

# Interaction of an atmospheric pressure plasma micro jet with water based liquids

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The plasma – aqueous solution interface represents a perfect environment for generating chemically active species with high potential in producing changes on the properties of the treated liquids. The current work studies the interaction of an atmospheric pressure micro jet and water based solutions. Characteristics of the liquids like electrical conductivity and pH are monitored. Furthermore, the influence of experimental parameters like discharge gas, treatment time, treated volume and discharge environment is investigated. Moreover, the work proposes the treated solutions as proper agents for organic colorants degradation.

## 1. Introduction

The study of the interactions between the gas discharges and the liquid state continues to be of high interest [1-4]. When plasma interacts with water based liquids, the process results in the formation of the so called plasma acid, the water containing the chemical products generated at the plasma-liquid interface. It is a complex liquid that has found multiple applications like catalyst in organic reactions [1], increasing plant growth agent [3], cancer cell death cause [4] and bacteria inactivation mean [5,6].

Atmospheric pressure plasma  $\mu$ -jets are suitable choices for many applications like surface activation, sterilization and wound healing. Their special characteristics: ability to generate many chemically active species, easiness of generation on any surface and facility to manipulate, low cost and simplicity also recommend them for liquid treatments.

The current work presents the effects of the interaction between a plasma  $\mu$ -jet generated at atmospheric pressure and the surface of water based liquids.

## 2. Experimental details

Figure 1 presents the schematics of the experimental set-up. The discharge reactor is composed of a capillary metallic tube (syringe needle, 0.6 mm i.d.) whose free end is placed at a distance of 4 mm above the treated liquid surface. It represents the single electrode of the system, being powered with high sinusoidal voltage (1.7 kV, 10.2 MHz) generated with a laboratory made free-running oscillator. The plasma power is 16 W. The second electrode, with a floating electric potential,

is represented by the liquid. The plasma gas (He or Ar) flows through the electrode with a flow rate of  $0.3 \text{ l min}^{-1}$  forming a  $\mu$ -jet discharge (shown in the insert for He) between the water surface and the electrode.

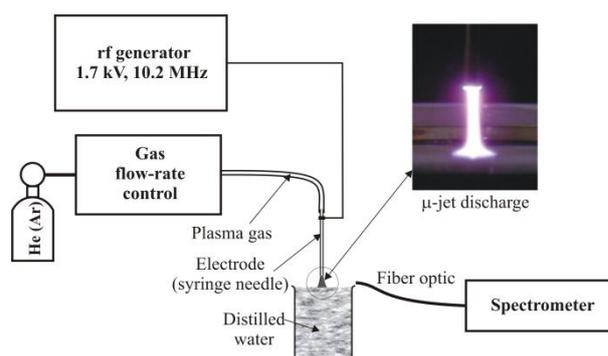


Fig. 1. Experimental set-up.

Distilled water volumes between 15 ml and 35 ml underwent plasma treatments for time intervals from 10 to 60 minutes. The temperature of the liquids was kept under  $40^\circ\text{C}$  by placing the water containers in a cold water bath. The plasma treated solutions were investigated by electrical conductivity, pH and absorption spectroscopy measurements. To evaluate the degradation effect of the plasma acid, the so treated distilled water was further mixed with methylene blue (MB) so that the final MB concentration was 0.001%. A control sample of the same concentration was also prepared using nontreated distilled water. All samples were stored in a closed, dark environment. UV-vis absorption spectroscopy was used to monitor the modifications produced by the water solutions to the

colorant. All absorption spectra were recorded using a Jasco V-630 UV-vis spectrophotometer.

Optical emission spectroscopy was used for plasma diagnosis. The emission spectra of the  $\mu$ -jet were collected with an HR4000CG-UV-NIR Ocean Optics High-Resolution Fibre Optic Spectrometer with the wavelength range of 254 – 965 nm. The electrical conductivity and the pH of distilled water before and after the plasma treatment were measured with a conductivity stick meter, Voltcraft LWT-02 (0-1999  $\mu\text{S cm}^{-1}$ ,  $\pm 2\%$ ) and a digital pH-meter, Voltcraft PH-100ATC (0-14 pH range and  $\pm 0.07$  precision), respectively.

