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Pre-Treatment of PFOA-Laden Synthetic Wastewater Via UV/Peroxydisulfate, UV/Peroxymonosulfate, and UV/Sulfite Processes: A Comparative Evaluation

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ABSTRACT

Introduction: Perfluorooctanoic acid (PFOA) is a persistent and toxic contaminant that requires effective degradation and defluorination strategies. Although several UV-based advanced oxidation and reduction processes have been investigated, direct comparisons under identical conditions are limited. In this study, we compared the degradation efficiency, mechanisms, and defluorination potential of three UV-based systems: UV/persulfate (UV/PDS), UV/peroxymonosulfate (UV/PMS), and UV/sulfite (UV/SS).

Materials and Methods: PFOA degradation experiments were conducted under 254 nm UV irradiation with an initial PFOA concentration of 0.24 mM and oxidant/reductant dosages of 1.0 mM. Reaction kinetics, transformation products, and fluoride generation were analyzed using LC-MS/MS and ion chromatography over a 6-hour treatment period.

Results: Direct UV photolysis was ineffective, achieving only 4% removal. Among the tested systems, UV/SS exhibited the highest performance, achieving 47% PFOA removal, compared with 24% and 31% for UV/PDS and UV/PMS, respectively. UV/PDS and UV/PMS primarily proceeded through oxidative radical pathways (sulfate and hydroxyl radicals), resulting in chain shortening and accumulation of shorter-chain perfluorinated carboxylic acids (PFHpA, PFHxA, PFPeA, PFBA, and TFA). In contrast, UV/SS operated through reductive pathways mediated by hydrated electrons, promoting sequential C–F bond cleavage and enhanced defluorination.

Conclusion: The UV/SS process demonstrated the greatest potential for PFOA pretreatment due to its ability to achieve true defluorination, whereas oxidative systems mainly transformed PFOA into persistent short-chain intermediates.

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Introduction

Perfluorooctanoic acid (PFOA), a well-known member of the per- and polyfluoroalkyl substance (PFAS) family, is recognized as one of the most persistent human-made contaminants in aquatic environments [1]. Its remarkable resistance to degradation is mainly attributed to the extremely strong carbon–fluorine (C–F) bond, with bond

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dissociation energies reaching 552 kJ/mol [2], together with its linear perfluorinated carbon structure and strong electron-withdrawing characteristics [3]. These properties make PFOA highly resistant to conventional physical, chemical, and biological treatment methods [4]. Although international regulations have promoted the gradual phase-out of PFOA, its widespread occurrence in the environment remains a major concern due to historical contamination, ongoing industrial releases, and incomplete removal during wastewater treatment [5].

Advanced oxidation processes (AOPs) and advanced reduction processes (ARPs) have attracted significant interest for the degradation of PFAS because they produce highly reactive radical species capable of initiating defluorination under appropriate conditions [6, 7]. However, the effectiveness of oxidative and reductive approaches differs considerably because of their distinct reaction mechanisms. Oxidative AOPs, including systems based on peroxydisulfate (PDS) or peroxymonosulfate (PMS) activated by ultraviolet light, generate sulfate radicals ($SO_4^{-\bullet}$) and hydroxyl radicals ($OH^{\bullet}$) [8]. These radicals possess strong redox potentials and can oxidize a wide range of organic pollutants in a relatively nonselective manner. For PFOA, however, oxidative reactions commonly promote decarboxylation of the carboxylate group, producing shorter-chain perfluorinated acids that remain persistent in the environment. As a result, although oxidative systems can decrease PFOA concentrations, they often achieve limited defluorination, which raises concerns about their effectiveness as independent technologies for complete PFAS destruction [9]. In contrast, reductive advanced reduction processes (ARPs), especially UV-activated sulfite systems, produce hydrated electrons (e_{aq}^{-}), which are highly powerful reducing agents with a strong tendency to react with fluorinated organic compounds [10]. These electrons can promote successive cleavage of C–F bonds through electron transfer reactions, enabling gradual defluorination and conversion of PFOA into less fluorinated [11] and potentially more biodegradable products. Recent research has shown that reductive treatments frequently provide greater defluorination efficiencies than oxidative approaches, particularly under optimized pH conditions and controlled radical scavenging environments [12].

Although UV-driven oxidative and reductive technologies have received increasing attention for PFAS treatment [11, 13-16], few studies have directly compared UV/PDS, UV/PMS, and UV/SS systems under the same experimental conditions. Existing research typically examines either oxidative or reductive radical pathways separately, which limits the ability to accurately assess the relative performance of these approaches in synthetic or real wastewater systems. In addition, factors such as water chemistry, radical scavenging effects, operating conditions, and reaction kinetics can significantly affect degradation efficiency [17]; however, these influences are seldom investigated comprehensively across multiple treatment methods.

In engineered wastewater treatment applications, there is an increasing demand for pretreatment methods capable of either significantly lowering PFOA concentrations or transforming the compound into intermediates that are easier to manage [18]. Complete mineralization within a single treatment unit is often difficult to achieve because of high energy demands, radical scavenging by coexisting contaminants, and the potential generation of unwanted byproducts [19]. Consequently, an effectively designed pretreatment step can be integrated with downstream biological or physicochemical treatment processes to enhance overall PFAS removal while minimizing operational challenges [20]. To be effective, such a pretreatment strategy should satisfy several key requirements: (i) efficient degradation of the original PFOA compound, (ii) limited production of toxic or persistent transformation products, and (iii) adaptability to varying wastewater compositions. Although UV/PDS, UV/PMS, and UV/SS have been investigated for the treatment of persistent organic contaminants, direct comparisons of these systems for PFOA degradation under identical experimental conditions remain limited.

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This study aims to address this important knowledge gap through a systematic comparison of three UV-based treatment processes. The research differentiates between oxidative radical systems, which produce $SO_4^{-\bullet}$ and $OH^{\bullet}$ radicals, and the reductive system that generates e_{aq}^{-}. Their performance is evaluated in terms of degradation kinetics, byproduct formation, and the degree of defluorination achieved. Particular emphasis is placed on identifying the transformation mechanisms associated with each process, including conditions where oxidative pathways tend to promote chain-shortening reactions and those where reductive pathways enable stepwise defluorination. The effects of key operational parameters—such as oxidant/reductant concentration, initial PFOA concentration, reaction time, and solution pH—are also investigated to better understand the mechanisms governing PFOA degradation and to inform practical considerations for process design and implementation.

Materials and Method

Chemicals and reagents

Perfluorooctanoic acid (PFOA, ≥98%) was obtained from Sigma-Aldrich and used as the target contaminant without further purification. Perfluoroheptanoic acid (PFHpA, $C_6F_{13}COOH$, > 99%), perfluorohexanoic acid (PFHxA, $C_5F_{11}COOH$, > 99%), perfluoropentanoic acid (PFPeA, C_4F_9COOH, > 99%), pentafluoropropionic acid (PFPrA, C_2F_5COOH, > 99%), heptafluorobutyric acid (PFBA, C_3F_7COOH, > 99%), and trifloroacetic acid (TFA, CF_3COOH, > 99%) were purchased from Agilent. Sodium persulfate ($Na_2S_2O_8$, PDS), peroxymonosulfate (HSO_5^-, PMS), and sodium sulfite (Na_2SO_3, SS) (as oxidant and reductant precursors) were all ACS reagent grade and purchased from Merck Company. All remaining chemicals were analytical grade and used without further purification. Ultrapure water with a resistivity of at least 18.2 MΩ·cm was used to prepare all solutions.

