Plasma Discharges Above and Below Water Surface Used for Bacterial Inactivation and Antibiotic Degradation in Drinking Water

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Abstract: Cold atmospheric plasma discharges, in air above air-water surface interface or in water below it with bubbles injection inside water, show interesting properties for water purification. Water parameters illustrate different values depending on discharge schemes. E-coli bacteria in water can be eliminated by plasma discharges occurring inside water faster than in air outside it. Degradations of DXC antibiotic in water solution are achieved in the two cases giving rise to degradation products dissociable by longer plasma exposure.

Keywords: Cold atmospheric plasma, Water purification, E-Coli, Doxycycline hydrate, Pharmaceuticals.

1. Introduction

Potable clean water is a valuable source of life. Purifying drinking water from biological and chemical pollutants is mandatory for consumers good life standards, [1]. Cold atmospheric plasma (CAP) can be a versatile tool capable of eliminating undesirable pollutants when conventional methods failed, [2]. Plasma discharges can be generated above (outside) or below (inside) air-water surface interface producing oxidizing elements and reactive species capable of eliminating many contaminants, [3]. We focus in this study on harmful bacteria elimination and on dissociation of pharmaceuticals contained in water by plasma discharges generated above and below water surface. In many developing countries bacterial polluted water is a major cause of diseases, [4], while in developed countries, accumulations in living bodies of even small amounts of common pharmaceuticals contained in drinking water, can cause severe health problems, [5]. As Parameters of water can vary during plasma treatment and in consequence plasma efficacy, [6], measurements of water parameters during discharges applied over and below water surface can help in decision making of the most suitable plasma discharge scheme achieving water purification through elimination of bacterial pathogens and degradation of pharmaceuticals in drinking water.

2. Experimental setup

Water to be treated of nearly 50 mL is contained in a 50 mL Pyrex glass container. Unless otherwise stated, tap water is used in experimentation to satisfy the same status as drinking water. Two types of plasma discharges are used namely above and below water surface.

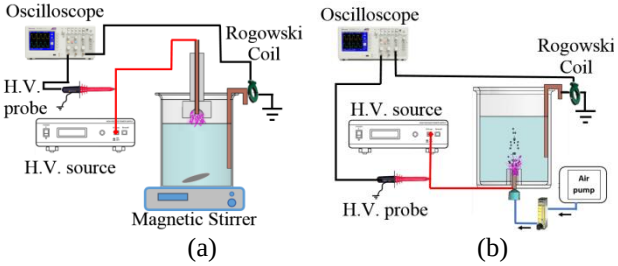


Fig. 1. Plasma discharges (a) above and (b) below water surface.

The first one, shown in Fig. 1-a, is a single pin-to-water electrode made by 1 mm tungsten wire located in air above air-water surface interface. The inter-distance between electrode tip and liquid interface is 3-5 mm.

The second one, shown in Fig. 1-b, is a water-electrode discharge with air bubbling system. The bias electrode consists of stainless steel syringe needle of 0.33 mm and 0.184 mm outer and inner diameters respectively. Active syringe length of 1.2 cm is inserted in a capillary glass tube of 1.5 cm long, 5 mm outer diameter and 0.5 mm inner one. The system of glass capillary tube and syringe is sealed in the bottom of the glass container so that it is submerged in water with rising air bubbles introduced by the syringe opening with 1 L/min flow rate.

The ground counter electrode made by a copper plate of dimensions 2 cm x 1 cm is submerged in water in the two arrangements. AC 5 kHz power supplies identical for the two discharges deliver 3 kV peak voltage and 2 mA average current.

3. Measurements of parameters of water during plasma exposure time periods

Water parameters are measured directly after plasma exposure. pH value of plasma treated water is measured by pH tester HI 98128, oxidation reduction potential (ORP) by HI 98120, total dissolved solids (TDS) and conductivity by HI 98129, all from Hanna Instruments (USA) equipped with built-in thermometers.

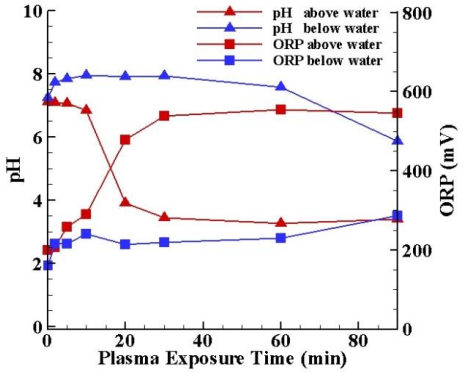


Fig. 2. pH and ORP with plasma.

