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2 **Microwave atmospheric pressure plasma jets for wastewater treatment:**  
3 **Degradation of methylene blue as a model dye**

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17 discharges; dye degradation; water treatments

18

19 **ABSTRACT**

20 The degradation of methylene blue in aqueous solution as a model dye using a non thermal  
21 microwave (2.45 GHz) plasma jet at atmospheric pressure has been investigated. Argon has  
22 been used as feed gas and aqueous solutions with different concentrations of the dye were  
23 treated using the effluent from plasma jet in a remote exposure. The removal efficiency  
24 increased as the dye concentration decreased from 250 to 5 ppm. Methylene blue degrades  
25 after different treatment times, depending on the experimental plasma conditions. Thus,  
26 kinetic constants up to  $0.177 \text{ min}^{-1}$  were obtained. The higher the Ar flow, the faster the  
27 degradation rate. Optical emission spectroscopy (OES) was used to gather information about  
28 the species present in the gas phase, specifically excited argon atoms. Argon excited species  
29 and hydrogen peroxide play an important role in the degradation of the dye. In fact, the  
30 conversion of methylene blue was directly related to the density of argon excited species in  
31 the gas phase and the concentration of hydrogen peroxide in the aqueous liquid phase. Values  
32 of energy yield at 50% dye conversion of  $0.296 \text{ g/kWh}$  were achieved. Also, the use of two  
33 plasma applicators in parallel has been proven to improve energy efficiency.

34

## 35 **1. Introduction**

36 In recent times there has been a dramatic increase in the amount of organic pollutants  
37 (volatile organic compounds, pharmaceuticals, organic dyes...) detected in water resources,  
38 thus representing a serious concern for the public health. Among these contaminants, dye  
39 wastewaters from the textile industry are particularly widespread (approx. 1 million kg of  
40 dyestuffs are emitted into the environment per year) (Foster et al., 2012) and pose numerous  
41 problems (affectation of photosynthesis in water plants, carcinogenicity, etc.). Consequently,  
42 the removal of colour from textile industry wastewaters represents a major environmental  
43 goal as it enables water reuse for further textile mill processing. However, dyes are designed  
44 to resist degradation and so this is not an easy task. Indeed, the new organic dyes coming to  
45 market have very stable molecular structures so conventional wastewater treatment techniques  
46 are usually ineffective for their degradation. As a consequence, new technologies for removal  
47 of dyes from wastewater have been investigated.

48 Advanced Oxidation Techniques and Processes (AOPs) are approaches allowing in situ  
49 decomposition of organic compounds in water through mineralization, i.e. conversion of the  
50 compound to carbon dioxide, water and inorganic intermediates (Glaze et al., 1987). AOPs  
51 have been developed to generate hydroxyl free radicals by different techniques (Al-Kdasi et  
52 al., 2004), and use these radicals as strong oxidants. More generally, the term AOP also refers  
53 to chemical processes and precursors that have high reduction potentials and either produce  
54 OH or directly attack organic molecules (ozone, atomic oxygen, excited nitrogen, ultrasound,  
55 UV light, and peroxide) (Foster et al., 2012). AOPs have been proven to be powerful and  
56 efficient treatment methods for degrading recalcitrant materials and toxic contaminants  
57 (Mohajerani et al., 2009).

58 In the last years, plasmas have begun to be employed to induce AOPs for water  
59 treatment purposes (Anpilov et al., 2001; Lukes et al., 2005; Sato and Yasuoka, 2008; Stratton

60 et al., 2015). More specifically, plasmas are sources of excited species, charged particles,  
61 radicals and UV radiation, among others, each of which are themselves advanced oxidation  
62 techniques (Foster et al., 2012). Different kinds of plasmas, using different configurations  
63 have been employed for water (and other liquids) treatment (Malik, 2010), particularly for the  
64 abatement of organic pollutants such as dyes (Clements et al., 1987; Yang et al., 2005;  
65 Magureanu et al., 2007; Dojčinović et al., 2011; Reddy et al., 2013), phenolic compounds  
66 (Sun et al., 2000; Krugly et al., 2015) and antibiotics (Magureanu et al., 2011; Kim et al.,  
67 2015).

68         Nowadays non-thermal plasmas, i.e. those whose electron temperature is different from  
69 the corresponding to ions and neutrals (gas temperature), are considered as a very promising  
70 technology. Their non-equilibrium properties including low power consumption and their  
71 ability to achieve enhanced gas phase chemistry at relatively low gas temperature, are  
72 responsible for the great attention that these plasmas have gained from an applied point of  
73 view and their extensive use in applications that require low temperatures, including material  
74 processing and synthesis, biomedical applications, and surface modification, among others  
75 (Park et al., 2001; Selwyn et al., 2001; Zille et al., 2015).

76         In particular, non-thermal atmospheric-pressure plasma jets/plumes play an increasingly  
77 important role in various plasma-assisted applications for several reasons (Walsh et al., 2006;  
78 Laroussi and Akan, 2007; Laroussi, 2009; Walsh et al., 2010; Lu et al., 2012). First of all, due  
79 to their practical capability in providing plasmas which are not spatially confined by  
80 electrodes and whose stability is not compromised by the presence of the sample to be  
81 processed. Plasma jets are able to generate stable discharges in a gas and then flush it to a  
82 separate region of reactive gas for processing applications (Walsh et al., 2006). This spatial  
83 separation enables a considerable flexibility in jet designs in order to achieve a good control in  
84 both plasma dynamics and reaction chemistry (Mora et al., 2010; Mora et al., 2011).

85 Secondly, because plasma jet configuration offers a chamberless delivery of downstream  
86 reaction chemistry if desired (Walsh et al., 2010). Finally, they are free from constraints  
87 imposed by vacuum-compatibility, as they operate at atmospheric pressure, being this an  
88 undeniable advantage in practical applications.

89 Atmospheric plasma jets can be generated in many different gases and using different  
90 electrical excitations. Several cold plasma jet devices have been designed; most of them are  
91 described in Laroussi and Akam review (Laroussi and Akan, 2007) although there are others  
92 more recently developed such as the plasmas generated by using nanosecond dc voltage  
93 pulses with kilohertz repetition frequencies as well as with sine-wave excitations in the  
94 kilohertz-to-megahertz range in pulsed or continuous mode (Chandana et al., 2015).

95 In the present work, we report for the first time on the design of a plasma jet reactor  
96 allowing liquid (water) treatment based on the use of a microwave (2.45 GHz) surface wave  
97 sustained discharge at atmospheric pressure (Ferreira and Moisan, 1993). This type of  
98 discharge generates non thermal plasmas with a high electron density (in the order of  $10^{14} \text{ cm}^{-3}$ ),  
99 and so a high reactivity (Henriques et al., 2011b). Microwave discharge reactors enable the  
100 generation of very stable and reproducible plasmas, that can operate over a broad range of  
101 experimental conditions (pressure, gas type, frequency, power, geometry), so being capable to  
102 produce copious and controlled amounts of active species. As far as the authors know, this is  
103 the first study where a microwave plasma jet of this type have been employed for water  
104 treatment.

105 More specifically, the reactor consisted of a plasma-jet over liquid configuration that  
106 was employed for degradation of methylene blue in aqueous solution. Remote exposure of the  
107 sample was done (Laroussi, 2009). In contrast to direct exposure (in which the sample is  
108 subject to all possible agents generated by the plasmas including heat, charged particles,

109 reactive neutrals, and electromagnetic radiation), in remote exposure the effect of charged  
110 particles on the water sample under treatment is weak as the sample is placed at some distance  
111 from the plasma and most of these species recombine before reaching it. The heat flux is also  
112 greatly reduced in this case, what leaves mainly the long-lived radicals to directly interact  
113 with the sample (Laroussi, 2009).

114

## 115 **2. Experimental part**

116

### 117 *2.1. Chemicals*

118 Methylene blue (MB) was selected as the model organic *contaminant* dye because of its  
119 stable molecular structure. Moreover, MB-laden waste water exhibit a high chroma and  
120 toxicity and has become an unmanageable industrial wastewater (Wang et al., 2013) whose  
121 treatment has being profusely studied in the last years. Methylene blue (Fig. S1) is a  
122 heterocyclic aromatic compound belonging to the phenothiazine family (C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl). It was  
123 purchased from Sigma-Aldrich and used without further purification.