Photoreactor setup

Photochemical reductive degradation experiments were performed in a cylindrical quartz batch reactor with a working volume of 1000 mL. A 16 W low-pressure mercury lamp (Philips Co.) emitting UV light at 254 nm was placed axially inside the reactor as the irradiation source. The reactor solution was continuously stirred with a magnetic stirrer to maintain uniform mixing. Throughout the experiments, the reaction temperature was maintained at room temperature (25–27 °C). Before initiating UV irradiation, the reaction mixture was stirred and allowed to equilibrate for 10 minutes.

Experimental procedures

UV/PDS, UV/PMS, and UV/SS processes

Batch experiments were conducted to investigate the degradation of PFOA in UV/PDS, UV/PMS, and UV/SS systems. A PFOA stock solution (0.24 mM) was prepared using ultrapure water and stored at 4 °C in the dark. Working solutions were freshly prepared by diluting the stock to the required concentration. Synthetic wastewater was formulated to represent simplified aqueous conditions and included selected inorganic ions. A simplified synthetic wastewater matrix was prepared using selected inorganic ions and humic acid to evaluate the influence of background constituents on PFOA degradation. Unless otherwise stated, the matrix-effect experiments were conducted at pH 7 with $[Cl^-]_0$ = 25 mM, $[CO_3^{2-}]_0$ = 15 mM, $[SO_4^{2-}]_0$ = 5 mM, $[H_3PO_4]_0$ = 10 mM, and $[HA]_0$ = 10 mg/L.The initial pH of the solutions was adjusted with 0.1 M HCl or NaOH.

The experimental design followed a one-factor-at-a-time approach, whereby the effect of each operational parameter was examined individually, while maintaining the remaining variables constant. In a typical run, a predetermined volume of the PFOA working solution (initial concentration of 0.24 mM) was placed in the reactor. Appropriate amounts of PS, PMS, or SS were then added to reach the desired concentrations (0.5–5 mM). The reaction was initiated by turning on the UV lamp. At specific time intervals (1–6 h), 5 mL samples were collected and immediately quenched to halt the reactions. A total of 250 samples were collected and analyzed. The collected samples were

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subsequently filtered through 0.22 µm membrane filters before being analyzed.

Control experiments

Control experiments were performed to identify the individual effects of each treatment component. These tests included (i) UV irradiation without added reagents (photolysis), (ii) PDS, PMS, or SS under dark conditions without UV exposure, and (iii) blank experiments conducted in the absence of oxidants or reductants. All other experimental parameters were maintained unchanged.

Analytical methods

PFOA quantification

PFOA and its intermediate products formed during degradation were analyzed using high-performance liquid chromatography coupled with mass spectrometry (HPLC-MS) (Waters Alliance 2695, Waters, USA) equipped with a Micromass Quattro Micro API mass spectrometer. Separation was carried out on a reverse-phase reverse-phase C18 column (Eurospher, 4.6 × 150 mm, 5 µm) maintained at 35 °C. The mobile phase consisted of water (A) and acetonitrile (B) at a ratio of 40:60, delivered at a flow rate of 0.3 mL/min. The injection volume was 3 µL.

The detection system operated in two modes: (1) multiple-reaction monitoring (MRM) with an electrospray ionization (ESI) source, where the ion source temperature was set to 130 °C and the desolvation temperature to 300 °C; and (2) full-scan mode with a scanning range of 100–500 (m/z) and a scan time of 5 minutes. Calibration curves were established using external standards over an appropriate concentration range, with correlation coefficients (R^2) greater than 0.99.

Fluoride ion analysis

The release of fluoride ions (F^-) was monitored to assess the extent of defluorination. Measurements were performed using ion chromatography (IC) with a conductivity detector. Calibration was performed using standard fluoride solutions. The defluorination efficiency was determined by comparing the amount of fluoride released with the theoretical maximum fluoride content in PFOA, as expressed in the Equation 1 [21]:

$$Defluorination\ efficiency = \frac{C_{F^-}}{C_0 \times 15} \times 100 \qquad (1)$$

C_{F^-} is the concentration of F^- in the solution, C_0 is the initial concentration of PFOA in the solution and the constant 15 represents the number of florine atoms in PFOA.

Transformation product identification

The selected samples were examined using LC-MS/MS to identify the possible transformation products generated during the degradation process. The obtained mass spectra were analyzed to propose likely degradation pathways, with particular emphasis on shorter-chain perfluorinated intermediates (PFIs).

Kinetic analysis

The degradation behavior of PFOA was evaluated using a pseudo-first-order kinetic model, as formulated in Equation 2.

$$-ln\left(\frac{C_t}{C_0}\right) = k_{obs}t \qquad (2)$$

where C_0 and C_t represent the concentrations of PFOA at the initial time and at time *t*, respectively, and K_{obs} denotes the apparent rate constant (h^{-1}). The rate constants were determined from the slopes of the linear regression plots.

Effect of operational parameters

The effects of major operational parameters on PFOA degradation were systematically evaluated. These parameters included: (i) oxidant/reductant concentration (PS, PMS, and SS) ranging from 0.5-5 mM, (ii) initial pH values between 3 and 11, (iii) initial PFOA concentrations of 0.024-0.36 mM and reaction times of 1–6 h, and (iv) the presence of background ions such as Cl^-, CO_3^{2-}, SO_4^{2-}, and H_3PO_4. Each variable was investigated individually while maintaining all other experimental conditions unchanged.

Quality assurance and data analysis

All experiments were performed in triplicates, and the results are presented as mean values accompanied by standard deviations. Calibration was routinely performed to maintain analytical

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reliability and accuracy. Data were analyzed using standard statistical approaches, and linear regression analyses were assessed based on correlation coefficient values (R^2).

Results

Degradation Performance of UV/PDS, UV/PMS, and UV/SS Processes

Preliminary control experiments were conducted using PDS alone, PMS alone, SS alone, and UV irradiation alone at 25 °C for 6 h to clarify the individual contributions of the oxidants and UV-activated species. As illustrated in Figure 1, negligible changes in PFOA concentration were observed in all control experiments, indicating that direct oxidation by PDS or PMS and direct photolysis were ineffective under the tested conditions.

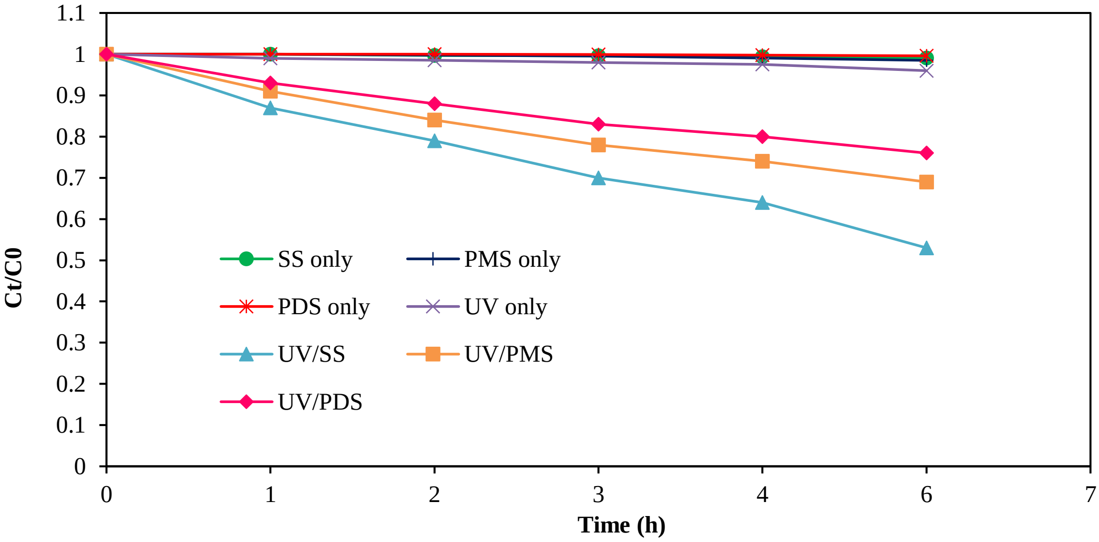

Figure 1: Degradation efficiency of PFOA in UV/SS, UV/PMS, and UV/PDS systems. Reaction conditions: $[PFOA]_0$ = 0.24 mM, $[SS]_0 = [PMS]_0 = [PDS]_0$ = 1 mM, and pH = 7.

