} = 4.0 \times 10^9$	29
57	$\text{SO}_4^{\cdot-} + \text{HClO} \longrightarrow \text{ClO}_2^{\cdot} + \text{SO}_3^{2-} + \text{H}^+$	$k_{57} = 2.79 \times 10^9$ (fitted)	Fitted
58	$\text{SO}_4^{\cdot-} + \text{ClO}_2^{\cdot} + \text{H}_2\text{O} \longrightarrow \text{ClO}_3^- + 2\text{H}^+ + \text{SO}_4^{2-}$	$k_{58} = 8.23 \times 10^9$ (fitted)	Fitted
59	$\text{ClO}_2^{\cdot} + \text{SO}_3^{2-} \longrightarrow \text{ClO}_2^- + \text{SO}_3^{\cdot-}$	$k_{59} = 7.8 \times 10^5$	29

60	$\text{SO}_3^{\cdot-} + \text{SO}_3^{\cdot-} \longrightarrow \text{S}_2\text{O}_6^{2-}$	$k_{60} = 2.4 \times 10^8$	20
61	$\text{ClO}^{\cdot} + \text{ClO}_2^{\cdot} \longrightarrow \text{ClO}^{\cdot} + \text{ClO}_2^{\cdot}$	$k_{61} = 9.4 \times 10^8$	29
62	$\text{Cl}^{\cdot} + \text{S}_2\text{O}_8^{2-} \longrightarrow \text{ClO}_2^{\cdot} + \text{byproducts}$	$k_{62} = 2.93 \times 10^8$ (fitted)	12
63	$\text{Cl}_2^{\cdot-} + \text{S}_2\text{O}_8^{2-} \longrightarrow \text{ClO}_2^{\cdot} + \text{byproducts}$	$k_{63} = 3.82 \times 10^4$ (fitted)	12
64	$\text{ClO}_3^{\cdot} \longrightarrow \text{byproducts}$	$k_{64} = 5.04 \times 10^{-6}$ (fitted)	Fitted
65	$\text{CO}_3^{\cdot-} + \text{ClO}^{\cdot} \longrightarrow \text{CO}_3^{2-} + \text{ClO}^{\cdot}$	$k_{65} = 5.1 \times 10^5$	29
66	$\text{CO}_3^{\cdot-} + \text{ClO}_2^{\cdot} \longrightarrow \text{CO}_3^{2-} + \text{ClO}_2^{\cdot}$	$k_{66} = 3.1 \times 10^7$	29
67	$\text{Cl}^{\cdot} + \text{CO}_3^{2-} \longrightarrow \text{Cl}^{\cdot} + \text{CO}_3^{\cdot-}$	$k_{67} = 5.0 \times 10^8$	32
68	$\text{Cl}^{\cdot} + \text{HCO}_3^{\cdot} \longrightarrow \text{Cl}^{\cdot} + \text{CO}_3^{\cdot-} + \text{H}^+$	$k_{68} = 2.2 \times 10^8$	32
69	$\text{Cl}_2^{\cdot-} + \text{CO}_3^{2-} \longrightarrow 2\text{Cl}^{\cdot} + \text{CO}_3^{\cdot-}$	$k_{69} = 1.6 \times 10^8$	32
70	$\text{Cl}_2^{\cdot-} + \text{HCO}_3^{\cdot} \longrightarrow 2\text{Cl}^{\cdot} + \text{CO}_3^{\cdot-} + \text{H}^+$	$k_{70} = 8.0 \times 10^7$	32
71	$\text{HClO} \longleftrightarrow \text{H}^+ + \text{ClO}^{\cdot}$	$\text{pKa}_4 = 7.6$	21
In the presence of HCO_3^{\cdot}			
72	$\text{SO}_4^{\cdot-} + \text{HCO}_3^{\cdot} \longrightarrow \text{CO}_3^{\cdot-} + \text{H}^+ + \text{SO}_4^{2-}$	$k_{72} = 3.60 \times 10^6$ (fitted)	36
73	$\text{SO}_4^{\cdot-} + \text{CO}_3^{2-} \longrightarrow \text{CO}_3^{\cdot-} + \text{SO}_4^{2-}$	$k_{73} = 6.5 \times 10^6$	37
74	$\text{HO}^{\cdot} + \text{HCO}_3^{\cdot} \longrightarrow \text{CO}_3^{\cdot-} + \text{H}_2\text{O}$	$k_{74} = 8.5 \times 10^6$	16
75	$\text{HO}^{\cdot} + \text{CO}_3^{2-} \longrightarrow \text{CO}_3^{\cdot-} + \text{OH}^{\cdot}$	$k_{75} = 4.2 \times 10^8$	16
76	$\text{HO}^{\cdot} + \text{CO}_3^{\cdot-} \longrightarrow \text{byproducts}$	$k_{76} = 3.0 \times 10^9$	6
77	$\text{H}_2\text{O}_2 + \text{CO}_3^{\cdot-} \longrightarrow \text{HCO}_3^{\cdot} + \text{HO}_2^{\cdot}$	$k_{77} = 4.3 \times 10^5$	29
78	$\text{CO}_3^{\cdot-} + \text{CO}_3^{\cdot-} \longrightarrow \text{byproducts}$	$k_{78} = 3.0 \times 10^7$	6
79	$\text{S}_2\text{O}_8^{2-} + \text{CO}_3^{\cdot-} \longrightarrow \text{CO}_3^{2-} + \text{S}_2\text{O}_8^{\cdot-}$	$k_{79} = 6.79 \times 10^8$ (fitted)	Fitted
80	$\text{H}_2\text{CO}_3 \longleftrightarrow \text{H}^+ + \text{HCO}_3^{\cdot}$	$\text{pKa}_5 = 6.3$	21
81	$\text{HCO}_3^{\cdot} \longleftrightarrow \text{H}^+ + \text{CO}_3^{2-}$	$\text{pKa}_6 = 10.3$	21
In surface water and waste water			
82	$\text{SO}_4^{\cdot-} + \text{NO}_3^{\cdot} \longrightarrow \text{NO}_3^{\cdot} + \text{SO}_4^{2-}$	$k_{82} = 3.6 \times 10^5$	29
83	$\text{HO}^{\cdot} + \text{NO}_3^{\cdot} \longrightarrow \text{NO}_3^{\cdot} + \text{HO}^{\cdot}$	$k_{83} = 4.0 \times 10^5$	38
84	$\text{Cl}^{\cdot} + \text{NO}_3^{\cdot} \longrightarrow \text{Cl}^{\cdot} + \text{NO}_3^{\cdot}$	$k_{84} = 7.1 \times 10^7$	38
85	$\text{NO}_3^{\cdot} + \text{NO}_3^{\cdot} \longrightarrow \text{N}_2\text{O}_6$	$k_{85} = 7.9 \times 10^5$	29
86	$\text{SO}_4^{\cdot-} + \text{HPO}_4^{2-} \longrightarrow \text{HPO}_4^{\cdot-} + \text{SO}_4^{2-}$	$k_{86} = 1.2 \times 10^6$	29
87	$\text{SO}_4^{\cdot-} + \text{H}_2\text{PO}_4^{\cdot} \longrightarrow \text{HPO}_4^{\cdot-} + \text{HSO}_4^{\cdot}$	$k_{87} = 6.0 \times 10^4$	29
88	$\text{HO}^{\cdot} + \text{HPO}_4^{2-} \longrightarrow \text{HPO}_4^{\cdot-} + \text{HO}^{\cdot}$	$k_{88} = 1.5 \times 10^5$	6
89	$\text{HO}^{\cdot} + \text{H}_2\text{PO}_4^{\cdot} \longrightarrow \text{HPO}_4^{\cdot-} + \text{H}_2\text{O}$	$k_{89} = 2.0 \times 10^4$	6
90	$\text{H}_2\text{O}_2 + \text{HPO}_4^{\cdot-} \longrightarrow \text{H}_2\text{PO}_4^{\cdot} + \text{HO}_2^{\cdot}$	$k_{90} = 4.3 \times 10^5$	6
91	$\text{HPO}_4^{\cdot-} + \text{Cl}^{\cdot} \longrightarrow \text{byproducts}$	$k_{91} = 5.0 \times 10^3$	29

