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Features and application of coupled cold plasma and photocatalysis processes for decontamination of water

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Abstract

Dielectric barrier discharge plasma and photocatalysis have been proposed as tools for decontamination of process water, especially in food industry. The present investigation aims to redefine and identify the features of coupling the two technologies in terms of degradation efficiency of a model compound. Results show that, when the process is carried out in plasma activated water in the presence of irradiated TiO₂, the efficiency of the integrated process is lower than the sum of the two processes acting separately. It is proposed that afterglow species, e.g. hydrogen peroxide and/or peroxyinitrites could be activated by UVA light irradiation producing hydroxyl radicals in the liquid phase. Even if TiO₂ limits this additional effect by acting as UVA screen barrier material, its decontamination efficiency under certain conditions results higher than that obtained with plasma systems. These results open the route to chlorine-free decontamination processes and redefine the application framework of this integrated approach.

35 **Keywords:** TiO₂ photocatalysis, Dielectric barrier discharge plasma, UVA light, process
36 intensification, water decontamination.

37

38 **1. Introduction**

39 The decontamination of fresh cut fruits and vegetables poses several safety issues and is challenging
40 due to the huge amount of drinking water needed (ca. 40 m³ per ton of product). In fact, these products
41 are generally eaten uncooked, and contamination could occur during different production steps
42 (Meireles et al., 2016). Chlorine is widely applied to this aim, but it does not generally afford
43 mineralization of residual antibiotics and/or pesticides eventually present and, worse still, produces
44 carcinogenic and mutagenic chlorinated compounds which then accumulate in the process water.

45 Different alternative approaches, mainly based on advanced oxidation processes, were deeply
46 investigated (Barbosa-Cánovas et al., 2017, Bhilwadikar et al., 2019). Among them, as witnessed by
47 the increasing number of published researches, the use of cold plasma under atmospheric conditions
48 could combine decontamination efficiency, process safety, and the need to preserve the organoleptic
49 features of the products (Berardinelli et al., 2016). In fact, glowing plasma discharge above the
50 aqueous phase to be decontaminated (plasma activated water, PAW) (Shen et al., 2016) has been
51 proposed as a viable alternative to chlorine based sanitizers. Various devices working in different
52 conditions (direct current, low frequency, radio frequency and microwave discharges), with peculiar
53 geometries, energy demand, and in the presence of various gas mixtures can be used to drive the
54 discharge. Among the low frequency plasma sources, Dielectric Barrier Discharge (DBD) devices
55 are, undoubtedly, the most investigated and industrialized non-equilibrium plasma generators. In a
56 DBD device the discharge is driven by applying alternating current between two electrodes often
57 characterized by a separation gap of few millimetres and by one or more dielectric layers. DBD
58 presents relevant advantages in terms of costs, flexibility, operating parameters (air as medium,
59 frequency and voltage), due to its simple and versatile electrode geometry (planar or circular) and its
60 ability to produce a stable discharge with negligible thermal effects (Tang et al., 2018). Moreover,

61 the separated configuration between electrodes and PAW limits corrosion phenomena, and avoids
62 contamination of water with heavy metals easily occurring in underwater systems such as plasma jet
63 devices, which are therefore unsuitable for food applications. Finally, the DBD plasma device is
64 known to produce higher amount of active species with respect to plasma jet glow discharges (Leduc
65 et al., 2010) due to its larger surface area. Reactive species are generated through collision
66 mechanisms in the gas phase. When air is used as working gas to generate non-equilibrium plasma
67 discharges, reactive oxygen species (ROS) and reactive nitrogen species (RNS) are formed. Ozone
68 (O_3), atomic oxygen (O) and hydroxyl radical (OH^\cdot) are the main ROS, while excited molecules of
69 N_2 and nitrogen oxide radicals are the main RNS characterizing a non-equilibrium plasma (Ragni et
70 al., 2010). Many authors investigated reactions involving these species in gas phase (Du et al., 2008,
71 Misra et al., 2016, Moreau et al., 2016, Yousfi et al., 2011) or in liquid phase for underwater devices
72 (Lukes et al., 2012, Sun et al., 2012, Tian et al., 2014). However, the interaction of plasma generated
73 in gas phase close to a liquid medium, and the distribution of active species in the liquid phase is less
74 understood (Jiang et al., 2016), although this information is crucial to understand and control the
75 decontamination capability of the system. Active species generated by the plasma discharge can
76 directly diffuse through the gas/liquid interface, or can be generated in the liquid phase by post-
77 discharge chemical reactions (Bruggeman et al., 2016, Zhou et al., 2018, 2016). The complexity of
78 this scenario has been mainly approached by numerical simulation techniques which allowed to
79 estimate mass transfer kinetic and other relevant parameters. For instance, numerical simulation
80 performed by Yusupov et al. (2013) showed that ROS possessed high penetrating power into a 500
81 molecule thick water layer. Liu et al. (2016) investigated the role of the air gap between the plasma
82 and the liquid medium and concluded that for gaps larger than 0.5 cm the concentration of active
83 species in the PAW steeply decreases. In almost all the experimental investigations the pH value of
84 the PAW reduces up to 3 - 3.5 after few minutes of discharge (Liu et al., 2010, Moreau et al., 2007).
85 The concentration of reactive species in the liquid phase depends on several factors such as the system
86 configuration, treatment time, discharge gap, carrier gas, applied voltage, and the electron energy

87 (Gurol et al., 2012, Pavlovich et al., 2013, Tian et al., 2015). In a recent review, it has been reported
88 that ozone, hydrogen peroxide, nitrite, nitrate, superoxide ions, and peroxyxynitrite are the active
89 species mainly present in PAW (Perinban et al., 2019).

90 Heterogeneous photocatalysis is one of the most studied advanced oxidation processes for
91 environmental purposes (Parrino et al., 2019). TiO_2 is widely used as the photocatalyst in these
92 applications due to its low cost, non-toxicity, stability and high activity. Briefly, under irradiation of
93 suitable wavelength, electrons and holes are generated in the conduction and valence bands of TiO_2 ,
94 respectively. Interfacial electron transfer with species adsorbed to or in proximity of the surface of
95 TiO_2 induces formation of highly oxidizing radical species such as hydroxyl, superoxide, nitrate
96 radicals and singlet oxygen (Parrino et al., 2018), which are mainly responsible for the degradation
97 and mineralization of pollutants (Hamrouni et al., 2020) and for inactivation of pathogens such as
98 bacteria, fungi, algae, viruses and microbial toxins (Kumar and Bansal, 2013, Zhu et al., 2018). In
99 particular, TiO_2 photocatalysis has been used for the disinfection of washing water coming from fresh
100 vegetables industry towards natural microflora and potentially pathogenic microflora (Selma et al.,
101 2008). Others research experiences refer about the bactericidal photocatalytic activity of TiO_2 on
102 carrots (Cho et al., 2007) and iceberg lettuce (Kim et al., 2007) with respect to both washing water
103 and vegetables decontamination.

