

Pulsed Plasma Treatment of Per- and Polyfluoroalkyl Substances (PFAS): Exploring the Roles of Oxidative Species

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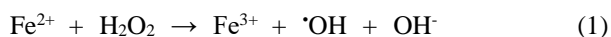
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Abstract: This study explores the synergy between a plasma process and various additives in enhancing the degradation of per- and polyfluoroalkyl substances (PFAS). The plasma-Fenton system, when combined with the cationic surfactant dodecyltrimethylammonium bromide (C12TAB), accelerates C-F bond cleavage, facilitates the oxidation of partially fluorinated byproducts, and promotes defluorination.

1. Introduction

Electrical discharge plasma is a promising technique for degrading per- and polyfluoroalkyl substances (PFAS) due to its ability to generate reactive species and photons capable of breaking the strong C-F bonds. While the process is highly effective at degrading long-chain PFAS, short-chain PFAS remain challenging because they do not concentrate at the gas-liquid interface. Sacrificial surfactants can enhance the mass transfer of short-chain PFAS to the plasma-liquid interface, enabling their degradation. However, complete defluorination remains elusive due to the formation of partially fluorinated intermediates.¹ These intermediates retain residual fluoride ions, lack surface activity, and limit further defluorination.

In this study, a pulsed gas-liquid electrical discharge reactor operating in argon was used to degrade perfluorobutane sulfonic acid (PFBS), a model PFAS compound with four carbon atoms. Experiments were conducted with the addition of ferrous ions which decompose plasma-generated hydrogen peroxide via the Fenton reaction (equation (1)) to produce OH radicals in the bulk liquid. These species were utilized to mineralize fluorinated intermediates.



2. Methods

Experiments were conducted in a gas-liquid electrical discharge plasma reactor with a point-plane electrode configuration. Argon gas was bubbled through a submerged diffuser, and discharges were generated above the liquid surface at -30 kV with a frequency of 60 Hz. The initial concentration of PFBS was 10 ppm.

3. Results and Discussion

Figure 1 compares the defluorination profiles of PFBS under various experimental conditions. In the absence of plasma (PFBS+Fenton case), Fenton reagent (iron and hydrogen peroxide) generated OH radicals, which are known to be ineffective towards the C-F bond cleavage, resulting in no defluorination. Plasma treatment without additives (PFBS case) resulted in 40% PFBS defluorination, while the addition of ferrous ions (PFBS+Fe²⁺ case) increased defluorination to 63%. The improvement is attributed to the additional OH radicals generated in the bulk liquid, which oxidized partially fluorinated intermediates formed during plasma treatment.

The addition of C12TAB significantly increased the initial defluorination rates of PFBS. In the absence of iron (PFBS+C12TAB case), 56% defluorination was achieved within the first 10 minutes of plasma treatment. This rapid defluorination is attributed to the enhanced transport of PFBS to the plasma-liquid interface facilitated by the cationic surfactant.¹ The degradation of PFBS likely generates organic, partially fluorinated intermediates that

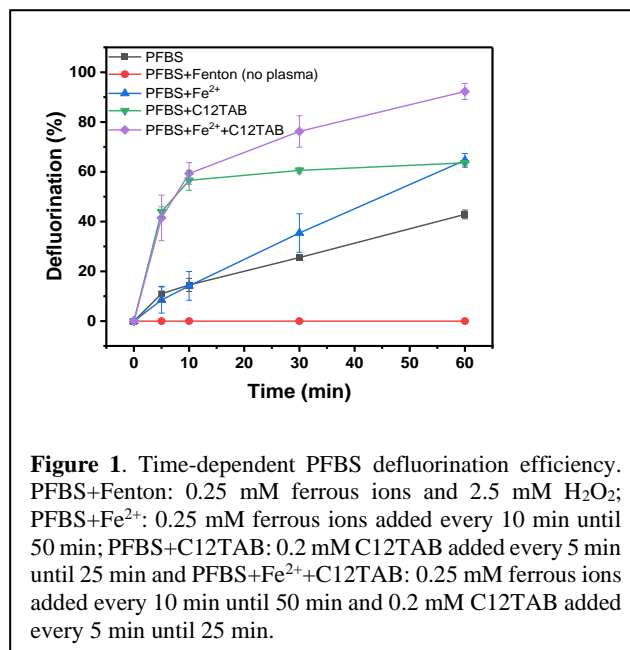


Figure 1. Time-dependent PFBS defluorination efficiency. PFBS+Fenton: 0.25 mM ferrous ions and 2.5 mM H₂O₂; PFBS+Fe²⁺: 0.25 mM ferrous ions added every 10 min until 50 min; PFBS+C12TAB: 0.2 mM C12TAB added every 5 min until 25 min and PFBS+Fe²⁺+C12TAB: 0.25 mM ferrous ions added every 10 min until 50 min and 0.2 mM C12TAB added every 5 min until 25 min.

are not surface-active and remain in the bulk liquid, where they can only be degraded through OH radical attack. The inability of plasma-generated OH radicals to fully oxidize these intermediates in the bulk liquid is believed to contribute to the observed plateau in defluorination rates. This has been demonstrated in the PFBS+Fe²⁺+C12TAB experiment, where the addition of C12TAB enhances the degradation of PFBS at the plasma-liquid interface, and ferrous ions facilitate the oxidation of partially fluorinated intermediates in the bulk liquid through the Fenton reaction.

4. Conclusion

The combination of surfactants and ferrous ions significantly enhances plasma-assisted PFAS defluorination. Surfactants are necessary for minimizing bulk liquid mass transport limitations and concentrating PFAS at the plasma-liquid interface. Once the PFAS is degraded by plasma, the generation of OH radicals in the bulk liquid becomes critical to fully defluorinate the fluorine-containing intermediates and achieve complete mineralization of the starting PFAS.

Acknowledgement

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References

1. Isowamwen, O., et al., Plasma-assisted degradation of a short-chain perfluoroalkyl substance (PFAS): Perfluorobutane sulfonate (PFBS). *Journal of Hazardous Materials*, 2023. **456**: p. 131691.