92	$\text{HPO}_4^{\cdot-} + \text{HPO}_4^{\cdot-} \longrightarrow \text{P}_2\text{O}_8^{4-} + 2\text{H}^+$	$k_{92} = 4.0 \times 10^8$	29
93	$\text{HPO}_4^{\cdot-} + \text{SO}_4^{2-} \longrightarrow \text{byproducts}$	$k_{93} = 1.0 \times 10^4$	29
94	$\text{SO}_4^{\cdot-} + \text{NOM} \longrightarrow \text{byproducts}$	$k_{94} = 2.35 \times 10^7 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$	39
95	$\text{HO}^{\cdot} + \text{NOM} \longrightarrow \text{byproducts}$	$k_{95} = 3.9 \times 10^8 \text{ M}_\text{C}^{-1} \text{ s}^{-1}$	8
96	$\text{SO}_4^{\cdot-} + \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{SO}_4^{2-}$	$k_{96} = 9.9 \times 10^8$	29
97	$\text{SO}_4^{\cdot-} + \text{Mn}^{2+} \longrightarrow \text{Mn}^{3+} + \text{SO}_4^{2-}$	$k_{97} = 2.0 \times 10^7$	29
98	$\text{HO}^{\cdot} + \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{HO}^-$	$k_{98} = 3.3 \times 10^8$	8
99	$\text{HO}^{\cdot} + \text{Mn}^{2+} \longrightarrow \text{Mn}^{3+} + \text{HO}^-$	$k_{99} = 3.0 \times 10^7$	8
100	$\text{H}_2\text{PO}_4^- \longleftrightarrow \text{H}^+ + \text{HPO}_4^{2-}$	$\text{pK}_\text{a7} = 7.2$	21
101	$\text{HPO}_4^{2-} \longleftrightarrow \text{H}^+ + \text{PO}_4^{3-}$	$\text{pK}_\text{a8} = 12.3$	21

Text S9. Kinetic Equations

Below are the kinetic equations of the main species used in the model. The pH calculation is based on the charge balance. Acid-base equilibrium of acids was calculated based on their pKa. The pH was calculated as the following equation which has also been used in our former works.⁴¹

$$10^{\text{pH}} + \text{total positive charge} - \text{total negative charge} - 10^{-(14-\text{pH})} = 0$$

Where the total positive or negative charge is the summary of all positive or negative charged radicals and ions.

$$\begin{aligned} \frac{d[\text{S}_2\text{O}_8^{2-}]}{dt} = & -r_{\text{UV},\text{S}_2\text{O}_8^{2-}} - k_1[\text{S}_2\text{O}_8^{2-}][\text{SO}_4^{\cdot-}] + k_2[\text{S}_2\text{O}_8^{\cdot-}][\text{SO}_4^{2-}] + k_3[\text{H}_2\text{O}][\text{S}_2\text{O}_8^{\cdot-}] + k_6[\text{SO}_4^{\cdot-}][\text{SO}_4^{\cdot-}] \\ & + k_7[\text{SO}_4^{\cdot-}][\text{S}_2\text{O}_8^{\cdot-}] - k_{14}[\text{S}_2\text{O}_8^{2-}][\text{HO}\cdot] + k_{18}[\text{SO}_5^{\cdot-}][\text{SO}_5^{\cdot-}] + k_{19}[\text{SO}_4^{\cdot-}][\text{SO}_5^{\cdot-}] - k_{33}[\text{S}_2\text{O}_8^{2-}][\text{CO}_3^{\cdot-}] \\ & - k_{66}[\text{Cl}\cdot][\text{S}_2\text{O}_8^{2-}] - k_{67}[\text{Cl}_2^{\cdot-}][\text{S}_2\text{O}_8^{2-}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{SO}_4^{\cdot-}]}{dt} = & 2 \cdot r_{\text{UV},\text{S}_2\text{O}_8^{2-}} - k_1[\text{S}_2\text{O}_8^{2-}][\text{SO}_4^{\cdot-}] + k_2[\text{S}_2\text{O}_8^{\cdot-}][\text{SO}_4^{2-}] - k_4[\text{SO}_4^{\cdot-}] + k_5[\text{HSO}_4^-][\text{HO}\cdot] \\ & - 2 \cdot k_6[\text{SO}_4^{\cdot-}][\text{SO}_4^{\cdot-}] - k_7[\text{SO}_4^{\cdot-}][\text{S}_2\text{O}_8^{\cdot-}] - k_{12}[\text{SO}_4^{\cdot-}][\text{H}_2\text{O}_2] - k_{13}[\text{SO}_4^{\cdot-}][\text{HO}_2\cdot] + k_{14}[\text{S}_2\text{O}_8^{2-}][\text{HO}\cdot] \\ & - k_{15}[\text{SO}_4^{\cdot-}][\text{HO}\cdot] - k_{16}[\text{SO}_4^{\cdot-}][\text{HSO}_5^-] + 2 \cdot k_{17}[\text{SO}_5^{\cdot-}][\text{SO}_5^{\cdot-}] - k_{20}[\text{SO}_4^{\cdot-}][\text{C}_7\text{F}_{15}\text{COO}^-] \\ & - k_{21}[\text{SO}_4^{\cdot-}][\text{C}_6\text{F}_{13}\text{COO}^-] - k_{22}[\text{SO}_4^{\cdot-}][\text{C}_5\text{F}_{11}\text{COO}^-] - k_{23}[\text{SO}_4^{\cdot-}][\text{C}_4\text{F}_9\text{COO}^-] - k_{24}[\text{SO}_4^{\cdot-}][\text{C}_3\text{F}_7\text{COO}^-] \\ & - k_{25}[\text{SO}_4^{\cdot-}][\text{C}_2\text{F}_5\text{COO}^-] - k_{26}[\text{SO}_4^{\cdot-}][\text{HCO}_3^-] - k_{27}[\text{SO}_4^{\cdot-}][\text{CO}_3^{2-}] - k_{34}[\text{SO}_4^{\cdot-}][\text{Cl}^-] + k_{35}[\text{SO}_4^{2-}][\text{Cl}\cdot] \\ & - k_{61}[\text{SO}_4^{\cdot-}][\text{ClO}^-] - k_{62}[\text{SO}_4^{\cdot-}][\text{ClO}_2\cdot] - k_{75}[\text{SO}_4^{\cdot-}][\text{NO}_3^-] - k_{79}[\text{SO}_4^{\cdot-}][\text{HPO}_4^{2-}] - k_{80}[\text{SO}_4^{\cdot-}][\text{H}_2\text{PO}_4^-] \\ & - k_{87}[\text{SO}_4^{\cdot-}][\text{NOM}] - k_{89}[\text{SO}_4^{\cdot-}][\text{Fe}^{2+}] - k_{90}[\text{SO}_4^{\cdot-}][\text{Mn}^{2+}] \end{aligned}$$

$$\frac{d[\text{S}_2\text{O}_8^{\cdot-}]}{dt} = k_1[\text{SO}_4^{\cdot-}][\text{S}_2\text{O}_8^{2-}] - k_2[\text{S}_2\text{O}_8^{\cdot-}][\text{SO}_4^{2-}] - k_3[\text{H}_2\text{O}][\text{S}_2\text{O}_8^{\cdot-}] - k_7[\text{SO}_4^{\cdot-}][\text{S}_2\text{O}_8^{\cdot-}] + k_{33}[\text{S}_2\text{O}_8^{2-}][\text{CO}_3^{\cdot-}]$$

$$\begin{aligned} \frac{d[\text{HO}\cdot]}{dt} = & k_3[\text{H}_2\text{O}][\text{S}_2\text{O}_8^{\cdot-}] + k_4[\text{H}_2\text{O}][\text{SO}_4^{\cdot-}] - k_5[\text{HO}\cdot][\text{HSO}_4^-] - 2 \cdot k_8[\text{HO}\cdot][\text{HO}\cdot] - k_9[\text{HO}\cdot][\text{H}_2\text{O}_2] \\ & - k_{10}[\text{HO}\cdot][\text{HO}_2\cdot] - k_{14}[\text{S}_2\text{O}_8^{2-}][\text{HO}\cdot] - k_{15}[\text{SO}_4^{\cdot-}][\text{HO}\cdot] - k_{28}[\text{HO}\cdot][\text{HCO}_3^-] - k_{29}[\text{HO}\cdot][\text{CO}_3^{2-}] \\ & - k_{30}[\text{HO}\cdot][\text{CO}_3^{\cdot-}] - k_{38}[\text{HO}\cdot][\text{Cl}^-] + k_{39}[\text{ClOH}\cdot] - k_{53}[\text{HO}\cdot][\text{Cl}_2^{\cdot-}] - k_{55}[\text{HO}\cdot][\text{HClO}] - k_{56}[\text{HO}\cdot][\text{ClO}^-] \\ & - k_{59}[\text{HO}\cdot][\text{ClO}^-] - k_{60}[\text{HO}\cdot][\text{ClO}_2\cdot] - k_{76}[\text{HO}\cdot][\text{NO}_3^-] - k_{81}[\text{HO}\cdot][\text{HPO}_4^{2-}] - k_{82}[\text{HO}\cdot][\text{H}_2\text{PO}_4^-] - k_{88}[\text{HO}\cdot][\text{NOM}] \\ & - k_{91}[\text{HO}\cdot][\text{Fe}^{2+}] - k_{92}[\text{HO}\cdot][\text{Mn}^{2+}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{H}_2\text{O}_2]}{dt} = & k_8[\text{HO}\cdot][\text{HO}\cdot] - k_9[\text{HO}\cdot][\text{H}_2\text{O}_2] + k_{11}[\text{HO}_2\cdot][\text{HO}_2\cdot] - k_{12}[\text{SO}_4^{\cdot-}][\text{H}_2\text{O}_2] - k_{31}[\text{H}_2\text{O}_2][\text{CO}_3^{\cdot-}] \\ & - k_{46}[\text{Cl}_2^{\cdot-}][\text{H}_2\text{O}_2] - k_{52}[\text{Cl}\cdot][\text{H}_2\text{O}_2] - k_{83}[\text{H}_2\text{O}_2][\text{HPO}_4^{\cdot-}] \end{aligned}$$

