Chemistry of Air, N$_2$, and O$_2$ Reverse Vortex Gliding Arc Plasma System

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ABSTRACT: Reactive oxygen species and nitrogen species are generated after water is treated with room temperature nonthermal plasma, generated by a reverse-vortex gliding arc discharge (GAD) plasmatron. In this short communication, we have investigated the chemical species in water treated with GAD plasma with a pH meter and UV spectroscopy.

KEY WORDS: antimicrobial solution, indirect plasma, nonthermal plasma, plasma chemistry, reactive oxygen species, reactive nitrogen species

I. INTRODUCTION

Nonequilibrium discharges have been extensively investigated for their ability to generate metastable antimicrobial solutions, primarily used for pathogen inactivation in liquid phase.[1–7] Recently, our group determined the chemically active species present in water treated by the floating-electrode dielectric barrier discharge (FE-DBD) plasma by a variety of analytical methods and proposed the chemicals responsible for antibacterial properties of this solution.[8,9] One of the key challenges that remains is the generation of plasma-treated water in large volume for the real-world applications. One of the methods for water processing is the treatment of water by using reverse-vortex gliding arc discharge (GAD). We report here the effects of GAD on pH and the chemical species in the treated water.

II. MATERIALS AND METHODS

A. Plasma Generation

A dielectric barrier discharge (DBD) technique was used to generate low temperature plasma. The DBD electrode was customized by covering the surface of 38 mm X 64 mm copper plate with a 1 mm-thick glass slide (Fischer Scientific Inc., Pittsburgh, PA) and insulating with silicone to prevent arcing. A custom-designed quartz treatment chamber (referred to as fluid holder), which can maintain a 1 mm liquid column, was used. The discharge gap for plasma treatments was fixed at 2 mm. The complete setup was pre-

viously described by the authors.[10,11] Characterization of plasma power generator was performed according to a reported procedure.[12] One mL of deionized water (MP Bio-medicals Inc., Solon, OH) was treated separately at different time points and collected immediately after plasma treatment to perform various tests.

The gliding arc discharge (GAD), utilized in this study, was previously described in detail by the authors.[13–17] Figure 1 shows the specific setup used in this work. A peri-staltic pump was used to supply the water to the plasmatron, and water from the chilled collection cup was recirculated to reach the desired level of pH. Arc rotation (and the
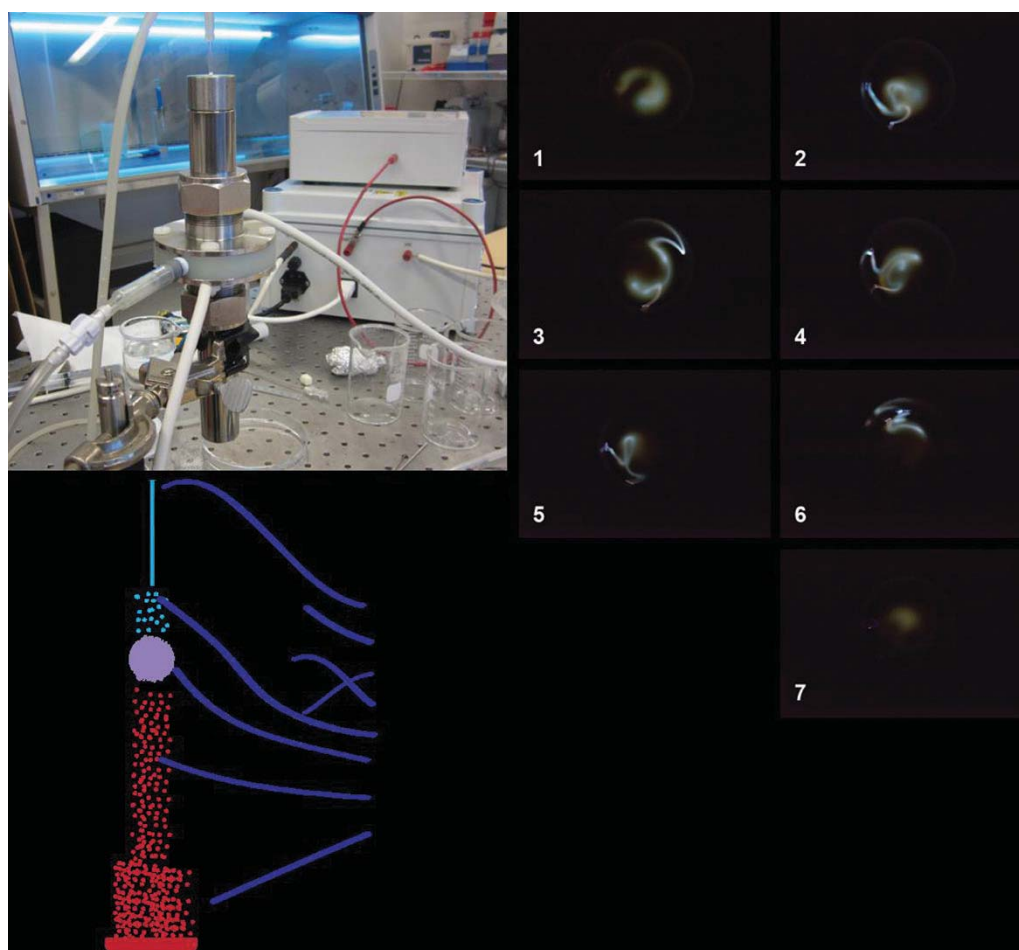