104 TiO_2 photocatalysis has been often integrated with other purification techniques such as biological
105 treatments (Parrino et al., 2019b), adsorption onto activated carbons (Cataldo et al., 2016), ozonation
106 (Camera-Roda et al., 2019), membrane separation (Toledano Garcia et al., 2018), among others.
107 Combination of cold plasma and photocatalysis is mainly reported for air purification systems. In
108 these cases, synergistic effects between the two technologies have been observed, mainly justified by
109 invoking the well-known synergy between TiO_2 photocatalysis and ozone (Parrino et al., 2013). For
110 instance, synergistic effects have been observed for the degradation of isovaleraldehyde (Palau et al.,
111 2015) and butyraldehyde (Gharib-Abou et al., 2016) in gas phase. Coupled photocatalysis-plasma
112 systems have been also applied for smoking rooms air deodorization (Ochiai et al., 2012), hospital

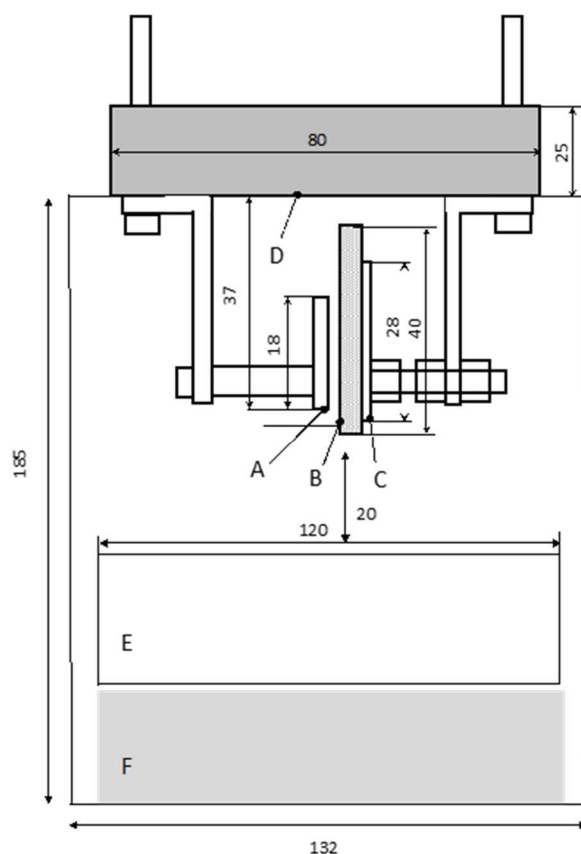
113 indoor air decontamination (Zadi et al., 2018), oxidation of mixtures of pollutants (Vorontsov et al.,
114 2012), and reduction of CO₂ into CO and O₂ at low temperatures (Mei et al., 2016).
115 On the other hand, only few researches deal with DBD plasma-photocatalysis systems for the
116 decontamination of liquid media. In most of these applications the plasma discharge is generated
117 underwater using point to plane geometry electrodes. The degradation of model pollutants such as
118 phenol, 4-chlorophenol, or tetracycline occurred faster than the single processes in most of the cases
119 when TiO₂ was suspended (He et al., 2014) or deposited on supports (Lukes et al., 2005). Similar
120 results have been obtained in such systems also for the inactivation of E. Coli by using microplasma
121 jet arrays and N₂, He, O₂ and air as the working gases (Zhou et al., 2016b). Only few reports deal
122 with the degradation of pollutants in liquid phase below the DBD plasma discharge acting in the head
123 space. For instance, Aziz et al. (2018) coupled different oxidation processes with DBD plasma in a
124 planar falling film reactor, and compared the integrated processes in terms of energy yield. Ghodbane
125 et al. (2014) reported on the degradation of the anthraquinone dye Acid Blue 25 by using DC glow
126 discharge and TiO₂ photocatalysis. However, in these reports the term synergy has been often used
127 to indicate a general increase of efficiency with respect to photocatalysis or plasma, but not with
128 respect to their sum. Moreover, as demonstrated by Camera Roda and Santarelli (2007) when synergy
129 between two processes exists, it depends primarily on the ratio between the rate of the two processes
130 operating separately under the same experimental conditions. This result, often disregarded, allowed
131 in this work to clarify the problem of synergy between TiO₂ photocatalysis and DBD plasma in non-
132 submerged systems, by rationally approaching the intensification problem.

133

134 **2. Material and methods**

135 Figure 1 schematically shows the discharge chamber. The external walls of the chamber were made
136 of Pyrex in order to allow external irradiation as below detailed.

137



138

139 **Figure 1.** Layout of the discharge chamber. A: cathode; B: glass plate; C: anode; D: fan; E: Pyrex
 140 reactor; F: magnetic stirrer. The reported values of dimensions are in millimetres.

141

142 The degradation of methylene blue (MB, Sigma-Aldrich, St. Louis, Mo, USA) was used as model
 143 reaction to evaluate the decontamination efficiency of the system. 200 mL of magnetically stirred
 144 MB aqueous solution (0.02 mM, if not otherwise specified) was placed in a Pyrex cylindrical reactor
 145 (inner diameter 120 mm; height 60 mm) positioned within the chamber. The free surface of the
 146 solution was ca. 20 mm below the gas plasma discharge. The discharge was generated by using a
 147 dielectric barrier discharge (DBD) device characterized by two parallel plate electrodes made of brass
 148 ($28 \times 12.6 \times 4.7$ mm) and stainless steel ($18 \times 9.9 \times 5.5$ mm), respectively. The brass electrode was
 149 covered by a thin sheet of glass ($40 \times 14.6 \times 0.05$ mm) working as dielectric barrier. Inside the
 150 chamber, a fan mounted at about 37 mm from the bottom of the stainless steel electrode was placed
 151 in order to direct the afterglow species towards the free surface of the methylene blue aqueous
 152 solution.

153 The discharge was driven by high voltage transformers and power switching transistors supplied by
154 a stabilized DC power supply (Elektro-Automatik GmbH & Co.KG, Viersen, Germany, EA-PS 2042-
155 06B) placed outside the chamber. Input voltage of 19.15 V (3.15 ± 0.5 A) and air as working gas were
156 considered.

157 The voltage output was characterized by a like-shaped sinusoidal waveform with a peak to peak value
158 of 13.8 kV (frequency around 46 kHz).

159 The concentration of MB during the treatments was measured by means of a Shimadzu UV-vis
160 spectrophotometer (Kyoto, Japan) which measured the absorbance at 663 nm of samples withdrawn
161 during the runs at fixed intervals of times. TiO₂ P25 (Evonik, Essen, Germany; specific surface area
162 $56 \text{ m}^2 \cdot \text{g}^{-1}$, 93% anatase, 7% rutile) was used as the photocatalyst for selected runs in amounts ranging
163 from 0.01 to $1 \text{ g} \cdot \text{L}^{-1}$ (Bellardita et al., 2017, 2018). Selected runs have been performed from 3 to 5
164 times and the reproducibility was better than 5%.