124

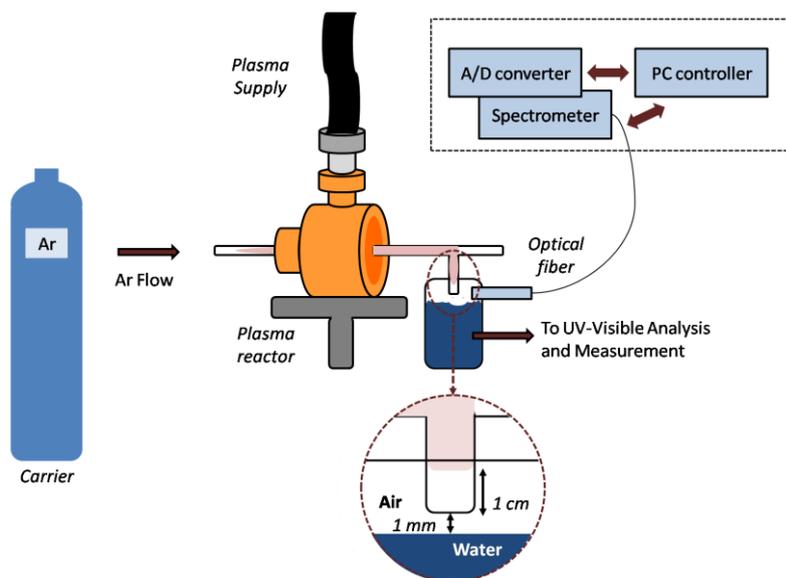
### 125 *2.2. Plasma reactor*

126 Fig. 1 shows the experimental set-up used for the generation of the plasma. A surfatron  
127 device (Moisan and Pelletier, 1992) was used to couple the energy coming from a microwave  
128 (2.45 GHz) generator (with a maximum stationary power of 200 W in continuous-wave  
129 mode) to the support gas (argon with a purity  $\geq 99.995$  %) within a quartz reactor tube of 1.5  
130 and 4 mm of inner and outer diameter, respectively, opened to the air as shown in Fig. 1.  
131 Surfatron was originally designed to generate cylindrical plasma columns inside straight  
132 dielectric tubes (Moisan and Pelletier, 1992), sustained by an azimuthally symmetric TM<sub>00</sub>  
133 surface wave mode (Henriques et al., 2011a). Nevertheless, in our experiments a T-shaped

134 tube with a closed end was employed in order to allow the plasma column go down through  
135 the vertical part of the tube and approach the water.

136

137



138

139 **Fig. 1.** Experimental set-up for the generation of plasma and OES measurements

140

### 141 2.3. Methods

142 In this work, the microwave power was set at 150 W and the argon flow rate (adjusted  
143 using a calibrated mass flow controller) ranged from 350 to 1400 sccm. The movable plunger  
144 and stubs permitted the impedance matching so that the best energy coupling could be  
145 achieved, making the power reflected back to the generator ( $P_r$ ) negligible (< 5%).

146 Plasma effluent downstream was directed to a solution of methylene blue (MB) dye in  
147 deionized water. The distance between the end of the plasma column and water was about 11  
148 mm, so that the sample suffered a remote plasma exposure (did not come in direct contact  
149 with the plasma at any time). Solutions with different MB concentrations (ranging from 5 to  
150 250 mg/L) were treated.

151 MB decomposition was monitored as a function of treatment time. In all cases, the water  
152 temperature never exceeded 55 °C. As shown in additional experiments, thermal degradation  
153 of the dye was negligible under these experimental conditions.

154

#### 155 2.4. Analysis

156 Optical Emission Spectroscopy (OES) techniques (sensitive, not invasive and very easy  
157 to implement tools) were employed to identify plasma active species reaching the water and  
158 triggering AOPs leading to dye degradation. Emission from the afterglow region next water  
159 was side-on collected using an optical fiber, and analyzed by using a Czerny-Turner type  
160 spectrometer of 1 m focal length equipped with a 2400 grooves/mm holographic grating and a  
161 photomultiplier (spectral output interval of 200-750 nm) as a detector. Spectra were recorded  
162 with a spectral resolution of 0.08 nm, and allowed us to gather information about different  
163 species that reach the water.

164 The degradation of the dye was followed by UV–visible absorption spectroscopy. Foster  
165 et al. (Foster et al., 2013) have shown that for methylene blue solutions this technique is a  
166 reasonable diagnostic to track actual dye concentrations. UV–visible absorption spectra of  
167 MB solutions before and after plasma treatment were measured by a spectrophotometer in the  
168 wavelength range 250–800 nm. The absorbance is proportional to the concentration of  
169 absorbing molecules, according to the Beer-Lambert law. The concentration of the dye in  
170 solution was determined from the absorption maximum at 668 nm, which was also employed  
171 for the calibration curves.

172 Conversion was calculated as:

$$173 \quad conv (\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

174 where  $C_0$  and  $C$  are initial and final concentrations of the MB solution, respectively.

175 The apparent kinetic constant ( $k$ ) was determined by fitting to a pseudo first order  
176 reaction:

$$177 \quad \ln\left(\frac{C_0}{C}\right) = kt \quad (2)$$

178 where  $t$  is the reaction time.

179 On the other hand, the energy yield, which measures the efficiency of the dye  
180 degradation process, has been defined as the ratio between the amount of methylene blue  
181 removed during plasma treatment and the consumed energy:

$$182 \quad \text{energy yield}(g / kWh) = Y = \frac{V(L) \times C_0(g / L) \times \text{conv}(\%) / 100}{P(kW) \times t(h)} \quad (3)$$

183 where  $V$  is the methylene blue solution volume and  $P$  is the microwave power supplied.

184 Peroxide-test strips (0.5–25 mg/L Mquant, Merck) based on a colorimetric method were  
185 used for  $H_2O_2$  determinations, and changes of pH and conductivity were measured with a  
186 Orion Star A329 (Thermo Scientific) digital meter. Test strips for ammonia (0.5-6.0 mg/L),  
187 nitrate (10-500 mg/L) and nitrite (1-80 mg/L) from Macherey-Nagel were also used.

188

### 189 **3. Results and Discussion**

#### 190 *3.1. OES spectra and plasma activated species*

191 The optical emission spectrum (Fig. S2) was measured downstream, 1 mm below the  
192 end of the plasma tube (position of the aqueous solution, see Fig. 1). Although this position  
193 was 11 mm distant from the end of the luminous plasma column and there was no apparent  
194 emission from this region, OES spectrum revealed the presence of some argon atomic (Ar I)  
195 system lines (696.54, 706.72, 738.40, 750.38, 763.51, 772.42 nm) corresponding to radiative  
196 de-excitations from  $4p$  and  $4p'$  to  $4s$  levels. Thus, the aqueous solution was placed at this  
197 separate region where some plasma species were still active and provide chemical reactivity.  
198 The plasma jet flushed out active species are able to reach the water.

199 Long-lived excited neutrals (argon metastables) should be likely the main energy  
 200 carriers for generation of new reactive species in the remote region of this microwave plasma  
 201 jet (Yu and Yasuda, 1998; Laroussi, 2009; García et al., 2010). At this region, pooling  
 202 Penning reactions of metastable argon atoms can generate argon atoms, argon ions  $\text{Ar}^+$  and  
 203 argon dimer ions  $\text{Ar}_2^+$  by means of metastable-metastable  $\text{Ar}^m$  ionization collisions and  
 204 metastable-metastable associative ionization (García et al., 2010).



207 and recombination reactions of ions  $\text{Ar}^+$  and  $\text{Ar}_2^+$  produce argon excited atoms  $\text{Ar}^*$ , justifying  
 208 the emission observed:



212 Although before reaching the water, plasma jet effluent came into contact with air,  
 213 emission lines corresponding to species containing nitrogen or oxygen (such as  $\text{N}_2$ ,  $\text{NO}$ ,  $\text{O}...$ )  
 214 were not detected. Particularly, energetic argon metastables ( $E \sim 11.5\text{-}11.8$  eV) are able to  
 215 cause excitation of nitrogen molecules through nearly-resonant excitation transfer reactions  
 216 leading to the emission of the Second Positive System ( $\text{C}^3\Pi_u - \text{B}^3\Pi_g$ ), typical of atmospheric  
 217 pressure argon plasma jets opened to the air (Jackson and King, 2003). The lack of these  
 218 emissions is probably a residence time issue due to the high speed of the plasma effluent in  
 219 this reactor (ranging between 3.3 and 13.2 m/s).

220 Optical emission spectroscopy techniques could not be used to measure plasma  
 221 characteristic parameters such as electron density, electron temperature or gas temperature in  
 222 this post-discharge region next to the water, because of the lack of emission of specific lines

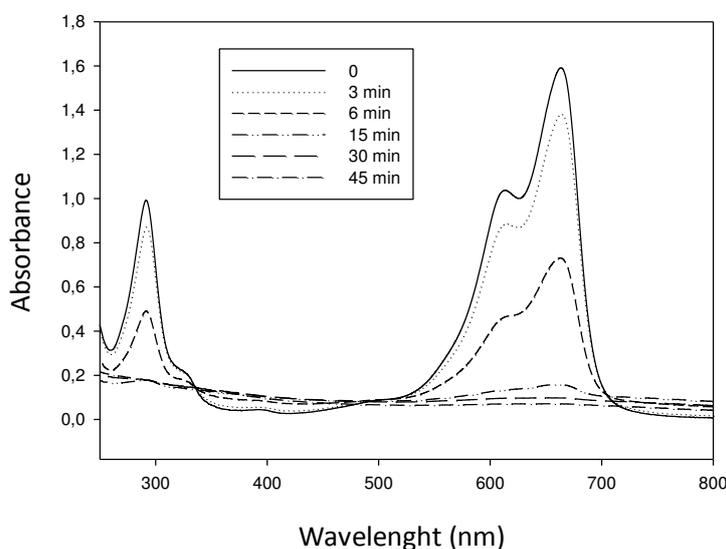
223 related to these diagnoses (Hydrogen Balmer Series lines or ro-vibrational bands of some  
224 molecular species such as OH, N<sub>2</sub>, CN...).

