

Non-Equilibrium Plasma Treatment of Liquids, Formation of Plasma Acid

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Abstract: Our experimental results indicate that direct exposure of deionized water to dielectric barrier discharge (DBD) plasma creates an acid (pH \approx 2) and a strong oxidizer. This study addresses the question: which acid is created in water by plasma treatment. Two major possibilities are considered: nitric/nitrous acid and an acid which consist of hydrogen cation (H⁺) and superoxide anion (O₂⁻), which for the lack of a better term we call *plasma acid*. The presence of nitric/nitrous acid in the water after plasma treatment in air is confirmed, although the observed pH \approx 2 cannot be completely explained by the production of nitric acid. Moreover, experiments with oxygen-plasma treatment of water also lead to high acidity, without production of nitrogen based acids. Therefore, O₂⁻, the conjugate base of the plasma acid, is at least partially responsible for both, lowering of the pH and the increase in the oxidizing power of the solution. Experiments indicate that peroxides such as H₂O₂ and O₂⁻, together with acidic environment are likely to be responsible for the oxidation properties of the plasma treated water. This plasma acid remains stable for at least a day, depending on the gas where plasma is generated, but the effect is temporal.

Keywords: non-thermal plasma, plasma treatment of liquids, DBD, dielectric barrier discharge, atmospheric pressure plasma, sterilization, disinfection, plasma medicine

1. Introduction

Ozonation and advanced oxidation processes utilizing effects of oxidative species and UV have been used to oxidize organics in solution phase [1-8]. It has also been widely documented that the exposure of organic molecules dissolved in water to various forms of plasma discharges leads to their oxidation [2-4]. These oxidation phenomena find applications ranging from environmental remediation [9-11] to water cleaning [12] and sterilization [1]. Oxidation also plays an important role in many industrial processes such as the conversion of methanol to formaldehyde [13-15].

It has been reported that water treated by various plasma discharges becomes acidic [16-20], which leads to antimicrobial effects [20-23]. The important question is which acid is created in water treated by

plasma. Oehmigen *et al.* [24] suggested that the acid created in water is nitric/nitrous acid and the antimicrobial properties observed are the result of synergetic action between H₂O₂ and nitric/nitrous acid. The goal of this study was to analyze plasma-treated deionized water without any organics presents to find out the source of acidity and oxidative ability of such water.

2. Experimental methods

To generate dielectric barrier discharge we used a quartz-protected copper electrode (0.5mm thick quartz) and power supply that were previously described by authors [25]. We build a small chamber containing plastic cap with a built in electrode and glass petri dish (inner diameter -37 mm, outer diameter - 40 mm). Air-tight environment was maintained and electrode height relative to the water

surface was adjustable. Water and gas were introduced into the chamber with syringe through four small self-sealing holes in the chamber cap. The bottom of the chamber was placed on a grounded aluminum plate and the liquid surface acted as a second electrode (**Figure 1**).

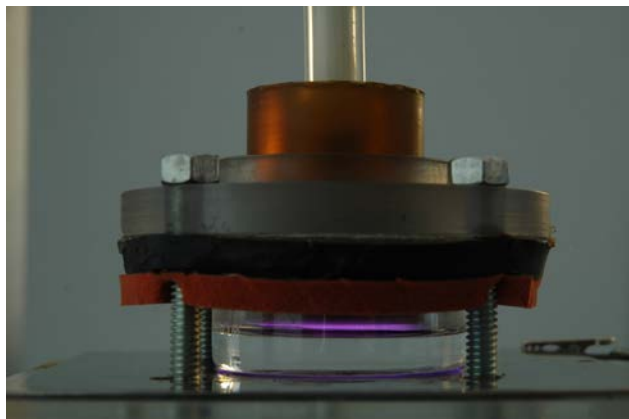


Figure 1: Experimental Setup – DBD electrode is placed in a closed glass chamber.

The chamber was filled with 10 ml of deionized water with an electrical resistance of 18M Ω . The gap between the electrode and the water surface was set to 1.5 mm. The pulsed voltage was 17 kV with 1.7 kHz pulse frequency. Treatment time was 15 min. Electrode diameter was 33 mm (25 mm copper, 33 mm with insulator), while the inner diameter of the container was 37 mm.

When experiments were done with a gas other than air, both water and the chamber were properly degassed.

For pH measurements, a micro pH electrode (Lazar Research Laboratories, Shelfscientific Model PHR-146 micro pH electrode, 1 mm tip and 2.8 mm diameter body) was used.

Overnight cultures of *E. coli* were diluted using phosphate buffered saline (PBS, 1X), to get a concentration of 10³ to 10⁵ colony forming units per milliliter (cfu/mL). Bacterial concentration was assessed by a standard dilution assay [26].