165 Irradiation was performed by means of six actinic Mercury UV-A lamps (Philips, Eindhoven, The
166 Netherlands; nominal power 14 W each, with emission peak at 365 nm) surrounding the chamber in
167 a hexagonal geometry. The radiation intensity of each lamp was ca. $7 \text{ W} \cdot \text{m}^{-2}$, as measured at the
168 reactor wall point nearest to the lamp by means of a Delta Ohm DO9721 radiometer equipped with a
169 UVA probe. After 10 minutes of plasma treatment the temperature inside the glass chamber reached
170 $33 \pm 1^\circ\text{C}$ (starting from ca. 26°C) and was constant during the treatment. The chemical
171 characterization of the atmosphere within the chamber in the presence of the discharge has been
172 elsewhere reported (Ragni et al., 2016).

173 Tests to unveil the role of peroxyxynitrite and hydrogen peroxide have been performed according to the
174 following procedures. Detection of H₂O₂ in the reacting mixture was performed by the titanium
175 peroxide method (Wolfe, 1962). Briefly, 5 mL of TiCl₄ (Sigma Aldrich, p.a.) were added to 5 ml of
176 a 6M aqueous solution of HCl at ice temperature and then diluted to 500 mL in 6M HCl. Aliquots of
177 this solution were added to the sample and the absorbance of the yellow titanium peroxy complex
178 (measured by means of a Shimadzu UV-vis spectrophotometer, Jasco V-570, Japan) was used to

179 check the presence of hydrogen peroxide. Peroxynitrite standard solutions were prepared by mixing
180 1 mL of sodium nitrite (0.3 M, Sigma Aldrich, p.a.), 1 mL hydrogen peroxide (0.7 M, Sigma Aldrich,
181 p.a.) and 0.5 mL of hydrochloric acid (0.6 M, Sigma Aldrich, 37%) as aqueous solutions. 0.5 mL of
182 an aqueous solution of sodium hydroxide (1.5 M, Sigma Aldrich, p.a.) was immediately added within
183 2-3 seconds to stabilize the solution. Nitrite ion was the limiting reactant, and to eliminate the excess
184 of H₂O₂, the solution was mixed with MnO₂ (Sigma Aldrich p.a.), left under stirring for 20 minutes,
185 and filtered. MB was added to the solution and the pH was adjusted to ca. 2 by adding HCl. Finally,
186 the solution was kept in the dark for 20 minutes and irradiated under UVA light (10 W UV LED,
187 supplied by GraceLightLed) for 5 minutes. The concentration of MB during the tests was measured
188 by UV-vis spectroscopy (Jasco V-570, Japan). Benzoic acid (Sigma-Aldrich, p.a.) has been used as
189 a molecular trap to highlight the presence of hydroxyl radicals in the reacting mixture, by monitoring
190 the formation of salicylic acid through fluorescence spectroscopy ($\lambda_{exc}= 270$ nm, Jasco FP-6300,
191 Japan).

192

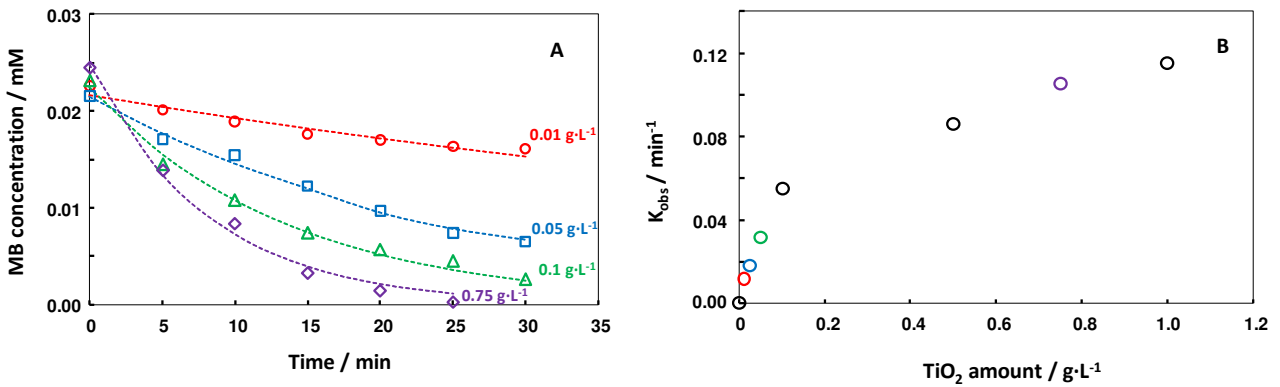
193 3. Results and discussion

194 Preliminary photocatalytic experiments were carried out at a fixed initial MB concentration by
195 changing the amount of TiO₂ and keeping constant the other experimental conditions. Results are
196 represented by symbols in Figure 2A. Experimental data have been fitted by using Eq. 1, as the
197 photocatalytic degradation of MB proceeds according to first order kinetics (Salehi et al. 2012).

$$198 \quad r = -\frac{dC_{MB}}{dt} = k_{obs}C_{MB} \quad (1)$$

199 where r is the reaction rate, C_{MB} the concentration of MB, and k_{obs} the observed apparent kinetic
200 constant. The values of the initial MB concentration and of k_{obs} have been obtained by fitting the
201 experimental concentration vs. time data by the least squares method. As it is evident the model
202 satisfactorily fits the experimental data. The obtained values of k_{obs} are reported in Figure 2B against
203 the TiO₂ amount suspended in the photocatalytic medium.

204



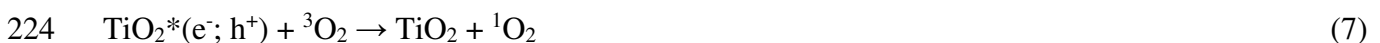
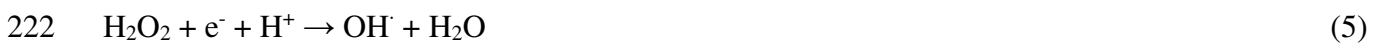
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206 **Figure 2.** MB photocatalytic degradation during irradiation time, for some representative runs carried
 207 out in the presence of different concentrations of TiO₂ (Panel A). The observed kinetic constants have
 208 been reported in Panel B against the amount of TiO₂ dispersed in the photocatalytic medium.

209

210 A linear behavior of the observed kinetic constant (see Eq. 1) for the photocatalytic reaction rate
 211 against the photocatalyst amount is apparent up to TiO₂ concentrations of ca. 0.1 g·L⁻¹ (see Panel B),
 212 while the curve tends to a plateau for higher TiO₂ amounts. The mechanism of the photocatalytic
 213 degradation of MB is well known, and readers are referred to the relevant literature for details (Dariani
 214 et al. 2016). Briefly, irradiating TiO₂ under UV light results in the formation of electron-hole pairs
 215 (Eq. 2). Highly oxidizing hydroxyl radicals, formed upon reduction of oxygen (Eq. 3-5) and water
 216 oxidation (Eq. 6), along with other reactive oxygen species (ROS) such as singlet oxygen (Eq. 7)
 217 (Parrino et al., 2018) are, in turn, mainly responsible for the degradation of MB.

