

Chemical analysis of reactive species and phenol degradation induced in static water by a DBD reactor driven by nanosecond pulses

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Abstract: In this work, the investigation of the reactive species produced in deionized water by an air dielectric barrier discharge driven by nanosecond pulses is presented. The role of pH and conductivity of the treated liquid on plasma induced chemical pathways have been highlighted for phosphate buffer solution and deionized water with phosphate electrolyte. Nitrites and nitrates concentrations were measured by means of ion chromatography, while hydrogen peroxide concentration was quantified using the titanium sulfate method. Phenol degradation was evaluated through high performance liquid chromatography (HPLC).

Keywords: dielectric barrier discharge, plasma activated water, reactive species, phenol degradation

1. Introduction

Numerous studies have reported on the antibacterial [1,2] and pollutant degradation [3] potential of plasma activated water (PAW); more recently, PAW was discovered to be able to affect plants' growth [4]. Driven by promising applicative results and with the aim of increasing the comprehension of fundamental aspects of plasma interaction with liquids, several groups have started to investigate the chemical composition and the chemical pathways induced, by plasma treatment in water, as well as in other liquids; significantly different chemical compositions were reported for different plasma sources and operating conditions [5,6], highlighting the necessity of thoroughly exploring the wide range of different effects of each specific plasma system.

The purpose of this work is the investigation of the reactive species produced in water by a dielectric barrier discharge (DBD) reactor driven by nanosecond pulses and enabling the treatment of static water in a closed and controlled environment. Three different liquids were treated: deionized water (DIW), phosphate buffer solution, and deionized water with phosphate electrolyte. Immediately after plasma treatment, nitrites (NO_2^-) and nitrates (NO_3^-) concentrations in the liquids were measured by means of ion chromatography, while hydrogen peroxides (H_2O_2) concentration was measured using the titanium sulfate method; the concentration of reactive species was also measured using analytic strips and results are here compared to better assess the reliability of this method. Moreover, post-treatment kinetics of reactive species was evaluated for DIW treated for 5 and 10 minutes. Finally, degradation of phenol in DIW and formation of hydroxylated and nitrated products of phenol were evaluated through HPLC analysis, also

performed immediately after plasma treatment.

2. Materials and methods

2.1. Plasma source

The DBD reactor, schematically represented in Fig. 1, consists of a borosilicate glass case acting both as liquid container and as dielectric barrier (thickness 2 mm).

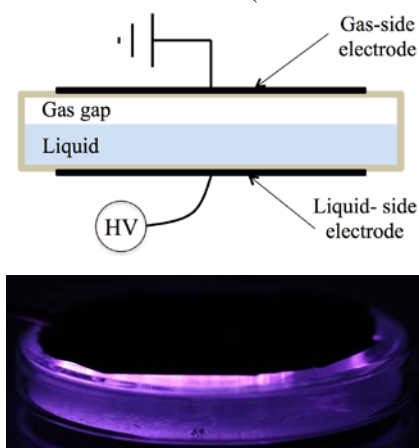


Fig. 1. Schematic (top) of the DBD reactor and photo of the plasma source during operation (bottom).

The volume of the source enables the treatment of up to 60 ml of static liquid in a closed environment; the amount of treated liquid determines the thickness of the gas filled gap. Two aluminum foils are used as electrodes; the liquid-side electrode is connected to a nanosecond pulsed high voltage generator, while the gas-side electrode is grounded. The plasma source is driven by a generator producing high voltage pulses with a slew rate of few kV/ns and 50 mJ of energy per pulse. Three different

liquids were treated in the DBD reactor: deionized water (DIW), phosphate buffer (PB), made dissolving Na_2HPO_4 and KH_2PO_4 in deionized water, and water solution containing an electrolyte, NaH_2PO_4 (NaH_2PO_4). pH and conductivity of untreated DIW were 5.5 and $1.5 \mu\text{S}/\text{cm}$, respectively. The conductivity of the PB and electrolyte solutions were adjusted in order to reach the same value measured in DIW after 10 min treatment ($1435 \mu\text{S}/\text{cm}$). All treatments were performed operating the source at a peak voltage of 20 kV and with a pulse repetition frequency of 1000 Hz. Experiments were carried out using 60 ml of liquid (resulting in a gas filled gap of 1 mm; air was used as gas) and different treatment times were tested (1, 2.5, 5 and 10 min).