$$\begin{aligned} \frac{d[\text{HO}_2\cdot]}{dt} = & k_9[\text{HO}\cdot][\text{H}_2\text{O}_2] - k_{10}[\text{HO}\cdot][\text{HO}_2\cdot] - 2 \cdot k_{11}[\text{HO}_2\cdot][\text{HO}_2\cdot] + k_{12}[\text{SO}_4^{\cdot-}][\text{H}_2\text{O}_2] - k_{13}[\text{SO}_4^{\cdot-}][\text{HO}_2\cdot] \\ & + k_{31}[\text{H}_2\text{O}_2][\text{CO}_3^{\cdot-}] + k_{46}[\text{Cl}_2^{\cdot-}][\text{H}_2\text{O}_2] - k_{47}[\text{Cl}_2^{\cdot-}][\text{HO}_2\cdot] + k_{52}[\text{Cl}\cdot][\text{H}_2\text{O}_2] + k_{83}[\text{H}_2\text{O}_2][\text{HPO}_4^{\cdot-}] \end{aligned}$$

$$\frac{d[O_2]}{dt} = k_7[SO_4^{\cdot-}][S_2O_8^{\cdot-}] + k_{10}[HO\cdot][HO_2\cdot] + k_{11}[HO_2\cdot][HO_2\cdot] + k_{13}[SO_4^{\cdot-}][HO_2\cdot] + 0.5 \cdot k_{14}[S_2O_8^{2-}][HO\cdot] + k_{17}[SO_5^{\cdot-}][SO_5^{\cdot-}] + k_{18}[SO_5^{\cdot-}][SO_5^{\cdot-}] + 0.5 \cdot k_{19}[SO_4^{\cdot-}][SO_5^{\cdot-}] + k_{47}[Cl_2^{\cdot-}][HO_2\cdot]$$

$$\frac{d[SO_5^{\cdot-}]}{dt} = k_{16}[SO_4^{\cdot-}][HSO_5^{\cdot-}] - 2 \cdot k_{17}[SO_5^{\cdot-}][SO_5^{\cdot-}] - 2 \cdot k_{18}[SO_5^{\cdot-}][SO_5^{\cdot-}] - k_{19}[SO_4^{\cdot-}][SO_5^{\cdot-}]$$

$$\frac{d[C_7F_{15}COOH]}{dt} = -k_{20}[SO_4^{\cdot-}][C_7F_{15}COOH]$$

$$\frac{d[C_6F_{13}COOH]}{dt} = k_{20}[SO_4^{\cdot-}][C_7F_{15}COOH] - k_{21}[SO_4^{\cdot-}][C_6F_{13}COOH]$$

$$\frac{d[C_5F_{11}COOH]}{dt} = k_{21}[SO_4^{\cdot-}][C_6F_{13}COOH] - k_{22}[SO_4^{\cdot-}][C_5F_{11}COOH]$$

$$\frac{d[C_4F_9COOH]}{dt} = k_{22}[SO_4^{\cdot-}][C_5F_{11}COOH] - k_{23}[SO_4^{\cdot-}][C_4F_9COOH]$$

$$\frac{d[C_3F_7COOH]}{dt} = k_{23}[SO_4^{\cdot-}][C_4F_9COOH] - k_{24}[SO_4^{\cdot-}][C_3F_7COOH]$$

$$\frac{d[C_2F_5COOH]}{dt} = k_{24}[SO_4^{\cdot-}][C_3F_7COOH] - k_{25}[SO_4^{\cdot-}][C_2F_5COOH]$$

$$\begin{aligned} \frac{d[CO_3^{\cdot-}]}{dt} = & k_{26}[SO_4^{\cdot-}][HCO_3^{\cdot-}] + k_{27}[SO_4^{\cdot-}][CO_3^{2-}] + k_{28}[HO\cdot][HCO_3^{\cdot-}] + k_{29}[HO\cdot][CO_3^{2-}] - k_{30}[HO\cdot][CO_3^{\cdot-}] \\ & - k_{31}[H_2O_2][CO_3^{\cdot-}] - 2 \cdot k_{32}[CO_3^{\cdot-}][CO_3^{\cdot-}] - k_{33}[S_2O_8^{2-}][CO_3^{\cdot-}] - k_{69}[CO_3^{\cdot-}][ClO\cdot] - k_{70}[CO_3^{\cdot-}][ClO_2\cdot] \\ & + k_{71}[Cl\cdot][CO_3^{2-}] + k_{72}[Cl\cdot][HCO_3^{\cdot-}] + k_{73}[Cl_2^{\cdot-}][CO_3^{2-}] + k_{74}[Cl_2^{\cdot-}][HCO_3^{\cdot-}] \end{aligned}$$

$$\frac{d[SO_3^{\cdot-}]}{dt} = k_{63}[ClO_2\cdot][SO_3^{2-}] - 2 \cdot k_{64}[SO_3^{\cdot-}][SO_3^{\cdot-}]$$

$$\begin{aligned} \frac{d[Cl\cdot]}{dt} = & -k_{34}[SO_4^{\cdot-}][Cl\cdot] + k_{35}[SO_4^{2-}][Cl\cdot] - k_{38}[HO\cdot][Cl\cdot] + k_{39}[ClOH\cdot] - k_{40}[ClOH\cdot][Cl\cdot] - k_{41}[Cl\cdot][Cl\cdot] \\ & + k_{42}[Cl_2^{\cdot-}] + 2 \cdot k_{44}[Cl_2^{\cdot-}][Cl_2^{\cdot-}] + k_{45}[Cl\cdot][Cl_2^{\cdot-}] + 2 \cdot k_{46}[Cl_2^{\cdot-}][H_2O_2] + 2 \cdot k_{47}[Cl_2^{\cdot-}][HO_2\cdot] + k_{48}[H_2O][Cl_2^{\cdot-}] \\ & - k_{51}[HClOH][Cl\cdot] + k_{52}[Cl\cdot][H_2O_2] + k_{53}[HO\cdot][Cl_2^{\cdot-}] + k_{54}[H_2O][Cl_2\cdot] + k_{57}[Cl\cdot][HClO] + k_{58}[Cl\cdot][ClO\cdot] \\ & + k_{67}[Cl_2^{\cdot-}][S_2O_8^{2-}] + k_{71}[Cl\cdot][CO_3^{2-}] + k_{72}[Cl\cdot][HCO_3^{\cdot-}] + 2 \cdot k_{73}[Cl_2^{\cdot-}][CO_3^{2-}] + 2 \cdot k_{73}[Cl_2^{\cdot-}][HCO_3^{\cdot-}] \\ & - k_{77}[Cl\cdot][NO_3\cdot] - k_{84}[Cl\cdot][HPO_4^{\cdot-}] \end{aligned}$$

$$\begin{aligned} \frac{d[Cl\cdot]}{dt} = & k_{34}[SO_4^{\cdot-}][Cl\cdot] - k_{35}[SO_4^{2-}][Cl\cdot] - k_{36}[H_2O][Cl\cdot] + k_{37}[ClOH\cdot][H^+] - k_{41}[Cl\cdot][Cl\cdot] + k_{42}[Cl_2^{\cdot-}] \\ & - 2 \cdot k_{43}[Cl\cdot][Cl\cdot] - k_{45}[Cl\cdot][Cl_2^{\cdot-}] + k_{50}[HClOH] - k_{52}[Cl\cdot][H_2O_2] - k_{57}[Cl\cdot][HClO] - k_{58}[Cl\cdot][ClO\cdot] \\ & - k_{66}[Cl\cdot][S_2O_8^{2-}] - k_{71}[Cl\cdot][CO_3^{2-}] - k_{72}[Cl\cdot][HCO_3^{\cdot-}] + k_{77}[Cl\cdot][NO_3\cdot] \end{aligned}$$

$$\frac{d[ClOH\cdot]}{dt} = k_{36}[H_2O][Cl\cdot] - k_{37}[ClOH\cdot][H^+] + k_{38}[HO\cdot][Cl\cdot] - k_{39}[ClOH\cdot] - k_{40}[ClOH\cdot][Cl\cdot] + k_{49}[HClOH]$$

$$\begin{aligned} \frac{d[Cl_2^{\cdot-}]}{dt} = & k_{40}[ClOH\cdot][Cl\cdot] + k_{41}[Cl\cdot][Cl\cdot] - k_{42}[Cl_2^{\cdot-}] - 2 \cdot k_{44}[Cl_2^{\cdot-}][Cl_2^{\cdot-}] - k_{45}[Cl\cdot][Cl_2^{\cdot-}] - k_{46}[Cl_2^{\cdot-}][H_2O_2] \\ & - k_{47}[Cl_2^{\cdot-}][HO_2\cdot] - k_{48}[H_2O][Cl_2^{\cdot-}] + k_{51}[HClOH][Cl\cdot] - k_{53}[HO\cdot][Cl_2^{\cdot-}] - k_{67}[Cl_2^{\cdot-}][S_2O_8^{2-}] - k_{73}[Cl_2^{\cdot-}][CO_3^{2-}] \\ & - k_{74}[Cl_2^{\cdot-}][HCO_3^{\cdot-}] \end{aligned}$$