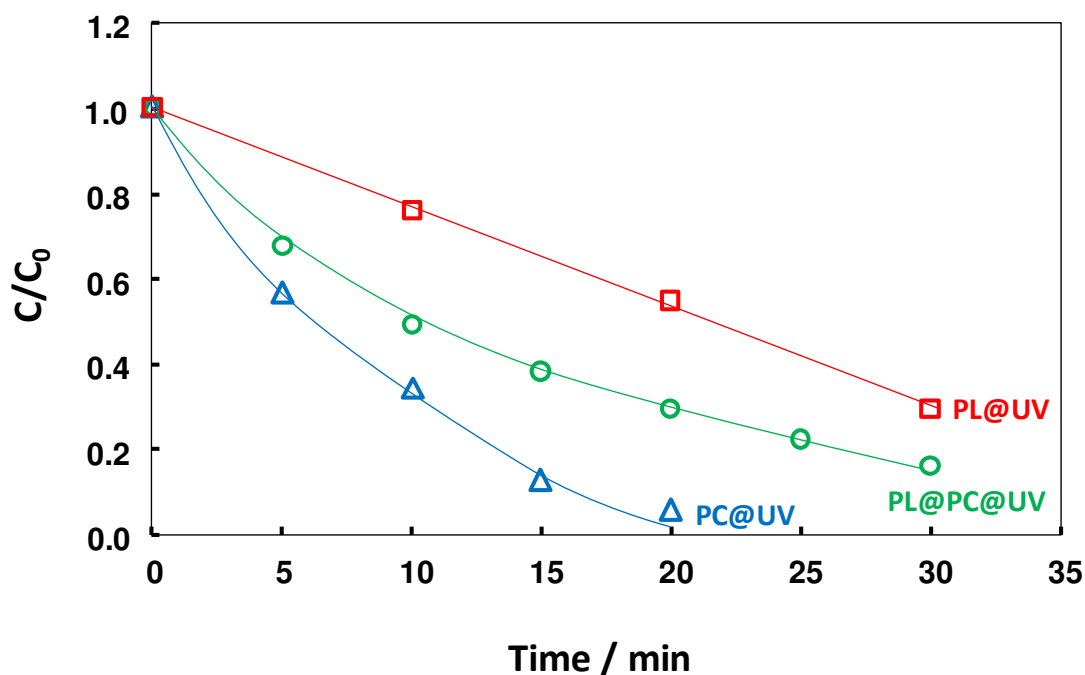
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225

226 We would like to stress here that the use of dyes should be avoided in photocatalysis when testing
227 novel photocatalysts under visible light irradiation (Yan et al., 2006). In fact, the complex
228 photochemistry of MB (Mitoraj et al. 2018) and the substrate dependent nature of photocatalysis (Ryu
229 and Choi, 2008, Parrino et al. 2017) could produce results of difficult interpretation. Moreover,
230 indirect photocatalytic mechanisms triggered by the excited triplet state of the dye could mask the
231 real activity of the photocatalytic material. In this case, however, TiO₂ is the main light absorbing
232 species due to the fact that the irradiation wavelength (centered at 365 nm) matches its absorption
233 band, and that at this wavelength range MB shows low absorption capability. Therefore, indirect
234 photocatalytic paths can be neglected in these conditions. Accordingly, blank tests performed by
235 irradiating MB solutions in the absence of TiO₂ did not result in appreciable MB degradation within
236 the considered time range.

237 In order to investigate the coupling between plasma treatment and photocatalysis, we performed the
238 photocatalytic degradation of MB under external UV light irradiation and in the presence of TiO₂, by
239 simultaneously switching on the plasma discharge within the system. Results are represented in
240 Figure 3 by the curve labelled as PL@PC@UV. Figure 3 reports also the MB degradation due to the
241 sole photocatalysis (PC@UV curve) and to the plasma treatment under simultaneous UV light
242 irradiation (PL@UV curve). Notably, all of the three runs reported in Figure 3 have been carried out
243 under UV irradiation, for the sake of comparison.



244

245 **Figure 3.** Normalized concentration of MB during reaction time for some representative runs of sole
 246 photocatalysis (PC@UV, blue triangles), plasma-UV (PL@UV, red squares), and plasma-
 247 photocatalysis (PL@PC@UV, green circles). Initial MB concentration $C_0 = 0.02$ mM, TiO_2 amount
 248 for the photocatalytic runs $0.75 \text{ g}\cdot\text{L}^{-1}$.

249

250 Under the given experimental conditions, the degradation rate of MB due to the sole photocatalysis
 251 is faster than the one induced by plasma and UV light. However, surprisingly, the MB degradation
 252 obtained when coupling plasma and photocatalysis is slower than that of photocatalysis alone, even
 253 if it is higher with respect to that of plasma and UV light. This implies that in this case the two
 254 technologies not only do not show any synergistic effect, but the simultaneous use of plasma and
 255 photocatalysis is detrimental with respect to the sole photocatalysis.

256 These results do not agree with those reported in literature in which, generally, the integration of
 257 plasma and photocatalysis results in process intensification. It is worth mentioning that low energy
 258 DBD plasma has been poorly investigated in literature and integration with photocatalysis has been
 259 carried out in gas phase but never in the head space above a photocatalytic liquid suspension as in
 260 this case. The reported synergy between plasma and photocatalysis for the degradation of model

261 compounds in gas phase, such as butyraldehyde and isovaleraldehyde, (Palau et al., 2015, Gharib-
262 Abou et al., 2016) has been justified by assuming that the ozone produced by plasma was the main
263 oxidant, and that its concomitant action with the irradiated TiO₂ increased the degradation rate with
264 respect to the sum of the single technologies (Camera-Roda et al., 2017). In fact, in the presence of
265 ozone only 1 electron (1 photon) is required to produce one OH radical (Eq. 8-9), while 3 electrons
266 (3 photons) are necessary in the presence of oxygen (Eq. 3-5).

267



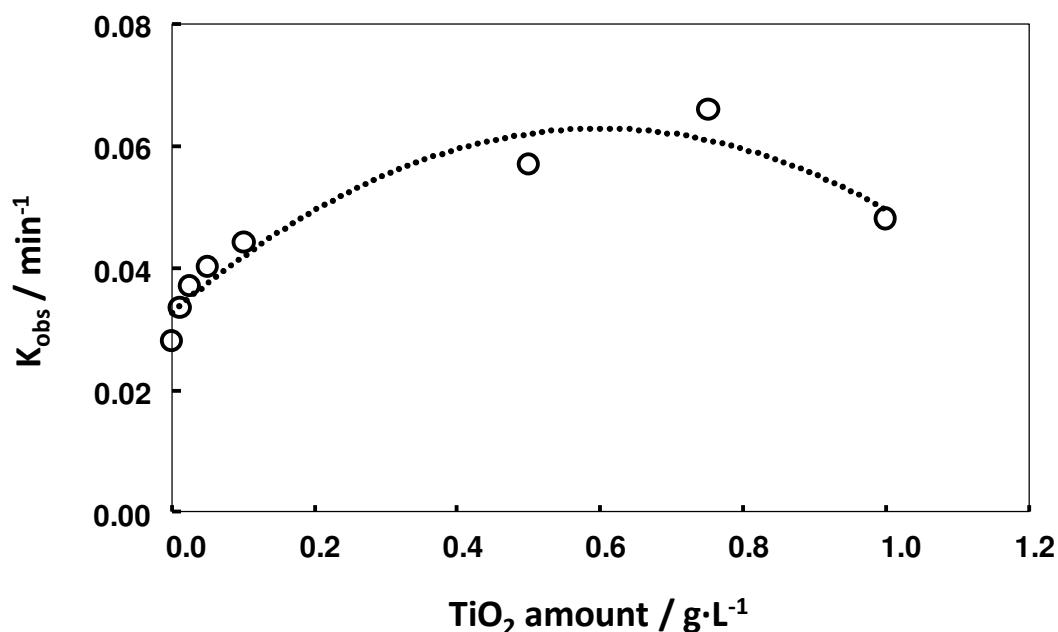
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271 The evident absence of synergy expressed in Figure 3 can be due to different reasons.