Figure 1 shows the degradation efficiencies of PFOA in the three UV-based systems. All systems achieved measurable PFOA degradation, although with markedly different efficiencies. After 6 h of reaction, the removal efficiencies were approximately 47%, 31%, and 24% for UV/SS, UV/PMS, and UV/PDS, respectively. These results indicate that the UV/sulfite (UV/SS) system exhibited the highest degradation efficiency among the investigated processes. In comparison, the control experiments showed negligible PFOA removal, confirming that UV irradiation is required to activate the oxidants or reductants and generate reactive species capable of degrading PFOA.

Overall, the degradation efficiencies followed the order: UV/SS > UV/PMS > UV/PDS.

PFOA Defluorination Kinetics

Defluorination was evaluated through the release of fluoride ions, which directly reflects C–F bond cleavage. Figure 2 shows that fluoride release followed the same order as PFOA degradation: UV/SS > UV/PMS > UV/PDS. In the UV/SS system, fluoride release increased from 4.0% after 1 h to 24.1% after 6 h, representing the highest defluorination among the investigated processes. In contrast, the UV/PMS and UV/PDS systems achieved lower fluoride release values of 16.2% and 11.8%, respectively, after 6 h of reaction.

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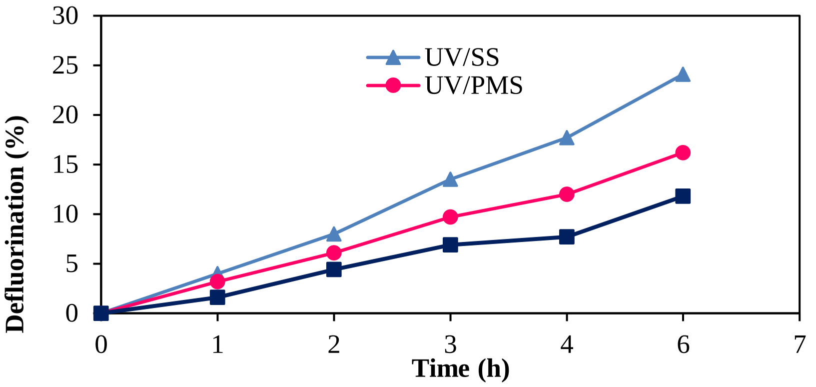

Figure 2: Defluorination rate of PFOA in UV/SS, UV/PMS, and UV/PDS systems. Reaction conditions: $[PFOA]_0$ = 0.24 mM, $[SS]_0 = [PMS]_0 = [PDS]_0$ = 1 mM, and pH = 7.

The defluorination data were fitted using pseudo-first-order and pseudo-second-order kinetic models (Table 1). For the UV/SS system, both models provided an excellent fit, with correlation coefficients of R^2 = 0.9957 and 0.9956 for the first-order and second-order models, respectively. The calculated first-order rate constant was K_1 = 0.0473 h^{-1}, indicating the fastest defluorination rate among the studied systems. In the UV/PMS system, the pseudo-second-order model showed a slightly better fit (R^2 = 0.9959) compared with the pseudo-first-order model (R^2 = 0.9928), with a first-order rate constant of K_1 = 0.0299 h^{-1}. The UV/PDS system exhibited the slowest kinetics, with K_1 = 0.0211 h^{-1}. The correlation coefficients were R^2 = 0.9887 and 0.9898 for the pseudo-first-order and pseudo-second-order models, respectively.

Overall, the kinetic results confirmed the trend: UV/SS > UV/PMS > UV/PDS, indicating that the UV/SS system achieved the most rapid and extensive PFOA defluorination.

Table 1. Kinetic parameters for PFOA defluorination in UV/SS, UV/PMS, and UV/PDS systems based on pseudo-first-order and pseudo-second-order model fitting of fluoride release during 6 h of UV irradiation. The rate constants and R^2 values indicate the relative defluorination performance of each process.

System	K_1 (h^{-1})	R^2 (1st)	K_2 (h^{-1})	R^2 (2nd)
UV/SS	0.047	0.995	0.054	0.995
UV/PMS	0.029	0.992	0.032	0.995
UV/PDS	0.021	0.988	0.022	0.989

Influence of operational factors on the removal efficiency

Effect of pH

The effect of pH on PFOA degradation and defluorination in the UV/SS, UV/PMS, and UV/PDS systems was evaluated at five initial pH values: 3, 5, 7, 9, and 11. The natural pH of the PFOA solution was approximately 4. As shown in Figure 3, the degradation performance of the three UV-based systems was influenced by the initial solution pH, although the extent and direction of this influence differed among the processes.

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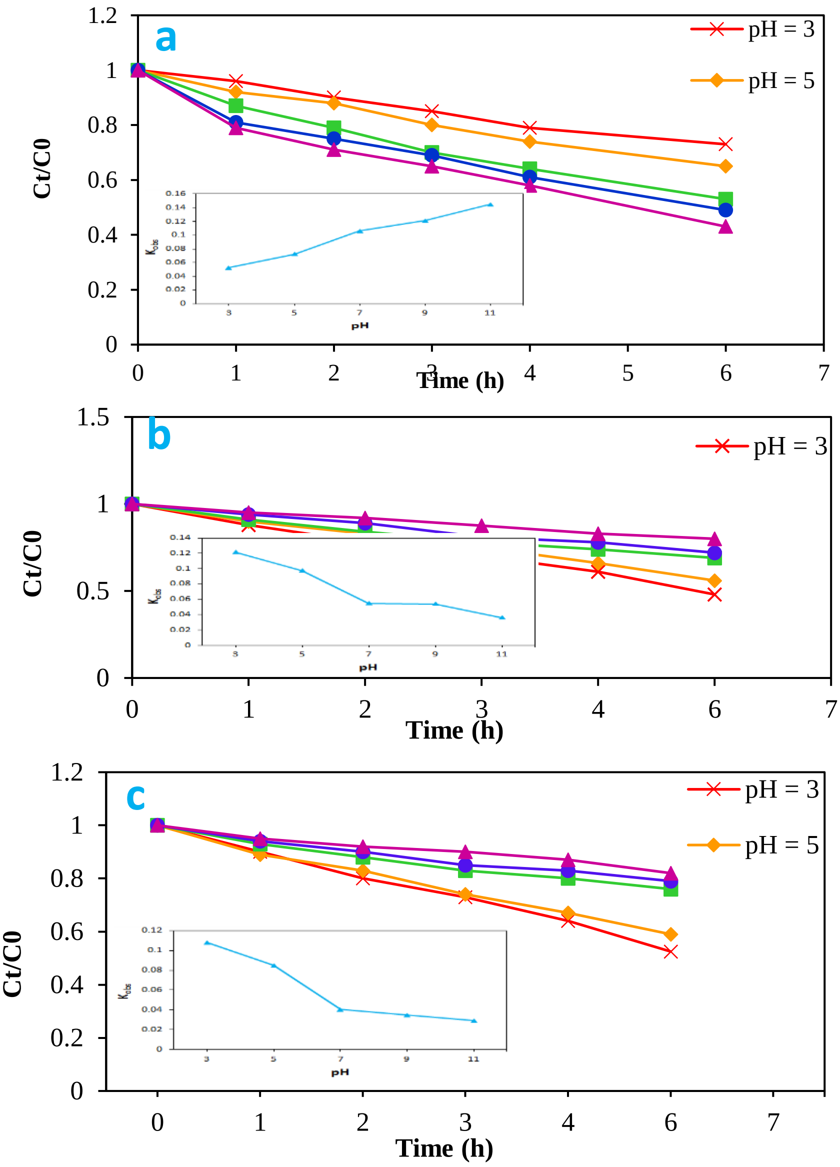

Figure 3: Effect of initial pH on the efficiency of UV/SS (a), UV/PMS (b), and UV/PDS (c) processes. Reaction conditions: $[PFOA]_0$ = 0.24 mM, and $[SS]_0$ = $[PMS]_0$ = $[PDS]_0$ = 1 mM.

