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DEGRADATION OF PARACETAMOL IN AQUEOUS SOLUTION BY NON THERMAL PLASMA

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In this study, the paracetamol degradation in water was investigated using Non Thermal Plasmas (NTP) created by Dielectric Barrier Discharges. The effects of the operating conditions (applied voltage, inlet gas composition) on the degradation were studied. A conversion rate higher than 90% was reached with an energy yield of 1 g/kWh. We showed that the efficiency of the process highly depends on electrical parameters and gas composition injected in the reactor containing the aqueous solution. The main produced species in water were nitrogen compounds, carboxylic acids and aromatic compounds.

1 Introduction

Pharmaceutical substances like paracetamol are frequently present in groundwater, and present a long-term risk for the environment and health [1]. We propose to use Advanced Oxidation Processes (AOPs) using Non Thermal Plasmas to degrade these drug residues. AOPs generally refer to a specific subset of processes which produces oxidizing species such as O, O₃, OH[•] and H₂O₂. AOPs can also involve TiO₂ catalysis, Fenton's reaction, and Non Thermal Plasma (NTP) [2,3]. Here, we use a NTP process which was generated by Dielectric Barrier Discharge, because they have proved to be effective for the production of oxidizing species. These processes have already been applied for the treatment of pharmaceutical compounds in aqueous media but differed in the type of plasma reactor [3,4]. To get a better understanding of degradation mechanisms, it is important to study the effects of the electrical parameters of the reactor and operating conditions on the treatment of pollutants and the generated products. So, in this work which deals with the treatment of paracetamol in liquid by non-thermal plasma process, the effects of the nature of the working gas into the solution and the plasma reactor operating parameters (voltage, power) on the conversion rate and the generated products were studied.

2 Experimental

The plasma reactor used was a multiple needle-to-plate configuration. The schematic diagram of the experimental setup has been previously described [5]. The volume of the treated solution was 40 mL of tap water with an initial paracetamol concentration of 20 mg/L. The initial pH of the solution was 7.2. The electrical discharge was powered by a high voltage amplifier driven by a function generator. The electrical measurements were performed using a high voltage and current probes and were displayed on an oscilloscope. Lissajous's method [6] was used to evaluate the consumed power. To quantify the paracetamol concentration in the solution, analyses were performed using an absorption UV-Visible spectrophotometer. The range concentrations of H₂O₂, NO₂⁻, NO₃⁻, were estimated during the treatment times with semi-quantitative test strips QUANTOFIX[®]. The degradation products were identified by High-Resolution Mass Spectra (HRMS) on a Q-TOF maXis mass spectrometer (Bruker[®]) [7].

3 Results and Discussion

3.1 Effects of operating conditions

In a previous paper [5], the effects of the amplitude of applied voltage on the conversion of paracetamol have been presented. It was shown that in an oxidative gas, a better conversion rate is obtained when the applied voltage is high, whatever the treatment times. The discharge regime must be streamer one [5], since the spark regime may lead to the disruption of the functioning of the reactor. The conversion rate, τ , and the energy yield, EY (g/kWh), of paracetamol degradation were calculated from equations (1) and (2), respectively, with C_0 , C_t concentrations (g.L⁻¹) of paracetamol in the solution at the beginning and the end of the time interval Δt (h), V is the volume of the solution (L) and P , the consumed power (kW).

$$\tau = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$EY = \frac{(C_0 - C_t) \cdot V}{\Delta t \cdot P} \quad (2)$$

Figure 1.a shows the conversion rates for various injected gas mixtures in function of the treatment time. These curves show that the composition of the injected gas plays an important role on the paracetamol degradation in the liquid. The highest conversion rate is obtained for 90% Ar+10% O₂ mixture, because the dissociation of O₂ enables the generation of oxidizing species such as O or O₃ in the gas phase and also OH[•] in the liquid phase to degrade the pollutant. Furthermore, the interest to combine an oxidative gas with argon, is to generate more easily the discharge, and to reduce the necessary applied voltage (*i.e.* ± 5 kV for the mixture 90% Ar + 10% O₂, ± 3.6 kV for the mixture 90% Ar + 10% air, and ± 6.8 kV for 100% air) due to a lowest breakdown voltage [8]. In absence of oxygen in the injected gas, no paracetamol degradation was observed [5]. The energy yield of the process therefore depended on the nature of the working gas and the diffusion of the produced species (figure 1b).