225

### 226 3.2. Influence of experimental conditions on the transformation of MB

227 The UV-visible spectra for an untreated MB solution and for plasma jet treated  
228 solutions during different time intervals in the range 3–45 min are shown in Fig. 2. In these  
229 experiments the initial dye concentration was 50 ppm, the solution volume was 40 mL and  
230 argon (gas feeding the plasma) was ran at a flow rate of 1400 sccm in the discharge. The  
231 absorption maxima intensity in the UV-visible spectra (at ca. 293, 609 and 668 nm) decreased  
232 with increasing treatment time and the solution became colourless after 30 minutes exposure  
233 to the plasma.

234



235

236 **Fig. 2.** UV-visible spectra for an untreated and plasma jet treated MB solution (50 ppm)  
237 during different time intervals

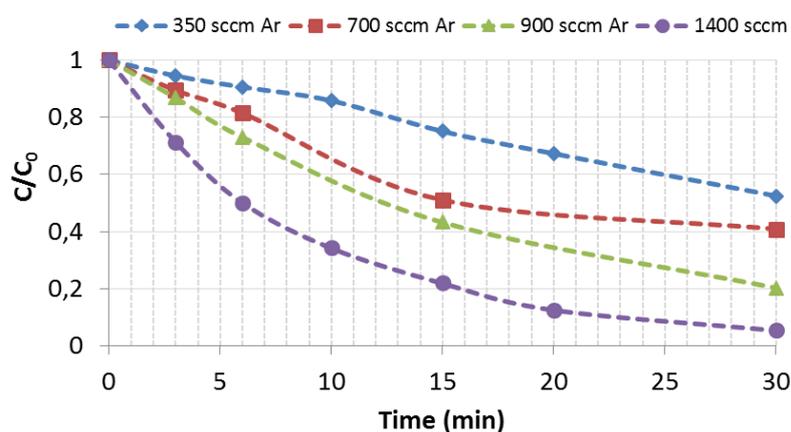
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239 Argon flow rate also had an important effect on the degradation of the dye, as illustrated  
240 in Fig. 3. The higher the argon flow rate, the faster the MB was decomposed. In order to

241 understand this fact, the intensity of Ar I line at 763.51 nm (proportional to the amount of  
242 argon atomic excited species reaching the water) was monitored for different argon flow rates  
243 (Fig.4). A linear increase was found as a result of the higher amount of plasma active species  
244 reaching the aqueous solution per unit of time (*vide infra*). In the range of experimental  
245 conditions studied, the energy efficiency of this reactor (measured from the energy yield at 50  
246 % conversion) increased with the argon flow rate (Fig. S3).

247 Under the reaction conditions studied, methylene blue degradation followed a pseudo-  
248 first-order kinetics. At an Ar flow rate of 1400 sccm, the apparent kinetic constant was 0.097  
249  $\text{min}^{-1}$  with a correlation coefficient ( $R^2$ ) of 0.997. This value is in the range of those found in  
250 the degradation of methylene blue in a pulsed tubular plasma reactor (Reddy et al., 2013) or  
251 an atmospheric pressure non-thermal plasma jet (Chandana et al., 2015), ca. between 0.03 and  
252  $0.15 \text{ min}^{-1}$ , and also in the degradation of reactive blue 19 in a needle-plate discharge system  
253 in argon and air, 0.017 and  $0.089 \text{ min}^{-1}$ , respectively (Sun et al., 2016). Much lower values  
254 (up to  $0.014 \text{ min}^{-1}$ ) were reported in a pulsed discharge plasma combined with activated  
255 carbon for the degradation of acid orange 7 (Guo et al., 2016).

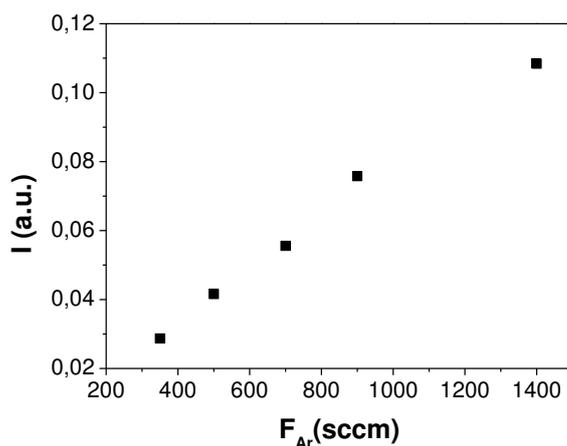
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257  
258

259 **Fig. 3.** Degradation of the dye over time (MB concentration 50 ppm) for plasma treatments  
260 using different argon flow rates

261



**Fig. 4.** Intensity of the Ar I line 763.51 nm measured next to the water for different argon flow rates

On the other hand, the possibility of improving plasma reactor efficiency in MB decomposition by operating with multiple plasma applicators in parallel was also investigated. For this purpose, a dual applicator using a sole surfatron was employed (Fig. S4). The source consisted of two identical quartz reactor tubes, and the total MW power injected to the system was kept at 150 W. The energy efficiency using dual-tube configuration (at 700 + 700 sccm) was much higher (with an energy yield at 50 % conversion of  $Y_{50\%} = 0.037$  g/kWh) than single-tube configuration (at 700 sccm) efficiency ( $Y_{50\%} = 0.012$  g/kWh).

Similar MB transformation curves over time were obtained for single-tube configuration reactor working at 1400 sccm and dual-tube configuration working at (700 + 700) sccm. A similar result was found for 700 sccm and (350 + 350) sccm in single and dual-tube configurations, respectively. From these results it can be inferred that, in the range of the argon flow rate considered, the amount of species reaching water rather than their speed played the most relevant role in the MB decomposition process. The slightly higher efficiency of dual versus single configuration could be most likely ascribed to the larger volume of humid air affected by the plasma in the former case. Thus, the apparent kinetic constant was

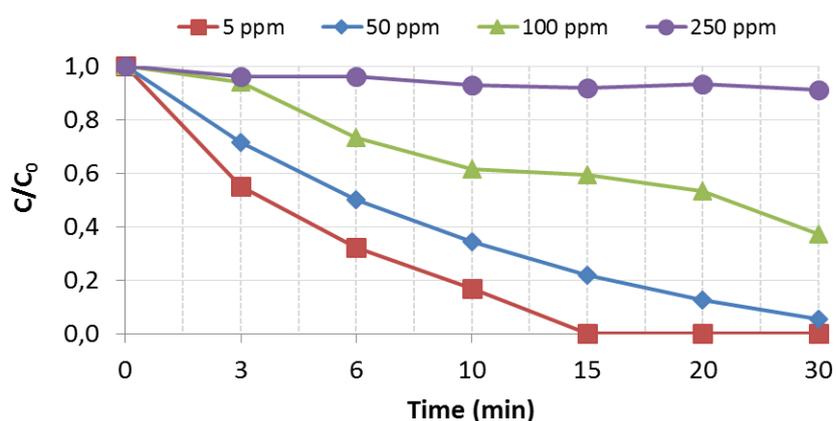
281 0.118 min<sup>-1</sup> for dual-tube configuration working at (700 + 700) sccm, whereas it was 0.097  
282 min<sup>-1</sup> for single-tube configuration reactor working at 1400 sccm.

283 The initial concentration of the dye in solution was another parameter affecting the MB  
284 degradation rate. The relative decomposition of methylene blue decreased with increasing the  
285 initial dye concentration (Fig. 5). Table 1 also illustrates that MB degradation at low dye  
286 concentration is much more effective in terms of the energy yield. Also, the apparent kinetic  
287 constant increased with the decrease in dye concentration from 0.097 min<sup>-1</sup> at 50 ppm to 0.177  
288 min<sup>-1</sup> at 5 ppm. At higher concentrations, likely intermediates formed can interact with each  
289 other and compete with dye decomposition (Zhu et al., 2014).

290 The degradation pathways of MB have been recently studied with hydroxyl radicals  
291 being a key factor during the process. Several intermediate compounds have been detected by  
292 demethylation, deamination and ring cleavage, among other reactions, and the resulting  
293 mixture has been shown to be totally nontoxic (Huang et al., 2010; Bansode et al., 2017)

294

295



296

297 **Fig. 5.** Degradation of the dye over time for plasma treatments of MB aqueous solutions  
298 of different initial concentrations (argon flow rate 1400 sccm).

299

300

301 **Table 1**302 Energy yield at 50 % conversion ( $F_{Ar} = 1400$  sccm).

