# Solar Photo-Persulfate Degradation of Perfluorooctanoic Acid (PFOA): A Promising Approach for Effective Contaminant Removal

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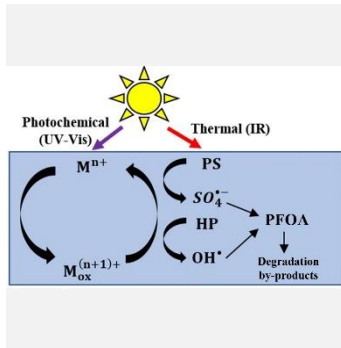
Perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) have significant environmental concerns due to their chemical durability, widespread distribution, and adverse effects on biological systems. Persulfate (PS) has emerged as a viable alternative to hydrogen peroxide (H_2O_2) for advanced oxidation processes, offering effective organic pollutant removal. This study investigates the photo-Persulfate degradation of PFOA under natural pH conditions, utilizing a solar simulator as the radiation source. The study evaluates the impact of key reaction variables: persulfate concentration (PS), iron dosage (Fe), temperature (T), and radiation level (Rad) on PFOA conversion. The results demonstrate the effectiveness of the photo-Persulfate process in degrading PFOA when ferrioxalate serves as the catalyst source. Operating the system with high radiation levels, the conversion of PFOA reaches approximately 70% after only 6 hours of reaction.

Introduction

Per-and polyfluoroalkyl substances (PFASs) have become ubiquitous across industries due to their unique properties, but their widespread use has raised significant environmental and health concerns. Human exposure to PFASs has been linked to various adverse health effects, including cancer, obesity, elevated cholesterol levels, immune suppression, and endocrine disruption. In response to regulatory pressures and the imperative to protect human health, industries are increasingly exploring more effective and efficient treatment technologies for PFASs. Moreover, current trends have shown that the destructive treatment processes, which offer degradation and mineralization of PFASs, are the most desirable process among researchers and policy makers. The potential application of solar radiation in addressing PFAS-related environmental and health challenges while meeting regulatory requirements is discussed [1,2].

In this work, perfluorooctanoic acid (PFOA), was selected as a model compound to study its abatement using an innovate photo-Persulfate process at natural pH conditions using ferrioxalate as catalyst source, which was enhanced with radiation coming from a solar simulator. Specifically, the effect of the main reaction variables: persulfate concentration (PS), iron dosage (Fe), pH, and radiation level (Rad), on PFOA conversion was evaluated. The evolution of the fluoride concentration in the reactive medium was used as a direct measure of the level of de-fluorination of PFOA and its fluorinated intermediates.

Material and Methods

The experiments were carried out in a borosilicate glass lab-flat plate photo-reactor with external recycling, irradiated from one side using a solar simulator (V_T=1.7 L). The local radiation flux averaged over the reactor window was 174.22 W m^{-2} (300-550 nm). Various analytical methods were employed to quantify Fe^{2+}, total Fe, PS, oxalate, fluoride ions, and PFOA. These included colorimetric methods, ion chromatography, and HPLC with a diode array detector [3]. For all the performed tests, an initial PFOA concentration of 40 mg L^{-1} was set. Samples were withdrawn at predefined time intervals over a total reaction time of 360 min.

Results and Discussion

Influence of Iron

The activation of persulfate through dissolved Fe^{2+} offers a promising approach for contaminant degradation, with lower activation energy requirements compared to other techniques. However, insufficient iron concentration leads to inefficient persulfate utilization, while excessive Fe^{2+} scavenge sulfate radicals, limiting the process's efficacy. Additionally, the rapid conversion of Fe^{2+} to Fe^{3+} after persulfate activation poses a challenge to sustained reaction kinetics. Here, we explore the role of radiation in mitigating this limitation by facilitating the reduction of Fe^{3+} back to Fe^{2+}. By considering the dimensions of the photo-reactor (optical length) used and the fraction of UV-Vis radiation available for the photochemical reduction of Fe^{+3}, an initial iron concentration of 10 mg L^{-1}, with an oxalate to iron molar ratio of 3:1, was selected (oxalate concentration was 47.3 mg L^{-1}). This ratio favours the formation of the ferrioxalate complex as the dominant iron species in the system, characterized by higher molar absorption coefficients [3].

Influence of pH

Higher removal efficiencies of PFOA are observed at lower pH values. Under alkaline conditions, sulfate radicals may react with hydroxide ions (OH$^-$) to generate additional hydroxyl radicals. It is well established that sulfate radicals possess higher redox potentials (2.5V~3.1 V) and longer lifetimes compared to hydroxyl radicals. Therefore, initially, the pH condition was set at 3 to maximize the generation and activity of sulfate radicals for efficient PFOA degradation.

