

Chemical Composition and Storage Stability of SDBD Air Plasma Activated Water (PAW)

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Abstract: The chemical composition and storage stability of SDBD air PAW was determined as a function of the operating conditions (plasma exposure time and plasma power). Increasing exposure time and plasma power led to a decrease in pH and an increase in temperature, nitrate and nitrite levels in the PAW. Hydrogen peroxide was not detected, irrespective of the treatment. While the pH and nitrate levels remained stable after 2 weeks at 4 °C, the nitrite levels decreased slightly, due to their instability under acidic conditions

Keywords: Plasma activated water, chemical species, operating conditions, storage stability

1. Introduction

A recent application of the cold plasma technology relies on the activation of water and liquids through their exposure to a plasma discharge, resulting in a cocktail of chemical reactive species causing the acidification of the media. Hydrogen peroxide, nitrates and nitrites have been reported as persistent species in the plasma activated water (PAW), also responsible for its antimicrobial activity [1].

The PAW provides a series of advantages over the direct plasma treatment: dose control, ease of implementation; storage capacity; on/offsite generation; possibility for self-sanitation and reactivation; and sustainable production. PAW has rapidly emerged as a value-added, niche opportunity for bio-based applications, including food decontamination, plant growth promotion (nitrogen fertiliser) and curing of meat products [2-4].

2. Objectives

The overall objective of the present study was to characterise the chemical composition of SBD air PAW as a function of the operating conditions (plasma exposure time and plasma power), as well as its stability under relevant conditions for industrial settings (2 weeks at 4 °C), in order to gain a better insight on its storage capacity for practical applications in e.g. food disinfection.

3. Materials and Methods

3.1 Cold plasma generation system

The plasma reactor used to generate the PAW is based on a surface barrier discharge (SBD) electrode set in a dielectric barrier discharge configuration (DBD) and coupled to the lid of the treatment chamber (176 x 174 x 48 mm), with a total discharge area of 15 cm². For 100 mL treatment volume, the distance between the liquid surface and the electrode was 44.8 mm (3.2 mm water column). The plasma generating source produced a sinusoidal signal at a frequency of 12 kHz. Plasma power (16, 26 or 36 W) was determined using the mean of the product between the applied voltage and current over 200 cycles. The system operates at atmospheric pressure, with room air as the plasma-inducing gas.

3.2 Determination of reactive species in the PAW

The Merck Spectroquant® test kits were used for the spectrophotometric determination of nitrates (#109713)

and nitrites (#114776) at 340 and 525 nm, respectively. The H₂O₂ concentration was determined with the titanium sulphate colorimetric method at 407 nm.

3.3 Experimental design

Plasma activation experiments were conducted with distilled water under standard/constant conditions of magnetic stirring (500 rpm) and initial volume (100 mL), pH (no adjustment, ≈ 5.3-6.0) and temperature (room temperature, ≈ 19-21 °C). A full factorial design was implemented (3 levels x 3 levels; at least in triplicate on independent days) to determine the effect on the concentration of reactive species in the PAW of:

- Voltage peak-to-peak (plasma power): 9 kV (16 W), 10 kV (26 W) and 11 V (36 W).
- Plasma exposure time: 5, 12.5 and 20 min.

The stability of the PAW (concentration of reactive species) after 24 h, 1 week and 2 weeks of storage at 4 °C was determined (in triplicate) for those tests carried out at 20 min exposure time (for the 3 values of plasma power).

4. Results and discussions

4.1. Chemical composition of the PAW

Figures 1-4 display the results (average and standard deviation) corresponding to the effect of plasma power (voltage peak-to-peak) and plasma exposure time on the pH, temperature (immediate reading), and nitrate and nitrite levels in the PAW, respectively. Hydrogen peroxide was not detected in the PAW samples (no significant difference with respect to the blank), irrespective of the treatment condition.

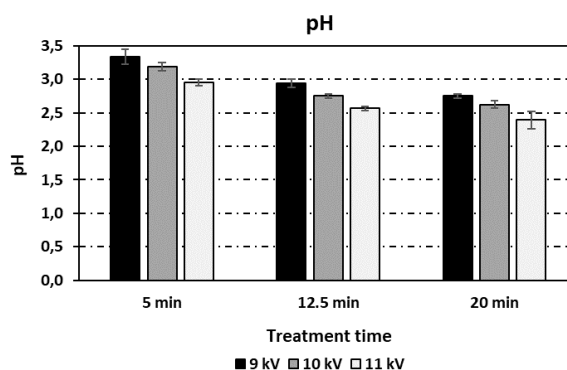


Fig. 1. Effect of the voltage peak-to-peak and exposure time on the pH values of the PAW

From Figure 1 it can be noticed that the pH of the PAW decreased as the exposure time and the voltage peak-to-peak increased. However, the change in the pH, at constant voltage, was slightly more pronounced for shorter exposure times (5 and 12.5 min). The reactive oxygen and nitrogen species in the plasma diffuse and dissolve in the liquid during the treatment and react with the water molecules giving rise to new chemical species, whose generation is subject to the release of hydrogen ions causing a reduction of the pH to values of up to 2.4 ± 0.1 , depending on the operating conditions.