Dye concentration (ppm)	$Y_{50\%}$ (g/kWh)
5	0.296
50	0.033
100	0.018
250	0.007 <sup>a</sup>

303 <sup>a</sup> Maximum value registered (50% conversion was not reached)

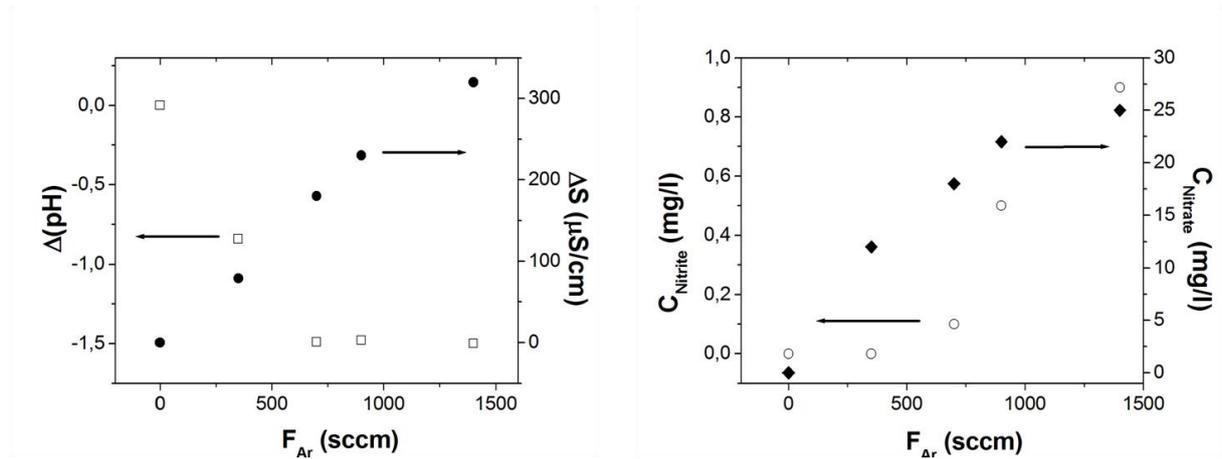
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305 *3.3. Plasma jet influence on water properties*

306 In order to gain further insight into the chemical activity of this plasma reactor, changes  
307 in deionized water properties induced by the application of the plasma afterglow were  
308 investigated. Thus, the ability of this plasma reactor to generate H<sub>2</sub>O<sub>2</sub>, and the changes of pH  
309 and conductivity in pure water caused by the treatment were studied. Since the most important  
310 pathway for H<sub>2</sub>O<sub>2</sub> formation is by combination of OH radicals, H<sub>2</sub>O<sub>2</sub> is considered as an  
311 indicator for hydroxyl radical formation in plasma in contact with water (Locke and Shih,  
312 2011; Magureanu et al., 2013). These radicals are very active species able to degrade organic  
313 pollutants. Plasma jet treatment generated H<sub>2</sub>O<sub>2</sub> species in water in all the cases studied  
314 (Table S1).

315 This plasma reactor was able to generate up to 5 mg/L of H<sub>2</sub>O<sub>2</sub> after 30 min treatment  
316 on a 40 mL water sample. This amount increased to 25 mg/L when the sample volume  
317 reduced to 8 mL. These amounts are similar to those found in other discharge processes  
318 (Yang et al., 2005). The energy yield for hydrogen peroxide formation for the most favourable  
319 case studied ( $F_{Ar} = 1400$  sccm) was 2.7 mg/(kW·h), falling in the range of the values reported  
320 for different electric discharges above liquids (Locke and Shih, 2011). The generation rate in  
321 this case was  $4.1 \cdot 10^{-4}$  g/h.

322 Two experiments consisting of a pure chemical treatment, i.e., without plasma, were  
 323 conducted to check the influence of H<sub>2</sub>O<sub>2</sub> in the degradation of MB. They were carried out  
 324 with H<sub>2</sub>O<sub>2</sub> concentrations of 10 and 100 mg/L for the treatment of 50 mg/L of MB and  
 325 revealed that there was no dye degradation under stirring for 30 min at room temperature.  
 326



327  
 328 **Fig. 6.** Changes of electrical conductivity and pH (left) and concentrations of nitrite and  
 329 nitrate (right) in water after plasma treatment as a function of argon flow rate

330  
 331 Conductivity of the water underwent an increase after plasma jet treatment as shown in  
 332 Fig. 6, having again a linear dependence with argon flow rate. This result can be explained by  
 333 the dissolution of species formed in the gas phase by the action of the plasma jet and  
 334 subsequent hydrolytic reactions in the liquid phase leading to the generation of different ions.  
 335 A small reduction of water pH was detected upon plasma jet exposure, also decreasing with  
 336 argon flow rate. Species NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> were detected in water upon plasma treatment (see  
 337 Fig. 6) and their formation usually involves an increase of the water acidity due to the  
 338 concomitant formation of H<sub>3</sub>O<sup>+</sup> ions (*vide infra*). The measured concentration of both NO<sub>2</sub><sup>-</sup>  
 339 and NO<sub>3</sub><sup>-</sup> were in the range of those reported by other authors in different discharge plasmas  
 340 in contact with water (Lukes et al., 2014). Moreover, ammonia was not detected in the water.  
 341

342 *3.4. Formation of H<sub>2</sub>O<sub>2</sub> species and methylene blue degradation*

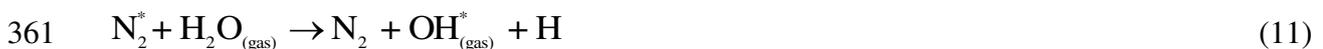
343 Combinations of charged particles, ozone, hydrogen peroxide and UV radiation have  
344 been shown as a way to produce hydroxyl radicals in water and to effectively degrade many  
345 organic compounds (Lukes and Locke, 2005). Plasma is a source of all these species. Ozone  
346 has been claimed to play an important role in the degradation of dyes (Yang et al., 2005).  
347 However, ozone formation is practically suppressed in air due to the reaction of oxygen atoms  
348 with nitrogen (Deng et al., 2013; Sun et al., 2016). In the present case, plasma jet mainly  
349 delivers argon excited species, photons and heat at the remote region next to water. Argon  
350 species (excited or metastables) striking on the water surface are likely leading to water  
351 dissociation in hydroxyl and hydrogen radicals at the interface region (Magureanu et al.,  
352 2008) (Fig. S5).



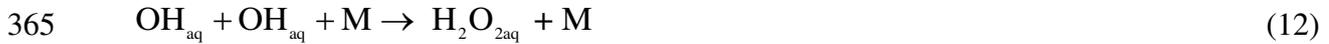
354 Also, as some water evaporation is expected, these reactions might also have taken  
355 place at the gas phase consisting of humid air. In this region (gas phase), plasma jet species  
356 should also be interacting with surrounding air molecules. Excitation transfer from argon  
357 metastables to ground state of molecular nitrogen is the main mechanism provoking nitrogen  
358 molecules excitation (Timmermans et al., 1998):



360 These species might cause further dissociation of water molecules (Magureanu et al., 2008):



362 OH species formed in the gas phase reach the water solvating, and so producing OH<sub>aq</sub>.  
 363 Finally, OH<sub>aq</sub> species in water react in the presence of a third molecule to give hydrogen  
 364 peroxide, eventually difusing to the bulk liquid (Locke and Shih, 2011) :



366 Since H<sub>2</sub>O<sub>2</sub> itself did not degrade MB, as discussed above, OH radicals will most likely  
 367 be the main reactive species responsible for the degradation of dye molecules. In the case of  
 368 the dual-tube configuration, a greater contact with the humid air and a bigger generation of  
 369 these species would explain the best efficiency for MB degradation of this approach.

370 On the other hand, the presence of nitrites and nitrates in treated water can be explained  
 371 by reactions implying long-lived species N<sub>x</sub>O<sub>y</sub> generated in the gas phase (where plasma came  
 372 in contact with air) solvating into the liquid (Lietz and Kushner, 2016). Reactions of N<sub>x</sub>O<sub>y</sub><sub>aq</sub>  
 373 (solvated) gave rise to formation of acids *HNO<sub>x</sub>aq* and explain the observed decrease in pH  
 374 upon the treatment with plasma (Lukes et al., 2014).



379

380 Finally, in order to gain an insight into the importance of these mechanisms, argon,  
 381 nitrogen and synthetic air were added in the gas region in contact to the liquid surface. The  
 382 external injection of argon gas into the region where the discharge makes contact with the  
 383 liquid improves slightly the MB conversion, unlike air or nitrogen, thus suggesting the role of  
 384 argon species in these processes (Fig. S6).

385 A linear dependence of the MB transformation on the density of Ar I (*4p*) species as  
386 inferred from argon emission was observed (Fig. S7). This supports the outstanding role of  
387 the abovementioned mechanism mediated by argon excited species. Thus, the larger the  
388 concentration of excited argon species, the higher the transformation of MB.

389

#### 390 **4. Conclusions**

391 In this work, the use of a microwave (2.45 GHz) plasma jet for treatment of MB-laden  
392 water was investigated. Dye degradation was followed by UV–visible spectroscopy, and  
393 Optical Emission Spectroscopy (OES) techniques (sensitive, non-invasive and very easily  
394 implementable tools) were employed to identify plasma active species triggering AOPs  
395 leading to dye degradation. The degradation of the dye methylene blue was more efficient at  
396 low dye concentration. Also, an increase in the argon flow rate produced a higher degradation  
397 rate and, in fact, the possibility of using two plasma applicators in parallel have been  
398 demonstrated. Indeed, multiple applicators were found to be slightly more efficient than a  
399 single applicator even with equal total flow and total input power. For sample volumes lower  
400 or equal to 50 mL, values of energy yield at 50 % of dye conversion ranged between 0.033  
401 and 0.296 g/kWh, among the best values reported in the literature (Sato and Yasuoka, 2008).  
402 The plasma reactor was able to generate hydrogen peroxide species in pure water, whose  
403 concentration increased with the plasma argon flow rate. For the most favourable case  
404 studied, the energy yield for H<sub>2</sub>O<sub>2</sub> formation was 2.7 mg/(kW·h), falling in the range of  
405 values reported in the literature for different electric discharges above liquids (Locke and  
406 Shih, 2011). Also, several experiments proved that argon excited species plays an important  
407 role in the formation of the active species that at last degrade the organic pollutant.

