The roles of neutral species and photons in plasma treatment of PFAS

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Abstract: Low-temperature plasmas effectively degrade long-chain poly- and perfluoroalkyl substances (PFAS). However, the degradation mechanisms and underlying chemical reaction pathways are not fully understood. This work utilizes an atmospheric pressure plasma jet – the COST jet – to explore the roles of non-charged reactive plasma species in PFAS degradation. Findings suggest that VUV generated by the plasma may be the key agent responsible for PFAS degradation.

1. Introduction

Atmospheric pressure plasmas effectively degrade long-chain PFAS compounds by breaking C-F bonds and shortening chain lengths until they are completely mineralized into fluoride ions. However, the exact mechanism and the reactive species responsible remain unknown.

This study employs the COST jet to investigate the role of non-charged species in PFAS degradation. The COST jet is well-suited for this task due to its parallel electrode configuration, which confines charged species within the electrode gap and allows only neutral species and photons to reach the gas-liquid interface. The jet was used to treat perfluorooctanoic acid (PFOA), a model long-chain PFAS contaminant with eight carbon atoms.

2. Methods

A COST jet driven by a 13.56 MHz RF power supply was used to treat 2.5 mL aqueous samples containing 50 ppm PFOA in a 12-well plate container for two hours. The jet operated at a power input of approximately 1 W for all experiments. Plasma was generated using helium gas and helium mixed with molecular gases such as nitrogen and oxygen. Gas mixture humidity was varied by passing helium through a water bubbler.

3. Results and Discussion

Results shown in Figure 1 indicate that adding molecular gases to helium plasma significantly enhances the degradation of PFOA. With pure helium, only ~ 20% of the staring PFOA concentration was degraded after 120 minutes of treatment. However, with the addition of 0.4% nitrogen or 0.6% oxygen, the removal increases to ~ 60%. Studies suggest that molecular gas additions reduce helium excimer intensities while increasing the photon intensities of atomic particles from these gases in the VUV range [1, 2]. Consequently, we hypothesize that the enhanced photon energy from these molecular gases controls the PFOA degradation.

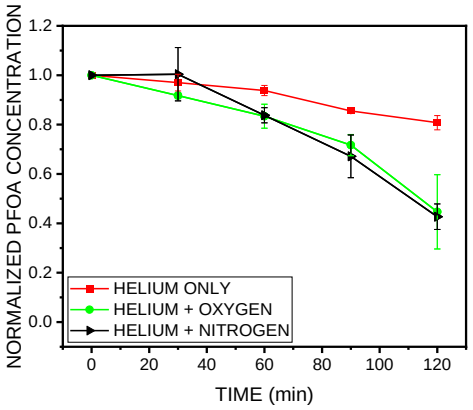

Fig. 1. Time-dependent degradation profiles of perfluorooctanoic acid (PFOA) in helium, helium-nitrogen (0.4%), and helium-oxygen (0.6%) plasmas.

4. Conclusion

Investigations into the roles of non-charged plasma species suggest that contrary to previous studies emphasizing solvated electrons, other species/agents may also contribute to PFAS degradation and defluorination. With aqueous electrons isolated by the COST jet configuration, the results indicate that energetic VUV photons transmitted to the aqueous solution might be responsible for the observed degradation.

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References

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