2.2. pH and conductivity measurements

pH and electrolytic conductivity measurements of plasma treated solutions were performed immediately after the treatment by means of pH and conductivity probes (WTW).

2.3. Reactive species concentration measurements

NO_2^- , NO_3^- and H_2O_2 concentrations in liquids were measured by means of both quantitative and semi-quantitative methods. H_2O_2 concentrations were measured quantitatively using the titanium sulfate test, while NO_3^- and NO_2^- concentrations were measured by means of ion chromatography [6]; samples were fixed immediately after being withdrawn from the plasma-treated solution to avoid the decomposition of the reactive species [6]. Moreover, analytic Quantofix test strips were used in order to collect semi-quantitative information on the reactive species concentration in treated DIW. For the case of DIW treated for 5 or 10 min, the post-discharge kinetics of reactive species (H_2O_2 , NO_2^- and NO_3^-) was also evaluated, measuring their concentrations at different times after plasma treatment (2, 4, 6, 8, 10, 12, 15, 18, 24, 30 and 36 min after the 5 min treatment and 1, 2, 3, 4, 5, 6, 8, 10 and 15 min after the 10 min treatment).

2.4. Phenol degradation

500 μM of phenol were added to DIW before plasma treatment in order to evaluate the phenol degradation and by-product formation; for the measurement of these species, a HPLC system with UV and fluorescence detection [6] was used. Different treatment times were tested (1, 2.5, 5 and 10 min).

3. Results and discussion

3.1. pH and conductivity measurements

pH and conductivity variation induced by plasma treatment are presented in Fig. 2: a strong acidification and increase of conductivity was induced by the plasma treatment of DIW and NaH_2PO_4 , while pH and conductivity of PB were only slightly affected by even the 10 min plasma treatment.

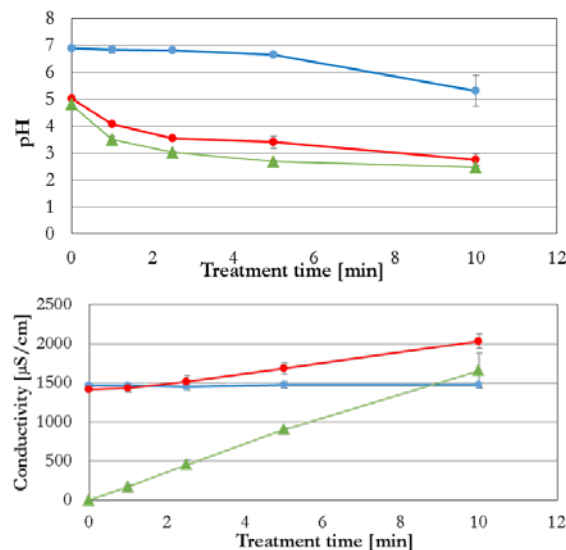


Fig. 2. pH (top) and conductivity (bottom) variation induced by plasma treatments of different duration in PB (blue), DIW (green) and NaH_2PO_4 (red).

3.2. Reactive species concentration measurements

H_2O_2 , NO_3^- and NO_2^- concentrations measured after plasma treatment of the different liquids (samples fixed immediately after being withdrawn from the plasma-treated solution) are reported in Fig. 3. An increase of H_2O_2 and NO_3^- concentrations was observed for increasing treatment times in all the treated liquids. With respect to NO_2^- concentration, a monotone increase was observed in PB for increasing treatment times, while for DIW and NaH_2PO_4 a lower concentration was measured after a 10 min treatment than after a 5 minutes one. This behaviour can be ascribed to the peroxy-nitration process that occurs in liquids with pH lower than 4 [6], like DIW and NaH_2PO_4 after plasma treatment.

3.3. Comparison of quantitative and semiquantitative analysis

A comparison between qualitative and semiquantitative measurements of reactive species is reported in Figs. 4, 5 and 6. Even if analytic strips are a less sophisticated measurement tool, in some of the considered cases the concentrations measured with quantitative methods falls within the range measured by the strips. Since measurements through analytic strips provide a range of concentration, they are represented in Figs. 4, 5 and 6 as colored bars.