408

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413

## 414 **References**

415

- 416 Al-Kdasi, A., Idris, A., Saed, K., Guan, C.T., 2004. Treatment of textile wastewater by  
417 advanced oxidation processes—a review. *Global nest: the Int. J* 6, 222-230.
- 418 Anpilov, A., Barkhudarov, E., Bark, Y.B., Zadiraka, Y.V., Christofi, M., Kozlov, Y.N.,  
419 Kossyi, I., Kop'ev, V., Silakov, V., Taktakishvili, M., 2001. Electric discharge in water as a  
420 source of UV radiation, ozone and hydrogen peroxide. *Journal of Physics D: Applied Physics*  
421 34, 993.
- 422 Bansode, A.S., More, S.E., Siddiqui, E.A., Satpute, S., Ahmad, A., Bhoraskar, S.V., Mathe,  
423 V.L., 2017. Effective degradation of organic water pollutants by atmospheric non-thermal  
424 plasma torch and analysis of degradation process. *Chemosphere* 167, 396-405.
- 425 Clements, J.S., Sato, M., Davis, R.H., 1987. Preliminary investigation of prebreakdown  
426 phenomena and chemical reactions using a pulsed high-voltage discharge in water. *IEEE*  
427 *Transactions on industry applications*, 224-235.
- 428 Chandana, L., Reddy, P.M.K., Subrahmanyam, C., 2015. Atmospheric pressure non-thermal  
429 plasma jet for the degradation of methylene blue in aqueous medium. *Chemical Engineering*  
430 *Journal* 282, 116-122.
- 431 Deng, X., Nikiforov, A.Y., Vanraes, P., Leys, C., 2013. Direct current plasma jet at  
432 atmospheric pressure operating in nitrogen and air. *Journal of Applied Physics* 113, 023305.
- 433 Dojčinović, B.P., Roglič, G.M., Obradović, B.M., Kuraica, M.M., Kostić, M.M., Nešić, J.,  
434 Manojlović, D.D., 2011. Decolorization of reactive textile dyes using water falling film  
435 dielectric barrier discharge. *Journal of hazardous materials* 192, 763-771.
- 436 Ferreira, C., Moisan, M., 1993. *Fundamentals and Applications*. Nato ASI Series, Series B,  
437 *Physics* 302.
- 438 Foster, J., Sommers, B.S., Gucker, S.N., Blankson, I.M., Adamovsky, G., 2012. Perspectives  
439 on the Interaction of Plasmas With Liquid Water for Water Purification. *IEEE Transactions*  
440 *on Plasma Science* 40, 1311-1323.
- 441 Foster, J.E., Adamovsky, G., Gucker, S.N., Blankson, I.M., 2013. A comparative study of the  
442 time-resolved decomposition of methylene blue dye under the action of a nanosecond  
443 repetitively pulsed DBD plasma jet using liquid chromatography and spectrophotometry.  
444 *IEEE Transactions on Plasma Science* 41, 503-512.
- 445 García, M., Varo, M., Martínez, P., 2010. Excitation of species in an expanded argon  
446 microwave plasma at atmospheric pressure. *Plasma Chemistry and Plasma Processing* 30,  
447 241-255.
- 448 Glaze, W.H., Kang, J.-W., Chapin, D.H., 1987. *The Chemistry of Water Treatment Processes*  
449 *Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation*. *Ozone: Science &*  
450 *Engineering* 9, 335-352.
- 451 Guo, H., Wang, H., Wu, Q., Zhou, G., Yi, C., 2016. Kinetic analysis of acid orange 7  
452 degradation by pulsed discharge plasma combined with activated carbon and the synergistic  
453 mechanism exploration. *Chemosphere* 159, 221-227.

454 Henriques, J., Tatarova, E., Dias, F., Ferreira, C., 2011a. Microwave N<sub>2</sub>-Ar plasma torch. II.  
455 Experiment and comparison with theory. *Journal of Applied Physics* 109, 023302.  
456 Henriques, J., Tatarova, E., Ferreira, C., 2011b. Microwave N<sub>2</sub>-Ar plasma torch. I. Modeling.  
457 *Journal of Applied Physics* 109, 023301.  
458 Huang, F., Chen, L., Wang, H., Yan, Z., 2010. Analysis of the degradation mechanism of  
459 methylene blue by atmospheric pressure dielectric barrier discharge plasma. *Chemical*  
460 *Engineering Journal* 162, 250-256.  
461 Jackson, G.P., King, F.L., 2003. Probing excitation/ionization processes in millisecond-pulsed  
462 glow discharges in argon through the addition of nitrogen. *Spectrochimica Acta Part B:*  
463 *Atomic Spectroscopy* 58, 185-209.  
464 Kim, K.-S., Kam, S.K., Mok, Y.S., 2015. Elucidation of the degradation pathways of  
465 sulfonamide antibiotics in a dielectric barrier discharge plasma system. *Chemical Engineering*  
466 *Journal* 271, 31-42.  
467 Krugly, E., Martuzevicius, D., Tichonovas, M., Jankunaite, D., Rumskaitė, I., Sedlina, J.,  
468 Racys, V., Baltrusaitis, J., 2015. Decomposition of 2-naphthol in water using a non-thermal  
469 plasma reactor. *Chemical Engineering Journal* 260, 188-198.  
470 Laroussi, M., 2009. Low-temperature plasmas for medicine? *IEEE Transactions on Plasma*  
471 *Science* 37, 714-725.  
472 Laroussi, M., Akan, T., 2007. Arc - Free Atmospheric Pressure Cold Plasma Jets: A Review.  
473 *Plasma Processes and Polymers* 4, 777-788.  
474 Lietz, A.M., Kushner, M.J., 2016. Air plasma treatment of liquid covered tissue: long  
475 timescale chemistry. *Journal of Physics D: Applied Physics* 49, 425204.  
476 Locke, B.R., Shih, K.-Y., 2011. Review of the methods to form hydrogen peroxide in  
477 electrical discharge plasma with liquid water. *Plasma Sources Science and Technology* 20,  
478 034006.  
479 Lu, X., Laroussi, M., Puech, V., 2012. On atmospheric-pressure non-equilibrium plasma jets  
480 and plasma bullets. *Plasma Sources Science and Technology* 21, 034005.  
481 Lukes, P., Clupek, M., Babicky, V., Janda, V., Sunka, P., 2005. Generation of ozone by  
482 pulsed corona discharge over water surface in hybrid gas-liquid electrical discharge reactor.  
483 *Journal of Physics D: Applied Physics* 38, 409.  
484 Lukes, P., Dolezalova, E., Sisrova, I., Clupek, M., 2014. Aqueous-phase chemistry and  
485 bactericidal effects from an air discharge plasma in contact with water: evidence for the  
486 formation of peroxyxynitrite through a pseudo-second-order post-discharge reaction of H<sub>2</sub>O<sub>2</sub>  
487 and HNO<sub>2</sub>. *Plasma Sources Science and Technology* 23, 015019.  
488 Lukes, P., Locke, B.R., 2005. Plasmachemical oxidation processes in a hybrid gas-liquid  
489 electrical discharge reactor. *Journal of Physics D: Applied Physics* 38, 4074.  
490 Magureanu, M., Bradu, C., Piroi, D., Mandache, N.B., Parvulescu, V., 2013. Pulsed corona  
491 discharge for degradation of methylene blue in water. *Plasma Chemistry and Plasma*  
492 *Processing* 33, 51-64.  
493 Magureanu, M., Mandache, N.B., Parvulescu, V.I., 2007. Degradation of organic dyes in  
494 water by electrical discharges. *Plasma Chemistry and Plasma Processing* 27, 589-598.  
495 Magureanu, M., Piroi, D., Gherendi, F., Mandache, N.B., Parvulescu, V., 2008.  
496 Decomposition of methylene blue in water by corona discharges. *Plasma Chemistry and*  
497 *Plasma Processing* 28, 677-688.  
498 Magureanu, M., Piroi, D., Mandache, N., David, V., Medvedovici, A., Bradu, C., Parvulescu,  
499 V., 2011. Degradation of antibiotics in water by non-thermal plasma treatment. *water research*  
500 45, 3407-3416.  
501 Malik, M.A., 2010. Water purification by plasmas: which reactors are most energy efficient?  
502 *Plasma Chemistry and Plasma Processing* 30, 21-31.

503 Mohajerani, M., Mehrvar, M., Ein-Mozaffari, F., 2009. An overview of the integration of  
504 advanced oxidation technologies and other processes for water and wastewater treatment. *Int J*  
505 *Eng* 3, 120-146.

506 Moisan, M., Pelletier, J., 1992. *Microwave Induced Plasmas, Plasma Technology, Vol. 4.*  
507 Elsevier Science Publishing, The Netherlands.

508 Mora, M., del Carmen García, M., Jiménez-Sanchidrián, C., Romero-Salguero, F.J., 2010.  
509 Transformation of light paraffins in a microwave-induced plasma-based reactor at reduced  
510 pressure. *international journal of hydrogen energy* 35, 4111-4122.

511 Mora, M., García, M.C., Jiménez - Sanchidrián, C., Romero - Salguero, F.J., 2011.  
512 Selectivity Control in a Microwave Surface - Wave Plasma Reactor for Hydrocarbon  
513 Conversion. *Plasma Processes and Polymers* 8, 709-717.

514 Park, J., Henins, I., Herrmann, H., Selwyn, G., Hicks, R., 2001. Discharge phenomena of an  
515 atmospheric pressure radio-frequency capacitive plasma source. *Journal of Applied Physics*  
516 89, 20-28.