Absorption spectra were measured using UV/VIS Spectrophotometer (Perkin-Elmer Model: Lambda 2).

3. Results and Discussion

Figure 2 presents pH values of deionized water as a function of the plasma treatment for two different gasses: air and oxygen. There was a rapid decrease in the acidity of deionized water from the initial pH of 7.43 \pm 0.15 to 2.01 \pm 0.18 after 15 min of treatment in both air and oxygen. This experimental results shows that when pure water (deionized water with an electrical resistance of 18M Ω) is treated with DBD plasma it becomes acidic; similar acidity was previously similar effect in air was previously reported by Oehmigen *et al* [24].

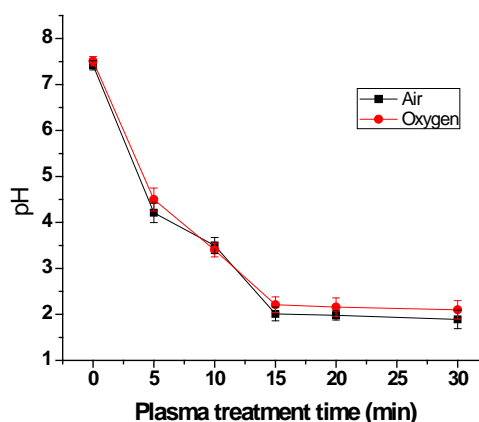


Figure 2: Variations of pH of deionized water after plasma treatment in two different gases: air, and oxygen.

Plasma treated water also becomes a strong oxidizer, whose oxidizing properties are demonstrated in Figure 3 for the case of *E.coli* inactivation.

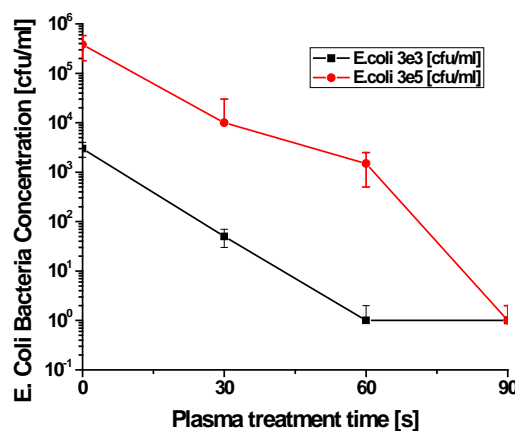


Figure 3: Results of *E.coli* inactivation by plasma treated water show that 60 s treatment was enough to inactivate 2x10³ cfu/ml *E.coli*.

Although the low pH values of water after plasma treatment has been shown before [16-19], it is still not clear what the source of acidity was. It was previously suggested that the acidity of plasma treated water might be the result of nitric and nitrous acid formation [24, 27]. However, as it is shown in Figure 2 pH drops in plasma treated liquid not only in air but also in oxygen environment: nitric acid formation cannot explain the acidity of plasma treated water in oxygen. Moreover, although the absorption peak at 300 nm (Figure 4), which is specific to nitric acid, was registered in all liquid samples, the intensity in the water sample treated in oxygen was significantly lower than the other two liquid samples.

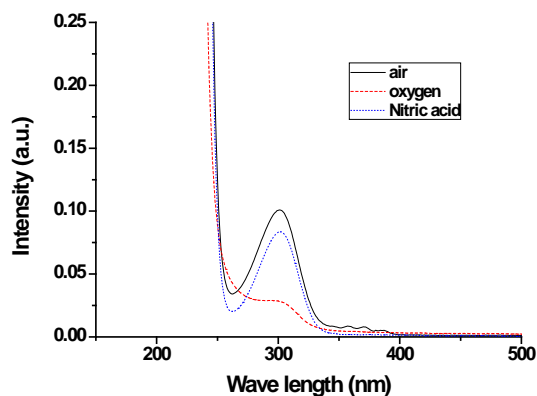


Figure 4: UV-VIS absorption spectra of nitric acid (pH=2.05) and water samples treated with plasma in air (pH=2.07) and in oxygen (pH=2.01).

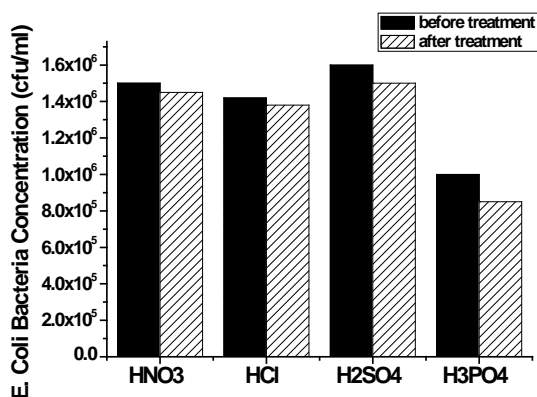


Figure 5: Results of *E.coli* inactivation by various acids at pH=2.

