Evolution of ONOOH and O_2NOOH in water treated with humid air plasma: detection, model and bactericidal effects

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Abstract: This study quantitatively analyzed peroxynitrous acid (ONOOH) and peroxynitric acid (O_2NOOH) in plasma-activated water. Results showed that O_2NOOH concentrations were significantly higher than ONOOH and increased with plasma treatment time. O_2NOOH primarily originates from gas-phase solvation or interfacial radical reactions. We discuss the impact of these results on the plasma-enabled inactivation of bacteria.

1. Introduction

Peroxynitrous acid (ONOOH) and peroxynitric acid (O_2NOOH) are increasingly recognized as playing important roles in the inactivation of wet-state microorganisms by atmospheric pressure air plasma [1-2]. However, quantitative studies of these two species in plasma-activated water (PAW) remain limited, and their role in bacterial inactivation remains often unclear.

2. Methods

A 2D microhollow DBD plasma array was used as described in detail in previous reports to treat 1 mL of 1% NaCl solution [3]. The source was operated at a discharge power of 5.4 W in humid air at a flow rate of 10 SLM at a distance of 22 mm from the solution. The ONOOH concentration was determined using the HKGreen-4I fluorescence probe [4]. O_2NOOH levels were evaluated using N,N-diethyl-1,4-phenylenediamine (DPD) using the signal differences before and after O_2NOOH decomposition. The decomposition was induced by adding 1 M phosphate buffer (pH 7.4).

3. Results and Discussion

The HKGreen-4I fluorescence probe showed high sensitivity for detecting ONOOH in PAW, with a detection limit of 0.05 μM. The DPD method demonstrated a detection limit of 1 μM for O_2NOOH. As shown in Fig. 1, significantly higher levels of O_2NOOH compared to ONOOH were found and may be due to the acidic conditions induced by plasma, which favor O_2NOOH accumulation but promote ONOOH decomposition.

A 1D liquid-phase reaction-diffusion model indicated that the reaction of H_2O_2 and NO_2^- under acidic conditions alone could not account for the measured levels of ONOOH and O_2NOOH. This suggests that the primary sources of these species in PAW are likely due to the solvation of gas-phase components or interfacial radical reactions, rather than reactions in the bulk liquid between H_2O_2 and NO_2^-. When additional constant gas-phase fluxes of the species were incorporated into the model, the predicted concentrations aligned well with experimental values (Fig. 1). We will discuss the impact of these findings on bactericidal decontamination. In tests on MRSA, the bactericidal performance of O_2NOOH and ONOOH was several hundred times higher under acidic conditions.

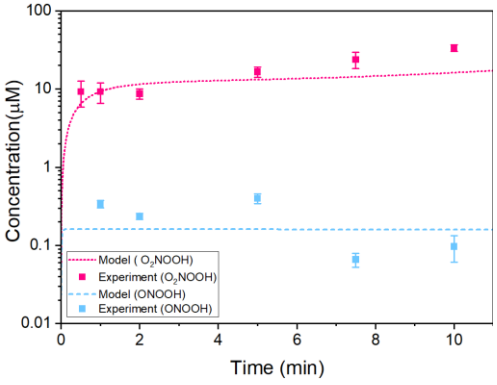

Fig. 1. Comparison of measured and simulated values of changes in ONOOH and O_2NOOH concentrations during treatment in humid air, 5.4 W, 1 mL 1% NaCl.

4. Conclusion

We reported methods that effectively quantified ONOOH and O_2NOOH in PAW. Plasma-induced acidic environments promoted O_2NOOH accumulation while suppressing ONOOH formation. The findings suggest that O_2NOOH in PAW predominantly originates from gas-phase solvation or interfacial radical reactions.

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