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Solar Activation of TiO2 Intensified with Graphene for **Degradation of Bisphenol-A in Water**

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13	J.M. Monteagudo ^a *, A. Durán ^a , E. Chatzisymeon ^b , I. San Martín ^a , S. Naranjo ^a
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17 18 19 20 21 22 23	 ^a Department of Chemical Engineering, Grupo IMAES, Escuela Técnica Superior de Ingenieros Industriales, Instituto de Investigaciones Energéticas y Aplicaciones Industriales (INEI)University of Castilla-La Mancha, Avda. Camilo José Cela 3, 13071 Ciudad Real (Spain). ^b Institute for Infrastructure and Environment, School of Engineering, The University of
24 25	Edinburgh, Edinburgh EH9 3JL, United Kingdom.
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29	* To whom correspondence should be addressed
30 31 32 33 34 35 36 37 38 39	Department of Chemical Engineering, Grupo IMAES Escuela Técnica Superior de Ingenieros Industriales, Instituto de Investigaciones Energéticas y Aplicaciones Industriales (INEI) University of Castilla-La Mancha, Avda. Camilo José Cela 3, 13071 Ciudad Real (Spain). Fax: 0034 926295361. Phone: 0034 926295300, ext: 3888 Email: josemaria.monteagudo@uclm.es

42 ABSTRACT

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44 Photocatalytic degradation of a Bisphenol-A (BPA) aqueous solution was achieved using titanium dioxide (TiO₂) and graphene-based TiO₂ photocatalysts activated by 45 46 solar light. First, a comparative study of the adsorption kinetics of BPA, in the presence 47 of both catalysts, as a function of pH was performed. Then, the effect of the initial BPA 48 concentration and catalyst loading was assessed and the optimal conditions for BPA 49 degradation by means of heterogeneous solar photocatalysis were determined. It was 50 observed that TiO₂ modified with 2 wt% graphene improved the photocatalytic 51 efficiency in terms of BPA mineralization. The TiO₂/graphene photocatalytic composite 52 achieved a 16% increase in the photocatalytic mineralization of the BPA solution under 53 solar light compared to un-doped TiO₂. This enhancement of photocatalytic efficiency is 54 a result of the increase of active sites for BPA adsorption, the more efficient harvesting 55 of solar light, and the inhibition of electron-hole recombination. The dynamic behavior 56 of hydroxyl radicals and dissolved oxygen in these systems was also discussed. Finally, 57 the roles played by hydroxyl radical, HO[•], superoxide radical anion, O_2^{\bullet} , and singlet 58 molecular oxygen, ¹O₂, were studied in both TiO₂ and TiO₂/graphene systems. It was found that O_2^{\bullet} were the main oxidative species in both systems. 59

60

61 *Keywords: bisphenol-A; TiO₂/graphene; oxidative species; solar light.*

63 1. INTRODUCTION

64

65 Bisphenol-A (BPA) is a well-known endocrine disrupting chemical (EDC) that has been 66 extensively detected in the environment. BPA can cause adverse health effects due to its 67 interference with the human and animal hormones (Schafer et al., 1999; Gultekin et al., 68 2009; Rubin, 2011; Rogers et al., 2013). Due to its xenobiotic nature, this molecule 69 cannot be completely degraded by the biological treatment processes used in wastewater 70 treatment plants (WWTPs) and it is therefore discharged intact into the environment 71 (Hu et al., 2007; Crain et al., 2007). Hence, an efficient treatment system for removing 72 BPA or its oxidation reaction intermediates from the aquatic environment remains a 73 pressing need for water industry and decision makers.

74

75 It is well-known that Advanced Oxidation Processes (AOPs) are effective methods for 76 treating organic pollutants in water. The efficacy of AOPs is based on the generation of 77 highly reactive free radicals, especially hydroxyl radicals (HO[•]) or sulfate radicals (SO₄[•]), which are capable of transforming bio-recalcitrant molecules into biodegradable 78 79 products. Among AOPs, heterogeneous photocatalytic degradation reactions using 80 semiconductor metallic oxides, such as TiO₂, as photocatalysts to destruct persistent 81 organic pollutants such as EDCs have been well studied (Esplugas et al., 2007; Durán et 82 al., 2009; Xekoukoulotakis et al., 2011). Reactive oxygen species, mainly hydroxyl radical, superoxide radical anion, O_2^{\bullet} , and singlet molecular oxygen, 1O_2 , which can 83 84 degrade a wide range of chemical contaminants in water, are generated during 85 photocatalytic processes. However, the production of photons by means of artificial light sources requires a substantial amount of electrical energy (Pérez et al., 2002). Solar 86 87 energy can be used, alternatively to UV lamps, as a more sustainable option in order to 88 reduce the energy and costs of the water treatment process. TiO₂-assisted photocatalytic