517 Reddy, P.M.K., Raju, B.R., Karuppiah, J., Reddy, E.L., Subrahmanyam, C., 2013.  
518 Degradation and mineralization of methylene blue by dielectric barrier discharge non-thermal  
519 plasma reactor. *Chemical Engineering Journal* 217, 41-47.

520 Sato, K., Yasuoka, K., 2008. Pulsed discharge development in oxygen, argon, and helium  
521 bubbles in water. *IEEE Transactions on Plasma Science* 36, 1144-1145.

522 Selwyn, G., Herrmann, H., Park, J., Henins, I., 2001. Materials processing using an  
523 atmospheric pressure, RF-generated plasma source. *Contributions to Plasma Physics* 41, 610-  
524 619.

525 Stratton, G.R., Bellona, C.L., Dai, F., Holsen, T.M., Thagard, S.M., 2015. Plasma-based water  
526 treatment: conception and application of a new general principle for reactor design. *Chemical*  
527 *Engineering Journal* 273, 543-550.

528 Sun, B., Sato, M., Clements, J., 2000. Oxidative processes occurring when pulsed high  
529 voltage discharges degrade phenol in aqueous solution. *Environmental science & technology*  
530 34, 509-513.

531 Sun, Y., Liu, Y., Li, R., Xue, G., Ognier, S., 2016. Degradation of reactive blue 19 by needle-  
532 plate non-thermal plasma in different gas atmospheres: Kinetics and responsible active  
533 species study assisted by CFD calculations. *Chemosphere* 155, 243-249.

534 Timmermans, E., Jonkers, J., Thomas, I., Rodero, A., Quintero, M., Sola, A., Gamero, A.,  
535 Van Der Mullen, J., 1998. The behavior of molecules in microwave-induced plasmas studied  
536 by optical emission spectroscopy. 1. Plasmas at atmospheric pressure. *Spectrochimica Acta*  
537 *Part B: Atomic Spectroscopy* 53, 1553-1566.

538 Walsh, J.L., Iza, F., Janson, N.B., Law, V., Kong, M.G., 2010. Three distinct modes in a cold  
539 atmospheric pressure plasma jet. *Journal of Physics D: Applied Physics* 43, 075201.

540 Walsh, J.L., Shi, J., Kong, M.G., 2006. Contrasting characteristics of pulsed and sinusoidal  
541 cold atmospheric plasma jets. *Applied Physics Letters* 88, 171501.

542 Wang, X., Li, Z., Zeng, J., Zhang, X., Lei, L., 2013. Improvement of atmospheric water  
543 surface discharge with water resistive barrier. *Plasma Chemistry and Plasma Processing* 33,  
544 691-705.

545 Yang, B., Zhou, M., Lei, L., 2005. Synergistic effects of liquid and gas phase discharges using  
546 pulsed high voltage for dyes degradation in the presence of oxygen. *Chemosphere* 60, 405-  
547 411.

548 Yu, Q., Yasuda, H., 1998. An optical emission study on expanding low-temperature cascade  
549 arc plasmas. *Plasma Chemistry and Plasma Processing* 18, 461-485.

550 Zhu, D., Jiang, L., Liu, R.-l., Chen, P., Lang, L., Feng, J.-w., Yuan, S.-j., Zhao, D.-y., 2014.  
551 Wire-cylinder dielectric barrier discharge induced degradation of aqueous atrazine.  
552 *Chemosphere* 117, 506-514.

553 Zille, A., Oliveira, F.R., Souto, A.P., 2015. Plasma treatment in textile industry. Plasma  
554 Processes and Polymers 12, 98-131.  
555  
556

**Table 1**[Click here to download Table: Table 1.docx](#)**Table 1**Energy yield at 50 % conversion ( $F_{Ar} = 1400$  sccm).

Dye concentration (ppm)	$Y_{50\%}$ (g/kWh)
5	0.296
50	0.033
100	0.018
250	0.007 <sup>a</sup>

<sup>a</sup>Maximum value registered (50% conversion was not reached)

Figure 1  
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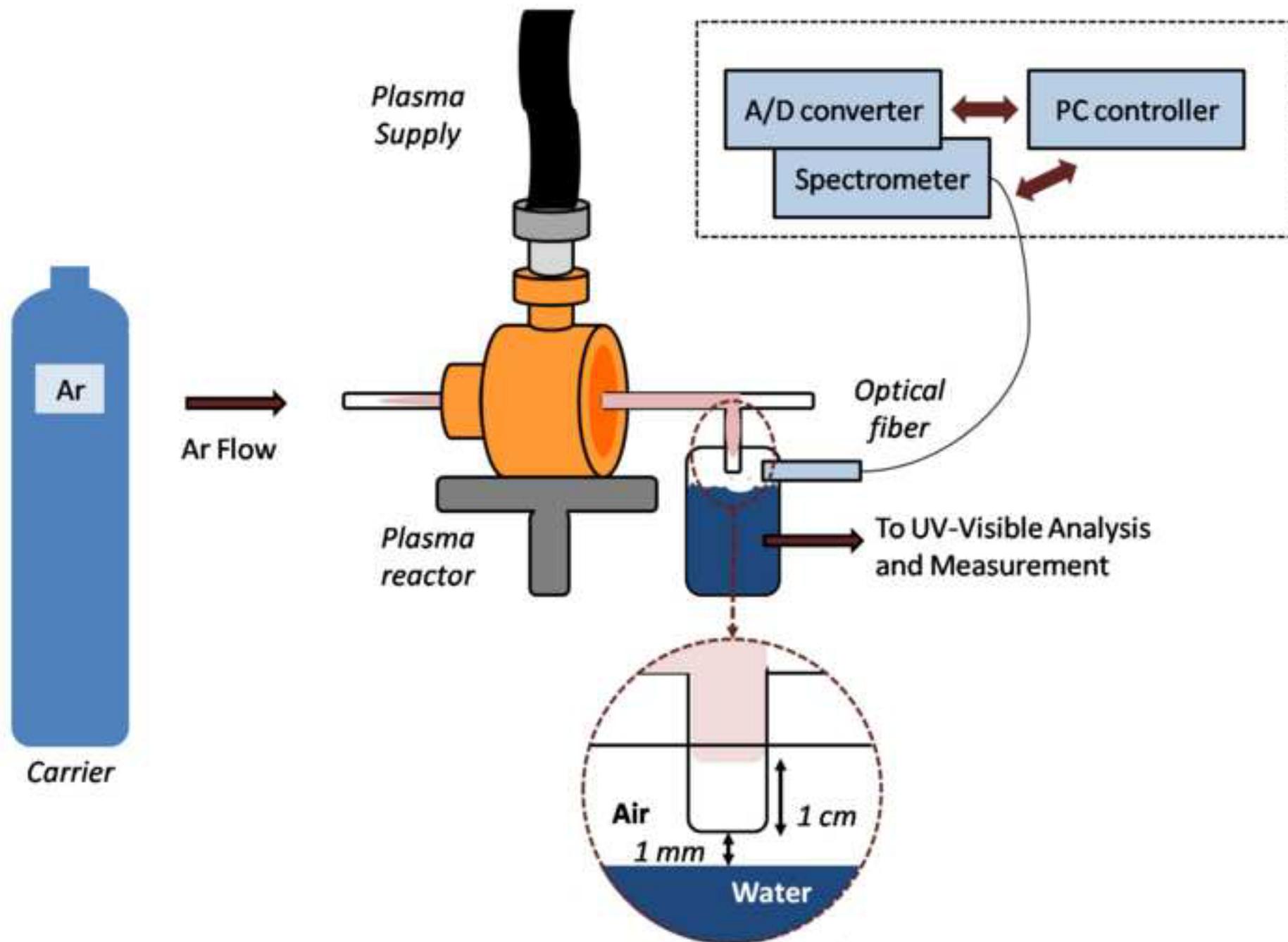


