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Plasma-induced chemistry in water electrosprayed through air corona and transient spark discharges

Z. Machala[1], B. Pongrác[1], H.-H. Kim[2], B. Tarabová[1], K. Tarabová[1], V. Martišovitš[1], M. Janda[1] and K. Hensel[1]

[1] *Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava, Slovakia*
[2] *Institute for Environmental Management Technology, AIST, Tsukuba, Japan*

Abstract: Bactericidal and biomedical effects of atmospheric pressure non-thermal (cold) plasmas mediated through aqueous solutions can be enhanced when air discharges are combined with water electrospray. The presence of the electrical discharge in the spraying area allows for very efficient mass transfer of plasma-generated active species into the water. We investigated the effect of the electrospraying of water in combination with positive DC corona discharge. Our key finding is that the discharge has a significant effect on the electrospray behavior and vice versa. Such water electrospray-air discharge (corona, transient spark) systems were demonstrated to be very efficient in inducing bactericidal and various chemical effects in plasma treated water.

Keywords: cold air plasmas, corona, spark, water electrospray, plasma activated water, water chemistry

1. Introduction

Biomedical effects of cold plasmas are typically mediated through water and aqueous solutions that are natural to cells. Cold plasmas generated in gases in contact with liquids produce reactive species that penetrate through the gas-liquid interface and are followed by formation of the secondary reactive species in the liquid. Air plasma – water interactions lead to the formation of *reactive oxygen and nitrogen species* (RONS) such as ozone O_3, hydroxyl (OH) radicals, and nitrogen oxides, NO and NO_2. Once they get into water solutions they generate hydrogen peroxide H_2O_2, nitrites NO_2^-, nitrates NO_3^-, peroxynitrites/peroxynitrous acid $ONOO^-$/ONOOH, which are accompanied by chemical changes (acidification) and antimicrobial effects [1-2]. Peroxynitrites are powerful oxidants that can oxidize many cellular components and together with the acidic pH are hypothesized to be responsible for the strong bactericidal effect that can be maintained in the plasma activated water for several hours/days after plasma treatment. [3-5]. We previously showed the correlation between the bactericidal effects in water by air transient spark with peroxynitrites detected by the fluorescence spectroscopy [5].

One way how to efficiently treat water by the cold plasma discharges is using the electrospraying phenomenon. Combination of the effect of water electrospray with the discharge enables the water flow directly through the high-voltage (HV) needle electrode into the active discharge region, where it is sprayed into small droplets. The presence of the plasma in the spraying area allows for very efficient mass transfer of plasma-generated reactive species into water [5-7]. In this regard, we investigated the effect of electrospraying in combination with the discharge under various conditions in details by using optical and electrical measurement techniques having capability of time-resolved visualization of fast phenomena. Our objective was to identify various modes of water electrospray combined with corona discharge by high-speed camera and supplement these measurements with the records of the discharge generation and propagation during the electrospray process by iCCD camera, photomultiplier tube responses, and oscilloscopic current measurements.

We also focused on the formation of RONS induced by plasma gas-liquid interaction in treated aqueous solutions. We measured formation of hydrogen peroxide, nitrites, nitrates, and dissolved ozone in water treated by ambient air DC-driven positive transient spark discharge with water electrospray or with water electrode. The chemistry was also investigated in synthetically prepared aqueous solution that should simulate the plasma treated water.

2. Experimental methods

The experimental set-up for electrical and optical diagnostics of the water electrospray system is depicted in Fig. 1 and has been described in detail along with materials and methodology in [5-9]. DC streamer corona or transient spark discharge was generated in ambient air at atmospheric pressure in point-to-plane geometry. The water solutions were driven through the high voltage electrode (hypodermic hollow needle with special cut tip) by the syringe pump. This allowed the water solutions to be electrosprayed directly through the active zone of the discharge. The electrospray enhanced the mass transfer of RONS into the treated liquid solutions [8].

For investigating the plasma-induced chemistry in water we tested various working solutions with different:

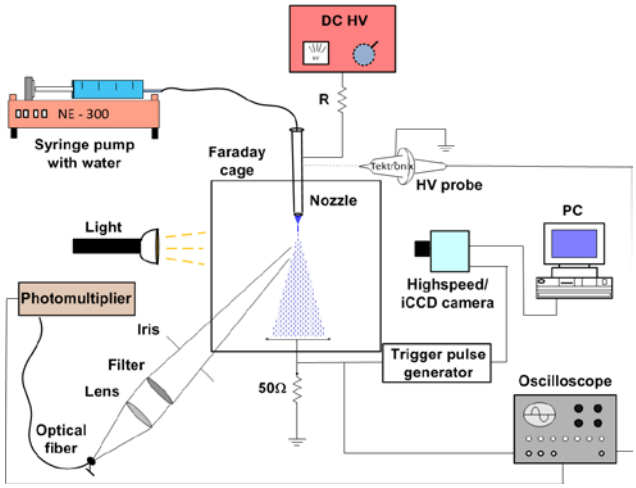

Fig. 1. Experimental set-up for investigations of electrospray of water, with a high-voltage hollow needle (nozzle) electrode enabling water spraying into the discharge.

