Plasma-Enhanced PFOA Degradation with Persulfate Activation

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Abstract: This study demonstrates the effective degradation of perfluorooctanoic acid (PFOA) and its byproducts using a non-thermal plasma process combined with persulfate (PS) oxidation and the cationic surfactant C12TAB (Dodecyltrimethylammonium bromide). The integrated approach achieved rapid PFOA destruction and over 90% defluorination efficiency, offering a promising solution for treating PFAS-contaminated water.

1. Introduction

Poly- and perfluoroalkyl substances (PFAS) are widely used in industry and have contaminated water sources for decades. The U.S. Environmental Protection Agency (USEPA) limits PFOA in drinking water to less than 4 parts per trillion (ppt) [1]. Meeting this strict standard requires new technologies to degrade PFAS and achieve near-complete defluorination, as partial defluorination can produce short-chain byproducts which could be as hazardous as their long-chain counterparts [2].

While studies have shown that plasma treatment with cationic surfactants degrades PFAS, defluorination efficiency remains below 50% [2]. This limitation is attributed to the formation of fluorinated byproducts that lack surface activity, causing them to remain in the bulk liquid and resist degradation.

In this work, persulfate (PS) and the surfactant C12TAB (Dodecyltrimethylammonium bromide) were integrated into the plasma treatment system to address these challenges. The surfactant is expected to transport non-surfactant-like intermediates to the plasma-liquid interface, while the decomposition of PS generates reactive sulfate radical anions capable of degrading these intermediates in the bulk liquid.

2. Methods

The experimental setup consisted of an argon-driven needle-to-plate pulsed plasma reactor with a tungsten high-voltage electrode and a grounded stainless-steel plate submerged in liquid. Argon was bubbled into the solution via a diffuser positioned above the grounded electrode. A high-voltage pulsed power supply was used to apply -30 kV at a frequency of 60 Hz. Each experiment treated 500 mL of PFOA solution in a semi-batch mode, recirculating the liquid through a heat exchanger to maintain a temperature of ~10°C. Samples were collected at regular intervals and analyzed using ultra-performance liquid chromatography-mass spectrometry (UPLC-MS).

3. Results and Discussion

Figure 1 shows the results of a 2-hour plasma treatment applied to a 10 mg/L PFOA solution. The treatment began with the addition of 5 mM PS, which facilitated the degradation of nearly all PFOA within the first 30 minutes. Subsequently, a total of 1.8 mM C12TAB was added to the solution in multiple steps, with 0.2 mM introduced every 10 minutes starting from t = 30 minutes. PFOA degradation
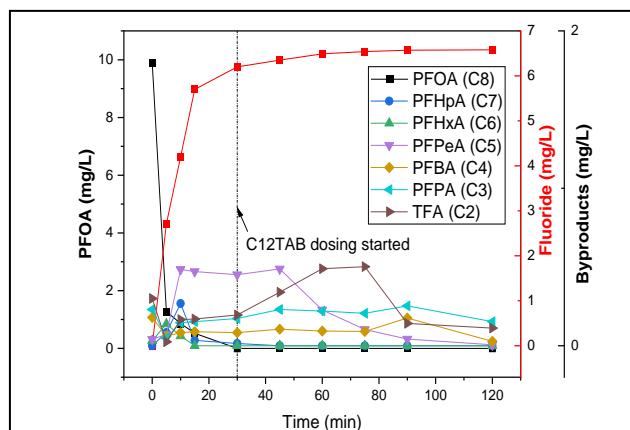

Fig. 1. Time-dependent concentration profiles of PFOA and its degradation byproducts including fluoride ions. Initial PFOA conc: 10 mg/L, PS: 5 mM (added at t=0 min), C12TAB: 1.8 mM (dosed 0.2 mM every 10 minutes starting at t=30 min).

occurs through the stepwise cleavage of C-C bonds, producing shorter-chain perfluoroalkyl carboxylic acids, while defluorination takes place via the breaking of C-F bonds, releasing fluoride ions (F^-) into the solution. Results reveal that all C5–C8 fluorinated byproducts were completely degraded by the end of the 2-hour treatment, leaving only trace amounts of PFBA and ultra-short-chain compounds in the solution. The fluoride yield results indicate a defluorination efficiency of over 90%.

4. Conclusion

The results of this study suggest that combining the non-thermal plasma process with persulfate oxidation in the presence of a cationic surfactant, such as C12TAB, is highly effective. This approach enables rapid destruction and defluorination of PFOA and its short-chain byproducts.

References
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