272 First of all, the diffusion of ozone from the gas phase (where it is generated) to the liquid phase could
273 limit the process. The ozone diffusion coefficient has been estimated by Jiang et al. (2013) being 1.75
274 $\cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$. Ozone can effectively oxidize MB at the gas-liquid interface or even within the first
275 liquid layers, but its action can be limited by mass transfer within the bulk of the solution. Notably,
276 in the present experimental set up only gentle magnetic agitation could be performed, as at higher
277 agitation speeds formation of water droplets within the electrodes destabilized the discharge.

278 As demonstrated in the relevant literature (Parrino et al., 2013), the synergy between photocatalysis
279 and ozone is dependent on the ratio between the rates of the single technologies. This aspect is
280 generally disregarded, whereas it might explain why in some cases the values of the intensification
281 factors measured by different researchers are very dissimilar. Therefore, in principle, opposite results
282 could be obtained also in this case by changing the rate of one of the two processes. In order to check
283 this hypothesis, we measured the MB degradation rate in the plasma-photocatalysis integrated system
284 at different TiO₂ concentrations. The apparent observed kinetic constants were determined
285 differentiating the experimental data at the initial time, by using a five points formula for equally

286 spaced points (Yeow et al., 2003, Lubansky et al., 2006). The obtained k_{obs} values versus the amount
287 of TiO_2 for the plasma-photocatalysis integrated process are reported in Figure 4.



288

289

290 **Figure 4.** Observed kinetic constants calculated at the initial time against the amount of TiO_2
291 for integrated runs with plasma and photocatalysis.

292

293 It is apparent that the initial rate of degradation of MB, proportional to the k_{obs} values, during the
294 coupled plasma-photocatalytic process increases with the amount of photocatalyst until a maximum
295 is reached. Thereafter, for TiO_2 concentrations higher than ca. $0.5\text{-}0.7\text{ g}\cdot\text{L}^{-1}$ the rate of the integrated
296 process decreases. The presence of a maximum indicates the existence of an optimum at which
297 photocatalysis and plasma can be used at the highest efficiency. On the other hand, such a behavior
298 is the typical result of two contrasting processes operating simultaneously during the integrated
299 process. As above reported (Figure 2B) the rate of photocatalysis increases until a plateau is reached.
300 Therefore, a second process, related to the plasma discharge and/or with UV light irradiation, must
301 contribute to MB degradation and its efficiency is supposed to decrease with increasing catalyst
302 loading.

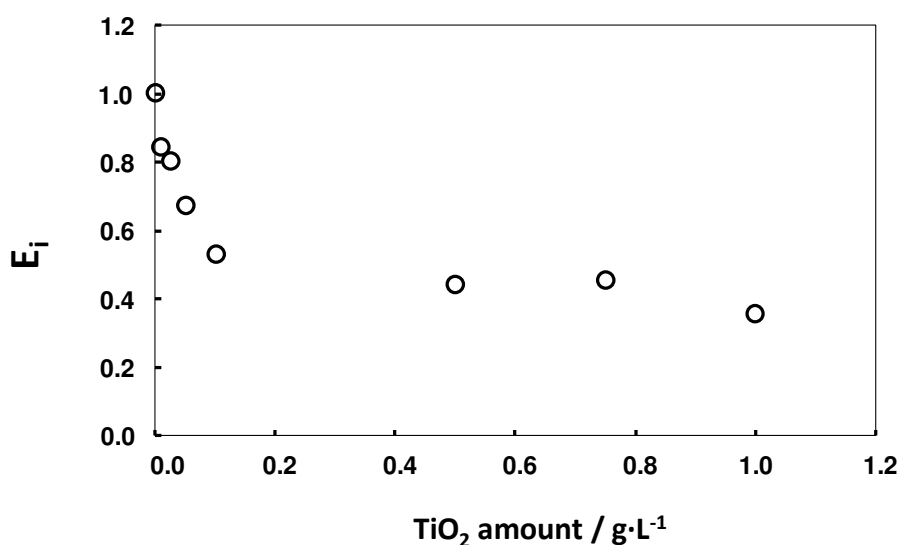
303 In order to evidence the nature of this second process, it is useful to define the following integration
304 factor (E_i) as in Eq. 10

305

$$306 \quad E_i = \frac{k_{obs}(PC@PL@UV)}{k_{obs}(PC@UV) + k_{obs}(PL@UV)} \quad (10)$$

307

308 Where $k_{obs}(PC@PL@UV)$ is the observed rate constant of the integrated plasma-photocatalysis
309 process, while $k_{obs}(PC@UV) + k_{obs}(PL@UV)$ is the algebraic sum of the rate constants of
310 photocatalysis and plasma-UV processes. In other words, E_i expresses at which extent the integrated
311 process is more (if $E_i > 1$) or less effective (if $E_i < 1$) with respect to the sum of the two processes
312 acting separately. In Figure 5 is reported the trend of the integration factor (E_i) at increasing TiO_2
313 amounts.



314

315 **Figure 5.** Trend of the integration factor E_i at increasing concentration of TiO_2

316

317 In the absence of photocatalysts, E_i is equal to 1 by definition. By increasing the amount of TiO_2 , the
318 integrated process is progressively less efficient than the sum of the two processes until, at a TiO_2
319 concentration of ca. $0.2 \text{ g}\cdot\text{L}^{-1}$, a plateau is reached. Two conclusions can be drawn from these results:
320 (i) a negative synergy is observed between plasma and photocatalysis under these conditions; (ii) the

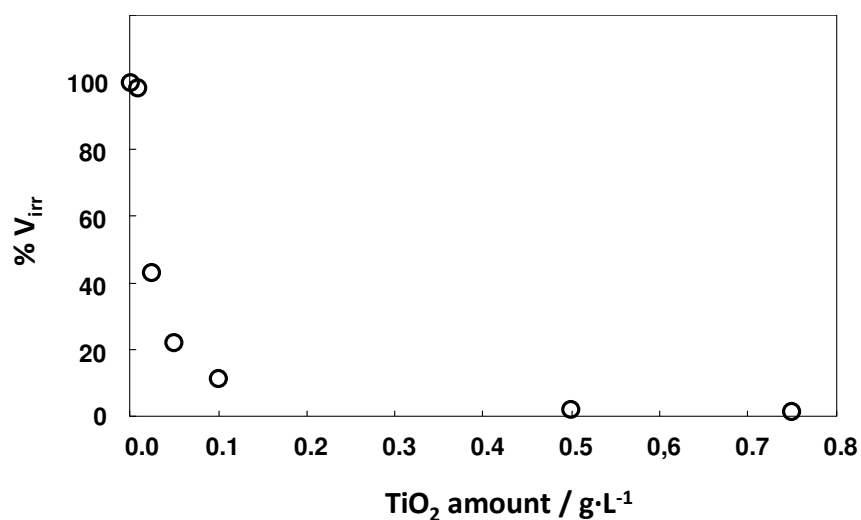
321 ozone induced oxidation process, known to provide a positive synergy when coupled with
322 photocatalysis, plays a minor role when photocatalysis acts together with DBD plasma.