$$\frac{d[Cl_2]}{dt} = k_{43}[Cl\cdot][Cl\cdot] + k_{44}[Cl_2^{\cdot-}][Cl_2^{\cdot-}] + k_{45}[Cl\cdot][Cl_2^{\cdot-}] - k_{54}[H_2O][Cl_2]$$

$$\frac{d[\text{ClO}^-]}{dt} = -k_{56}[\text{HO}\cdot][\text{ClO}^-] - k_{58}[\text{Cl}\cdot][\text{ClO}^-] - k_{59}[\text{HO}\cdot][\text{ClO}^-] - k_{61}[\text{SO}_4^{\cdot-}][\text{ClO}^-] + k_{65}[\text{ClO}\cdot][\text{ClO}_2^-] - k_{69}[\text{CO}_3^{\cdot-}][\text{ClO}^-]$$

$$\frac{d[\text{ClO}\cdot]}{dt} = k_{55}[\text{HO}\cdot][\text{HClO}] + k_{56}[\text{HO}\cdot][\text{ClO}^-] + k_{57}[\text{Cl}\cdot][\text{HClO}] + k_{58}[\text{Cl}\cdot][\text{ClO}^-] - k_{65}[\text{ClO}\cdot][\text{ClO}_2^-] + k_{69}[\text{CO}_3^{\cdot-}][\text{ClO}^-]$$

$$\frac{d[\text{ClO}_2\cdot]}{dt} = k_{59}[\text{HO}\cdot][\text{ClO}^-] - k_{60}[\text{HO}\cdot][\text{ClO}_2\cdot] + k_{61}[\text{SO}_4^{\cdot-}][\text{ClO}^-] - k_{62}[\text{SO}_4^{\cdot-}][\text{ClO}_2\cdot] - k_{63}[\text{ClO}_2\cdot][\text{SO}_3^{2-}] + k_{65}[\text{ClO}_2\cdot][\text{ClO}\cdot] + k_{66}[\text{Cl}\cdot][\text{S}_2\text{O}_8^{2-}] + k_{67}[\text{Cl}_2^{\cdot-}][\text{S}_2\text{O}_8^{2-}] + k_{70}[\text{CO}_3^{\cdot-}][\text{ClO}_2^-]$$

$$\frac{d[\text{ClO}_2^-]}{dt} = k_{63}[\text{ClO}_2\cdot][\text{SO}_3^{2-}] - k_{65}[\text{ClO}\cdot][\text{ClO}_2^-] - k_{70}[\text{CO}_3^{\cdot-}][\text{ClO}_2^-]$$

$$\frac{d[\text{ClO}_3^-]}{dt} = k_{60}[\text{ClO}_2\cdot][\text{HO}\cdot] + k_{62}[\text{ClO}_2\cdot][\text{SO}_4^{\cdot-}] - k_{68}[\text{ClO}_3^-]$$

Table S2. Characteristics of the Water Samples^a

water	pH	DOC	Cl ⁻	NO ₃ ⁻	PO ₄ ³⁻	H ₂ CO ₃	Fe ²⁺	Mn ²⁺
SW ^b	7.15	0.198	0.120	0.048	0.039	1.074×10 ⁻²	2.21×10 ⁻⁴	1.08×10 ⁻⁴
WW ^b	7.82	1.474	1.512	0.857	0.578	1.074×10 ⁻²	5.83×10 ⁻⁴	1.71×10 ⁻⁴

^aDOC unit = mM_C (DOC_{SW} = 2.38 mg/L and DOC_{WW} = 17.69 mg/L); Other concentration unit = mM; The concentration of CO₃²⁻ and HCO₃⁻ were calculated by assuming carbonate species were in equilibrium with atmospheric CO₂. The initial pH of SW and WW were 6.34 and 7.35 with the addition of PS and PFOA. ^bThe light absorbance of background constituents of SW and WW are 0.011 cm⁻¹ and 0.085 cm⁻¹, respectively.

Table S3. Pseudo-First Order Rate Constants for the Reaction Between PFOA and PS and Degree of Defluorination and Mineralization in UW^a

concentrations of PS	<i>k_{obs}</i>	defluorination (%)	mineralization (%)	final pH
5	0.18	19.94	15.00	2.81
10	0.28	32.58	17.24	2.44
15	0.30	41.29	28.97	2.35
20	0.30	45.65	41.37	2.25
30	0.30	41.45	33.18	2.04

^aPS unit was mM; *k_{obs}* unit was h⁻¹; the initial pHs = 4.09 ± 0.02.

Table S4. SD Values of Major Species for the Kinetic Model of PFOA Degradation in the UV-PS System^a

Kinetic model				In the presence of HCO_3^-		In the presence of Cl^-			
[PS]	SD_{PS}	SD_{PFOA}	SD_{pH}	$[\text{HCO}_3^-]$	SD_{PFOA}	$[\text{Cl}^-]$	SD_{PFOA}	SD_{Cl^-}	$\text{SD}_{\text{ClO}_3^-}$
5	0.65	0.20	0.12	5	0.19	0.5	0.11	0.02	0.15
10	0.50	0.12	0.11	10	0.13	1	0.12	0.14	0.23
15	0.50	0.16	0.09	15	0.04	2	0.11	0.52	0.30
20	0.47	0.27	0.10	25	0.06	3	0.13	0.54	0.31
30	0.33	0.16	0.09						

^aUV intensity was $2.88 \times 10^{-7} \text{ Einstein} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$; PFOA initial concentration was $150 \mu\text{M}$; system pH was not adjusted; the unit of PS, HCO_3^- and Cl^- was mM.

Table S5. Theoretical Mass Balance of Carbon and Fluorine for PFOA and Its Products

Time (h)	Total Carbon (mM)						
	[PFOA] _C	[PFHpA] _C	[PFHeA] _C	[PFPeA] _C	[PFBA] _C	[PFPrA] _C	[Total] _C
0	1.17 ^b	0	0	0	0	0	1.17
0.5	1.07	6.76×10 ⁻²	8.76×10 ⁻³	0	0	0	1.15
1	9.66×10 ⁻¹	1.69×10 ⁻¹	2.73×10 ⁻²	6.15×10 ⁻³	0	0	1.17
2	6.67×10 ⁻¹	2.99×10 ⁻¹	6.04×10 ⁻²	2.00×10 ⁻²	1.08×10 ⁻³	0	1.05
3	4.83×10 ⁻¹	3.58×10 ⁻¹	7.03×10 ⁻²	3.29×10 ⁻²	2.61×10 ⁻³	0	9.47×10 ⁻¹
4	3.58×10 ⁻¹	3.70×10 ⁻¹	9.67×10 ⁻²	4.33×10 ⁻²	2.93×10 ⁻³	4.69×10 ⁻⁵	8.71×10 ⁻¹
6	2.04×10 ⁻¹	3.38×10 ⁻¹	1.14×10 ⁻¹	5.21×10 ⁻²	4.40×10 ⁻³	2.45×10 ⁻⁴	7.12×10 ⁻¹
8 ^a	1.69×10 ⁻¹	2.81×10 ⁻¹	9.94×10 ⁻²	5.55×10 ⁻²	5.04×10 ⁻³	3.92×10 ⁻⁴	6.10×10 ⁻¹
Time (h)	Total Fluorine (mM)						
	[PFOA] _F	[PFHpA] _F	[PFHeA] _F	[PFPeA] _F	[PFBA] _F	[PFPrA] _F	[Total] _F
0	2.19	0	0	0	0	0	2.19
0.5	2.01	1.26×10 ⁻¹	1.61×10 ⁻²	0	0	0	2.16
1	1.81	3.14×10 ⁻¹	5.01×10 ⁻²	1.11×10 ⁻²	0	0	2.18
2	1.25	5.56×10 ⁻¹	1.11×10 ⁻¹	3.59×10 ⁻²	1.89×10 ⁻³	0	1.95
3	9.06×10 ⁻¹	6.65×10 ⁻¹	1.29×10 ⁻¹	5.91×10 ⁻²	4.58×10 ⁻³	0	1.76
4	6.71×10 ⁻¹	6.87×10 ⁻¹	1.77×10 ⁻¹	7.79×10 ⁻²	5.12×10 ⁻³	7.81×10 ⁻⁵	1.62
6	3.83×10 ⁻¹	6.27×10 ⁻¹	2.08×10 ⁻¹	9.37×10 ⁻²	7.70×10 ⁻³	4.08×10 ⁻⁴	1.32
8 ^c	3.16×10 ⁻¹	5.23×10 ⁻¹	1.82×10 ⁻¹	9.99×10 ⁻²	8.82×10 ⁻³	6.53×10 ⁻⁴	1.13

^a The measured mineralization carbon at 8 h was 0.31 mM. Total carbon of PFOA and its products was calculated using their concentrations measured by HPLC. ^b [TOC]_{measured} = 1.07 mM. ^c The measured F⁻ concentration in the solution at 8 h was 0.89 mM.