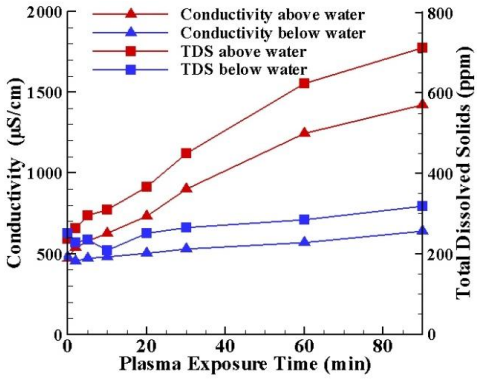


Fig. 3. Conductivity and TDS with plasma.

Depending on plasma discharge schemes, changes occur in water parameters as pH, ORP, TDS, Conductivity with plasma exposure time, as shown in Figs 2 and 3. In general, pH decreases with plasma exposure time for discharge above water, while it remains nearly constant for discharge below water. ORP exhibits an inverse behaviour with pH for different plasma exposure time in the two plasma discharge schemes.

Dissolved oxygen (DO) is measured by 970-DO2 meter from Jenway (UK). H_2O_2 concentration in treated water is quantified employing test strips from Macherey-Nagel Quatofix peroxide (Germany). Nitrate is measured using Brucine method, [7]. When a water sample containing nitrate ion is treated with Brucine in sulfuric acid, a yellow solution results. The concentration of nitrate is calculated based on absorbance at 410 nm. Nitrite is measured using modified Griess method, [8]. By adding sulfanilic acid reagent and hydrochloride reagent to water sample and mixing, reddish purple colour is formed, concentration of nitrite may be calculated based upon absorbance at 520 nm.

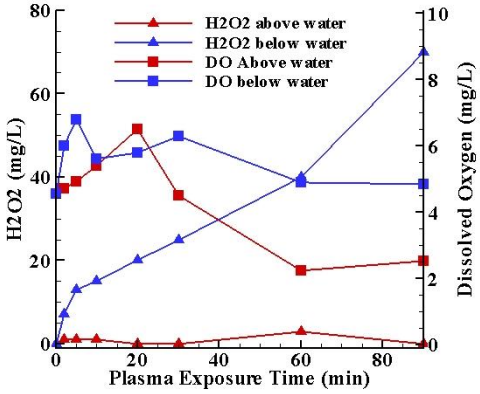


Fig. 4. H_2O_2 and DO with plasma

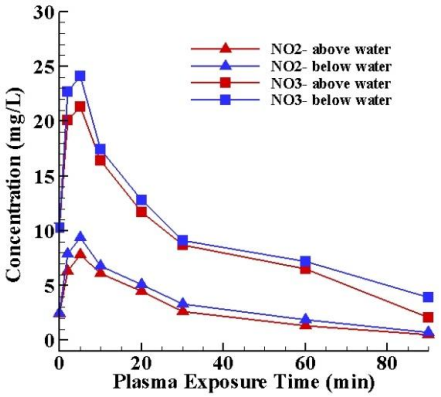


Fig. 5. Nitrate and nitrite with plasma.

In Fig. 4, Hydrogen peroxide H_2O_2 and dissolved oxygen DO are measured. H_2O_2 has negligible value for discharge above water, while it increase continuously below water. DO begins to increase and then decreases. along time for the two cases.

In Fig. 5, Nitrate and Nitrite are measured after application of plasma discharge above and below water.

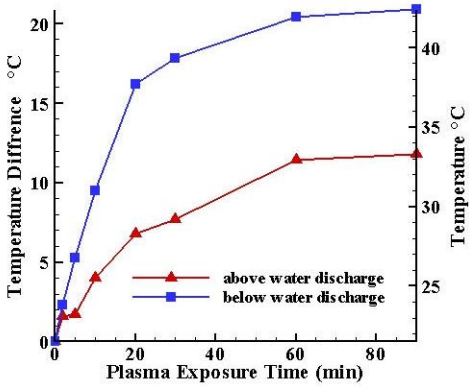
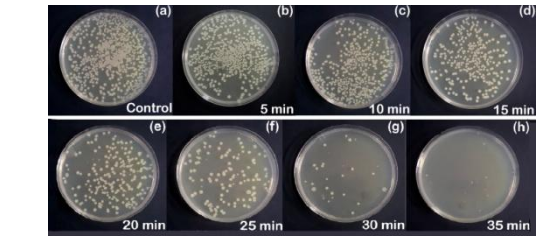


Fig. 6. Temperature difference ΔT and absolute temperature of water with plasma above and below

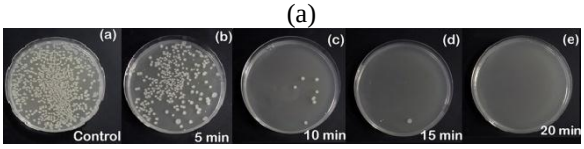
Fig. 6, shows the water temperature difference ΔT before and after plasma exposure and the absolute water temperature at different plasma exposure time periods for discharges above and below water surface.