323 The detrimental effect of TiO₂ on the plasma induced MB degradation is necessarily due to the
324 interaction between TiO₂ and some species generated by the discharge which then dissolve in the
325 reacting suspension. In this regard, it should be noted that the pH of the solution changed from around
326 6 to 3 within the first 15 minutes of discharge and UV-vis spectra of the solutions showed the presence
327 of nitrate and nitrite ions according to literature (Ragni et al., 2016).

328 Blank photocatalytic tests of MB degradation performed in the presence of nitrate and nitrite ions,
329 while maintaining constant the other conditions, did not show significant differences, indicating that
330 these ions, generated upon the plasma discharge, are not directly responsible for the observed
331 behavior. Regardless of their nature, the oxidizing species produced by the plasma discharge are
332 deactivated by the presence of TiO₂. This can occur by interaction of these species with the
333 photogenerated charges at the surface of TiO₂, or simply because TiO₂ acts as UV light screen, thus
334 reducing their direct photochemical activation. If the second hypothesis holds, the extent of the effect
335 of plasma during photocatalysis should be dependent on the portion of the reactor effectively
336 irradiated. In fact, the higher is the concentration of TiO₂, the lower is the penetration of the light and
337 the smaller is the volume of the reactor where irradiation is effective.

338 To tackle this issue, for each photocatalyst concentration we calculated the mean free photonic path
339 (i.e. the radius of the reactor annulus well irradiated, at which the optical thickness is equal to 1) as
340 the ratio between the radius of the reactor and the optical thickness. Note that the optical thickness is
341 equal to the specific extinction coefficient of TiO₂ P25 at 365 nm ($5.8 \cdot 10^4 \text{ cm}^2 \cdot \text{g}^{-1}$) multiplied by the
342 photocatalyst concentration and by the radius of the reactor (Satuf et al., 2005). In this way it is
343 possible to estimate the percentage of the photoreactor effectively irradiated ($\%V_{\text{irr}}$) at each
344 photocatalyst concentration. Results are reported in Figure 6.

345



346

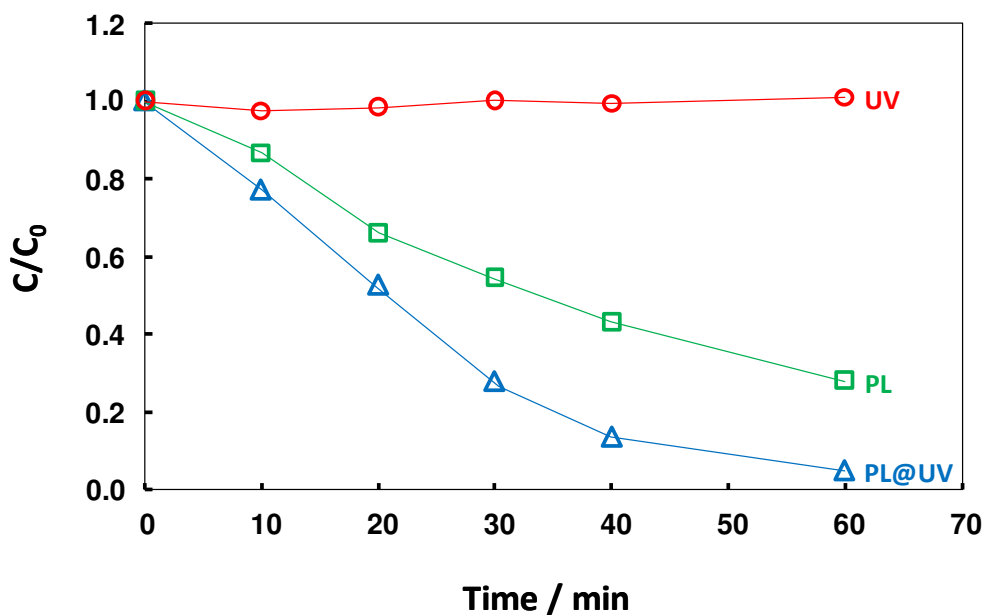
347 **Figure 6.** Percentage of reactor volume effectively irradiated at different TiO₂ concentrations of the
 348 suspension.

349

350 Results show that in the absence of the photocatalyst the whole volume is effectively irradiated (%V_{irr}
 351 = 100), while increasing the photocatalyst concentration results in a steep decrease of the portion of
 352 volume effectively irradiated until, for TiO₂ amounts higher than ca. 0.2 g·L⁻¹, the decrease is
 353 negligible and a plateau is reached. It is evident that while the rate of photocatalysis reaches a plateau
 354 for TiO₂ concentrations higher than 0.75 g·L⁻¹ (Figure 2B), the trend of the integration factor E_i
 355 (Figure 5) is similar to that of the percentage of volume well irradiated (Figure 6), as it reaches a
 356 plateau at ca. 0.2 g·L⁻¹. This evidence supports the hypothesis that TiO₂ simply acts as a screen during
 357 the integrated plasma-photocatalysis process and that some of the photoactive species produced by
 358 the discharge are simply activated by UV light.

359 As a further proof of the existence of UV light absorbing species generated by the plasma discharge
 360 and contributing to MB degradation, we performed the plasma treatment in the absence of TiO₂, with
 361 and without UV light irradiation. Results are shown in Figure 7.

362

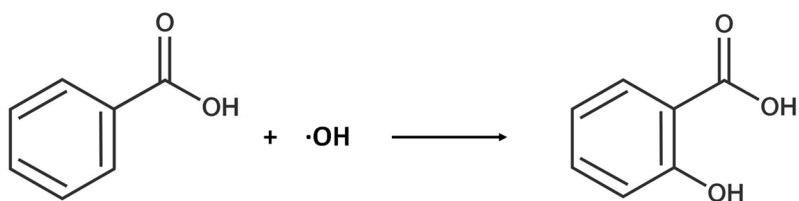


363

364 **Figure 7.** Normalized concentration of MB during time for runs performed under sole UV light
 365 irradiation (red circles, UV), by the sole plasma discharge treatment (green squares, PL), and by
 366 plasma discharge treatment performed under simultaneous UV light irradiation (blue triangles,
 367 PL@UV).