In the UV/SS system, PFOA degradation increased with increasing pH. The K_{obs} increased from 0.0524 h^{-1} at pH 3 to 0.145 h^{-1} at pH 11. Consistently, the remaining PFOA fraction after 6 h decreased from 0.73 at pH 3 to 0.43 at pH 11 (Figure 3a). These results indicate that alkaline conditions enhanced PFOA removal in the UV/SS process. In contrast, the UV/PMS system showed improved PFOA degradation under acidic conditions. The K_{obs} decreased from approximately 0.12 h^{-1} at pH 3 to 0.035 h^{-1} at pH 11 (Figure 3b). The degradation profiles also showed that PFOA removal after 6 h was highest at pH 3 and gradually declined as pH increased. At pH 3, the PFOA concentration decreased to 0.48 of its initial value, whereas only about 20% removal was observed at pH 11. Similar observed rate constants at pH 7 and 9 suggested a plateau in system activity under near-neutral to moderately alkaline conditions, followed by a further decrease at pH 11. The UV/PDS system exhibited a similar pH-dependent trend to UV/PMS. The K_{obs} decreased from 0.11 h^{-1} at pH 3 to 0.03 h^{-1} at pH 11 (Figure 3c), indicating that acidic conditions were more favorable for PFOA degradation. Under acidic conditions, particularly at pH 3–5, more than 45% PFOA degradation was

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achieved within 6 h. However, degradation efficiency declined progressively as pH increased.

Overall, the pH-dependent degradation trends differed between the reductive and oxidative systems. The UV/SS system performed best under alkaline conditions, whereas the UV/PMS and UV/PDS systems showed higher degradation efficiencies under acidic conditions.

Influence of initial PFOA concentration

The effect of the initial PFOA concentration (*[PFOA]₀*) on degradation performance was evaluated over a concentration range of 0.024–0.36 mM in the UV/SS, UV/PMS, and UV/PDS systems. The experiments were conducted at a fixed oxidant/reductant concentration of 1 mM and pH 7, as shown in Figure 4.

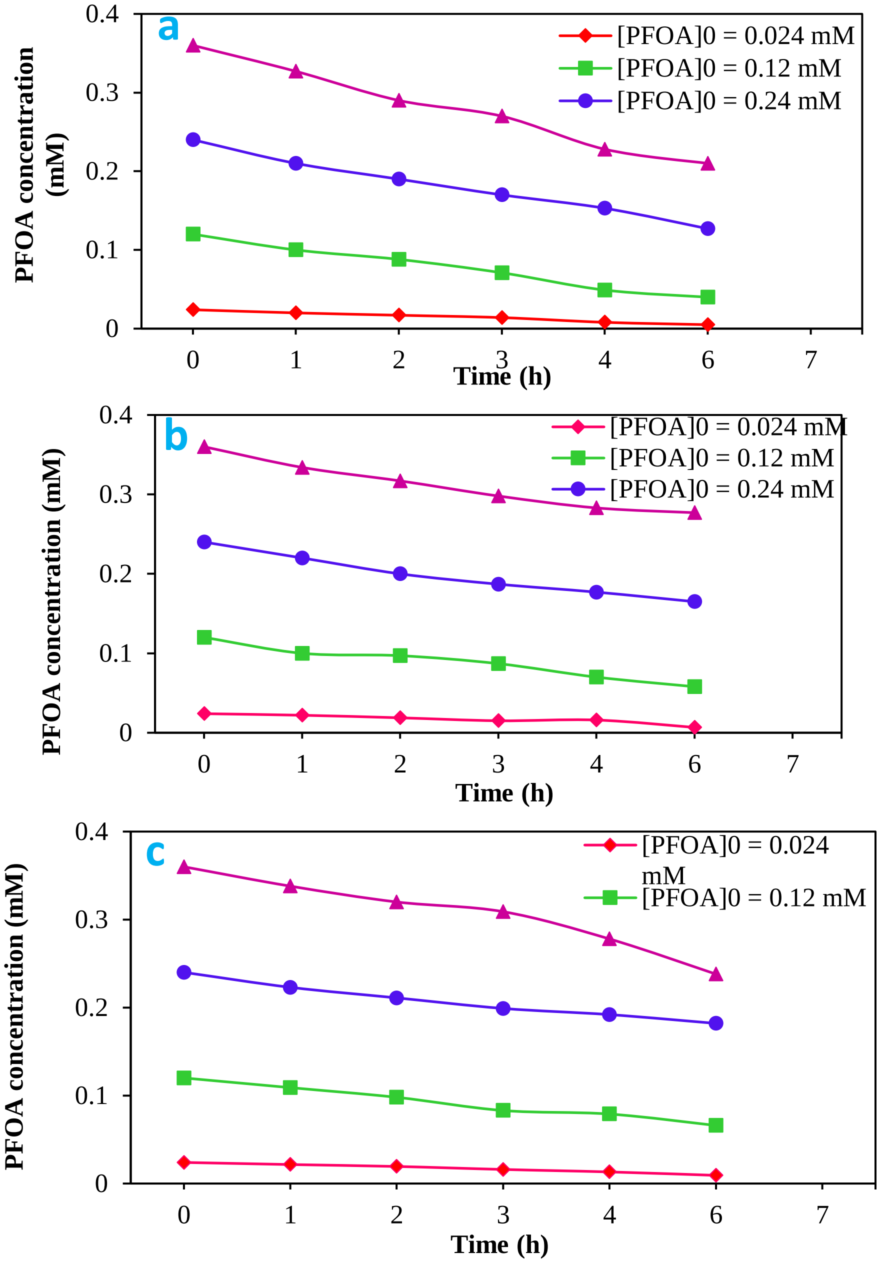

Figure 4. Effect of initial concentrations of PFOA on the efficiency of UV/SS (a), UV/PMS (b), and UV/PDS (c) processes. Reaction conditions: $[PFOA]_0$ = 0.024, 0.12, 0.24, and 0.36 mM, $[SS]_0 = [PMS]_0 = [PDS]_0$ = 1 mM, and pH = 7.

The UV/SS system exhibited the highest degradation efficiency among the three treatment

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processes. At the lowest initial PFOA concentration of 0.024 mM, the PFOA concentration decreased to 0.005 mM after 6 h, corresponding to approximately 79.2% removal (Figure 4a). When the initial PFOA concentration was increased to 0.36 mM, the remaining PFOA concentration reached 0.21 mM, and the removal efficiency decreased to 41.7%. The UV/PMS system also showed a decrease in degradation efficiency as the initial PFOA concentration increased. At 0.024 mM, PFOA removal reached 72.1%, with 0.0067 mM PFOA remaining after 6 h (Figure 4b). However, at 0.36 mM, the removal efficiency decreased sharply to 23.1%. Similarly, the UV/PDS system showed reduced degradation efficiency at higher initial PFOA concentrations. At 0.024 mM, the UV/PDS system achieved 61.2% removal, whereas at 0.36 mM, removal decreased to approximately 33.9% (Figure 4c).