FIG. 1: Gliding arc discharge (GAD) water treatment photograph (top left), schematic of the electrode construction (bottom), and photographs of the plasma discharge development (top right). The discharge photos were taken with a Nikon D800e camera with 105 mm lens at f32 with shutter speed of 1/8000; these are consecutive photos of the same arc, taken over 1 second period, with initial arc development,[1] elongation,[2–6] and extinguishment.[7]

plasma gas composition) was maintained by a mass-flow controller with compressed air, nitrogen, and oxygen as working gases.

B. Instrumentation for Chemical Analysis

An ultrasensitive pH probe attached to a Thermo Orion Research Digital pH meter (Thermo Fisher Scientific, Waltham, MA) was used to measure plasma treatment-associated pH changes in fluid over time. UV-Vis spectroscopy results were obtained from a spectrometer (SPD-20A, Shimadzu, Japan).

III. EXPERIMENTAL

A. Parameters

Water flow was set to 66.7 or 33.3 mL/min, and introduced to compare the influence of the different flow on the treatment effect in air plasma. 66.7 mL/min was used in oxygen or nitrogen plasma. The water was circulated through plasma up to four times. Other parameters were:

Gas pressure: 13 PSI;
DC power source:
Voltage: 15 ~ 16 kV in air or nitrogen, 17 ~ 18 kV in oxygen for plasma ignition
    and ~ 400 V to sustain the DC arc;
Current: 0.28 ~ 0.3 mA in air or nitrogen, 0.27 mA in oxygen.

IV. RESULTS AND DISCUSSION

The pH change of water in three plasma regimes (air, N_2, and O_2), is shown in Fig. 2. The most notable observation of plasma-treated water is that the pH decreased from neutral to acidic (Fig. 2) in air plasma, but showed essentially no change in O_2 or N_2 plasma. It was shown previously that the pH decrease in air plasma was due to the nitrous acid (HNO_2) and nitric acid (HNO_3) that are generated from NO_2 and NO in the plasma, respectively.[1,10,18] These results are consistent with those reported on DBD-treated water.[13]