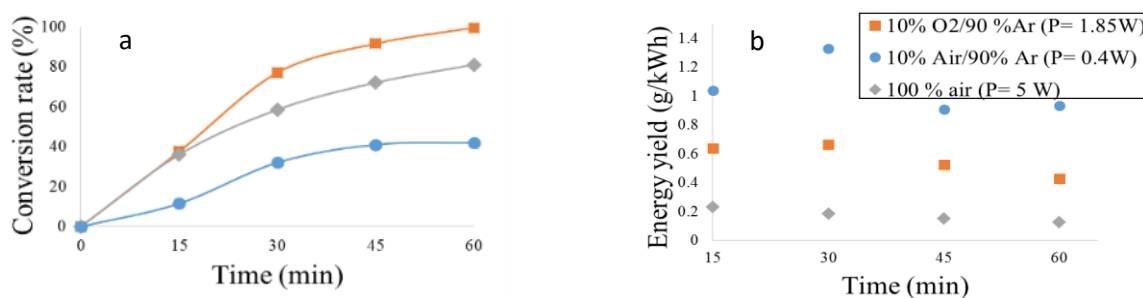


Figure 1: Effects of the injected gas composition and treatment duration on a) Paracetamol conversion rates and b) energy yields.

We observe that the injected power strongly depends on the injected gas. With the mixture 10% O₂+90% Ar, we obtained the highest τ , but its EY is lower than the one in the mixture 10% air+Ar, because of a higher power injected. The plasma process used in this work is not yet fully optimized, and this study allows to obtain a good paracetamol degradation with an energy yield in the range of 0.2 and 1.4 g/kWh. Brillas *et al* [9] obtained an energy yield of 0.82 g/kWh, in good agreement with our results.

3.2 Generated products

The concentrations of NO₃⁻, NO₂⁻, H₂O₂ and pH were estimated every 15 min during one hour of paracetamol treatment, the results obtained after 60 minutes of treatment are displayed in

Table 1. H_2O_2 is an oxidizing species which can react non-selectively [10]. In this work, we observe that the measured concentrations of H_2O_2 in the treated solutions are similar in all the studied conditions. An increase of the treatment duration leads to a higher concentration of H_2O_2 . The production of NO_3^- and NO_2^- does not seem to be linked to the degradation of paracetamol. Indeed in Ar- O_2 mixtures, these species are not produced despite the high conversion of paracetamol obtained. In presence of air, the concentrations of NO_3^- and NO_2^- increase over time, reaching values of 100 and 5 mg/L, respectively, after one hour of treatment.

Table 1: Ranges of concentrations of NO_3^- , NO_2^- , H_2O_2 and pH measured in the liquid.

Time (min)	90% Ar + 10% O_2				90% Ar + 10% air				100 % Air			
	$[\text{NO}_3^-]$ mg.L ⁻¹	$[\text{NO}_2^-]$ mg.L ⁻¹	$[\text{H}_2\text{O}_2]$ mg.L ⁻¹	pH	$[\text{NO}_3^-]$ mg.L ⁻¹	$[\text{NO}_2^-]$ mg.L ⁻¹	$[\text{H}_2\text{O}_2]$ mg.L ⁻¹	pH	$[\text{NO}_3^-]$ mg.L ⁻¹	$[\text{NO}_2^-]$ mg.L ⁻¹	$[\text{H}_2\text{O}_2]$ mg.L ⁻¹	pH
60	0	0	10-25	6.9	25-50	5-10	10-25	5.7-6	50-100	0-1	10-25	6-6.3

Figure 2 shows the absorption spectra of the paracetamol for different treatment time, and various inlet gas. An absorption band, observed around 210 nm, corresponds to the presence of NO_3^- and NO_2^- in the treated liquids [11]. These results are in agreement with the concentrations of NO_3^- and NO_2^- previously measured. These compounds are not produced in the absence of N_2 in the injected gas as shown in Figure 2b.