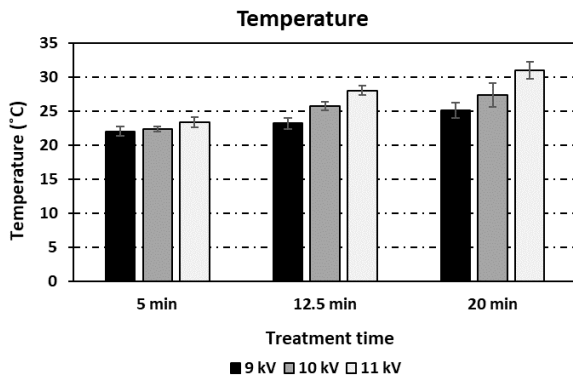


Fig. 2. Effect of the voltage peak-to-peak and exposure time on the temperature of the PAW

Figure 2 shows that the temperature of the PAW (immediate reading after plasma treatment) increased towards the plasma exposure time and the voltage peak-to-peak. A maximum temperature of 30.9 ± 1.2 °C was reached for the most severe conditions of plasma power and exposure time, and no variations in the volume of water before and after activation were recorded.

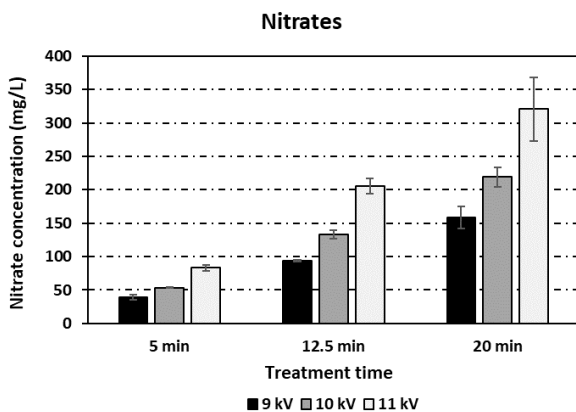


Fig. 3. Effect of the voltage peak-to-peak and exposure time on the nitrate levels in the PAW

Overall, the nitrate concentration increased significantly towards both variables, reaching the highest values ($320 \pm$

47.8 mg/L) under conditions of 11 kV voltage peak-to-peak (36 W plasma power) and 20 min of plasma exposure.

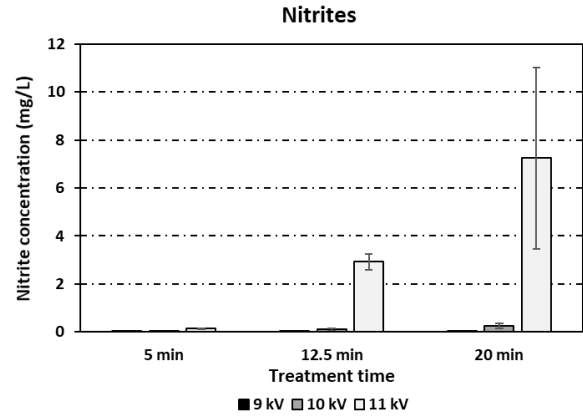


Fig. 4. Effect of the voltage peak-to-peak and exposure time on the nitrite levels in the PAW

The nitrite concentration followed a similar evolution with respect to the treatment duration and plasma power, although its presence was much lower than the nitrate levels (7.2 ± 3.8 mg/L). For example, for voltages peak-to-peak of 9 and 10 kV, the nitrite concentration was practically negligible. In the case of 11 kV, its presence was appreciable for exposure times of 12.5 and 20 min, although the variability between replicates was relatively high. This behaviour is attributed to the instability of nitrites under acidic conditions, which form nitrous acid, later decomposed into nitrates and nitrogen oxide.

4.2. Stability of PAW during Storage at 2-4°C

Figures 5-7 display the results (average and standard deviation) corresponding to the stability of the PAW (pH and nitrate and nitrite concentrations) generated at 9, 10 and 11 kV voltage peak-to-peak (16, 26, and 36 W plasma power) and 20 min of plasma exposure time, after 24 hours, 1 week and 2 weeks of storage at 4 °C, with the aim to simulate conditions relevant for industrial settings.