In all three treatment systems, the percentage removal decreased as the initial PFOA concentration increased. However, the absolute amount of PFOA degraded increased with increasing initial concentration. For example, in the UV/SS system, approximately 0.019 mM PFOA was removed at an initial concentration of 0.024 mM, whereas nearly 0.15 mM was degraded at an initial concentration of 0.36 mM. Overall, the degradation efficiency followed the order: UV/SS > UV/PMS > UV/PDS, with all systems showing reduced percentage removal at higher initial PFOA concentrations.

Effect of oxidant or reducing agent concentration

The effect of oxidant/reductant concentration on PFOA degradation in the UV/SS, UV/PMS, and UV/PDS systems was investigated by varying the reagent dosage from 0.5 to 5 mM. The corresponding pseudo-first-order rate constants (K_{obs}) were determined to compare the degradation kinetics among the three systems. As illustrated in Figure 5, increasing the oxidant or reducing agent concentration improved the degradation rate of PFOA in all systems, although the degree of enhancement depended on the treatment process.

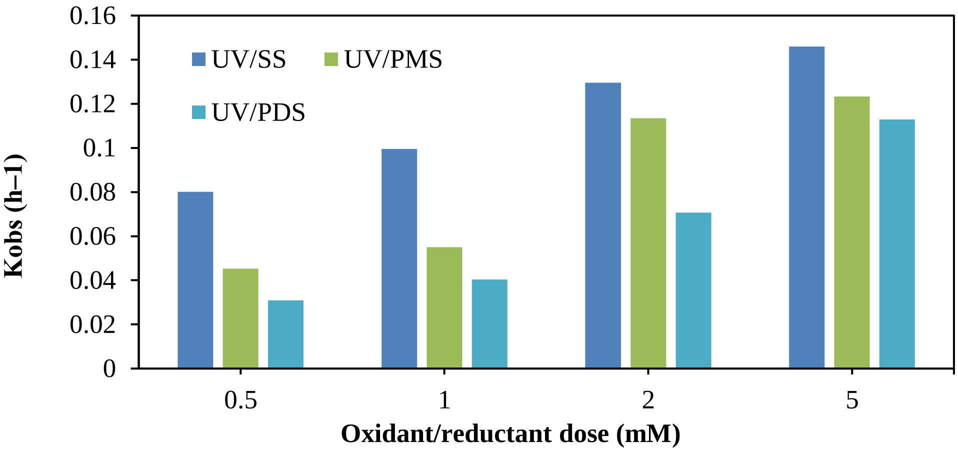

Figure 5. Effect of initial concentrations of SS, PMS, and PDS on the efficiency of UV/SS, UV/PMS, and UV/PDS processes. Inset: Variation of k_{obs} (h^{-1}) with $[SS]_0$, $[PMS]_0$, and $[PDS]_0$. Reaction conditions: $[PFOA]_0 = 0.24$ mM, reaction time = 6 h, and pH = 7.

In the UV/SS system, K_{obs} increased progressively from 0.0801 h^{-1} at 0.5 mM sulfite to 0.146 h^{-1} at 5 mM sulfite. The UV/SS process showed relatively high rate constants even at the lowest sulfite dosage, indicating strong PFOA degradation performance across the tested concentration range. However, the increase in K_{obs} became less pronounced above 2 mM, suggesting that further increases in sulfite concentration produced only limited additional improvement.

In the UV/PMS system, the degradation rate increased with increasing PMS concentration. The K_{obs} value rose from 0.0453 h^{-1} at 0.5 mM PMS to 0.1234 h^{-1} at 5 mM PMS. A pronounced increase in

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the rate constant was observed when the PMS concentration increased from 1 to 2 mM, indicating a substantial acceleration of PFOA degradation within this dosage range. At higher PMS concentrations, particularly at 5 mM, the improvement in degradation rate became less significant.

Similarly, the UV/PDS system exhibited enhanced degradation kinetics as the PDS concentration increased. The K_{obs} value increased from 0.0309 h^{-1} at 0.5 mM PDS to 0.1129 h^{-1} at 5 mM PDS. Compared with UV/PMS, the UV/PDS system showed lower reaction rates at lower oxidant dosages. However, at higher oxidant concentrations, particularly 5 mM, the K_{obs} values for UV/PMS and UV/PDS became relatively similar. Overall, increasing the concentration of SS, PMS, or PDS enhanced PFOA degradation, with the general kinetic performance following the order: UV/SS > UV/PMS > UV/PDS.

Effect of co-existing anions

The effects of common background water constituents on PFOA degradation were investigated in the UV/SS, UV/PMS, and UV/PDS systems at pH 7 over a reaction period of 6 h. The tested matrix constituents included inorganic anions (Cl^-, CO_3^{2-}, SO_4^{2-}, and H_3PO_4) and humic acid (HA), as shown in Figure 6.

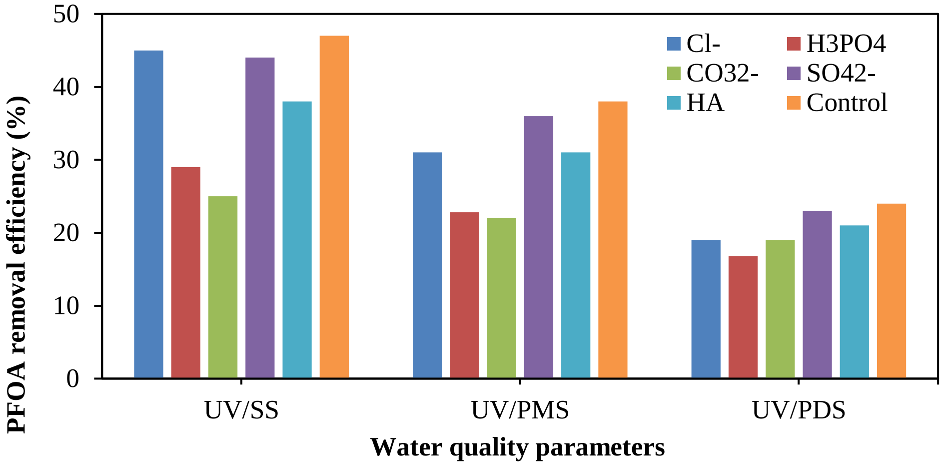

Figure 6. Effect of initial HA and inorganic anions on the percentage removal of PFOA in 6 h. Reaction conditions: $[PFOA]_0 = 0.24$ mM, $[SS]_0 = [PMS]_0 = [PDS]_0 = 1$ mM, $[HA]_0 = 10$ mg/L, $[Cl^-]_0 = 25$ mM, $[H_3PO_4]_0 = 10$ mM, $[CO_3^{2-}]_0 = 15$ mM, $[SO_4^{2-}]_0 = 5$ mM, and pH = 7.

Under control conditions without added background constituents, PFOA removal efficiencies were 47% for UV/SS, 38% for UV/PMS, and 24% for UV/PDS. These results confirmed that UV/SS exhibited the highest PFOA removal efficiency under near-neutral conditions.

The addition of co-existing ions and dissolved organic matter generally inhibited PFOA degradation in all three systems, although the extent of inhibition varied depending on the treatment process and matrix component. Overall, the sensitivity to water matrix interference followed the order: UV/SS > UV/PMS > UV/PDS.