Table S6. Q_R analysis for Cl^- impact on contaminants degradation in $\text{SO}_4^{\cdot-}$ based AOPs ^a

k_R	[R] = 150 μM			[R] = 50 μM		
	[Cl ⁻] = 2	[Cl ⁻] = 1	[Cl ⁻] = 0.5	[Cl ⁻] = 2	[Cl ⁻] = 1	[Cl ⁻] = 0.5
1.0×10^4	1.60×10^{-6}	3.19×10^{-6}	6.38×10^{-6}	5.32×10^{-7}	1.06×10^{-6}	2.13×10^{-6}
1.0×10^5	1.60×10^{-5}	3.19×10^{-5}	6.38×10^{-5}	5.32×10^{-6}	1.06×10^{-5}	2.13×10^{-5}
1.0×10^6	1.60×10^{-4}	3.19×10^{-4}	6.38×10^{-4}	5.32×10^{-5}	1.06×10^{-4}	2.13×10^{-4}
1.0×10^7	1.59×10^{-3}	3.18×10^{-3}	6.34×10^{-3}	5.32×10^{-4}	1.06×10^{-3}	2.12×10^{-3}
1.0×10^8	1.57×10^{-2}	3.09×10^{-2}	3.90×10^{-2}	5.29×10^{-3}	1.05×10^{-2}	2.08×10^{-2}
1.0×10^9	1.38×10^{-1}	2.42×10^{-1}	3.90×10^{-1}	5.05×10^{-2}	9.62×10^{-2}	1.75×10^{-1}
1.0×10^{10}	6.15×10^{-1}	7.61×10^{-1}	8.65×10^{-1}	3.47×10^{-1}	5.15×10^{-1}	6.80×10^{-1}
1.0×10^{11}	9.41×10^{-1}	9.70×10^{-1}	9.85×10^{-1}	8.42×10^{-1}	9.14×10^{-1}	9.55×10^{-1}
k_R	[R] = 10 μM			[R] = 1 μM		
	[Cl ⁻] = 2	[Cl ⁻] = 1	[Cl ⁻] = 0.5	[Cl ⁻] = 2	[Cl ⁻] = 1	[Cl ⁻] = 0.5
1.0×10^4	1.06×10^{-7}	2.13×10^{-7}	2.13×10^{-7}	1.06×10^{-8}	2.13×10^{-8}	4.26×10^{-8}
1.0×10^5	1.06×10^{-6}	2.13×10^{-6}	2.13×10^{-6}	1.06×10^{-7}	2.13×10^{-7}	4.26×10^{-7}
1.0×10^6	1.06×10^{-5}	2.13×10^{-5}	2.13×10^{-5}	1.06×10^{-6}	2.13×10^{-6}	4.26×10^{-6}
1.0×10^7	1.06×10^{-4}	2.13×10^{-4}	2.13×10^{-4}	1.06×10^{-5}	2.13×10^{-5}	4.26×10^{-5}
1.0×10^8	1.06×10^{-3}	2.12×10^{-3}	2.12×10^{-3}	1.06×10^{-4}	2.13×10^{-4}	4.24×10^{-4}
1.0×10^9	1.05×10^{-2}	2.08×10^{-2}	2.08×10^{-2}	1.06×10^{-3}	2.12×10^{-3}	4.24×10^{-3}
1.0×10^{10}	9.62×10^{-2}	1.75×10^{-1}	1.75×10^{-1}	1.05×10^{-2}	2.08×10^{-2}	4.08×10^{-2}
1.0×10^{11}	5.15×10^{-1}	6.80×10^{-1}	6.80×10^{-1}	9.62×10^{-2}	1.75×10^{-1}	2.99×10^{-1}
^a [R] is the concentration of target compound; second order rate constant of Cl^- with $\text{SO}_4^{\cdot-}$ is $4.7 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$; [Cl ⁻] unit = mM.						

Table S7. Q_R analysis for carbonate species impact on contaminants degradation in $\text{SO}_4^{\cdot-}$ based AOPs ^a

k_R	[R] = 150 μM			[R] = 50 μM		
	[HCO ₃ ⁻] =	[HCO ₃ ⁻] =	[HCO ₃ ⁻] =	[HCO ₃ ⁻] =	[HCO ₃ ⁻] =	[HCO ₃ ⁻]
	10	3	1	10	3	= 1
1.0×10^4	4.17×10^{-5}	1.39×10^{-4}	4.16×10^{-4}	1.39×10^{-5}	4.63×10^{-5}	1.39×10^{-4}
1.0×10^5	4.16×10^{-4}	1.39×10^{-3}	4.15×10^{-3}	1.39×10^{-4}	4.63×10^{-4}	1.39×10^{-3}
1.0×10^6	4.15×10^{-3}	1.37×10^{-2}	4.00×10^{-2}	1.39×10^{-3}	4.61×10^{-3}	1.37×10^{-2}
1.0×10^7	4.00×10^{-2}	1.22×10^{-1}	2.94×10^{-1}	1.37×10^{-2}	4.42×10^{-2}	1.22×10^{-1}
1.0×10^8	2.94×10^{-1}	5.81×10^{-1}	8.06×10^{-1}	1.22×10^{-1}	3.16×10^{-1}	5.81×10^{-1}
1.0×10^9	8.06×10^{-1}	9.33×10^{-1}	9.77×10^{-1}	5.81×10^{-1}	8.22×10^{-1}	9.33×10^{-1}
1.0×10^{10}	9.77×10^{-1}	9.93×10^{-1}	9.98×10^{-1}	9.33×10^{-1}	9.79×10^{-1}	9.93×10^{-1}
1.0×10^{11}	9.98×10^{-1}	9.99×10^{-1}	9.998×10^{-1}	9.93×10^{-1}	9.98×10^{-1}	9.99×10^{-1}
k_R	[R] = 10 μM			[R] = 1 μM		
	[HCO ₃ ⁻] =	[HCO ₃ ⁻] =	[HCO ₃ ⁻] =	[HCO ₃ ⁻] =	[HCO ₃ ⁻] =	[HCO ₃ ⁻]
	10	3	1	10	3	= 1
1.0×10^4	2.78×10^{-6}	9.26×10^{-6}	2.78×10^{-5}	2.78×10^{-7}	9.26×10^{-7}	2.78×10^{-6}
1.0×10^5	2.78×10^{-5}	9.26×10^{-5}	2.78×10^{-4}	2.78×10^{-6}	9.26×10^{-6}	2.78×10^{-5}
1.0×10^6	2.78×10^{-4}	9.25×10^{-4}	2.77×10^{-3}	2.78×10^{-5}	9.26×10^{-5}	2.78×10^{-4}
1.0×10^7	2.78×10^{-3}	9.17×10^{-3}	2.70×10^{-2}	2.78×10^{-4}	9.25×10^{-4}	2.77×10^{-3}
1.0×10^8	2.70×10^{-2}	8.47×10^{-2}	2.17×10^{-1}	2.78×10^{-3}	9.17×10^{-3}	2.70×10^{-2}
1.0×10^9	2.17×10^{-1}	4.81×10^{-1}	7.35×10^{-1}	2.70×10^{-2}	8.47×10^{-2}	2.17×10^{-1}
1.0×10^{10}	7.35×10^{-1}	9.03×10^{-1}	9.65×10^{-1}	2.17×10^{-1}	4.81×10^{-1}	7.35×10^{-1}
1.0×10^{11}	9.65×10^{-1}	9.89×10^{-1}	9.96×10^{-1}	7.35×10^{-1}	9.03×10^{-1}	9.65×10^{-1}

^a [R] is the concentration of target compound; [HCO₃⁻] is the concentration of carbonate species; second order rate constant of HCO₃⁻ with SO₄^{·-} is $3.6 \times 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$; [HCO₃⁻] unit = mM.

Table S8. SD Values of the Model Predictions for Different Species in Real Water Samples

water	SD_{PFOA}	SD_{Cl^-}	$SD_{\text{ClO}_3^-}$	SD_{pH}
SW	0.10	0.82	0.40	0.15
WW	0.19	0.50	0.18	0.20

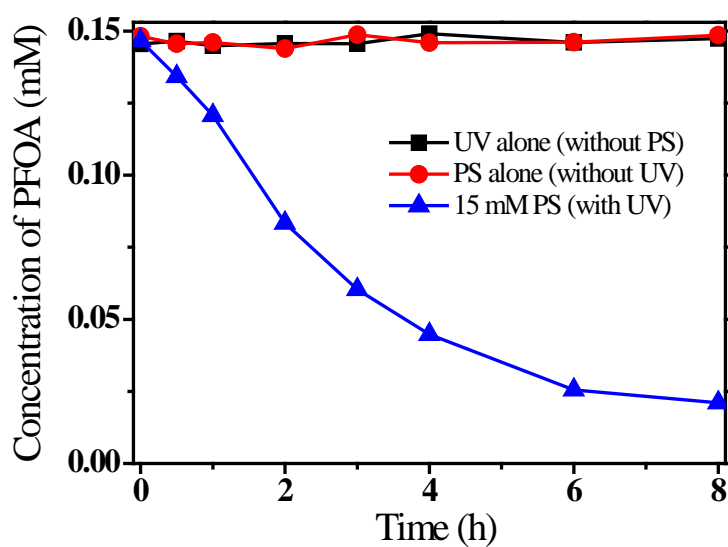


Figure S1. PFOA degradation under direct photolysis, direct PS oxidation and exposure to UV-PS in UW. Conditions: [PFOA] = 150 μ M (62.11 mg·L⁻¹), PS dosage = 15mM, UV intensity = 2.88×10^{-7} Einstein·L⁻¹·s⁻¹, without pH adjustment.