The UV-Vis spectra of water before and after plasma treatment is shown in Fig. 3. The air plasma generated a broad featureless peak at 360 nm after passing through the plasma zone for the first and second times (Fig. 3A), after which the peak turned into a group of five peaks in the range of 330–390 nm, which is characteristic of HNO_2.[19] Based on the literature and the formation of HNO_2 at lower pH after the third flow through to the tube, we suggest that the featureless peak at 360 nm is NO_2^- since the pH of the solutions was above 4 when water flowed the first and second times.[13] While a lower pH was observed after the third flow, when NO_2^- was turned to HNO_2, a new peak at 302 was also observed, which was attributed to HNO_3. This is consistent with Traylor
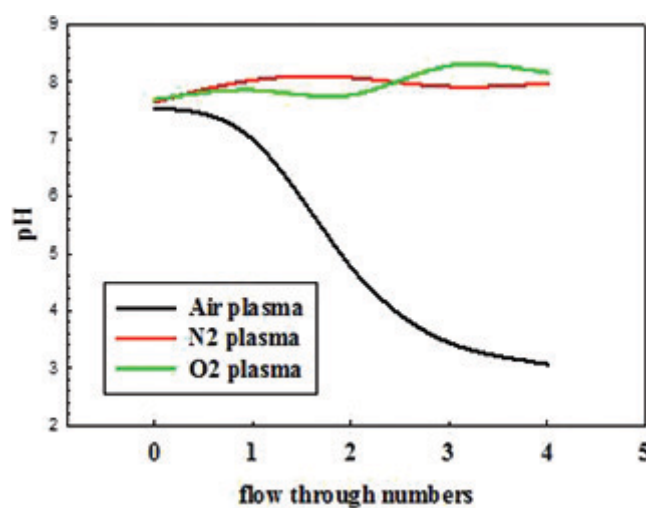
FIG. 2: pH change of the deionized water vs. number of flows through the plasmatron at 66.7 mL/min in air, N2, and O2 plasma
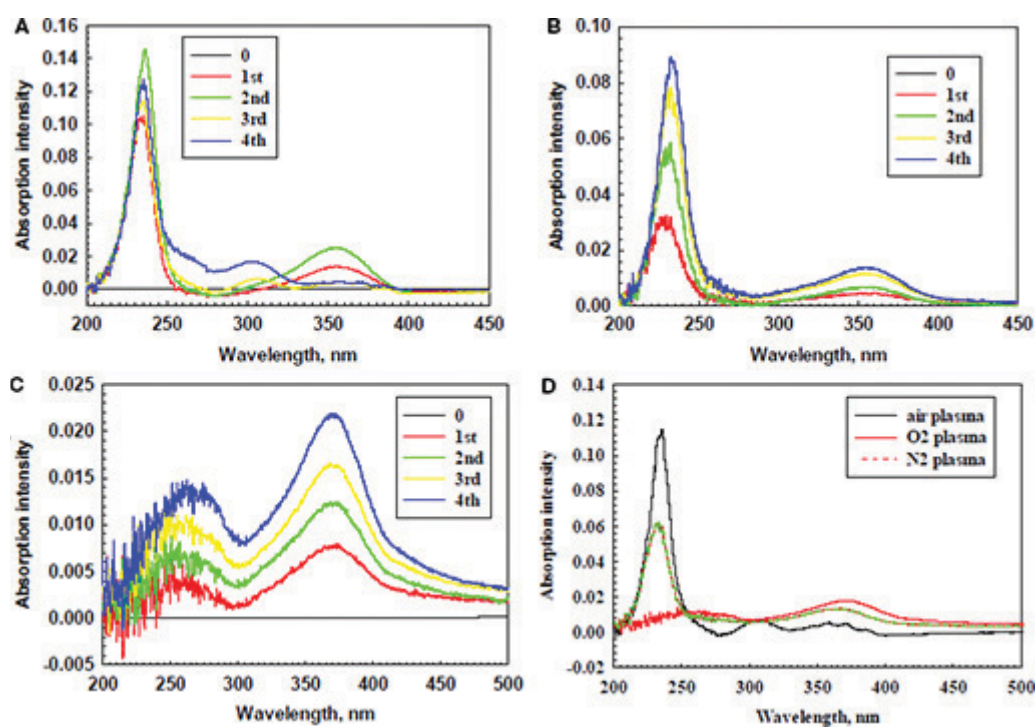

FIG. 3: UV-Vis curves of deionized water treated with A) air plasma; B) N2 plasma; C) O2 plasma; and D) all three plasmas after third flow through

et al. that on initial treatment with air plasma, both HNO_2 and HNO_3 are generated from deionized water.[20]