368

369 It is evident that UV light alone does not induce MB degradation. Contrarily, plasma discharge in the
 370 absence of external UV light irradiation results in ca. 40% degradation of MB after 30 minutes of
 371 irradiation, while the degradation reached ca. 70% in the same time when the solution is externally
 372 irradiated. This result confirms that the plasma discharge produces species that are activated by UV
 373 light. To unravel the mechanism underlying this effect, we checked the presence of OH radicals in
 374 the irradiated and non-irradiated suspensions in the presence of the plasma discharge. We perform
 375 the experiments by only substituting MB with benzoic acid, under otherwise identical conditions. In
 376 fact, in the presence of OH radicals, benzoic acid is hydroxylated to salicylic acid according to Eq.
 377 11.

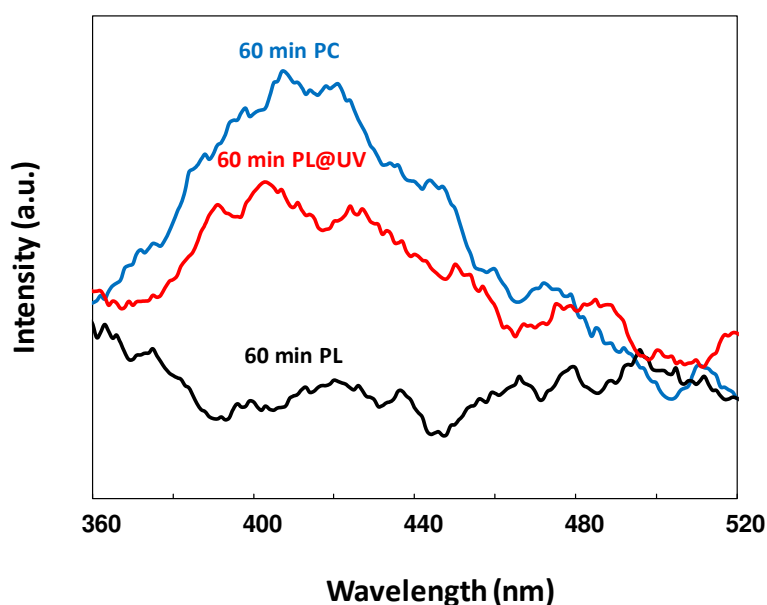


378

(11)

379 The presence of salicylic acid has been detected by measuring its fluorescence at 410 nm. Results are
 380 shown in Figure 8.

381



382

383 **Figure 8.** Fluorescence spectra of samples of reacting suspension for runs carried out in the
 384 presence of 0.5 mM of benzoic acid after 60 minutes of plasma treatment (black curve), of plasma
 385 under external UV light irradiation (red curve), and of photocatalytic treatment without plasma and
 386 with 0.1 g·L⁻¹ TiO₂ (blue curve). Excitation wavelength: 270 nm.

387

388 Notably, a quantitative comparison of the spectra was not possible due to the influence of the different
 389 treatments on the composition of the suspension. However, it can be seen that salicylic acid could be
 390 detected in the presence of irradiated TiO₂ (blue curve), and in the presence of the plasma discharge,
 391 only if the solution was externally irradiated. On the contrary, salicylic acid was virtually absent when
 392 the plasma treatment was performed under dark conditions.

393 Formation of hydroxyl radicals by means of photocatalysis is well documented and occurs according
394 to Eqs. 2-6.

395 The absence of hydroxyl radicals when the solution was treated by plasma under dark conditions is
396 reasonable, by considering that hydroxyl radicals eventually formed in the discharge zone could not
397 live enough to reach the bulk of the solution beneath. In fact, the life time of OH radicals is reported
398 to be in the order of magnitude of microseconds (Perinban et al., 2019).

399 On the other hand, when plasma discharge was performed under external UV irradiation, the
400 formation of salicylic acid could be detected, thus indicating that hydroxyl radicals are responsible
401 for the enhanced MB degradation observed when plasma was performed under UV irradiation with
402 respect to the dark conditions.

403 This finding justifies the previously observed detrimental behaviour of TiO₂ when plasma and
404 photocatalysis simultaneously operated. In fact, photochemical reactions triggered by UVA light
405 absorbing species must be the responsible for the observed formation of hydroxyl radicals.

406 Direct detection of these species was not straightforward at this step of research, by considering their
407 possible transient nature. However, some hypotheses can be proposed, while further investigation are
408 ongoing to afford definitive proofs.

409 OH radicals could form from hydrogen peroxide (Cataldo, 2014) which undergo photolysis at any
410 wavelength lower than 380 nm with a quantum yield Φ ranging between 1 and 1.5, according to Eq.
411 12.

412



414

415 However, during plasma treatment the amount of H₂O₂ in the liquid phase was lower than the
416 detection limit (1 μM) of the method based on titanium peroxocomplexes described in the
417 experimental part. On the other hand, as the absence of evidence is not evidence of absence, it cannot
418 be excluded that hydrogen peroxide could be present at lower concentrations or for times shorter than

419 those of analysis. In fact, the presence of hydrogen peroxide has been often reported in similar
420 systems, even if at concentrations closer to the detection limit (Ragni et al., 2016).

421 Nitrate ions photolysis could be excluded as a source of hydroxyl radicals as photons below 300 nm
422 (required for this reaction) are cut off by Pyrex glass (Parrino et al., 2016).

423 The presence of nitrite ions in solution with MB under UV irradiation did not result in MB
424 degradation. Therefore, nitrite ions alone are not responsible for the observed production of hydroxyl
425 radicals.

426 Peroxynitrite ion is reported among the species that can be present in the aqueous phase below the
427 plasma discharge (Tarabová et al., 2019). Peroxynitrite (ONOO^-) can be formed by reaction of
428 superoxide and nitric oxide radicals (Eq. 13) formed after glow (Goldstein and Merényi, 2008).
429 Notably the life time of the superoxide radical is long enough (ca. 5 seconds) in aqueous solution and
430 is easily protonated to hydroperoxyl radical at pH lower than 4.8 (Eq. 14) (Bielski et al., 1985).

431



434

435 Moreover, peroxynitrite can be formed by reaction of nitrite and hydrogen peroxide according to Eq.
436 15 (Saha et al., 1998).