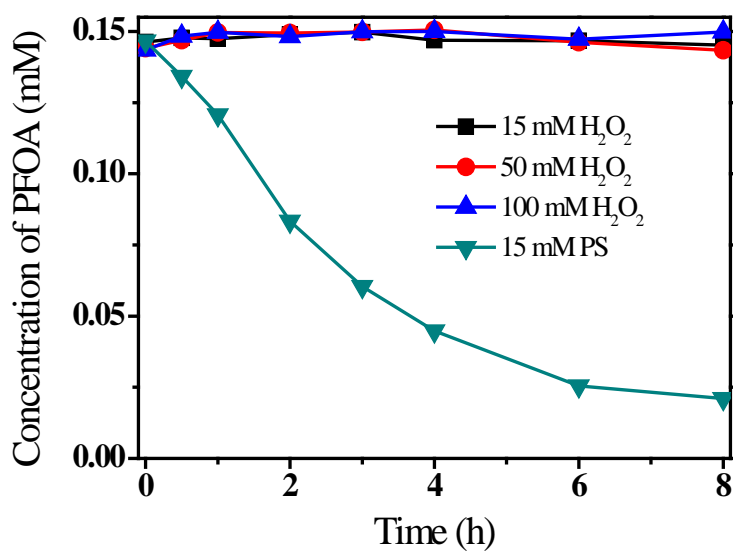


Figure S2. Comparison of PFOA degradation under different concentrations of H₂O₂ alone and 15 mM PS alone in UW. Conditions: [PFOA] = 150 μ M (62.11 mg·L⁻¹), UV intensity = 2.88×10^{-7} Einstein·L⁻¹·s⁻¹, without pH adjustment.

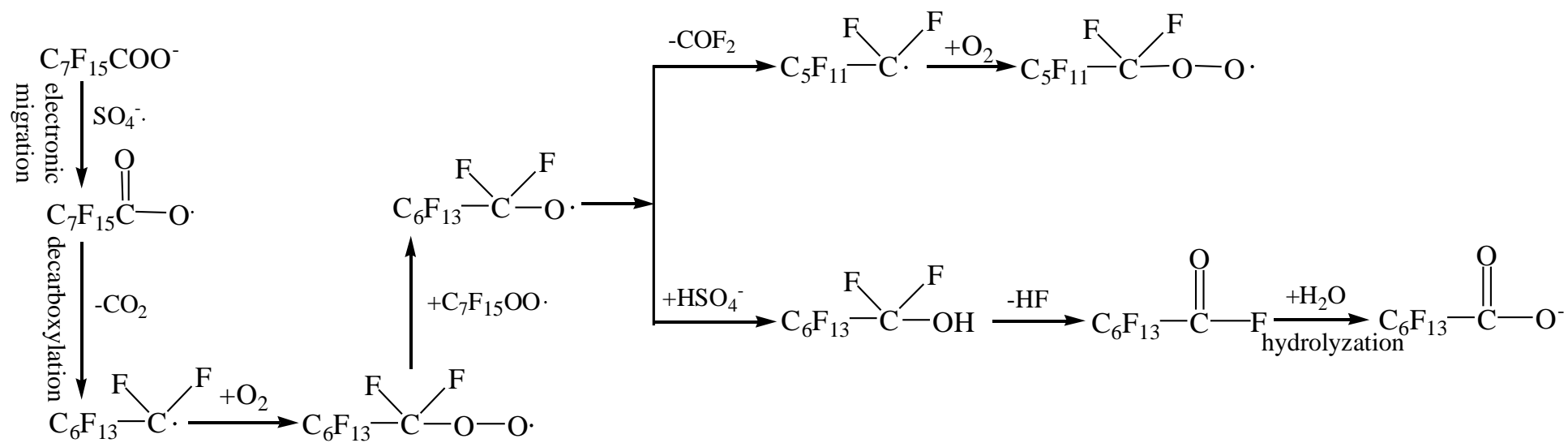


Figure S3. Scheme of PFOA degradation pathways during UV-PS treatment process.

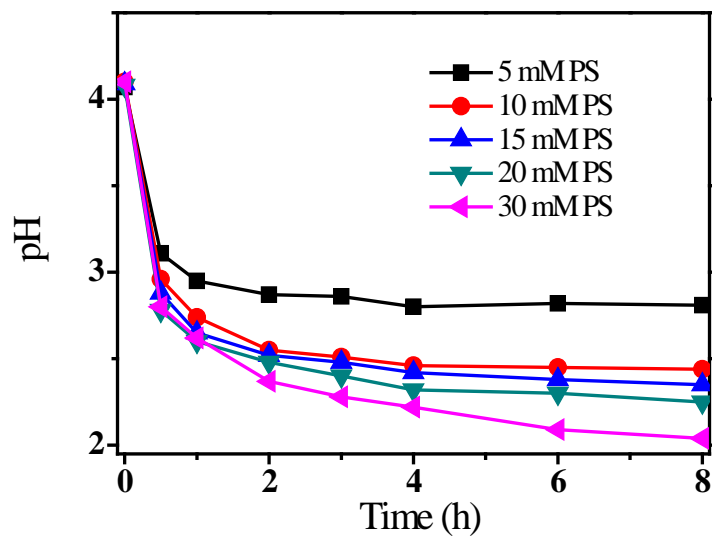


Figure S4. pH variation during the degradation process of PFOA under different concentrations of PS. Conditions: [PFOA] = 150 μ M (62.11 $\text{mg}\cdot\text{L}^{-1}$), UV intensity = 2.88×10^{-7} Einstein $\cdot\text{L}^{-1}\cdot\text{s}^{-1}$, without pH adjustment.

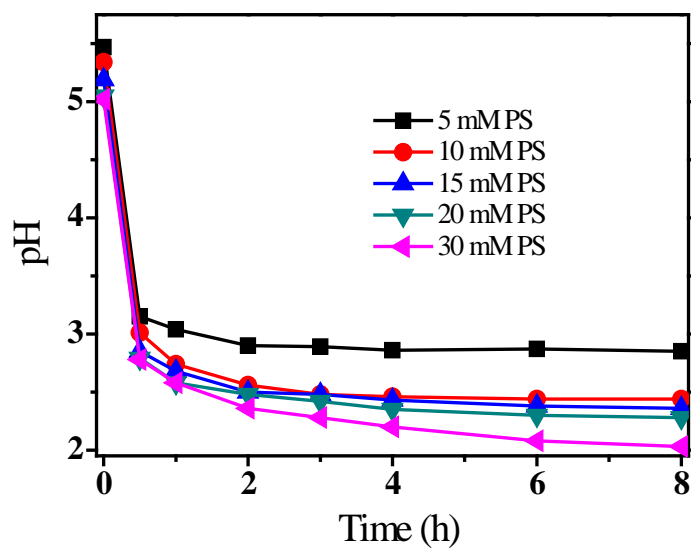


Figure S5. pH variation during the decomposition process of PS without PFOA addition. Conditions: UV intensity = 2.88×10^{-7} Einstein $\cdot\text{L}^{-1}\cdot\text{s}^{-1}$, without pH adjustment.

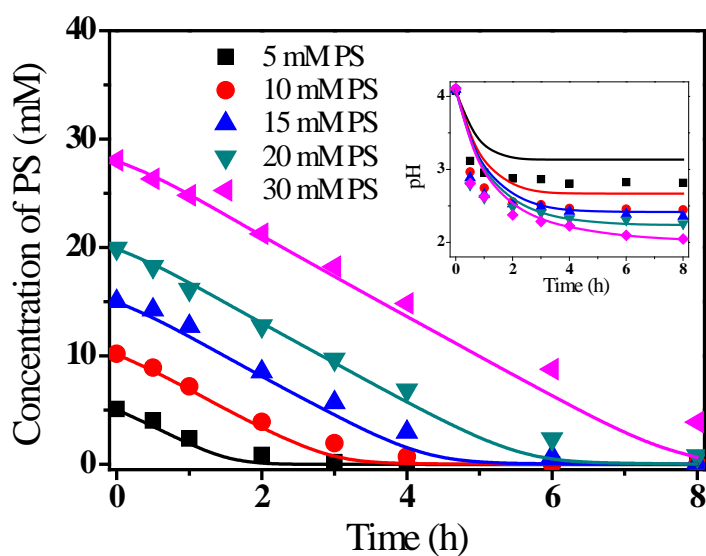


Figure S6. Concentration profiles for the decay of PS during the UV-PS treatment process in UW. The dots are experimental data, and the solid lines represent the model fits. Conditions: UV intensity = 2.88×10^{-7} Einstein \cdot L $^{-1}\cdot$ s $^{-1}$, without pH adjustment.