The presence of chloride ions (Cl^-) at 25 mM caused only a slight decrease in PFOA degradation in the UV/SS system, reducing removal from 47% to 45%. In the UV/PMS and UV/PDS systems, stronger inhibition was observed, with removal efficiencies decreasing to approximately 31% and 19%, respectively. The addition of phosphate (10 mM H_3PO_4) caused a more pronounced inhibitory effect in all systems. PFOA removal decreased to approximately 29% for UV/SS, 23% for UV/PMS, and 17% for UV/PDS. The addition of carbonate (CO_3^{2-}) at 15 mM produced the strongest inhibition, particularly in the UV/SS and UV/PMS systems. PFOA removal efficiencies decreased to approximately 25% for UV/SS, 22% for UV/PMS, and 19% for UV/PDS. The presence of sulfate ions (SO_4^{2-}) at 5 mM caused only minor

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changes in PFOA degradation. The removal efficiencies remained close to the control values, at approximately 44% for UV/SS, 36% for UV/PMS, and 23% for UV/PDS. The addition of HA at 10 mg/L also inhibited PFOA degradation in all systems. The removal efficiencies decreased to approximately 38% for UV/SS, 31% for UV/PMS, and 21% for UV/PDS. During the reaction, the characteristic brownish-yellow color of HA gradually diminished, indicating that HA itself underwent decomposition under UV irradiation.

The intermediate and reaction mechanisms

LC-MS/MS characterization confirmed the formation of chain-shortened perfluoroalkyl acids (PFAAs) during PFOA degradation in all investigated systems. The detected intermediates included PFHpA, PFHxA, PFPeA, PFBA, and ultimately trifluoroacetic acid (TFA). These products indicate that PFOA degradation did not occur through direct mineralization in a single step, but rather through sequential transformation reactions involving progressive shortening of the perfluoroalkyl chain.

In the UV/PDS system, the detected intermediates followed the sequence:

PFOA → PFHpA → PFHxA → PFPeA → PFBA → TFA

This product distribution demonstrates continuous carbon-chain shortening through fragmentation and carbon-loss processes. The formation of shorter-chain PFAAs was accompanied by fluoride ion release and CO_2 evolution, confirming that defluorination and decarboxylation occurred during degradation.

In the UV/PMS system, a similar sequence of chain-shortened intermediates was observed. PFOA was progressively transformed into PFHpA, PFHxA, PFPeA, PFBA, and finally TFA. The similarity of the product distribution to that observed in the UV/PDS system indicates that both peroxysulfate-based oxidation systems promote stepwise degradation of PFOA through the formation of shorter-chain perfluorinated carboxylic acids.

In the UV/SS system, LC-MS/MS analysis also confirmed the formation of PFHpA, PFHxA, PFPeA, PFBA, and TFA. Although the detected products were similar to those found in the oxidative UV/PMS and UV/PDS systems, the UV/SS process exhibited a different dominant reaction pathway because degradation was mainly associated with reductive defluorination rather than oxidative fragmentation.

Discussion

PFOA degradation and defluorination

The negligible PFOA removal observed in the control experiments highlights the high chemical stability of this compound. The persistence of PFOA is mainly attributed to its highly fluorinated carbon chain and the exceptional strength of its C–F bonds, which makes it resistant to conventional oxidation processes and direct photolysis [22].

The superior degradation performance of the UV/SS system can be attributed to its reductive reaction pathway. Under UV254 irradiation, sulfite generates e_{aq}^- along with smaller amounts of $OH^\bullet$[23]. Hydrated electrons are among the most powerful reductants in aqueous systems ($E^\circ \approx -2.9\ V$) and are highly effective at initiating C–F bond cleavage through reductive defluorination [24]. Previous studies have reported that UV/sulfite systems can induce rapid degradation of PFOA accompanied by significant fluoride release, demonstrating that reductive pathways are particularly effective for PFAS destruction [10]. Similarly, investigations involving PFOA substitutes such as GenX have shown that UV/SS systems outperform oxidative UV/persulfate processes, emphasizing the key role of hydrated electrons in PFAS degradation [16].

In contrast, the UV/PDS and UV/PMS systems mainly operate through sulfate radical–driven oxidation mechanisms. Although $SO_4^{-\bullet}$ and $OH^\bullet$ are strong oxidants, they are generally less effective for degrading PFOA because the molecule lacks easily oxidizable functional groups and is resistant to electrophilic radical attack. Consequently, both UV/PDS and UV/PMS systems achieved only moderate degradation over the 6 h reaction period, which is consistent with previous studies showing that persulfate-based oxidation alone is insufficient

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for rapid PFOA degradation [10, 16].

Defluorination, evaluated through fluoride ion release, provides direct evidence of C–F bond cleavage and represents a more rigorous indicator of PFOA mineralization than the disappearance of the parent compound alone [25]. In the UV/SS system, the higher defluorination efficiency indicates that hydrated electrons effectively promote sequential C–F bond cleavage and extensive defluorination. UV irradiation of sulfite generates e_{aq}^{-} together with hydrogen atoms ($H^{\bullet}$) and sulfite-derived radicals ($SO_3^{-\bullet}$), which collectively contribute to reductive degradation pathways [26]. Previous studies have demonstrated that UV/sulfite systems can achieve complete PFOA degradation within 20 min and up to 77.5% defluorination after 6 h, highlighting the strong capability of this process for PFAS destruction [10]. By contrast, the lower fluoride release observed in the UV/PMS and UV/PDS systems suggests that oxidative degradation primarily leads to partial transformation and the formation of intermediate products rather than extensive cleavage of C–F bonds. Although UV-activated persulfate systems can facilitate some defluorination, sulfate radicals and hydroxyl radicals are generally less effective than hydrated electrons in breaking the strong C–F bonds of highly fluorinated compounds [13].

The kinetic analysis also supports these mechanistic interpretations. The higher rate constant obtained for the UV/SS system indicates a faster defluorination process, consistent with the strong reductive capability of hydrated electrons. In contrast, the slower kinetics observed in the UV/PMS and UV/PDS systems reflect the limitations of oxidative radical pathways in attacking the highly stable PFOA structure.

Overall, these results demonstrate that reductive processes driven by hydrated electrons in the UV/SS system provide a more effective pathway for PFOA degradation and defluorination than oxidative persulfate-based systems, highlighting the potential of advanced reduction processes for the treatment of persistent PFAS contaminants [10, 16].

Influence of operational factors

Effect of pH

The pH-dependent behavior of the UV/SS system can be attributed to the characteristics of sulfite-based advanced reduction processes. Under UV irradiation, sulfite is activated to produce highly reactive reducing species, particularly e_{aq}^{-} [11]. The enhanced degradation observed at alkaline pH suggests that sulfite species participate more efficiently in the formation of reductive radicals and electrons under basic conditions, thereby improving the reductive degradation and defluorination of PFOA. Since PFOA is highly fluorinated and electron-deficient, it is generally more susceptible to reductive attack than oxidative degradation [27]. Therefore, the improved removal at higher pH likely results from increased production of reductive intermediates and more effective C–F bond cleavage.

For the UV/PMS system, the enhanced performance under acidic conditions is likely associated with more efficient UV activation of PMS and greater availability of strong oxidizing radicals, particularly $SO_4^{-\bullet}$ [28]. These reactive species can promote oxidative degradation, including defluorination and chain-shortening reactions involved in PFAS transformation. In contrast, at neutral and alkaline pH, radical scavenging, reduced oxidant stability, and less favorable PMS speciation may lower the effective radical concentration, thereby slowing PFOA degradation. Changes in PFOA speciation with increasing pH may also contribute to the reduced degradation efficiency under more basic conditions. Overall, acidic conditions appear to be the most favorable for PFOA degradation in the UV/PMS system.