### 3. Results

The emission spectra of the discharge in the region placed at the plasma-liquid interface offers information about the chemically active species generated in the plasma. Besides the characteristic emission of the plasma gas (He or Ar), emission lines and bands of hydrogen, oxygen, nitrogen and OH radical are very prominent in the discharge emission. The spectra were also used for estimating the energy of the particles in the discharge.

In the plasma-liquid contact region, chemically active species like hydrogen peroxide, nitrogen oxides, superoxide and hydroxyl radical are generated [2-8]. They interact with the distilled water resulting in changes of the pH and the electrical conductivity of the treated solution. Furthermore, modifications in the molecular structure of the liquid are determined. The UV-vis absorption measurements highlight the formation of nitric acid in the treated liquids through the presence of an absorption peak at 301 nm (Fig.2).

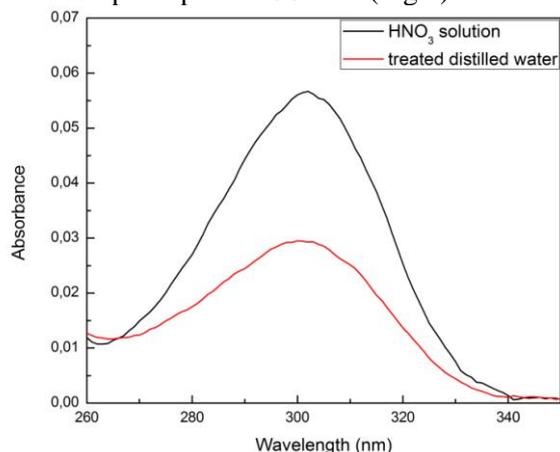


Fig. 2. Absorbance at 301 nm of a nitric acid solution of 0.035% and a distilled water sample treated for 40 minutes.

The effect on the properties of the treated liquids of some experimental parameters like the type of the

discharge gas, the treatment time, the environment surrounding the discharge (air or the same gas that is used for plasma generation) and liquid volume are also investigated showing that each one of them is very important for the final properties of the treated solutions. The augmentation of the treatment time as well as the decrease of the treated volume has as consequence higher electrical conductivities, lower pH values and higher nitric acid concentrations of the aqueous solutions. Depending on the treatment time or the initial volume of the treated water, the pH suffers a severe drop from 5.9 pH units to values smaller than 3, while the conductivity strongly increases from 2  $\mu\text{S cm}^{-1}$  to values bigger than 2000  $\mu\text{S cm}^{-1}$ . Further, the time stability of the liquids with the new characteristics is verified. It was observed that the new properties of the treated solutions are stable for more than one month.

The modifications generated by the plasma treatment to the distilled water render the  $\mu$ -jet as an important candidate for some applications like organic dyes degradation or nanoparticles synthesis. The effects of the plasma acid on methylene blue were investigated by absorption spectroscopy. It was shown that the plasma treated distilled water is able to gradually reduce the MB concentration, until the complete degradation of the colorant in 2 days (Fig. 3).



Fig. 3. MB samples (MB mixed with distilled water treated for 50 minutes – left; control – right) two days after preparation.

### 4. Conclusions

The plasma  $\mu$ -jet used in this study was proved to be an efficient tool for inducing changes in water based liquids that underwent treatment. Important features of the liquids like electrical conductivity, pH and chemical composition change when exposed to plasma treatment. The nitric acid formation in the aqueous solutions represents the main cause of the pH drop and conductivity increase for the treated solutions.

Moreover, the results obtained for methylene blue diluted in distilled water treated with plasma

show that the plasma acid serves as a proper degradation agent for organic dyes.

## 5. References

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