

Plasma Degradation of Surfactant Molecules at the Gas-Liquid Interface

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Abstract: As surfactants, PFAS residing on the surface of water can be efficiently degraded during plasma treatment by electrons, heavy particles, and photons produced by surface ionization waves. In this paper, plasma degradation of a surrogate surfactant molecule C_3F_8 was investigated using a 2-dimensional models. Plasma degradation of PFOA was investigated using a global model for long term assessments.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are called forever chemicals due to their strong carbon-fluorine bonding and surfactant-like character that enables them to persist in the environment. Atmospheric Pressure Plasma Jets (APPJs) have the potential to effectively dissociate PFAS molecules on the liquid surface through direct interaction with energetic plasma produced species (electrons, ions, photons) and in-water plasma produced reactivity. However, the mechanisms for degradation are not well understood. In this work, APPJ interactions with water contaminated with PFAS-like and PFAS molecules were computationally investigated to quantify these processes.

2. Description of the Models

An argon plasma jet onto water was simulated using *nonPDPSIM* (2-dimensional model) and *Global-Kin* (0-dimensional model). In the 2-D model, -15kV was applied for 70 ns with 0.5 cm electrode-water gap. C_3F_8 was present on the water surface as a surrogate molecule of a surfactant, which is dissociated into primarily C_2F_6 and secondarily CF_3 by electron and heavy particle impact, and by photolysis. In the 0-D model, a complete mechanism for PFOA degradation was implemented to investigate plasma treatment over minute timescales.

3. Plasma Degradation of Surfactants

The ionization wave propagates along the water surface charging the surface negatively and forming anode-like sheath on the surface. (See Fig. 1.) While the sheath can accelerate electrons onto water, the dominant mechanism for C_3F_8 dissociation was photolysis. This is due to the limited penetration depth of electrons, as well as the photon flux being 3 to 4 times higher than the electron flux. The rate of electron impact dissociation was an order of magnitude greater than by ion impact, while excited species had a minor impact.

Long-chain surfactant PFOA mostly exists in ionized form in water [3], and therefore the degradation of its

conjugate base ($C_7F_{15}COO^-$) was addressed in the 0-D model. For example, solvated electrons can break the C-F bond by replacing fluorine atoms with hydrogen atoms (H-F exchange). Photons can initiate chain shortening through sequential steps of decarboxylation - hydroxylation - elimination - hydrolysis (DHEH) mechanism [4-5]. For direct interaction with gas-phase plasmas, the cross section of the conjugate base was assumed to be the same as that of PFOA, as electron, photon, and heavy particle encounter the hydrophilic portion of the molecule which remains the same after the long-chain surfactant donates a proton.

4. Concluding Remarks

In this work, dissociation sources of surfactants residing on the water surface were investigated in negatively pulsed plasma jet system which produces a surface ionization wave across the surface. While the anode-like sheath allows the electrons to strike the liquid surface, the surrogate molecule C_3F_8 was primarily dissociated by photons. To investigate the degradation of PFOA, the reaction mechanism for its conjugate base was included in 0-D model. The C-F and C-C bond was weakened by H-F exchange and DHEH mechanism as well as the impacts of electrons, heavy particles, and photons.

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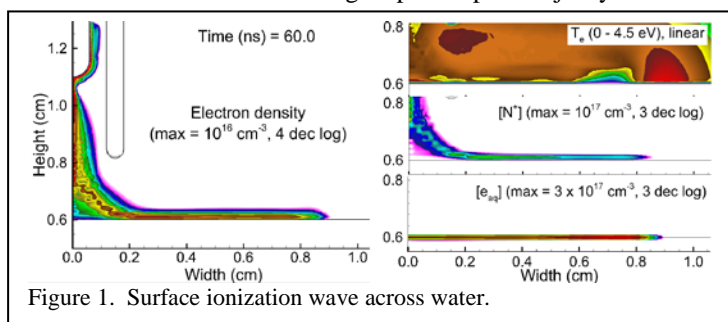


Figure 1. Surface ionization wave across water.