Similarly, the UV/PDS process performed more effectively under acidic conditions. At low pH, UV activation of persulfate more readily generates $SO_4^{-\bullet}$ [28], which are strong oxidants capable of contributing to PFOA degradation. As pH increases, $OH^{\bullet}$ become more dominant due to persulfate hydrolysis [29]. However, hydroxyl radicals are generally less selective and less effective toward PFOA than sulfate radicals [21]. Therefore, the decline in the observed rate constant with increasing pH can be

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explained by a shift from sulfate radical-dominated oxidation to hydroxyl radical-dominated pathways. This interpretation is consistent with previous findings. Lei et al. (2020) reported an approximately 55% decrease in PFOA defluorination efficiency when the pH was increased from 3 to 9 [30]. This decline was attributed to two main factors. First, under alkaline conditions, sulfate radicals react more readily with hydroxide ions, resulting in the conversion of sulfate radicals to hydroxyl radicals (Equations 3 and 4) [31].

$$SO_4^{-\bullet} + H_2O \rightarrow SO_4^{2-} + OH^{\bullet} + H^{+} \qquad (3)$$

$$SO_4^{-\bullet} + OH^{-} \rightarrow SO_4^{2-} + OH^{\bullet} \qquad (4)$$

Second, the oxidation potential of hydroxyl radicals decreases with increasing pH, from approximately 2.8 V under acidic conditions to 1.8 V under neutral conditions, which reduces their capacity for PFOA defluorination [32]. Therefore, pH control is critical for maximizing sulfate radical generation and improving the degradation of persistent fluorinated contaminants in UV/PMS and UV/PDS systems.

Influence of Initial PFOA Concentration

The initial contaminant concentration is an important factor in advanced oxidation and reduction processes because it affects the ratio between reactive species and target pollutant molecules. The decrease in percentage removal with increasing PFOA concentration observed in all three systems suggests that the availability of reactive species became increasingly limited relative to the pollutant load.

The superior performance of the UV/SS system is mainly attributed to the generation of e_{aq}^{-} through sulfite photolysis (SO_3^{2-}) [26]. Because PFOA is highly electron-deficient, it is more susceptible to reductive defluorination by hydrated electrons than to oxidative degradation pathways [27]. However, as the initial PFOA concentration increased, the fixed sulfite dosage and UV intensity likely produced an insufficient amount of hydrated electrons relative to the higher pollutant concentration. In addition, PFOA molecules and degradation intermediates may compete for available e_{aq}^{-}, producing a saturation effect that limits the overall degradation efficiency.

The lower effectiveness of the UV/PMS and UV/PDS systems compared with UV/SS is associated with the dominant reactive species generated in these systems. UV/PMS and UV/PDS primarily produce $SO_4^{-\bullet}$ and $OH^{\bullet}$. Although sulfate radicals are strong oxidants, PFOA is highly resistant to oxidative degradation due to the high C–F bond energy of approximately 485 kJ/mol and the electron-withdrawing nature of fluorine atoms [33]. Therefore, oxidative radical attack proceeds more slowly than the hydrated electron-driven reductive degradation pathway in the UV/SS system [16].

The observation that the absolute amount of PFOA degraded increased with increasing initial concentration, while the percentage removal decreased, indicates that higher pollutant concentrations may enhance the probability of contact between PFOA molecules and reactive species. However, because UV intensity and oxidant/reductant dosage were held constant, the total production of reactive species remained limited. As a result, the fixed reactive species supply became insufficient for achieving high fractional removal at elevated PFOA concentrations.

The decline in degradation efficiency at higher PFOA concentrations may also be explained by the shielding or internal filter effect (IFE) [34]. At elevated concentrations, PFOA and its transformation intermediates can compete with sulfite, PMS, or PDS for UV light absorption. This competition reduces the effective photochemical activation of the reagents and lowers the quantum yield of reactive species formation. Consequently, fewer hydrated electrons or radical species are available for PFOA degradation, leading to lower removal efficiencies at higher initial pollutant concentrations.

Influence of initial oxidant or reducing agent concentration

The enhancement of PFOA degradation with increasing oxidant or reducing agent concentration can be attributed to greater production of reactive

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species under UV irradiation. However, the extent of improvement differed among the UV/SS, UV/PMS, and UV/PDS systems because each process generates different dominant reactive species and follows distinct degradation pathways.

In the UV/SS system, the increase in K_{obs} with increasing sulfite concentration is mainly attributed to enhanced generation of e_{aq}^- under UV irradiation. These highly reductive species play a key role in cleaving the strong C–F bonds of PFOA through reductive defluorination pathways [11]. The comparatively high rate constant observed even at 0.5 mM sulfite indicates that UV/SS is highly effective for initiating PFOA degradation. However, the smaller increase in K_{obs} above 2 mM suggests that excessive sulfite may not proportionally improve degradation efficiency. This behavior may be related to electron scavenging, recombination reactions, or competition among reactive intermediates, which can limit the effective availability of reductive species at higher sulfite concentrations. For the UV/PMS system, increasing PMS dosage promotes the generation of $SO_4^{-\bullet}$ and $OH^\bullet$ under UV activation [35.] These oxidizing species are primarily responsible for PFOA degradation in UV/PMS. The marked increase in K_{obs} between 1 and 2 mM PMS suggests that a threshold concentration may exist, above which radical production becomes sufficient to substantially accelerate degradation. However, the reduced improvement at higher PMS concentrations, such as 5 mM, may be explained by radical self-quenching or scavenging of reactive radicals by excess PMS, which lowers the effective radical concentration available for PFOA attack. The UV/PDS system showed a similar concentration-dependent enhancement, as PDS activation under UV irradiation generates sulfate radicals that drive oxidative degradation. The lower K_{obs} values for UV/PDS at lower oxidant dosages may be due to slower UV activation of PDS compared with PMS [36]. At higher PDS concentrations, increased oxidant availability enhances sulfate radical formation, leading to improved degradation performance. The convergence of K_{obs} values for UV/PMS and UV/PDS at 5 mM suggests that sufficient oxidant availability can partially compensate for the slower activation of PDS.

Overall, reagent dosage plays an important role in controlling reactive species production and PFOA degradation kinetics. While higher SS, PMS, and PDS concentrations generally improved degradation, the diminishing increase in K_{obs} at elevated dosages indicates that excessive reagent addition may not be proportionally beneficial due to scavenging, recombination, or saturation effects.

Effect of co-existing anions and HA

Reactive radicals can interact with both organic and inorganic constituents present in water. Therefore, common water matrix components, including inorganic anions (Cl^-, CO_3^{2-}, SO_4^{2-}, and H_3PO_4) and dissolved organic matter such as HA, may compete with the target contaminant for reactive species and either enhance or inhibit degradation kinetics [37].

The stronger sensitivity of the UV/SS system to matrix constituents can be explained by its reliance on highly reactive and short-lived reductive species, particularly e_{aq}^- and sulfur-centered radicals. These species are readily scavenged by background water constituents. In contrast, UV/PMS and UV/PDS continuously generate oxidative radicals such as $SO_4^{-\bullet}$ and $OH^\bullet$ through peroxysulfate activation, making them comparatively less sensitive to some matrix interferences.

The limited inhibitory effect of chloride in the UV/SS system suggests that Cl^- is a relatively weak scavenger of e_{aq}^- and sulfur-centered reducing radicals under near-neutral conditions [11]. However, chloride caused greater inhibition in the oxidative UV/PMS and UV/PDS systems. This reduction is likely due to the reaction of Cl^- with $SO_4^{-\bullet}$ and $OH^\bullet$, forming secondary chlorine radicals such as $Cl^\bullet$ and $Cl_2^{-\bullet}$ [38]. These chlorine radicals are generally less reactive toward PFOA, diverting part of the radical flux away from direct PFOA degradation.

