Degradation of Perfluorooctanoic Acid (PFOA) via DC- driven Pin-to-Water Atmospheric Pressure Plasma

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Abstract: In this study, we report the degradation of Perfluorooctanoic acid (PFOA) by a DC-driven pin-to-water Atmospheric Pressure Plasma (AAP). Short-lived reducing species (H· and the e_{aq}) were shown to responsible for degrading a significant percentage of the PFOA. The products of degradation of PFOA were further determined and quantified.

1.Introduction

The forever chemical known as PFOA is an emerging pollutant in waste, ground and drinking water [1]. Literature has indicated that hydrated electrons generated by AAPs upon reaction with liquid water are responsible for the breakdown of PFOA [1, 2]. In this study, we probed the chemical reaction pathways for the breakdown of PFOA by the reducing species, the H· radical and the hydrated electron at different pH's. pH plays an important role as the H· radical is the conjugate acid of the hydrated electron with a pKa of 9.6 [3]. The degradation products were identified and quantified using targeted and non-targeted analysis techniques.

2. Methods

The pin-to-water discharge plasma ignited in Ar gas [4] had a positive polarity while 40 ml of a 20 µM solution of PFOA in water with different additives acted as the cathode. Treatment times ranged from 0 to 120 minutes and the plasma power was 11 (±1) W. Scavengers isopropanol and sodium nitrate were used to target the reducing species in their active pH ranges. The percentage degradation and the products of degradation were quantified using targeted Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) analysis. Non-targeted analysis via LC High Resolution Mass Spectrometry (HRMS) was used to measure other degradation products.

3. Results and Discussion

PFOA degradation was 50% in 30 minutes and 80% in 120 minutes. In the presence of a surfactant cetyltrimethylammonium bromide (CTAB), PFOA was degraded 75% in 1 minute and 90% in 30 minutes. PFOA degradation was reduced by 51% in the presence of 7 mM isopropanol at a pH of 2.89. 25 mM sodium nitrate reduced the degradation of PFOA by 64% at a pH of 10. Perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), and perfluoroheptanoic acid (PFHpA) were detected and quantified as likely degradation products of PFOA using AAP. Non-targeted analysis suggests potential substitutions and rearrangements of the parent PFOA is occurring.

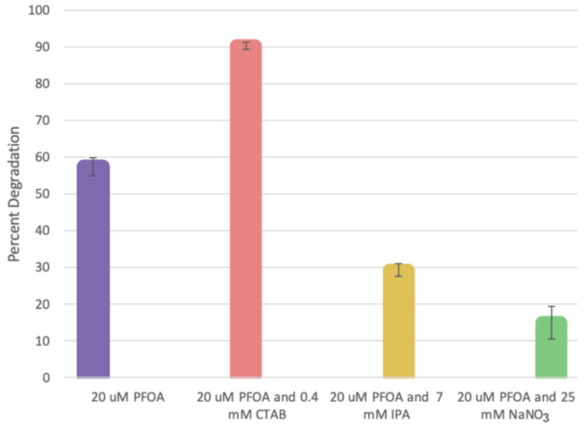

Fig. 1 Percentage Degradation of PFOA

4. Conclusion

A pin to water discharge Argon plasma is a promising technology for the degradation of PFOA. PFOA degradation was 80% in 120 min. CTAB allows for much faster degradation of PFOA. 90% degradation occurred in 30 min. Scavengers of the hydrated electron and the H· radical in their effective pH ranges suppressed the degradation of PFOA suggesting an important contribution of these reactive species in the PFOA degradation.

Acknowledgement

The Minnesota Department of Health performed the analysis of various degradation products of PFOA. We are grateful to the Department of Chemistry, Hamline University for funding this project.

References

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