The concentrations of HNO_3 and HNO_2 in water after the third flow-through were 0.13 mM and 0.26 mM, respectively, according to the Beer-Lambert Law, which is used to calculate the concentrations of an analyte in a solution,

$$a = \varepsilon\, bc \tag{1}$$

where a is the measured absorbance, b the path length (1 cm), and c the concentration of the analyte in the solution. ε is the extinction coefficient of the analyst at specific wavelengths. The extinction coefficients of HNO_3 and HNO_2 are 70 M^{-1} cm^{-1} at 300 nm and 23 at 354 M^{-1} cm^{-1} nm, respectively.[21]

The pKa of HNO_2 is 4×10^{-4} M, which contributes 0.19 mM H^+, so a total of 0.32 mM of H^+ (i.e., pH = 3.49), was produced in the solution after the third flow-through. This pH is consistent with the pH of 3.44 observed from the measurement from pH meter.

The concentration of HNO_3 increases with the increased treatment times from one to four (Fig. 4), while the pH values decrease. This is understandable since, with the increasing treatment time, the circulating water absorbs more NOx produced in air plasma, which were absorbed and converted into HNO_3, resulting in the decreasing pH.

Oxygen or nitrogen plasma was generated separately to treat water, comparing with the air plasma as shown in Fig. 3 (B)–(D). Figure 3 (B) shows a board peak at 360 nm in N_2 plasma, which is the same as that in air plasma. Again, this is the peak of NO_2^-. However, one difference from that of air plasma was that no characteristic signal of HNO_2 was observed. The lack of the formation of HNO_2 is consistent with the pH change of
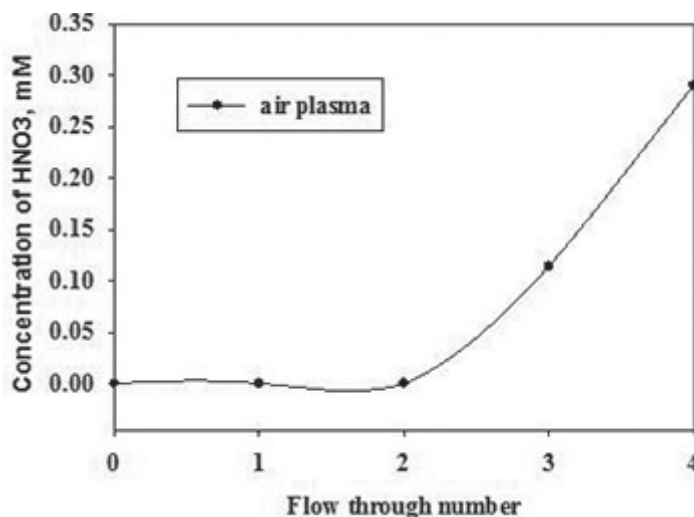

FIG. 4: Concentration of HNO3 vs. the flow-through number

air and N_2 plasma (i.e., the pH of water after air plasma treatment decreased, but slightly increased after the N_2 plasma treatment).

For O_2 plasma, the reported reactive oxygen species (ROS) in water were mainly O_2^-, H_2O_2, ·OH radical, and O_3. Therefore, the peak at 260 nm in our experiment should be attributed to either H_2O_2, O_3, or ·OH radical since they all appear at around 260 nm. We did not observe HO_2 from the UV spectra, which is at around 230 nm.[22] Other than the known species at the 260 nm, a new peak at 375 nm was observed, which does not belong to any of the above-mentioned ROS. This differs from 360 of NO_2^- in air or N_2 plasma for two reasons: 1) the peak position is not the same; 2) NO_2^- also has an intense peak at around 225 nm, which was not observed from the O_2-plasma-treated water in this experiment. The attribution of this peak is unknown at this stage. It will be further studied and reported in due course.

V. CONCLUSION

We report that the pH changes and the reactive oxygen species and nitrogen species generated after water is treated with a reverse-vortex gliding arc discharge (GAD) plasmatron are similar to those from a traditional DBD device. The information builds a foundation for the studies of the antimicrobial property of the water treated with GAD plasmatron.

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