Figure 5 shows *E.coli* inactivation by various acids with acidity of pH=2. Almost no inactivation observed for all acids. Figure 5 indicates that acidic

environment by itself usually does not have bacteria inactivation properties. Under the same pH conditions both weak acids (H_3PO_4) and strong acids (HCl , H_2SO_4) resulted in poor bacteria inactivation, consistent with the previous findings [24]. This shows that an oxidizer which may have no influence on acidity is present in the liquid treated by plasma. One of such oxidizers is H_2O_2 which can be produced in the plasma acid in fairly high concentration (Figure 6). H_2O_2 is considered a strong oxidizer, especially in acidic environment [28]. Another oxidizer that is present in plasma acid is O_2^- (superoxide anion). Adding superoxide dismutase enzyme (SOD) to plasma acid results in H_2O_2 concentration increase (Equation 1) and pH increase to 4 (results not shown).

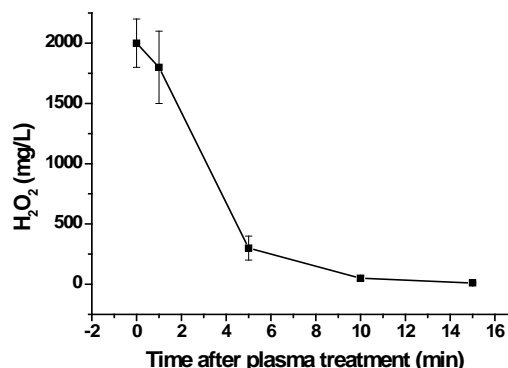
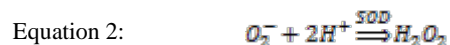


Figure 6: Results of hydrogen peroxide concentration measurements after plasma treatment.

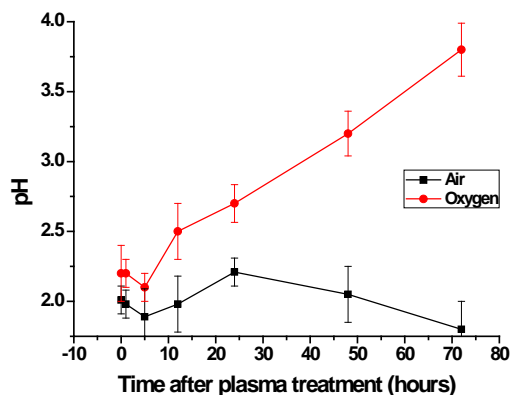


Figure 7: Results of pH changes of deionized water as a function of time after plasma treatment.

Thus plasma acid may consist of H^+ ions and O_2^- as a conjugate base. Together with H_2O_2 it has very strong oxidizing properties.

We assessed stability of plasma acid by following pH change after plasma treatment. Figure 4 presents variations of pH over approximately 70 hours waiting time after the plasma treatment in air and in oxygen. Deionized water treated in air, shows stable pH values over time of approximately pH=2, while water treated in oxygen increases pH almost linearly after reaching a local minimum at t=5 hours.

4. Conclusions

Strong oxidizing liquid is produced by direct exposure of deionized water to dielectric barrier discharge (DBD) plasma. While oxidizing properties and acidity remain stable for days, these effects are temporal. Plasma acid's oxidizing power may be linked to the significant lowering of its pH. Although nitric acid can be present in the solution, especially when it is treated in air plasma, the observed low pH (2.0) is partially caused by superoxide anion O_2^- , which also contributes to oxidizing power of the solution. Changing the gas used in plasma treatment can influence pH stability and oxidizing properties of the plasma-treated water. We suggest plasma acid — hydrogen cation H^+ and superoxide anion O_2^- — as the cause of water acidification following plasma-treatment. Strong oxidizing properties are attributed to peroxides present in the water such as hydrogen peroxide H_2O_2 and superoxide O_2^- that together with acidic environment result in strong oxidizing solution.

Plasma acid, as a stable oxidizer, is likely to be used in many applications ranging from food sterilization to cleaning of pipes and filters. Plasma acid is easy to use for oxidation of materials on hard-to-reach surfaces or surfaces with complex topology (skin folds and pores, for example). In many of these applications it may be desirable to produce a liquid that has a strong oxidizing potential and is capable of maintaining its oxidative power over a reasonably long time period. At the same time, it may be desirable for this liquid to eventually dissipate its

oxidative power in order to safely dispose of the remaining material.

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