4. Results of bacterial elimination in water with plasma

E-coli gram negative bacteria, which represents the most common bacteria encountered in polluted water, is chosen in this study. In order to isolate only one type of bacteria, 50 ml of distilled water was sterilized by autoclaving at 121℃ for 20 minutes. When water temperature become appropriate for inoculation by E-coli (30-40℃), broth culture of E-coli was added to the water to be treated by plasma and turbidity was visually adjusted to 0.5 McFarland (turbidity standard). After plasma discharge, specimen from water was taken. Subculture was done on MacConkey agar. Isolated colonies was cultured on glass tubes containing nutrient broth incubated aerobically at 37℃ for 24 hours. Next morning, tubes was briefly vortexed to make homogenous bacterial suspension. Counts was performed according to plate counting method. Plates were then analyzed for the presence of colonies and growth was expressed as colony forming units (CFU)/ml.



(a)



(b)

Fig. 6. Petri dishes of E- coli culture at different treatment times for plasma (a) above water and (b) below water.

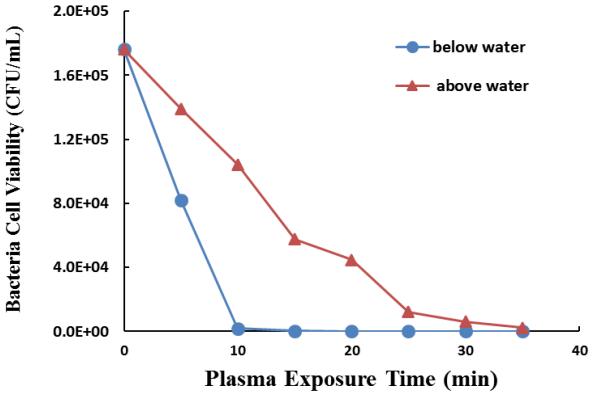


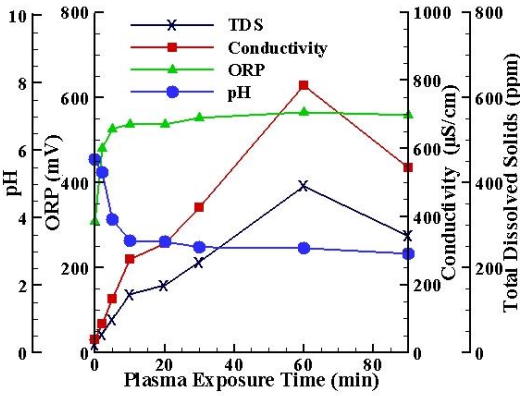
Fig. 7. Bacterial cell viability versus plasma exposure time for plasma above and below water

In Fig. 6 we can see the bacterial cultures for different plasma exposure times as compared to untreated control sample for the two types of plasma discharges.

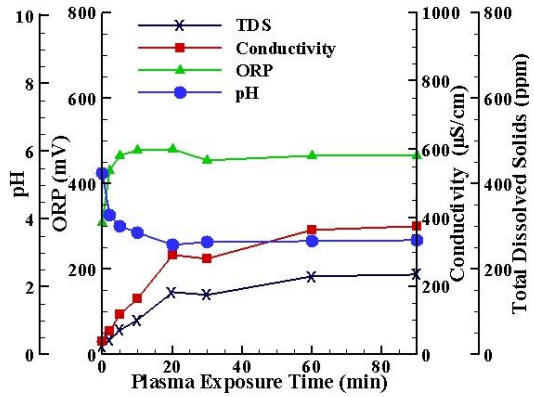
Fig. 7 shows the decay of colony forming units per mL versus plasma exposure times. One can calculate the D value for discharge above water as 18.8 min, and below water as 4.7 min, which indicates a faster killing rate of bacteria with discharge under water.

5. Results of antibiotic degradation in water with plasma

High proportion of Doxycycline hydrate (DXC) could be found in groundwater, surface water and soil due to its ineffective biodegradability. The decomposition of DXC in aqueous solution was examined by plasma discharges above and below water surface. We use 50 mL solution with concentration of 50 mg/L DXC in distilled water.