437



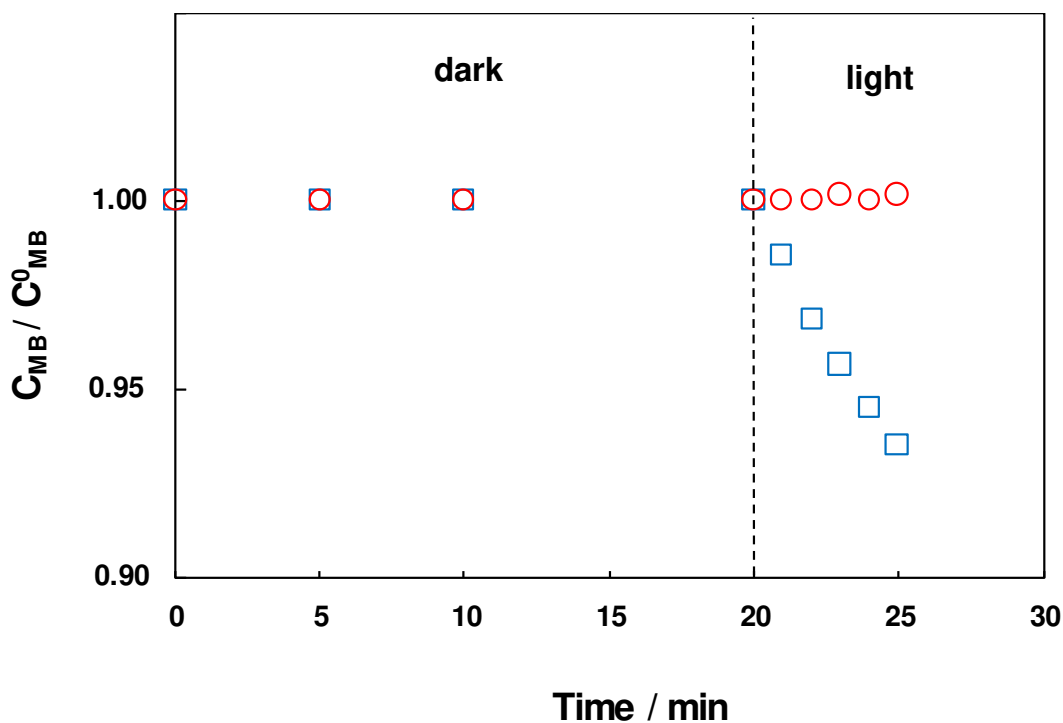
439

440 By considering that the pH of the MB solution is acidic (ca. 3), it is probable that peroxynitrite is
441 present in its protonated form in solution. In fact, pKa of peroxynitrous acid is ca. 6.8. Peroxynitrous
442 acid is a highly oxidizing and nitrating agent. It is rather unstable with respect to its corresponding
443 anion, and it easily undergoes homolytic rupture to NO_2 and hydroxyl radical. By considering that
444 the peroxynitrite shows an absorption band with a maximum at 302 nm which can extends up to 390

445 nm, it is possible that production of hydroxyl radicals could be sped up under UVA irradiation.
446 Coddington et al. (1999) report the formation of hydroxyl radicals by decomposition of peroxyxynitrite
447 ions in aqueous solution. Beckman et al. (1990) observed that peroxyxynitrite rapidly decomposes once
448 protonated with a half-life of 1.9 s at pH 7.4 thereby generating a strong oxidant with reactivity similar
449 to hydroxyl radical. Khan et al. (2000) reported the decomposition of peroxyxynitrite to nitroxyl anion
450 and singlet oxygen. However, Martinez et al. (2000) soon later observed that formation of singlet
451 oxygen could be observed only in the presence of traces of hydrogen peroxide. Most of the reports
452 concern the behaviour of peroxyxynitrite under dark conditions, while few is known about its
453 photochemical behaviour. Recently Thøgersen et al. (2015) investigated the primary photochemistry
454 of peroxyxynitrite aqueous solutions irradiated at 266 nm by transient absorption spectroscopies. More
455 than 90% of the peroxyxynitrite was dissociated after 400 ps and the dominant path was the formation
456 of superoxide anion radical and nitrogen monoxide. To the best of our knowledge the effects of
457 radiation at longer wavelengths have been poorly investigated. To the aim of our work, it was
458 interesting to ascertain if UVA irradiation could affect the degradation of MB in the presence of
459 peroxyxynitrite ions and/or hydrogen peroxide. Further investigation is ongoing in order to detail the
460 mechanistic aspects of this behaviour.

461 Figure 9 shows the normalized concentration of MB under dark and under UVA irradiation in the
462 presence and in the absence of peroxyxynitrite ions. Notably, the pH of the as prepared standard solution
463 was ca. 12. Blank tests allowed to determine that MB degradation, at this pH value, proceeded both
464 under dark conditions and (faster) under UVA irradiation even in the absence of peroxyxynitrite.
465 Therefore, the tests in Figure 9 have been performed by acidifying the solution containing MB at pH
466 ca. 3 (i.e. the pH of the MB solution under plasma discharge) by means of HCl (0.7 M solution)
467 addition prior to starting the test.

468



469

470 **Figure 9.** Normalized concentration of MB versus time in acidified (pH = 3) peroxyxynitrite standard
 471 solution (blue squares) and in the absence of peroxyxynitrite (red circles) under dark and under UV
 472 light irradiation.

473

474 Addition of HCl resulted in an immediate drop of MB concentration, possibly due to direct
 475 peroxyxynitrous acid formation that induced oxidation (not shown in Figure 9). Thereafter, the MB
 476 concentration was stable under dark and the pH was constant at ca. 3. The solution was maintained
 477 in the dark for twenty minutes and the concentration of MB did not decrease as it is evident from
 478 Figure 9. However, under UVA irradiation the concentration of MB decreased of ca. 8% after 5
 479 minutes in the presence of peroxyxynitrite, while remained constant in its absence.

480 Blank tests performed in the absence of peroxyxynitrite but in the presence of H₂O₂ afforded similar
 481 results (not shown). Even if hydrogen peroxide was removed from the peroxyxynitrite solution by
 482 passing it through powdered MnO₂, and its concentration was monitored by the titanium peroxide
 483 method, the presence of H₂O₂ at concentration lower than the detection limit cannot be excluded in
 484 the present experimental conditions. However, the present tests suggest that peroxyxynitrite and/or

485 hydrogen peroxide could be tentatively proposed as the active species responsible for the enhanced
486 MB degradation observed when plasma discharge acts under UVA irradiation.

487

488 **4. Conclusions**

489 The interaction between photocatalysis and the plasma discharge generated above the liquid
490 suspension by means of a DBD device, has been investigated by monitoring the degradation of
491 methylene blue in the aqueous phase as a model reaction. Results showed an optimum in the
492 efficiency of MB degradation obtained by coupling plasma and photocatalysis exists for TiO₂
493 concentrations of ca. 0.5 g·L⁻¹. This bell behaviour, however, indicates the existence of two
494 contrasting processes simultaneously acting during the integrated process. In fact, increasing the
495 amount of TiO₂ results in higher photocatalytic activity but, at the same time is detrimental as far as
496 the joint effect of plasma and photocatalysis is concerned. In fact, the efficiency of the integrated
497 process with respect to the sum of the two processes acting separately decreases with increasing the
498 TiO₂ concentration in the reacting mixtures. This finding has been related with the production of
499 active species absorbing UVA light which in turn generate hydroxyl radicals in the aqueous solution,
500 as demonstrated by fluorescence spectroscopy. Accordingly, in the absence of TiO₂, irradiating the
501 aqueous solution above which the plasma is glowed enhances the degradation rate of MB with respect
502 to the simple use of plasma. Experimental results show that peroxyntrous acid and/or hydrogen
503 peroxide generated upon the action of plasma could be responsible for the observed behaviour.
504 Notably, due to the substrate dependent nature of photocatalytic reactions, further investigation in the
505 presence of different pollutants is required to obtain a full picture of the complex interplay between
506 plasma and photocatalysis. However, these preliminary results define the terms of interaction between
507 plasma and photocatalysis and show that the integration of these technologies under opportune
508 conditions could be a promising alternative to the use of chlorine for the disinfection of fresh cut
509 vegetables in the food processing chain.

510

511 **Competing interest statement**

512 The authors have no competing interests to declare.

513

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