According to the Figure 5, the pH of the PAW remained stable during refrigerated storage, for all the conditions tested (2.4 ± 0.1 for 11 kV and 20 min exposure).

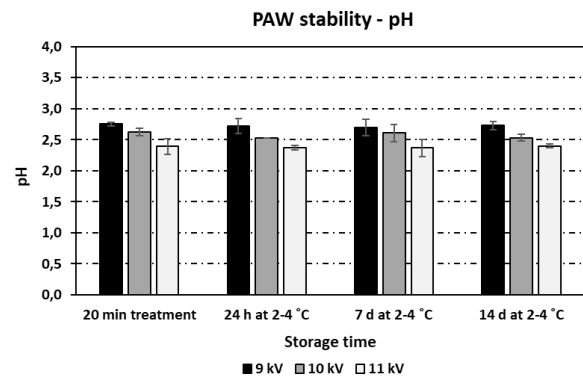


Fig. 5. Stability of PAW (pH) during storage at 4 °C

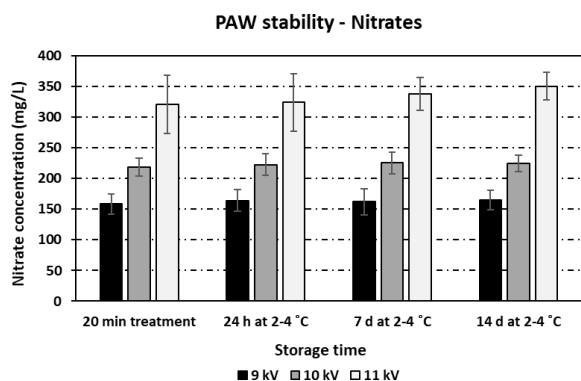


Fig. 6. Stability of PAW (nitrate concentration) during storage at 4 °C

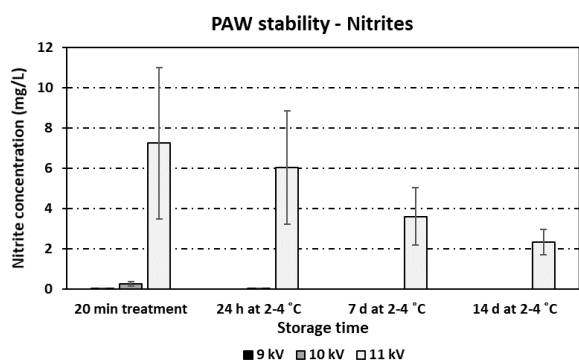


Fig. 7. Stability of PAW (nitrite concentration) during storage at 4 °C

The nitrate levels remained relatively stable (350.1 ± 2.4 mg/L) and the nitrite concentration decreased steadily (also its variability) during storage at 4 °C, which is attributed to the acidic pH of the PAW, leading to the decomposition of nitrites into nitrates and nitrogen oxide. A recent study (plasma jet) assessing PAW antimicrobial activity as a function of the storage conditions (-80, -20, 4 and 25 °C for 1, 3, 7, 15, 30 days) reported that the concentration of reactive species in the PAW (hydrogen peroxide, nitrites and nitrates) decreased as the storage time increased and such a decrease was more pronounced at higher storage temperatures [5].

5. Conclusions

Chemical composition of the PAW

- Hydrogen peroxide was not detected in the PAW, regardless of the treatment conditions, albeit it is recognised as one of the persistent species in the PAW and commonly associated to its antimicrobial activity.
- The pH of the PAW decreased (up to 2.4 depending on the operating conditions) as the exposure time and plasma power increased, due to the generation of reactive species causing the release of hydrogen ions.
- The temperature of the PAW (immediate reading) increased as the plasma exposure time and plasma power increased.

- The nitrate levels in the PAW increased with increasing exposure time and plasma power, reaching their maximum concentration (320 mg/L) at 11 kV voltage peak-to-peak (36 W plasma power) and 20 min of plasma exposure. The nitrite concentration followed a similar trend, although their presence was much lower (7.2 mg/L) and variability much higher than that for nitrates, due to the nitrites instability under acidic pH.

Stability of the PAW during storage at 4 °C

- While the pH and nitrate concentration in the PAW remained stable after 2 weeks of storage at 4 °C, the nitrite concentration decreased steadily, due to the acidic pH of the PAW leading to the decomposition of nitrites into nitrates and nitrogen oxide.
- The (at least) 2 week storage capacity of the PAW will confer an operational margin to food producers to cope with the volatile supply and demand.

6. References

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