The inhibitory effect of phosphate can be attributed to radical scavenging and changes in reactive intermediate behavior. At pH 7, phosphate mainly exists as $H_2PO_4^-/HPO_4^{2-}$ [39]. These species can compete with PFOA for $SO_4^{-\bullet}$ and $OH^\bullet$ in the

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UV/PMS and UV/PDS systems, reducing the steady-state radical concentration available for oxidation. In the UV/SS system, the pronounced decline in removal efficiency may also result from quenching of hydrated electrons by phosphate species [11].

Carbonate produced the strongest inhibition among the tested inorganic constituents. At pH 7, carbonate is primarily present as bicarbonate (HCO_3^-), which is widely recognized as an effective scavenger of e_{aq}^- [11]. Reactions involving carbonate or bicarbonate can generate carbonate radicals ($CO_3^{-\bullet}$) [40]. These carbonate-centered radicals are less reactive toward highly fluorinated carboxylic compounds such as PFOA. As a result, carbonate/bicarbonate species reduce the availability of both reductive species in UV/SS and oxidative radicals in UV/PMS and UV/PDS, thereby decreasing degradation efficiency.

The minimal effect of sulfate is expected because SO_4^{2-} has low reactivity toward the primary reactive species involved in PFOA degradation. In addition, sulfate is a final product generated during PMS and PDS activation, making it less likely to interfere directly through radical scavenging. The slight variations observed after sulfate addition may therefore be related mainly to changes in ionic strength and solution activity coefficients rather than direct reactions with reactive species.

Dissolved organic matter is a major constituent of natural aquatic systems, and HA is commonly used as a representative model substance [41]. HA inhibited PFOA degradation through two main mechanisms. First, HA can absorb UV light, reducing UV penetration and thereby limiting sulfite photolysis as well as PMS/PDS activation [26]. Second, HA competes with PFOA for reactive species because its aromatic and phenolic functional groups readily react with $SO_4^{-\bullet}$ and $OH^{\bullet}$ [42], and reductive transient species [43, 44] generated in the UV/SS system. The observed fading of HA color during irradiation supports the occurrence of HA transformation or decomposition during treatment. Previous studies have reported that HA may enhance the degradation of perfluorinated compounds by helping maintain elevated concentrations of e_{aq}^- in the reaction system [45]. However, such a promoting effect was not observed in the present study, as HA addition did not enhance PFOA degradation in any of the investigated systems.

Identification of intermediates

PFOA degradation in the UV/PDS, UV/PMS, and UV/SS systems proceeded through radical-mediated pathways, but the dominant reactive species differed among the processes and governed both degradation behavior and intermediate formation.

In the UV/PDS system, persulfate photolysis under 254 nm irradiation generates $SO_4^{-\bullet}$ as the main oxidizing species (Equation 5) [46]:

$$S_2O_8^{2-} + h\vartheta \rightarrow 2SO_4^{-\bullet} \qquad (5)$$

These radicals, together with secondary $OH^{\bullet}$, initiate attack at the carboxylate group of PFOA, promoting decarboxylation, defluorination, and stepwise chain shortening. The detection of PFHpA, PFHxA, PFPeA, PFBA, and TFA supports a sequential oxidation pathway.

In the UV/PMS system, irradiation of HSO_5^- produces both $SO_4^{-\bullet}$ and $OH^{\bullet}$. Sulfate radicals are considered the principal species responsible for initiating PFOA degradation because of their relatively selective oxidation behavior [47], while hydroxyl radicals mainly contribute to non-selective oxidation of intermediates [48]. As in UV/PDS, degradation followed a progressive chain-shortening route, yielding PFHpA, PFHxA, PFPeA, PFBA, and TFA.

In contrast, the UV/SS system proceeded mainly through a reductive pathway. UV activation of sulfite generated e_{aq}^- and sulfite radical species, with e_{aq}^- acting as the dominant reactive species. These hydrated electrons promoted reductive defluorination of PFOA, followed by hydrogen/fluorine exchange, C–F bond cleavage, protonation, and decarboxylation [49]. The same series of short-chain intermediates was detected, but their formation occurred through reductive rather than oxidative transformation.

Thus, the main difference among the three

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systems lies in the identity of the reactive species: UV/PDS and UV/PMS are mainly oxidative systems, while UV/SS is primarily reductive. This explains the stronger defluorination capability of the sulfite-based system and the chain-shortening behavior observed in the peroxysulfate-based systems. Overall, although the mechanisms differ, all three processes followed a similar degradation sequence involving intermediate formation, carbon-chain shortening, fluoride release, and eventual formation of TFA. The detection of these intermediates confirms that PFOA degradation occurred through multistep transformation rather than direct photolysis, and it also highlights the need to consider the fate of short-chain PFAS products, especially in oxidative systems.

Conclusions

General conclusion

A comparative assessment of UV-driven treatment systems showed that PFOA degradation is highly dependent on the predominant reactive species formed within each process. Exposure to 254 nm UV light alone produced only minimal degradation, emphasizing the remarkable resistance of PFOA to direct photolysis. However, the incorporation of oxidizing or reducing agents substantially improved PFOA transformation, with the UV/SS process exhibiting the highest degradation and defluorination efficiencies among the evaluated systems.

The enhanced performance of the UV/SS system underscores the critical role of reductive mechanisms involving hydrated electrons, which effectively promote stepwise cleavage of C–F bonds and increase fluoride ion release. In comparison, the UV/PMS and UV/PDS systems mainly generated sulfate and hydroxyl radicals, which promoted oxidative degradation pathways, leading predominantly to the formation of shorter-chain perfluorinated byproducts.

Kinetic evaluations further confirmed the superior reactivity of the UV/SS process, while analysis of the transformation products verified that oxidative systems primarily proceeded through chain-shortening mechanisms. These observations highlight the importance of considering defluorination in addition to parent compound removal when evaluating the effectiveness of PFAS treatment technologies.

Overall, the findings suggest that the UV/SS process represents a promising strategy for improving PFOA degradation and may serve as an effective pretreatment option for persistent PFAS contamination in aquatic environments.

Future directions

Future research should focus on validating these findings in real wastewater matrices, examining performance at environmentally relevant PFAS concentrations, and systematically investigating the influence of dissolved oxygen and other coexisting constituents on the treatment efficiency. Further studies are required to quantify transformation intermediates, assess their toxicity, and optimize reaction conditions to maximize defluorination and minimize the accumulation of persistent by-products. Such studies are essential for determining the practical applicability of UV-based processes, particularly UV/SS, for sustainable PFAS treatment.

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Conflict of Interest

The authors declare that they have no competing interests.

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Ethical Considerations

As this study involved no human or animal participants, all research activities, including fieldwork, sampling, and data analysis, were carried out with minimal ecological disruption and in full adherence to ethical scientific standards.

Ethics Approval and Consent to Participate

The study was approved by the Ethics Committee of the Iran University of Medical Sciences (Code of

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Consent for Publication

This manuscript contains no personal information about the individuals.

Availability of Data and Material

All data generated or analyzed during this study are included in this article.

Authors' Contributions

Ali Behnami contributed to the conceptualization, methodology design, data collection, formal analysis, and writing the initial manuscript draft. Mojtaba Pourakbar contributed to the methodology design, conceptualization, formal analysis, and writing the initial manuscript draft. Khaled Zoroufchi Benis was responsible for validating data and reviewing and editing. Mahdi Farzadkia contributed to the visualization and validation of data. Roshanak Rezaei Kalantari contributed to the visualization and validation of data. Mojtaba Yeganeh was responsible for formal analysis and data collection. Ali Esrafili contributed to the conceptualization, methodology design, formal analysis, and validation of data. Mitra Gholami was responsible for conceptualization, methodology design, visualization, validation of data, writing the initial manuscript draft, and reviewing and editing.

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