- **buffering activity:** buffered solutions – phosphate buffer (PB), phosphate buffered saline (PBS); non-buffered solutions – NaH_2PO_4 (low concentration, mimicking tap water) and NaCl (physiological) solutions;
- **pH:** acidic solutions (pH 3.3 – 3.5, prepared in H_3PO_4); neutral solutions (pH 6.8 – 7.4, prepared in PB/PBS)

RONS in plasma treated water (PAW) were detected mostly by colorimetric methods (UV/VIS absorption spectrometer UV-1700 SHIMADZU):
1. Hydrogen peroxide H_2O_2: Pertitanic acid, absorption maximum 407 nm, in the presence of NaN_3 [5]
2. Nitrites NO_2^- and nitrates NO_3^-: Griess reagents, absorption maximum 540 nm.
3. Ozone: Indigo dye, absorption maximum 600 nm, is supposed to be bleached by reaction with O_3 [10].

3. Results and discussion

3.1. Imaging of corona discharge and electrospray

We investigated the corona discharge generation during the intermittent electrospray of water. Fig. 2 shows different stages of the electrospraying event and the discharge propagation from 0 to 3 ms.

The glow corona is first visible at the tip of the water cone (column 1). As the water cone gradually elongates and creates the filament which propagates axially towards the grounded electrode, the bright spot of the glow corona remains present at the tip of this filament and propagates with it (column 2). After the detachment of the elongated water fragment, and the contraction of the water meniscus back towards the nozzle, the glow corona disappears (column 3). Finally, after a few ms, a new cone is formed, and the filamentary discharge occurs from the cone tip (column 4).

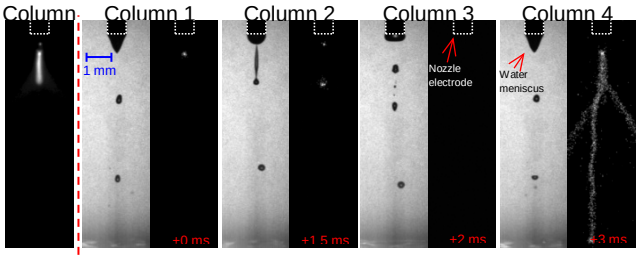

Fig. 2. iCCD time sequence images of electrospray of water (illuminated, columns 1-4 with exposure time 10 µs) with corona discharge (dark, columns 1-4 with exposure time 100 µs) in spindle mode for water conductivity 500 µS/cm, + 6 kV, gap 1 cm, 0.6 mm inner diameter. iCCD dark image in column 0 with exposure time 5 s represents an integrated emission over the long period with many droplet formation cycles. [8]

The dark image in column 0 represent an integrated emission over the long period (5s) with many cycles of droplet formation and corona discharge on the water cone tip during this intermittent electrospraying mode, and its movement with elongating water filament. The image also represents the visual appearance of the discharge during the electrospray.

We showed that the appearance of the corona on the water filament tip is primarily the electric field effect due to the various curvatures of this water filament tip [8].

3.2. Electrosprayed droplet size and time of flight

The fast camera image sequences enabled us to estimate the average time of flight (time between the water filament disintegration and the droplet fall on the grounded electrode) in 1 cm gap and the sizes of the sprayed water droplets between the electrodes. For instance, in the case of low conductivity water (2 µS/cm) this average time of flight is ~100 µs for the first incoming droplets from the head of the filament, and ~2.5 ms for the last one. The characteristic size of the water droplet (approximating to a spherical shape) vary approximately from <10 µm to ~250 µm in diameter. The droplet size becomes larger with higher liquid conductivities (~190-280 µm for 400 µS/cm). The same applies to the time of flight which becomes longer (from ~2.7-6.3 ms for 400 µS/cm). Since the droplets are formed by disintegration of the thin water filament, the sizes of droplets are determined by this filament thickness. The time of flight is related with the velocity of filament propagation and its length before disintegration. Both of these parameters (filament length and filament elongation velocity) decrease with the water conductivity, as described elsewhere [8-9].