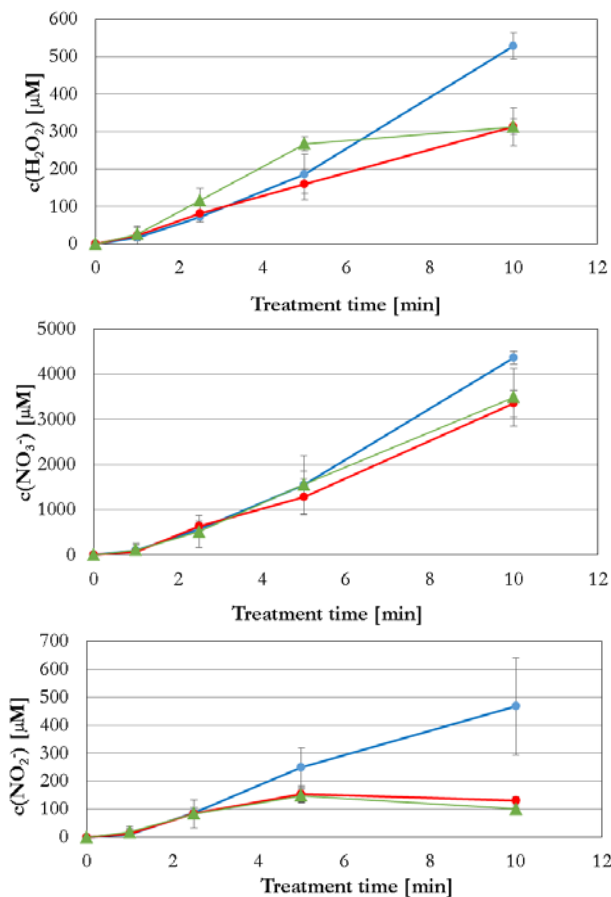


Fig. 3. H_2O_2 (top), NO_3^- (middle) and NO_2^- (bottom) concentrations induced by plasma treatments of different duration in PB (blue), DIW (green) and NaH_2PO_4 (red).

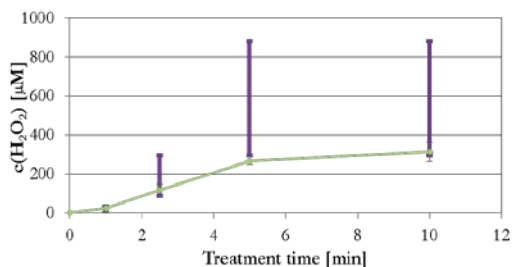


Fig. 4. H_2O_2 concentration induced by plasma treatments of different duration in DIW measured by means of titanium sulfate test (quantitative method, green) or analytic strips (semi-quantitative method, purple).

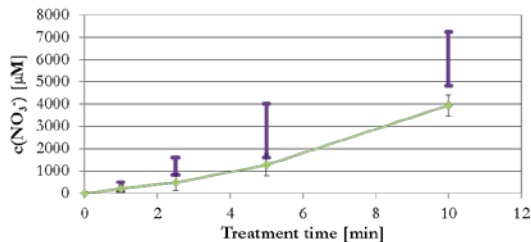


Fig. 5. NO_3^- concentration induced by plasma treatments of different duration in DIW measured by means of ion chromatography (quantitative method, green) or analytic strips (semi-quantitative method, purple).

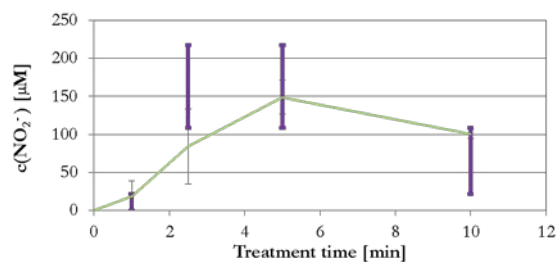


Fig. 6. NO_2^- concentration induced by plasma treatments of different duration in DIW measured by means of ion chromatography (quantitative method, green) or analytic strips (semi-quantitative method, purple).

Post-discharge kinetics of reactive species in PAW

The time evolution of reactive species concentration in DIW was recorded at different times after plasma treatment. Post-discharge kinetics for 5 min and 10 min plasma treatments are reported in Fig. 7. In both cases a decrease of H_2O_2 and NO_2^- concentrations was found; NO_2^- concentration fell under the detection limit 24 min after the 5 min treatment and 6 min after the 10 min treatment. This behaviour can be appointed to the lower pH registered for DIW after 10 min treatment than after 5 min treatment, which enhances the peroxyxynitrite reaction mechanism.

