Preliminary Study of a Non-thermal Plasma for the Degradation of the Paracetamol Residue in Water

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Abstract—This paper deals with the challenging research topic of the use of low-temperature plasmas at atmospheric pressure for the treatment of pharmaceutical residues in water. The low-temperature plasmas were generated in a multiple needle-to-plate reactor. Using ICCD imaging and electrical measurement, two distinct discharge regimes were identified. Optical Emission Spectroscopy (OES) measurements evidenced the OH production and enabled determination of the rotational temperature. An analgesic (paracetamol) in aqueous solution was treated with this reactor, and its conversion rate was 81% after 60 min of treatment.

Keywords-Advanced oxidation processes (AOP), non-thermal plasma (NTP), paracetamol degradation in water

I. INTRODUCTION

The presence of low concentrations of various pharmaceutical substances in industrial effluents and surface water has been evidenced in several studies indicating their poor biodegradability in sewage treatment plants [1]-[3]. Due to their properties and composition (chemical formula and the number of aromatics present in the molecules), the presence of pharmaceutical residues in water can have substantial health effects on humans and may also affect aquatic organisms. Consequently, their presence in water is an important issue in environmental research. Their removal has been performed with Advanced Oxidation Processes (AOPs) such as the Fenton process, UV oxidation, assisted photochemistry, and Non-Thermal Atmospheric pressure Plasma (NTAP), since these processes are efficient at producing highly reactive species especially OH and O₃, [4]–[8]. Thanks to their strong oxidizing power, with a standard reduction potential higher than 2 V, these species can efficiently oxidize the pollutants, leading to their removal.

In recent decades, the interest of NTP technologies for the abatement of aqueous pollutants has greatly increased. They were successfully applied for the treatment of pharmaceutical compounds in liquid effluents [9]–[12] in laboratory conditions. Many discharge configurations have been used; for example, discharges in contact with the liquid, inside the liquid or post-discharge [13], [14]. In liquid-discharge direct contact, UV radiation added to the oxidizing species can act effectively on complex chemical compounds (such as drug residues in liquid effluents) [3].

In this paper, we present a preliminary study on the application of Dielectric Barrier Discharges (DBD) in a needle-toplate configuration to treat drug residues in aqueous liquids. Firstly, optical and electrical diagnostics of a needle-to-plate DBD discharge were performed. The discharge morphology was investigated using ICCD imaging; the production of

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OH radicals in two distinct regimes was compared, and the rotational temperature was determined thanks to OH radical and N_2 emission spectra.

Finally, a multiple needle-to-plate discharge configuration was used for the treatment of a paracetamol solution in several experimental conditions (nature of the injected gas and amplitude of the applied voltage).

II. EXPERIMENTAL SETUP AND METHODOLOGY

Fig. 1 displays a schematic diagram of the experimental device used for the paracetamol treatment by a multiple needle-to-plate configuration.

The needle-to-plate configuration was placed inside a vessel made of PVC enabling control of the working gas. The lower electrode was a copper film deposited on a dielectric epoxy plate that was in contact with the liquid. The inlet gas (air, Ar, or N_2) was injected through the upper electrodes (capillary needles with inner diameter of 0.4 mm) by mass flow-meter controllers (El-Flow Bronkhorst[®]) with a total gas flow rate maintained at 100 standard cubic centimeter per minute (sccm).

The discharges were generated at the tip of the needles above the liquid. The distance between the electrodes and the



Fig. 1. Scheme of the multiple (9) needle-to-plate experimental apparatus for the drug treatment.

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Fig. 2. Experimental setup for OES and ICCD imaging measurements.