(a) Above



(b) Below

Fig. 8. DXC Solution parameters for plasma discharges (a) above, (b) below solution surface

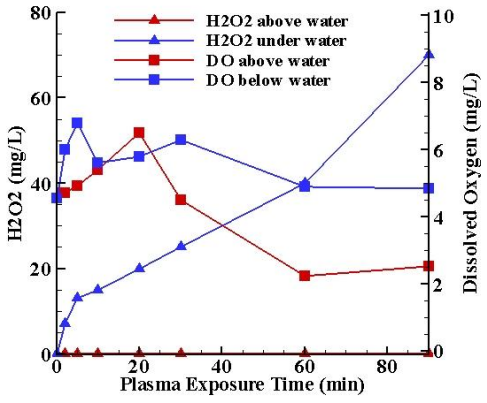
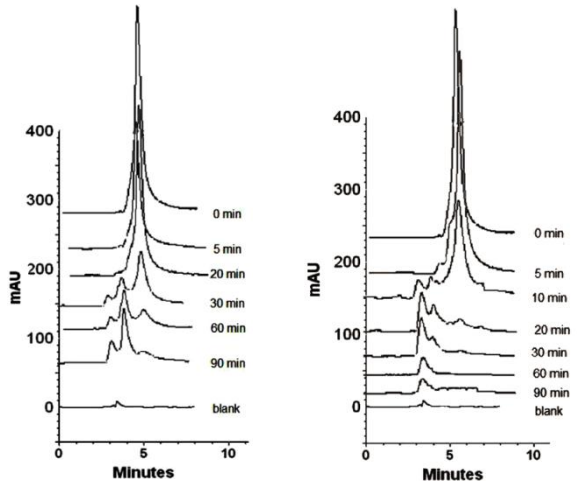


Fig. 9. H_2O_2 and DO for plasma above and below.

During DXC solution treatment by plasma, water parameters as pH, ORP, TDS and conductivity are shown in Fig. 8 for plasma above and below water surface. We can note that the solution parameters don't vary as much for the two discharge schemes. Fig. 9 shows H_2O_2 and DO of the solution for discharges above and below water surface.

The degradation of DXC during plasma treatment was assessed by UV-Vis spectrophotometer Cary 6000 from Agilent (USA) in the wavelength range 190–500 nm.

The concentrations of DXC is analyzed by Thermo HPLC system from Thermo Electron Corp. (Bellefonte, PA, USA) with a Thermo Hypersil C18 column (250 mm×4.6mm I.D, 5µm particle size column), and detection wavelength of Photo diode array (PDA) detector was set in 347 nm for DXC. The mobile phase was mixture of acetonitrile and phosphate buffer (pH=3.5) in ratio of (40:60, v/v) for DXC and in an isocratic mode at flow rate 1.0 ml/min.



(a) (b)

Fig. 10. Chromatograms of DXC concentrations for plasma (a) above, (b) below solution surface

Fig. 10 shows chromatograms of DXC concentrations where counts in milli Absorbance Unit (mAU) are plotted versus acquisition time for different plasma treatment time intervals, above and below solution surface.

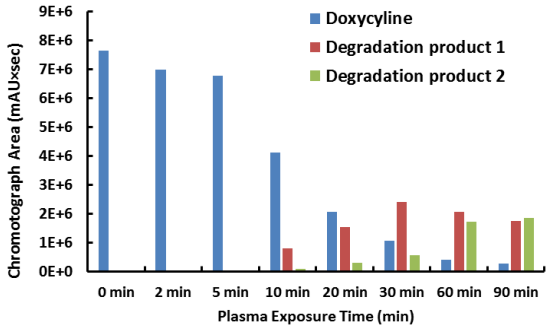


Fig. 11 (a)

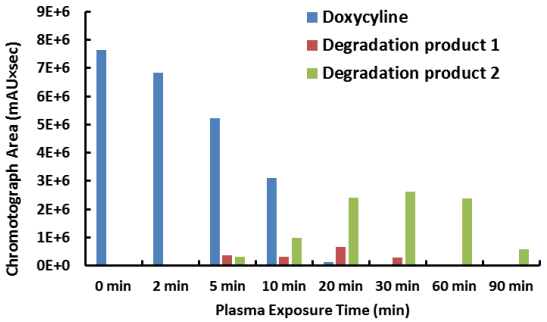


Fig. 11 (b)

Fig. 11. Degradation peaks area for plasma (a) above and (b) below solution surface

Fig. 11 shows degradation peaks area for discharges above and below solution surface. Two degradation products appeared as result of DXC integration.

6. Conclusion

Discharges at the bottom of discharge vessels with air bubbles reveal to be more efficient in bacteria killing and antibiotic degradation. For below water plasma exposure DXC is completely removed (100 %) after 30 min plasma exposure. While for above water plasma exposure DXC is partially removed (70 %) after 90 min plasma exposure. With degradation of DXC, two degradation products appear. For discharge under water, one of them is eliminated completely after 60 min and the other is eliminated by about 70% after 90 min. In the two cases, after plasma exposure time of 90 min, the drug solutions have been left for two days in ambient conditions. We observe then that degradation products are completely diapered from sample solutions.

7. Acknowledgements

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8. References

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