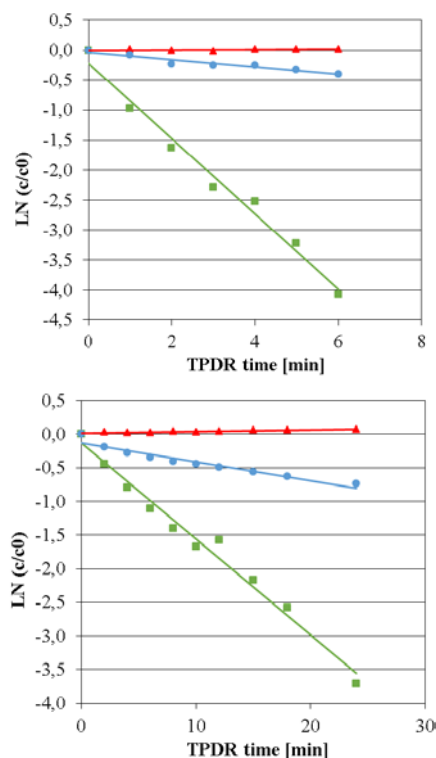


Fig. 7. Post-discharge kinetics of NO_2^- (green), H_2O_2 (blue) and NO_3^- (red) concentrations in DIW after 10 min (top) and 5 min (bottom) plasma treatments.

3.4. Phenol degradation

Plasma treatment containing was observed to induce a reduction of the concentration of phenol in DIW (initial concentration 500 μM): the longer is the treatment time, the lower is the final concentration of phenol (Fig. 8); the degradation of phenol is accompanied by the formation of hydroxylated and nitrated products of phenol (HQ: hydroquinone, HBQ: hydroxybenzoquinone, BQ: 1,4-benzoquinone, CC: catechol, 4-NCC: 4-nitrocatechol, 2-NHQ: 2-nitrohydroquinone, 4-NP: 4-nitrophenol, 2-NP: 2-nitrophenol), as shown in Fig. 8.

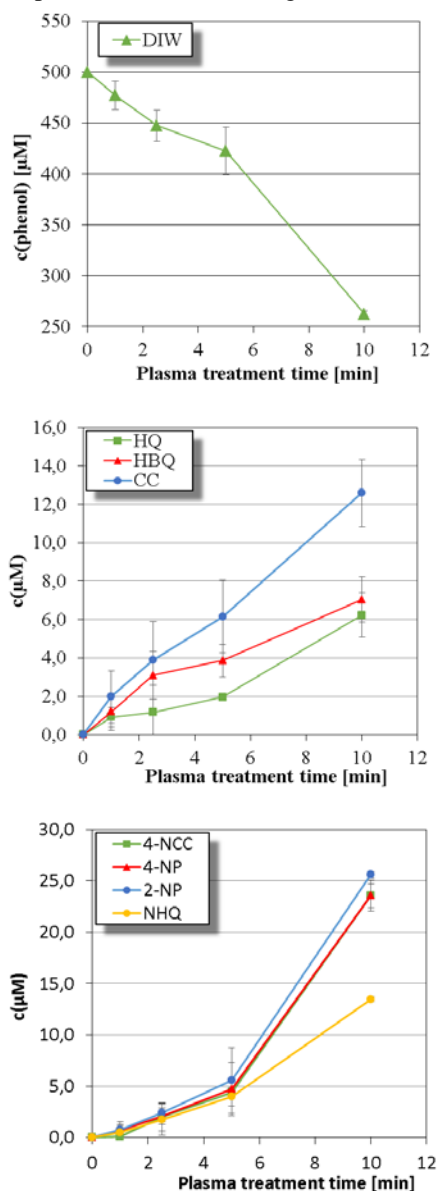


Fig. 8. Phenol (top), hydroxylated (middle) and nitrated (bottom) products concentrations induced by plasma treatments of different duration in DIW containing phenol.

4. Conclusions

The reactive species produced in deionized water (DIW) by an air DBD reactor driven by nanosecond pulses was presented. It was observed that pH and electrolytic conductivity had great effect on the liquid chemistry induced by the treatment: under acidic conditions at pH lower than 4, decomposition of NO_2^- by H_2O_2 occurred via peroxyxynitrite reaction mechanism. Moreover, for plasma treatment of DIW containing phenol, a significant degradation of phenol and the consequent formation of secondary hydroxylated and nitrated products were detected by means of HPLC.

5. Acknowledgment

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6. References

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