surface of the liquid can be adjusted from 0 to 10 mm. The volume of the solution to be treated was 40 mL of tap water containing 0.8 mg of paracetamol (the initial concentration of paracetamol was thus 20 mg/L). The initial pH of the solution was 8. The electrical discharge was powered by a high voltage (HV) amplifier (Trek® 20/20C) driven by a function generator (TG4001 TTI®). The electrical measurements were performed using high voltage (PE20KV Lecrov^{\mathbb{R}}) and current (CT-C5 Magnelab[®]) probes and were displayed on an oscilloscope (DPO 3054 Tektronic[®]). A single needleto-plate configuration operating in the same conditions was used to perform OES measurements and ICCD imaging (Fig. 2). To acquire optical emission spectra, a spectrometer (Acton SP2750 from Princeton Instruments®) with a grating of 600 gr/mm was used with an ICCD camera (PiMax 4 from Princeton Instruments[®]). An apparatus function of this spectroscopic device was measured using the 543 nm green line of a helium-neon laser. Due to the weakness of the discharge radiation, an accumulation of 10000 was used for each spectrum. To determine the rotational temperature, the experimental spectra were compared to the simulated ones from SPECAIR[®] [15]. To observe the morphology of the discharges as a function of the operating conditions, discharge imaging was performed using an ICCD camera (iStar from ANDOR Technology[®]) with a lens of 100 mm in focal length and an exposure time of 200 μ s.

To quantify the paracetamol concentration in the solution to be treated, analyses were per-formed using a UV-Visible absorption spectrometer (Cary 60 UV-Vis Agilent Technologies[®]). The concentration of paracetamol in the solution was determined from the absorption maximum at 243.9 nm [16]. According to the Beer-Lambert law, the absorbance A (also called optical density, unitless), at wavelength λ , is given by the formula (1):

$$A = -\log\left(\frac{I}{I_0}\right) = \varepsilon lc \tag{1}$$

where I/I_0 is the transmittance of the solution (unitless); ε is the molar extinction coefficient (L·mg⁻¹·cm⁻¹), which depends on the wavelength, the chemical nature of the medium and temperature; l is the optical path length in the solution to be analyzed (cm); c is the mass concentration of the paracetamol in the solution (mg/L).



Fig. 3. ICCD imaging of streamer regime (exposure time: 200 μ s). U_{p-p} = 8 kV; air flow rate 10 sccm.

III. RESULTS AND DISCUSSION

A. Discharge evolution and morphology

The operation of a DBD discharge is well known but to describe the operation of our specific DBD, we need to recall some principles very briefly. A DBD generally works with AC voltage: when the voltage exceeds a given threshold to provide a sufficiently strong electric field, a micro discharge begins in the form of a filament. The discharge current deposits electrical charges on the dielectric surface, inducing an electrical field. The electrical field is in opposition to the applied field, leading the extinction of the micro-discharge. Then, another micro-discharge begins either because the applied voltage has sufficiently evolved, or elsewhere where the total field is strong enough. A current corresponding to each streamer is therefore a very fast pulse of the order of 100 ns and with a low amplitude, less than 100 mA.

In our specific case, the electrical charges reach firstly tap water which is a good conductor. The charges should be distributed throughout the volume of the water and should be scattered over the entire surface of the dielectric; the induced field is therefore much lower and the limitation effect on the discharge current is weak. Consequently, with tap water on the dielectric surface, the current can be much stronger.

In this study, instead of a sine wave, we opted for a square wave with a rise time of about 100 V/ μ s. When the voltage amplitude is low, a filamentary discharge forms, as shown in Fig. 3. This picture was recorded with an exposure time of 200 μ s and it integrates all the filaments of the discharge for about a half cycle of the applied voltage whose frequency is 2 kHz (Fig. 4).

Each filament has a diameter of about 100 μ m and a lifetime of the order of several tens of ns [17]. This type of discharge is called Streamer Regime in the present work. The peak to peak voltage amplitude (U_{p-p}) for this discharge was 8 kV.

For a higher amplitude, for example 14 kV in U_{p-p} , the current is much stronger and a rectilinear ionization channel is formed under the tip (Fig. 5). This channel carries a significant amount of energy and water under the tip evaporates.

It should be noted that the current is not a single broad pulse, but always a train of rapid pulses, as shown by the



Fig. 4. Voltage and current waveforms in streamer regime ($U_{p-p} = 8$ kV, f = 2 kHz).



Fig. 5. ICCD imaging in spark regime (exposure time: 200 μ s). $U_{p-p} = 14$ kV; air flow rate 10 sccm.



Fig. 6. Voltage and current waveforms in streamer regime ($U_{p-p} = 14$ kV, f = 2 kHz).

current waveform in Fig. 6.