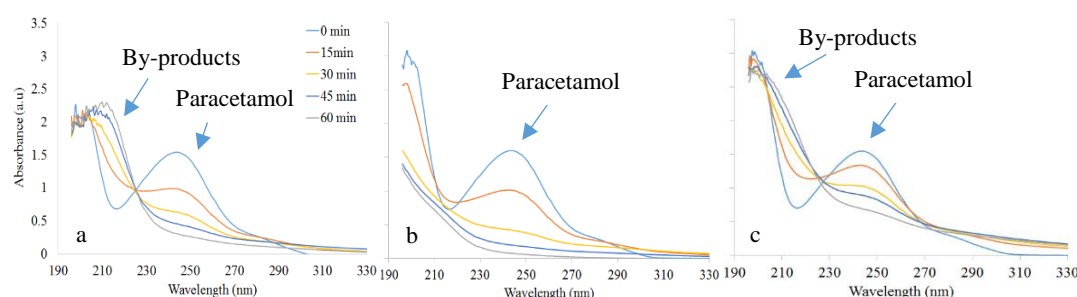


Figure 2. Absorption spectra in function the composition of the injected gas a) air ($U = \pm 6.8$ kV); b) 90% Ar + 10% O_2 ($U = \pm 5$ kV); c) 90% Ar + 10% air ($U = \pm 3.6$ kV).

A complete analysis of the generated products was performed by HRMS. Table 2 presents a non-exhaustive list of the main detected degradation products among about 70 ones.

Table 2. List of identified compounds by HRMS which are similar to literature.

mode	experimental m/z	Attempt of identification	Molecular formula	formula
Negative	103.004	Malonic acid [12,13]	$\text{C}_3\text{H}_3\text{O}_4^-$	
Negative	145.014	acetonedicarboxylic acid	$\text{C}_5\text{H}_5\text{O}_5^-$	
Negative	166.051	hydroxy-4-(Nacetyl)-aminophenol [12]	$\text{C}_8\text{H}_8\text{NO}_3^-$	
Positive	200.055	[12,14]	$\text{C}_8\text{H}_{10}\text{NO}_5^+$	
Negative	214.035	[12]	$\text{C}_8\text{H}_8\text{NO}_6^-$	

All the compounds presented in table 2 are common to the treatments using three gas compositions. Different families of molecules from paracetamol degradation have been identified, including compounds similar to those observed from the degradation of paracetamol in some AOPs [12-15] and also in NTP processes [3]. In addition to the aromatic compounds listed in Table 2, nitrophenol, aminophenol, and hydroquinone were also detected and carboxylic acids (*i.e.* acetic, succinic, muconic, and maleic acids) were identified. Nitrites and nitrates were also detected only for the 100% air and 10% air + 90% Ar. The formation of carboxylic acids during the degradation of paracetamol can explain the acidification of the samples as reported in Table 1.

4 Conclusion

This study was about the treatment of paracetamol in aqueous solution by non-thermal plasma. The effects of the nature of the working gas on the conversion rate and the produced species were presented. The highest conversion close to 99% was obtained for a gas mixture of O₂-Ar with an EY of 0.7 g/kWh. A better energy yield of 1.4 g/kWh was obtained for gas mixture of air-Ar. The dissociation of O₂ in the plasma and the diffusion of produced species in the liquid are necessary steps in the process. The energy yield of the process, strongly depends on the experimental conditions as the consumed power which in turn depends on the composition of injected gas. In the liquid phase, analysis shows that nitrites, nitrates, carboxylic acids, and aromatic compounds are the main degradation products. The perspectives of this work will be to optimize the process with the study of the influence of the concentration and the volume of the solution. A comparison of this process to another one in post-discharge, like an ozone generator, is scheduled to find out the influence of other generated species in addition to ozone.

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