Knowing the typical droplet size and time of flight is important in water decontamination applications when considering the mass transfer of plasma generated active species into the water droplets while they are sprayed through the discharge. Our results on bio-decontamination

of water in streamer corona or transient spark showed that even such short times of flight enable efficient mass transfer of air plasma generated RONS in the sprayed water to induce significant bactericidal effects [5-6]. In addition, water activated by the electrospray with very low flow rates (~0.05 ml/min) demonstrated enhanced bactericidal effects when sprayed on the surfaces [7]. The key is probably in very high surface to volume ratio of the droplets.

3.3. Influence of the water conductivity on the corona properties

Depending on the water conductivity, various spray properties were observed: pointy, prolonged, and fast spreading water filaments for lower conductivity; in contrast to rounder, broader, and shorter quickly disintegrating filaments for higher conductivity. When the conductivity increased the breakdown voltage for corona-to-spark transition decreased (Fig. 3).

Since the highly conductive liquid acts as a good conductor, the electric field is stronger on the highly conductive water meniscus. The discharge is thus permitted to occur at the liquid surface and the discharge activity on the water filament tip is then enhanced as the filament proceeds toward the ground electrode.

For poorly conductive liquids, the liquid acts more as an insulator and the electrical resistance of the growing water filament suppresses the corona activity on its surface. So the discharge is forced to occur on the metal electrode. Subsequently, the spark does not occur until the higher voltage [9].

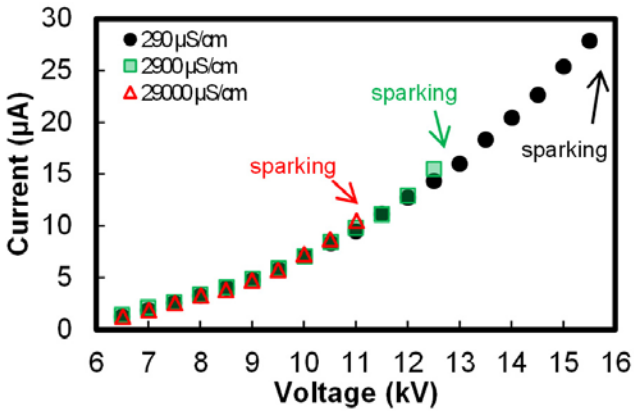

Fig. 3. I-V characteristics of the electrospray with corona discharge. Different breakdown voltages for corona-to-spark transition are due to different conductivities. [9]

3.4. Chemistry induced in water electrosprayed through air discharges

Chemical and bactericidal effects induced by plasma in water upon electro-spraying through DC-driven positive transient spark discharge in air were investigated. Inactivation of *E. coli* bacteria in water was determined in dependence on pH (controlled by buffers) and correlated with chemical changes induced in water, namely generation of RONS that play significant roles in cell physiology and many medical therapies [1]. The discharges in humid air (or air with water microdroplets) produce OH radicals, nitrogen oxides and in some cases ozone, resulting in the formation of hydrogen peroxide, nitrites, nitrates (Fig. 4), peroxynitrites and pH changes in the sprayed water. The degree of inactivation and oxidative damage of bacteria increased with the increasing acidity of the solution. Acidified nitrites (i.e. nitrous acid) interacting with hydrogen peroxide were determined as the most important bactericidal RONS agents in plasma-treated water leading to peroxynitrites (peroxynitrous acid) [3,5].

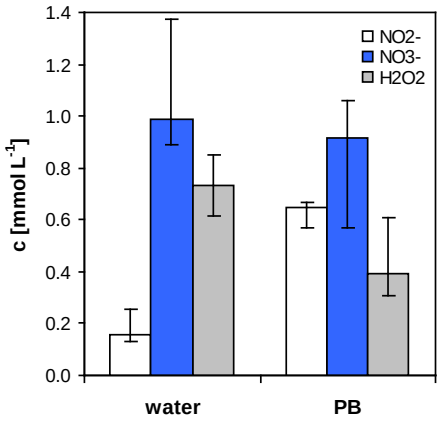

Fig. 4. Nitrite (NO_2^-), nitrate (NO_3^-) and hydrogen peroxide (H_2O_2) concentrations measured in NaH_2PO_4 solution (model tap water, acidification occurs) and PB solution (no acidification occurs) solutions air transient spark plasma treatment via electrospray. [5]

In the specific case of low power corona discharge with water electrospray, the bactericidal effect of ozone dissolved in water may play an important role. Since the diffusive solubility of ozone in water is relatively low, the interaction of non-thermal plasma with the micrometric droplets of water in the spraying area allows for very efficient mass transfer of ozone into the water.