This type of discharge is called Spark Regime in the present study.



Fig. 7. Optical Emission Spectroscopy in spark regime and streamer regime. Air flow rate = 10 sccm.

B. OES results in single needle configuration

Optical emission spectra were obtained from both spark and streamer regimes, in the 293-318 nm range of ultraviolet radiation (Fig. 7).

OH and N_2 molecular bands can be easily identified. It can be seen that the production of OH in spark regime is quite high while that in the streamer regime is negligible. This great difference is probably due to water evaporation in Spark regime as mentioned above, since the water molecules promote OH production, as described below. Locke et al. [4] showed, according to the reactions below, the different pathways of the formation and destruction of OH radical (Eqs. 2-7) from H₂O decomposition.

$$H_2O + e \longrightarrow H_2O^* + e$$
 (2)

$$H_2O^* + H_2O \longrightarrow H + OH + H_2O$$
 (3)

$$H + H_2 O^* \longrightarrow H_2 + OH$$
(4)

$$OH + H_2O^* \longrightarrow H_2O_2 + H$$
(5)
$$H + OH + H_2O \longrightarrow H_2O + H_2O$$
(6)

$$e + H_2O \longrightarrow H^- + OH$$
(7)

As shown in Fig. 8, experimental emission spectra were

fitted with simulated ones by using the SPECAIR[®] software [15].

From the comparison between experimental and simulated spectra, the rotational temperature, T_{rot} , in the discharge can be estimated. In Spark Regime, T_{rot} was about 1800K, while in Streamer Regime it was about 450K. The latter temperature was obtained from the N₂ bands alone, while the former was deduced by taking into account both the N₂ and the OH bands.

C. Paracetamol degradation

The treatment of paracetamol solutions by DBD was studied using the 9 needle-to-plate reactor. To study the effects of the inlet gas on paracetamol degradation in aqueous solution, various inlet gases (air, Ar and N_2) were injected, keeping the total flow rate at 100 sccm. Locke et al. [4] showed that the OH radical is a reactive species that can rapidly and efficiently degrade many organic compounds. In our reactor, the spark



Fig. 8. Simulated and experimental emission spectra in: (a) spark regime and (b) streamer regime.

mode enables a high production of OH radicals. We therefore started our treatment with a Spark regime discharge. However, with the 9 needle-to-plate configuration, a large amount of water vapor was produced, leading to dysfunctioning of the discharges due to water condensation on the reactor wall. Consequently, the treatment reported here was per-formed in the streamer regime, with a peak-to-peak voltage amplitude of 13.6 kV and a frequency of 500 Hz. Using the Lissajous method, the average power was estimated to be 1 W.

As indicated above, the initial concentration of paracetamol was 25 mg/L and the total liquid volume was 40 mL. The paracetamol concentration in the solution was measured by UV-visible absorption as a function of the treatment time with an air gas flow (Fig. 9).

We observe that the paracetamol absorption decreases as a function of time during the plasma treatment; this shows a degradation of paracetamol in the solution. A conversion rate of about 81% was obtained after 60 min of plasma treatment. This rate is underestimated since one can note a rise in the absorption for λ around 220 nm, due to by-products produced during the plasma treatment. These by-products (nature and concentration) need to be determined in order to ensure that the species produced are not toxic for the environment. This identification is scheduled in the perspectives of this work.

In Fig. 10, we report the conversion rate as a function of time. The conversion rate was about 35% after 15 minutes of treatment corresponding to 7 mg of paracetamol remediated. Knowing the mean power of 1 W, the energy yield can be



Fig. 9. Paracetamol degradation with a gas flow of air.



Fig. 10. Conversion rates of paracetamol and the natural logarithm of the remaining concentration of paracetamol in the solution as functions of the treatment time.

estimated to be 2 g/kWh. On increasing the treatment duration, the energy yield decreases slightly; for instance, for 45% conversion, the energy yield is about 1.8 g/kWh. This value is much smaller than the one (21 g/kWh) reported by Panorel et al. [11].