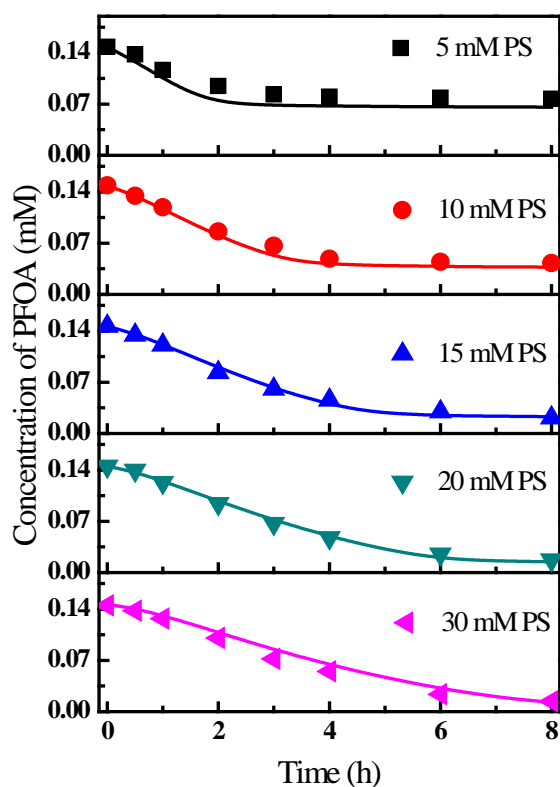


Figure S7. The degradation of PFOA under different concentrations of PS in UW. The dots are experimental data, and the solid lines represent the model fits. Conditions: [PFOA] = 150 μ M (62.11 mg \cdot L $^{-1}$), UV intensity = 2.88×10^{-7} Einstein \cdot L $^{-1}\cdot$ s $^{-1}$, without pH adjustment.

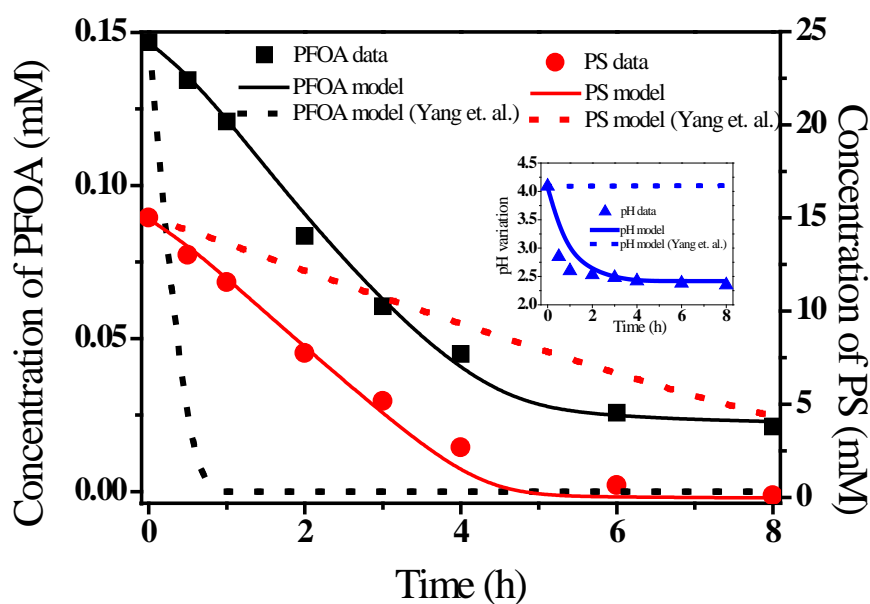


Figure S8. Comparison of the calculated concentration profiles of PFOA, PS and, pH obtained by our model and Yang et al.'s model. The dots are data. The solid lines represent the model fits of this work, and the dash lines are Yang et al.'s model. Conditions: [PFOA] = 150 μM ($62.11 \text{ mg}\cdot\text{L}^{-1}$), PS dosage = 15mM, UV intensity = $2.88 \times 10^{-7} \text{ Einstein}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$, without pH adjustment.

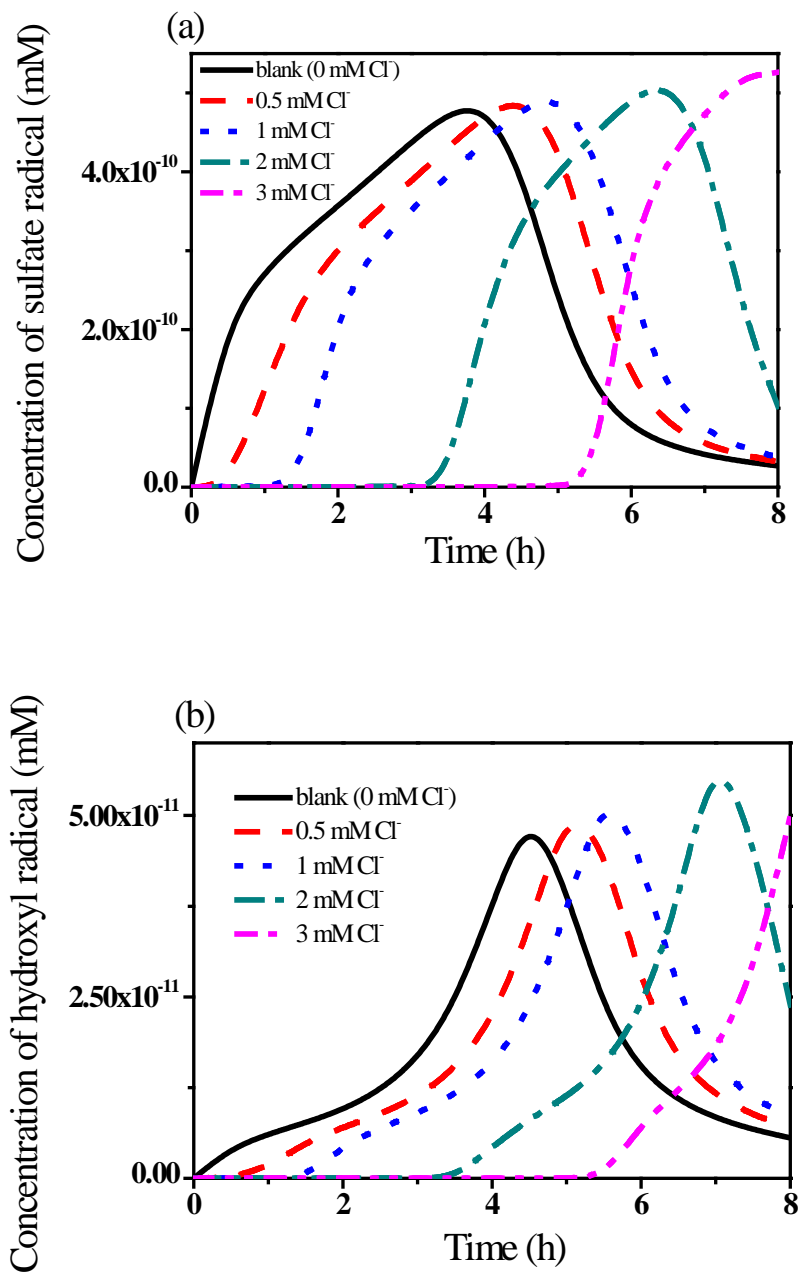


Figure S9. (a) Model predicted $\text{SO}_4^{\cdot-}$ distributions in the UV-PS system under different concentrations of Cl^- . (b) Model predicted HO^{\cdot} distributions in the UV-PS system under different concentrations of Cl^- . Conditions: PS dosage = 15 mM, UV intensity = 2.88×10^{-7} Einstein $\cdot\text{L}^{-1}\cdot\text{s}^{-1}$, without pH adjustment.

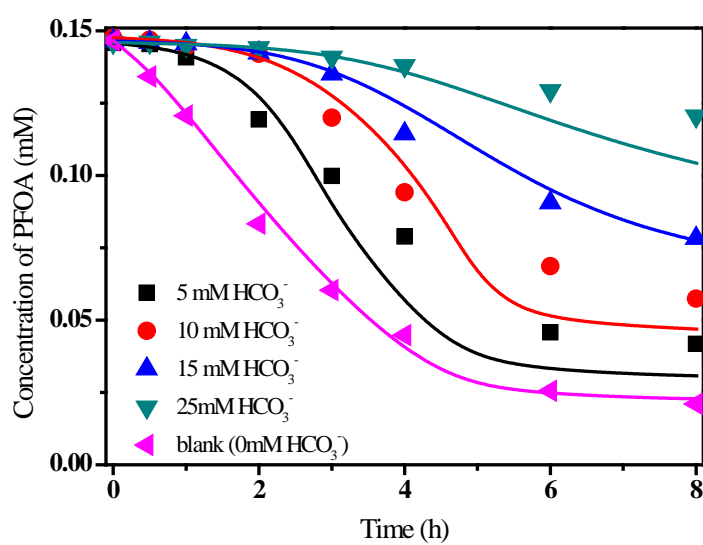


Figure S10. The degradation of PFOA under different carbonate species concentrations. The dots are experimental data, and the solid lines are the model fits. Conditions: [PFOA] = 150 μM (62.11 $\text{mg}\cdot\text{L}^{-1}$), PS dosage = 15mM, UV intensity = 2.88×10^{-7} Einstein $\cdot\text{L}^{-1}\cdot\text{s}^{-1}$, without pH adjustment.