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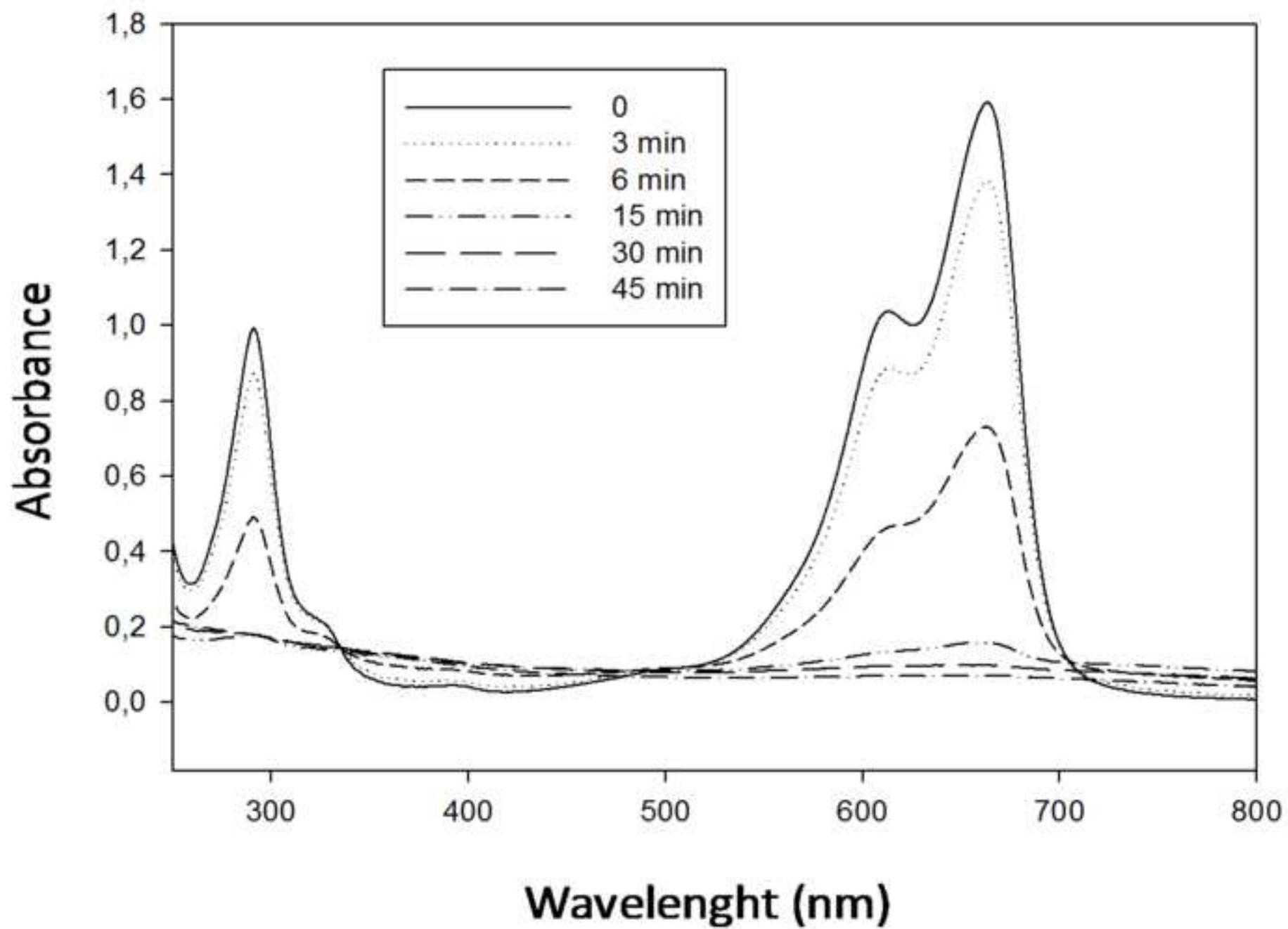


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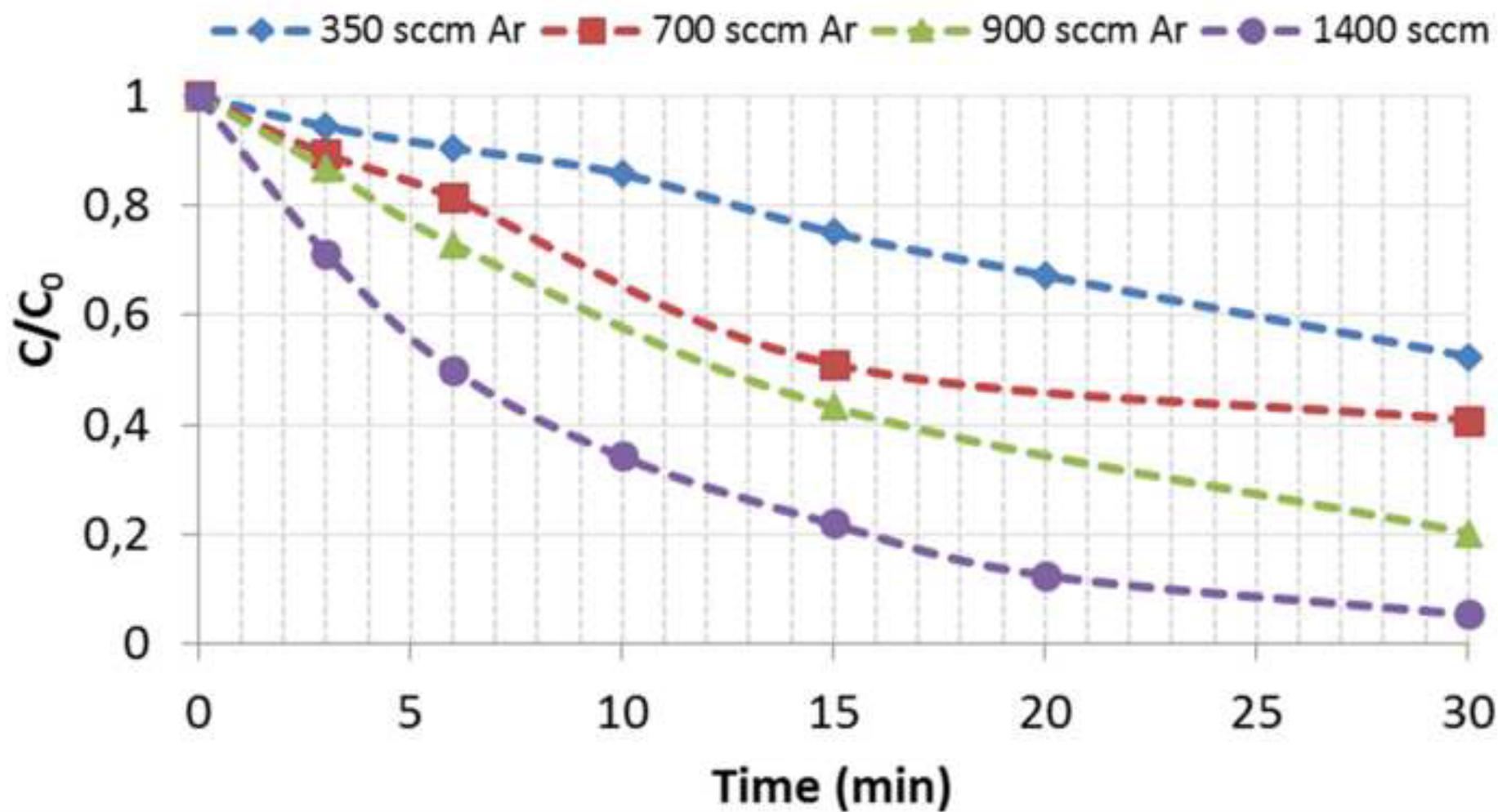


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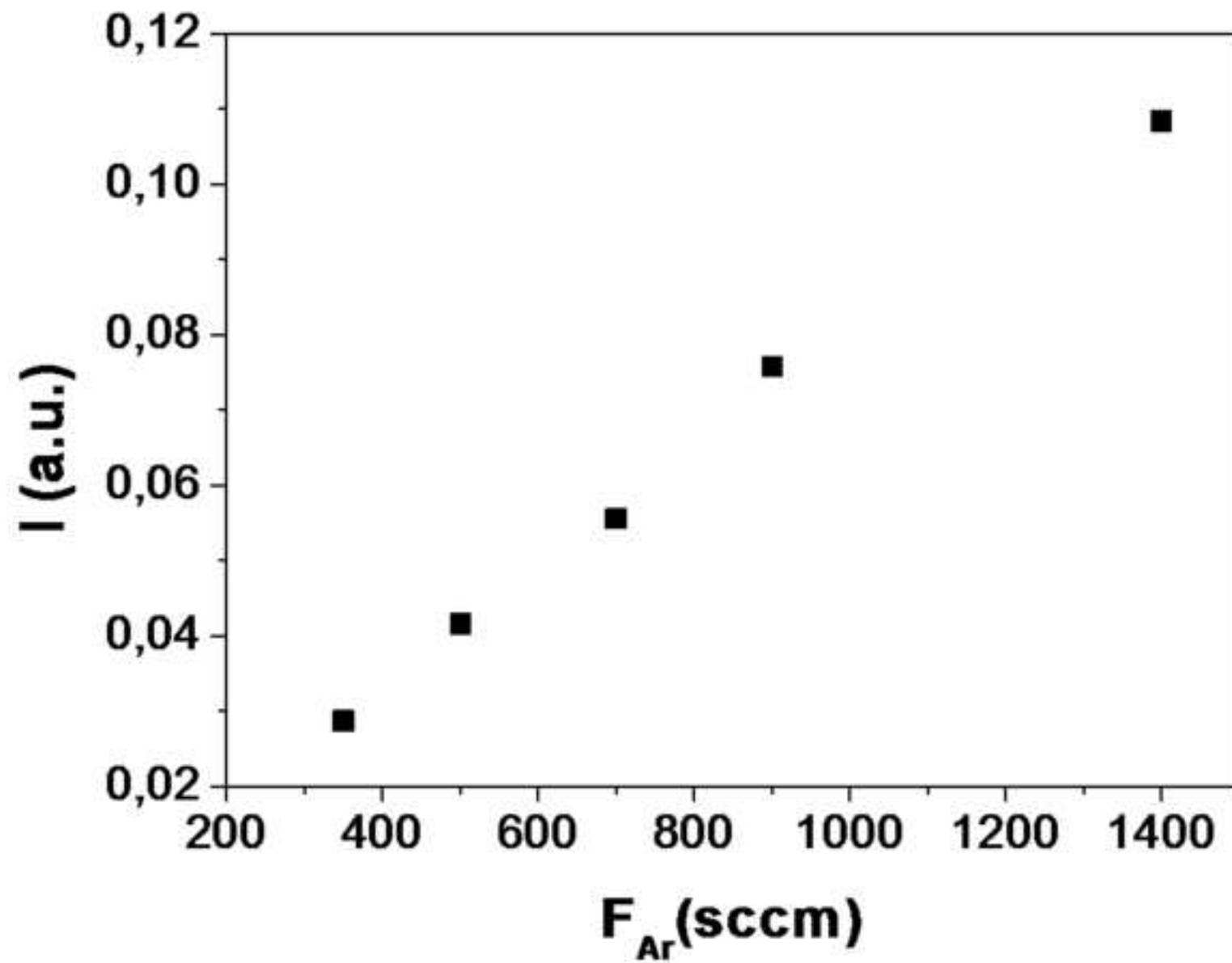