If we calculate the natural logarithm of the remaining concentration of paracetamol in the solution, and plot it as a function of time (Fig. 10), it can be seen that the curve obtained is a straight line with a negative slope. So, paracetamol degradation follows a 1st order reaction as described below. In this case, for the paracetamol decomposition reaction, we have:

$$v = -\frac{\mathrm{d}[\mathbf{para}]}{\mathrm{d}t} = k[\mathbf{para}] \tag{8}$$

$$\ln\left(\frac{[\text{para}]}{[\text{para}]_0}\right) = -kt \tag{9}$$

where t the treatment time (min), [para] the mass concentration of paracetamol at time t, and [para]₀ the initial mass concentration of paracetamol (mg/L). v is the kinetic rate (mg·L⁻¹·min⁻¹), and k the rate constant (min⁻¹). In our experimental conditions, the rate constant is 2.7×10^{-2} min⁻¹.

In air, paracetamol degradation can be due to reactions between the paracetamol and OH, O, O_3 and other species produced in the liquid. Note that the main oxidizer should be ozone in our case. Nitrogen compounds could also play a role in paracetamol degradation. To determine the effects of the



Fig. 11. Paracetamol degradation with a gas flow of a) argon and b) nitrogen. $[paracetamol]_0 = 25 \text{ mg/L}.$

latter species, experiments were also performed with injected gases without O_2 (i.e. in pure argon or N_2).

Fig. 11 give the absorption spectra in the UV range of paracetamol with Ar or N2 as a function of time, and show that the drug concentration remains almost unchanged.

Moreover, in experiments with pure N2, the same byproducts as those observed in air experiments seem to be produced inducing a stronger absorption in the 200-210 nm range. These by-products could be nitrogen compounds dissolved in water as NO_2^- or NO_3^- [18].

As discussed previously, OH detected by OES (Fig. 8) seems to be mainly produced from locally vaporized water due to the discharge impact on the liquid surface. This could explain the higher intensities of OH produced in spark regime where a higher localized injected energy promotes water vaporization and water dissociation in the discharge, as observed in the multi-needle configuration.

As shown by OES measurements (Fig. 7), in streamer regime with air as working gas, the production of OH is very weak. With argon as working gas, the discharge also produces oxidizers, at least OH [19], but this discharge has no effect on the drug in our experiment. These results show that O₂ injection in the plasma is necessary in our operating conditions to remove the pollutant from the liquid. The first active species generated O-atoms and O₃ from O₂ dissociation (Eqs. 10 and 11) which were transferred to the liquid to produce secondary radicals before reactions with the pollutant or to directly react

with the paracetamol.

$$O_2 + e \longrightarrow O + O + e$$
(10)
$$O + O_2 + M \longrightarrow O_3 + M$$
(11)

$$O + O_2 + M \longrightarrow O_3 + M$$
 (11)

Evidence for the presence of O₃ was verified by Fourier Transform Infra-Red (FTIR) spectroscopy in the outlet gas when air was injected in the 9 needles configuration in the streamer regime.

IV. CONCLUSION

This work has reported a study of the discharges generated in a needle-to-plate reactor and the first test of this reactor for the treatment of paracetamol in an aqueous liquid.

In the first step of this work, the microdischarges were characterized using a single needle-to-plate configuration. Two plasma regimes (spark and streamer regimes) were identified and investigated. OH production was promoted in spark mode with a rotational temperature close to 1800K. In streamer regime, OH production was much lower and T_{rot} was low (450K).

To treat the paracetamol solution, a multi-needle-to-plate reactor was used, while the discharge was in streamer regime to obtain a microdischarge at the tip of each needle. Various inlet gases were injected: air, N2 and Ar.

The main results are the following:

- A conversion rate of 81% in air was obtained. •
- Energy yield was about 1.8 g/kWh at 45% conversion.
- To increase the efficiency of the paracetamol treatment, the discharges must be generated in oxygenated gas to promote the production of O-atoms and/or O₃ and to increase the paracetamol degradation. In N₂ or Ar, no conversion was obtained, indicating that the OH production is not enough.
- The paracetamol degradation followed globally a 1st order reaction.

To optimize the process, the perspectives of this work are:

- The identification and the characterization of the oxidative species responsible for the pollutant degradation;
- The improvement of the energy yield;
- The identification and the quantification of the byproducts generated and their chemical pathways.

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