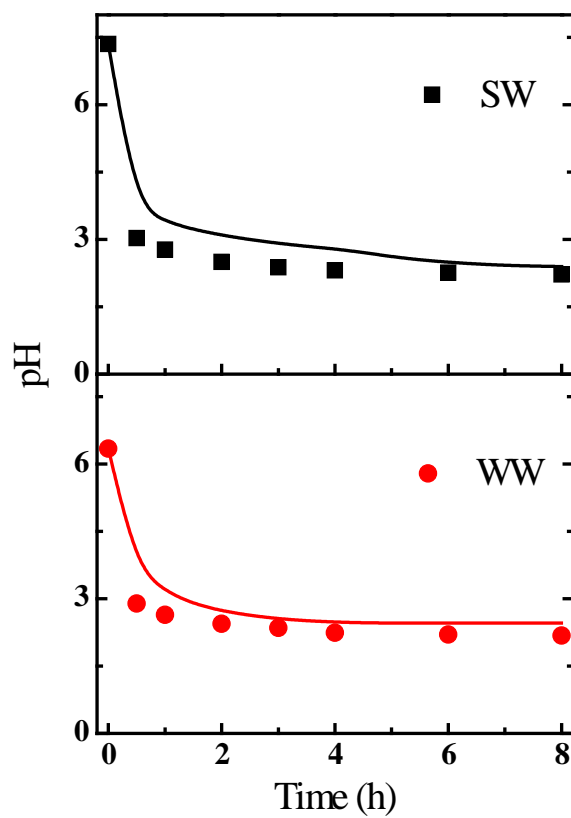


Figure S11. The predicted pH variation in SW (surface water) and WW (waste water) samples. The dots are data. The solid lines represent the model predictions. Conditions: [PFOA] = 150 μM (62.11 $\text{mg}\cdot\text{L}^{-1}$), PS dosage = 15mM, UV intensity = 2.88×10^{-7} $\text{Einstein}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$, without pH adjusting.

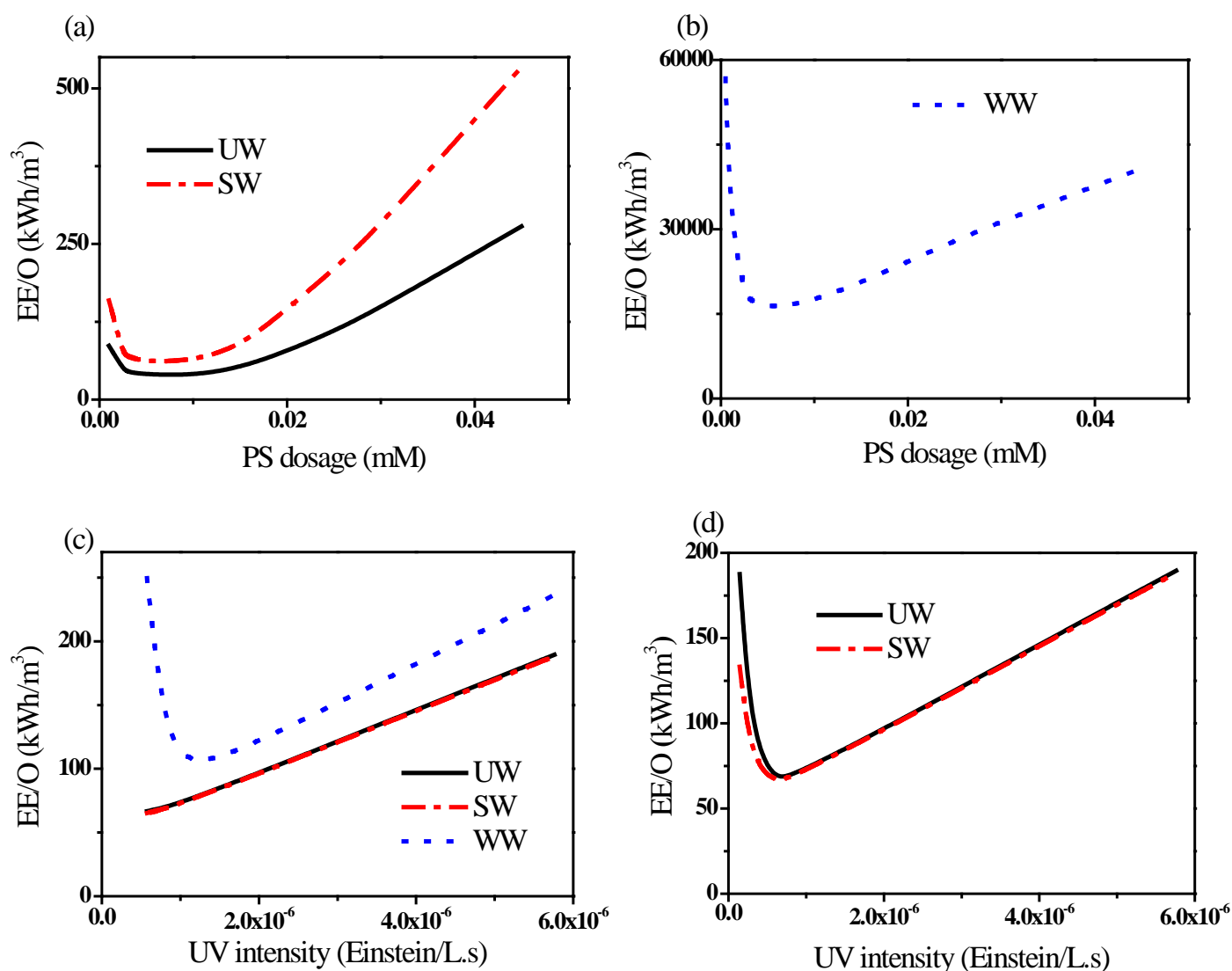
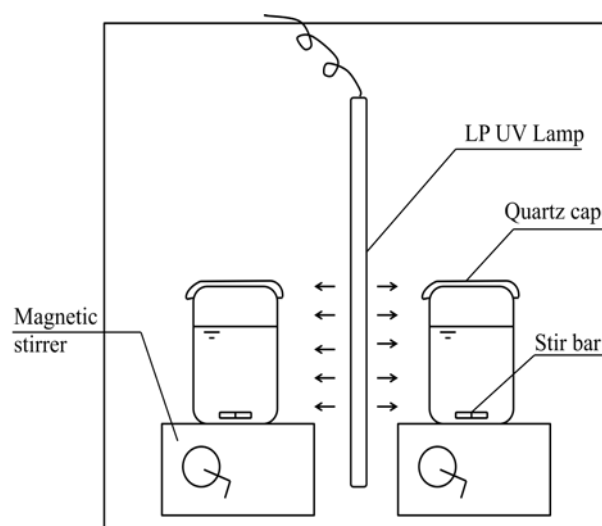
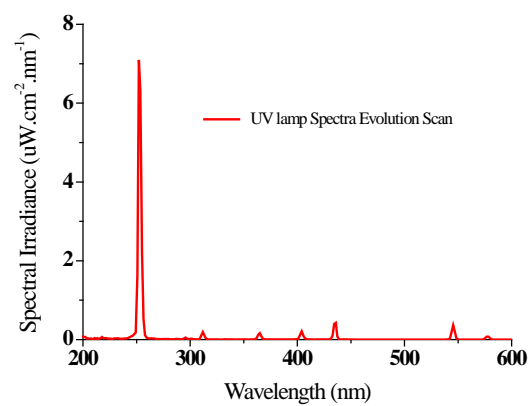


Figure S12. (a) EE/O vary with PS doses for UW (ultra pure water), SW (surface water). (b) EE/O vary with PS doses for WW (waste water). Conditions: [PFOA] = 150 μM ($62.11 \text{ mg}\cdot\text{L}^{-1}$), UV intensity = $2.88 \times 10^{-7} \text{ Einstein}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$. (c) EE/O vary with UV intensity for WW. (d) EE/O vary with UV intensity for UW and SW. Conditions: [PFOA] = 150 μM ($62.11 \text{ mg}\cdot\text{L}^{-1}$), [PS] = 15 mM.



(a) UV experimental set-up



(b) UV lamp spectrum

Figure S13. Schematic diagram of UV experimental set-up and the spectrum of UV lamp.

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