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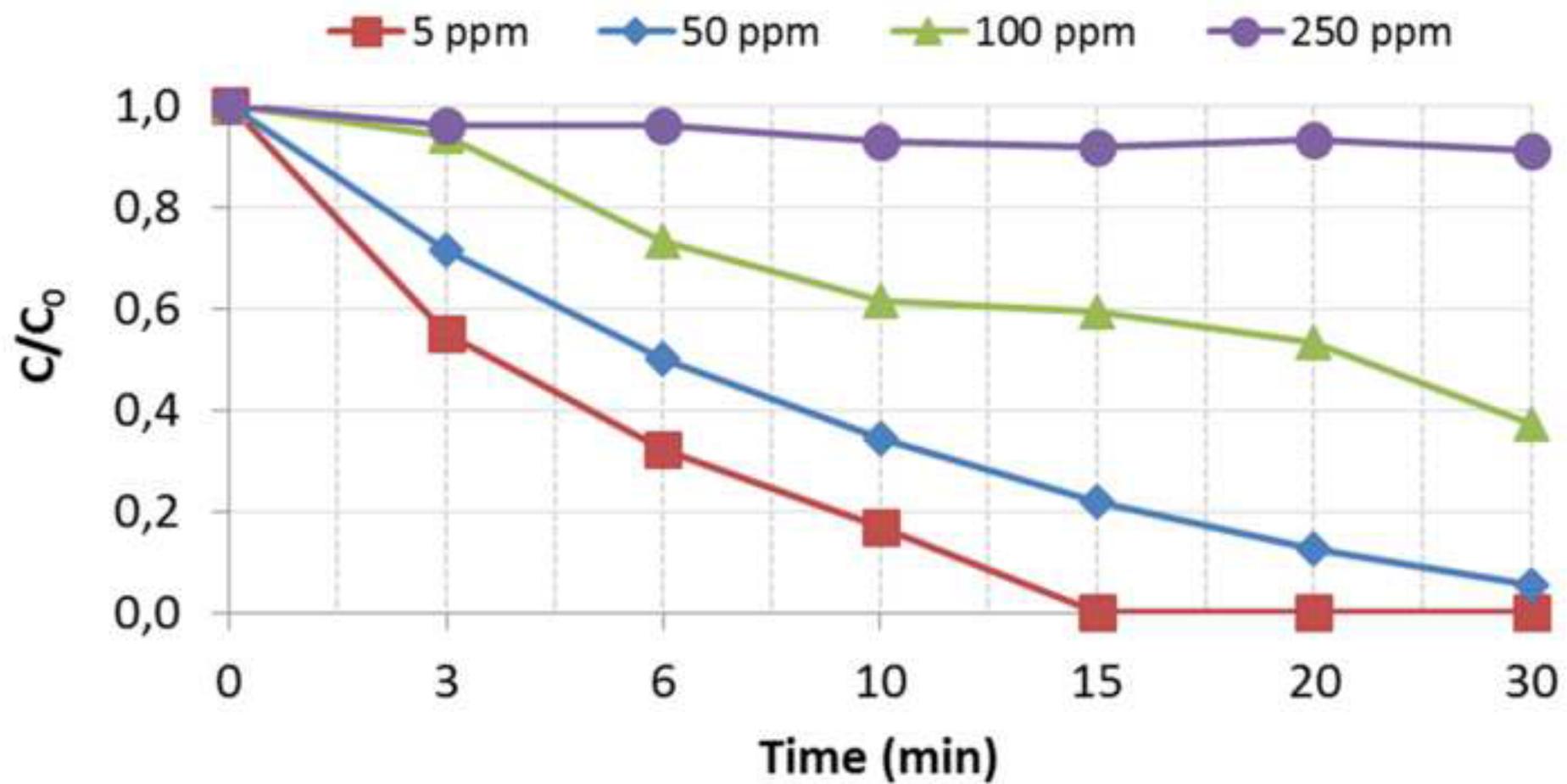
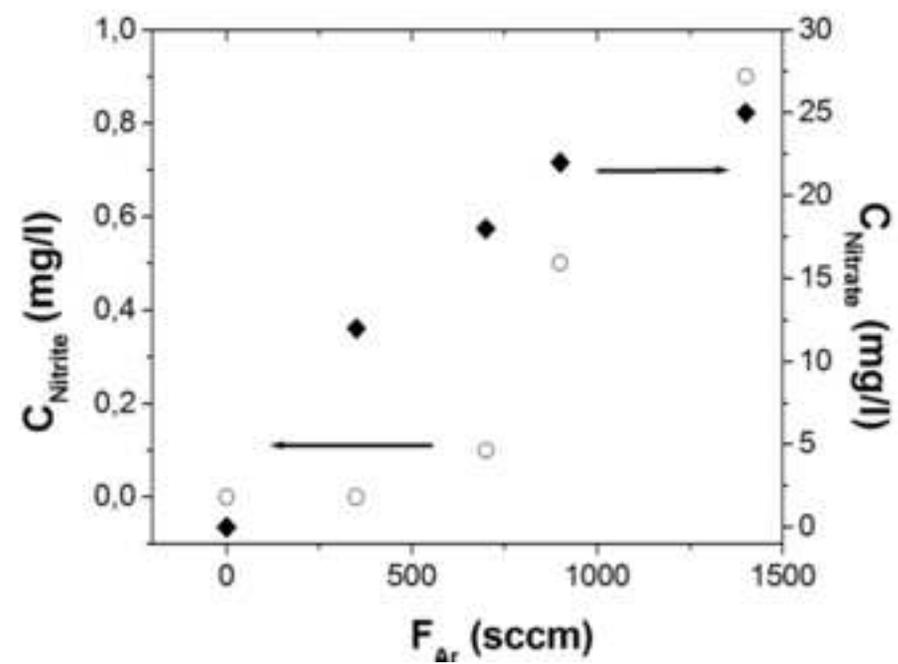
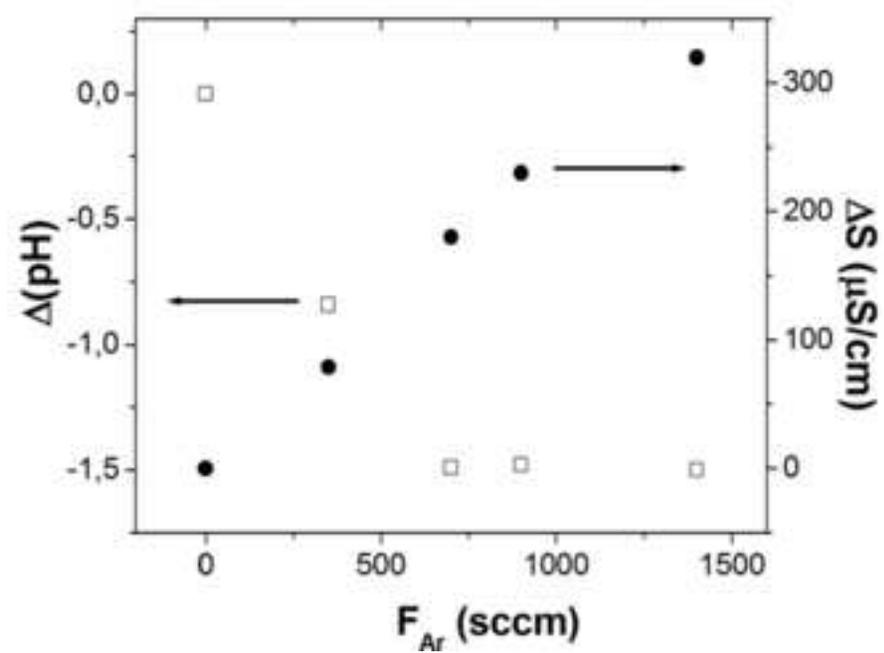


Figure 6  
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## FIGURE CAPTIONS

**Fig. 1.** Experimental set-up for the generation of plasma and OES measurements

**Fig. 2.** UV–visible spectra for an untreated and plasma jet treated MB solution (50 ppm) during different time intervals

**Fig. 3.** Degradation of the dye over time (MB concentration 50 ppm) for plasma treatments using different argon flow rates

**Fig. 4.** Intensity of the Ar I line 763.51 nm measured next to the water for different argon flow rates

**Fig. 5.** Degradation of the dye over time for plasma treatments of MB aqueous solutions of different initial concentrations (argon flow rate 1400 sccm).

**Fig. 6.** Changes of electrical conductivity and pH (left) and concentrations of nitrite and nitrate (right) in water after plasma treatment as a function of argon flow rate

**Supplementary Material**

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