3.5. Evolution of H_2O_2 and nitrites in the plasma treated water and the dissolved ozone detection

In order to better understand the chemical evolution in the plasma treated water, a water solution of 1 mM H_2O_2 + 1 mM $NaNO_2$ at pH 3.3 (or 6.8) was used to chemically mimic the plasma treated water (or PB). We measured the time developments of H_2O_2 and NO_2^-, as shown in Figure 5. At pH 6.8 (Fig. 5b), the concentrations of H_2O_2 and NO_2^- were time-stable, unlike at pH 3.3 (Fig. 5a), where we observed the temporal decay of these species, which is due to the reaction between H_2O_2 and NO_2^- via formation of peroxynitrites occurring under acidic conditions [3]:

$$NO_2^- + H_2O_2 + H^+ \rightarrow O=NOOH + H_2O \qquad (1)$$

We previously observed the dissolved ozone in the PAW by the indigo method and detected the concentrations 0.6-0.8 mg/L of dissolved ozone in the

plasma treated deionized water. Because the TS discharge treatment bleached the indigo more than 1000 ppm ozone bubbled through the deionized water in much higher concentrations, we revisited the selectivity of the indigo method in the simulated plasma treated water solution with similar chemical composition and pH as the TS plasma treated water but with no presence of ozone (Fig. 5). Interestingly, we detected "apparent ozone" even in this simulated solution without plasma treatment where no ozone could have been present. The degradation of the indigo dye in the solution without ozone was most likely caused by the formation of·OH created as a decay product of peroxynitritrous acid at low pH:

$$O = NOOH \leftrightarrow {}^{\cdot}OH + NO_2^{\cdot} \qquad (2)$$

This result support the fact that the indigo method is not selective to ozone in PAW and more examination is needed to truly measure ozone and determine reasons for indigo bleaching. It seems that ozone reacts with nitrites in plasma treated water [11].

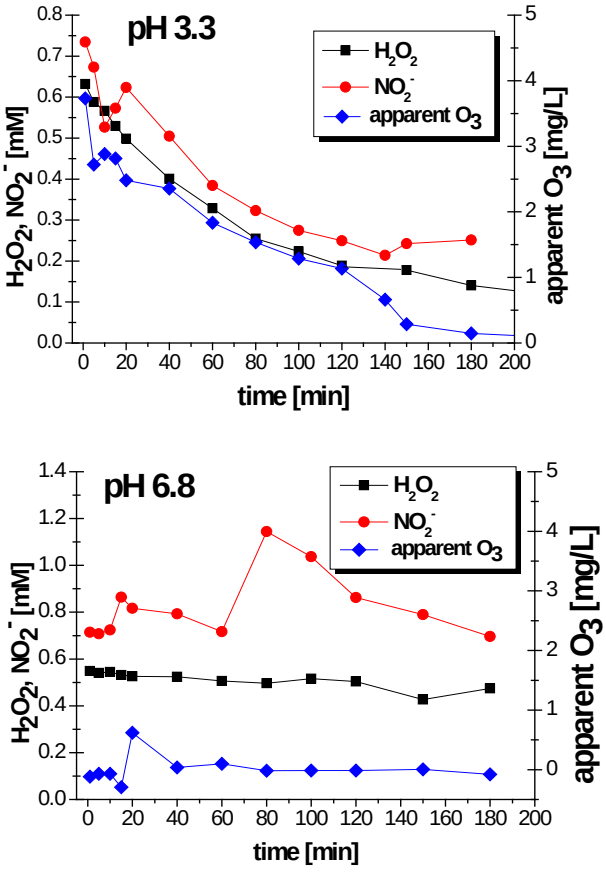

Fig. 5. Time developments of important reactive species in the simulated plasma treated water at pH 3.3 (a) and pH 6.8 (b). Apparent ozone means bleaching of the indigo dye.

4. Summary

Decontamination of water polluted with organic and microbial pollutants, and biomedical effects on cells mediated through aqueous solutions can be efficiently achieved by using various non-thermal plasma discharges. These effects can be enhanced when air discharges are combined with water electrospray.

We investigated the effect of the electrospraying of water in combination with positive DC corona discharge in atmospheric air. Our key finding is that the discharge has a significant effect on the electrospray behavior and vice versa. The appearance of the corona on the water filament tip is primarily the electric field effect due to the various curvatures of this water filament tip. Water conductivity and volume flow rate are very important parameters determining the electrospraying mode and its interaction with the discharge. [8-9]

The presence of the electrical discharge generating non-thermal plasma in the spraying area allows for very efficient mass transfer of plasma-generated reactive oxygen and nitrogen species into micrometric water droplets with very high surface to volume ratio [5-9]. Therefore, the water electrospray-air discharge system was demonstrated to be very efficient in inducing bactericidal and various chemical effects in the treated water.

5. Acknowledgement

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