Influence persulfate dosage

The initial persulfate concentration plays a significant role in the removal of organic pollutants in the photo-persulfate oxidation system. Increasing persulfate

concentration enhances degradation, as more sulfate radicals are produced, leading to faster pollutant degradation. However, there is a threshold to the effectiveness of increasing persulfate concentration. This limitation is attributed to the recombination of excess sulfate radicals and the reaction between sulfate radicals and excess persulfate. Therefore, further increases in persulfate concentration do not lead to additional pollutant degradation. Based on these considerations and the bibliographic references consulted, a PS/PFOA molar ratio of 100:1 was selected as a starting point (PS=1855 mg L^{-1}).

The pathway of PFOA degradation

Various reaction mechanisms associated with the decomposition of PFOA are documented in the literature. Although the reaction intermediates could not be identified in the laboratory tests conducted, a reaction mechanism is proposed below (see Table 1, Eqs. 1 to 5) based on the experimental evidence available. The proposed sequence of reactions for PFOA de-fluorination mechanisms involves the gradual removal of one CF$_2$ unit in each step. Decarboxylation and subsequent formation of unstable alcohols have been suggested as the predominant mechanisms in the de-fluorination process mediated by persulfate. These reactions are thought to proceed continuously with an abundant supply of sulfate radicals and hydroxyl radicals until complete decomposition is achieved [4].
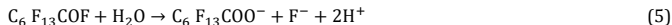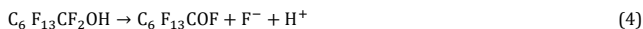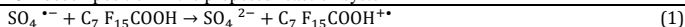
Figure 1 depicts the temporal evolution of the relative concentrations of PFOA and PS, along with the percentage of de-fluorination achieved (expressed as the fraction of experimental fluoride ions found in the samples relative to the initial theoretical value for 40 mg L^{-1} of PFOA). It's important to note two distinct kinetic behaviours. In the initial reaction stage, rapid degradation of the contaminant is observed, with conversion reaching close to 50% within just 180 minutes of reaction and a PS consumption of 12%. However, during this initial period,

the de-fluorination rate is very low, reaching a percentage of less than 5%. Thus, the de-fluorination rate is much lower than the corresponding PFOA degradation rate, indicating that PFOA is not entirely transformed into fluoride ions. Therefore, the formation of various intermediates of short-chain perfluoroalkyl carboxylates (C2-C6) is likely occurring. In a second reaction stage (from 180 min to 360 min of reaction), a significant reduction is observed in the decomposition rate of PFOA (only the conversion of PFOA increases by 20%) and in PS consumption (near 3%). However, a substantial increase in the de-fluorination rate of the system is observed, reaching a fraction of 25% for 360 min of reaction. Therefore, the influence of hydroxyl radicals is transcendental (Eq. 3, Table 1). Considering the need to achieve higher levels of de-fluorination (mineralization), the necessity of adding an auxiliary oxidizing agent (hydrogen peroxide) to the system is being analyzed. Laboratory studies are currently underway to reinforce this hypothesis.
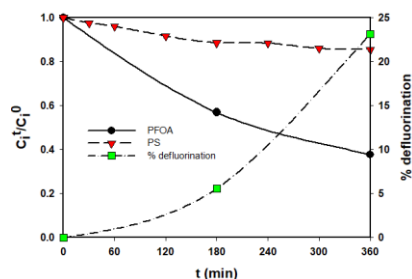
Figure 1. Relative concentrations of PFOA and PS, and the percentage of de-fluorination achieved. Conditions: pH=3, T= 50 °C, PS=1855 mg L^{-1}, Fe^{+3}=10 mg L^{-1}, Oxa=47.3 mg L^{-1} (molar ratio of Fe/Oxa = 1/3).

Table 1. Proposed pathway for PFOA decomposition in the proposed reaction system

$SO_4{}^{\bullet-} + C_7F_{15}COOH \rightarrow SO_4{}^{2-} + C_7F_{15}COOH^{+\bullet}$	(1)
$C_7F_{15}COOH^{+\bullet} \rightarrow C_7F_{15}{}^{\bullet} + CO_2 + H^+$	(2)
$C_7F_{15}{}^{\bullet} + {}^{\bullet}OH \rightarrow C_6F_{13}CF_2OH$	(3)
$C_6F_{13}CF_2OH \rightarrow C_6F_{13}COF + F^- + H^+$	(4)
$C_6F_{13}COF + H_2O \rightarrow C_6F_{13}COO^- + F^- + 2H^+$	(5)

Conclusions

Perfluorooctanoic acid (PFOA) poses environmental and health risks, needing effective remediation strategies. In this study, we demonstrated the successful degradation of PFOA using an innovative photo-Persulfate process, employing ferrioxalate as an iron source and a solar simulator. Among the studied variables, radiation level exerted the largest effect on PFOA conversion, highlighting its significance in the process. Ongoing investigations aim to elucidate the reaction mechanism and assess the feasibility of scaling up the process using pilot plant-scale solar reactors.

References
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