89 degradation of several organic contaminants by solar light has been successfully used. 90 This was found to be an economically viable process since solar energy is an abundant 91 natural energy source and can be used instead of artificial light sources which are costly and hazardous (Konstantinou and Albanis, 2003; Robert et al., 2004). TiO₂ has a wide 92 band gap (anatase E_{bg} = 3.2 eV or λ < 387 nm) and requires UV excitation (energy equal 93 94 to or greater than the band-gap) to form electron-hole pairs. The conduction band 95 electrons are able to reduce dissolved oxygen to generate superoxide radical, O_2^{\bullet} , hydroperoxyl radicals, HO₂[•], and through subsequent reduction reactions, hydrogen 96 peroxide, H_2O_2 , and hydroxyl radical, HO^{\bullet} . The valence band holes, h^+ , are able to 97 98 oxidize water to form HO[•]. The drawbacks of solar photocatalysis are that the UV radiation received by the earth is only around 5% of the entire solar energy spectrum 99 100 and the photogenerated electron-hole pairs have fast recombination rates. In this sense, 101 the efficiency of solar photocatalysis can be improved by doping TiO₂ composites with 102 materials, such as graphene (Kumordzi et al., 2016), in order to expand the catalyst 103 band-gap to the visible light region of the solar spectrum (λ > 400 nm) and prevent 104 electron-hole pair recombination (Fukahori et al., 2003; Bellobono et al., 2005; Ni et al., 105 2007; Fujishima et al., 2008). The use of graphene is of great scientific interest due to 106 its excellent properties such as chemical inertness, stability in both acidic and basic 107 mediums, its abundance and large surface area (2630 m^2/g) (Upadhyay et al., 2014).

108

BPA degradation has been previously investigated in many oxidative treatment processes, such as UV/H_2O_2 and UV/persulfate (Yoon et al., 2012). A comparative study on the oxidative degradation of BPA by Fenton reagent, UV, UV/H_2O_2 and Ultrasound has been also reported (Young et al., 2013). The removal of BPA by means of UV, UV/H_2O_2 , $UV/K_2S_2O_8$ and UV/Na_2CO_3 processes was also studied (SánchezPolo et al., 2013). F–TiO₂–RGO nanocomposites were examined for BPA degradation under UV light illumination (Luoa et al., 2015). TiO₂/graphene/Cu₂O was applied in the photoelectrocatalytic oxidation of BPA under artificial visible light irradiation (Yanga et al., 2016). The catalytic ability of TiO₂–reduced graphene oxide hybrid (TiO₂ – RGO) in photocatalysis using an artificial 365 nm light and ozonation combined system to degrade BPA was also investigated (Liao et al., 2016).

120

121 However, to the best of our knowledge, the application of graphene-TiO₂ composites 122 irradiated by natural solar light for BPA degradation has not been studied yet. 123 Therefore, further studies are required in this area to develop a more sustainable and 124 cost efficient treatment technology. The aim of this work is to investigate BPA 125 mineralization reactions by using solar photocatalytic oxidation in the presence of TiO_2 126 and TiO₂/graphene composites. First, the influence of pH on BPA adsorption kinetics for both TiO₂ and TiO₂/graphene composites was investigated. Then, the effects of 127 128 various process parameters, such as initial concentrations of BPA and suspended 129 photocatalysts as well as the type of the catalyst on mineralization reactions were 130 evaluated. Afterwards, the dynamic behavior of HO[•] radicals and the profile of 131 dissolved oxygen in both catalytic systems were determined. Finally, the roles played by different reactive oxidative species such as HO[•], $O_2^{\bullet-}$ and 1O_2 , in both TiO₂ and 132 133 TiO₂/graphene systems were evaluated using appropriate scavengers.

- 134
- 135 2. EXPERIMENTAL
- 136

137 *2.1. Materials*

BPA (CAS No: 80-05-7) (Fig. 1a), p-benzoquinone, sodium azide and ethanol (99.5%)
were purchased from Sigma-Aldrich. Aeroxide® TiO₂ P25 was supplied by Evonik
Industries and graphite powder (natural, microcrystal grade, product no. 14736) was
purchased from Alfa Aesar. Tert-butyl alcohol was purchased from Panreac. All
chemicals were used as received without further purification. The pH of the wastewater
in each test was adjusted using H₂SO₄ and NaOH solutions.

145

146 2.2. Photocatalyst preparation and characterization

147

148 Graphite oxide, GO, was obtained from graphite powder through the modified 149 Hummers method (Hummers and Offeman, 1958; Hassan et al., 2013). GO was 150 dissolved in a water/ethanol (2:1) solution followed by 60 min ultrasound treatment. 151 Then, a calculated amount (to obtain concentrations of 1, 2 and 3 wt% of graphene) of 152 commercial TiO₂ nanoparticles (P25) was added to the GO solution, which was 153 continuously stirred for 3 h. The mixture was transferred to a Teflon-lined autoclave, 154 and the hydrothermal process was performed at 120 °C for 15 h. During this process, 155 GO could be reduced to graphene and the deposition of TiO_2 was achieved. Then, the 156 obtained composites were centrifuged, rinsed with deionized water, and dried at 60°C. 157 The prepared samples are denoted as TiO_2 /graphene.

158

159 Structural analyses of TiO₂ and TiO₂/graphene samples were determined by X-ray 160 Diffraction (XRD) using a PHILIPS X'Pert MPD PW 3040 analyzer with a Cu 161 KAlpha1 radiation. Ultraviolet-visible (UV-Vis) spectra were collected in a Cary 100 162 diffuse reflectance UV-Vis spectrophotometer. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100Plus microscope. The specific
surface area, pore size and pore volume of the samples was measured with BrunauerEmmett-Teller (BET) method using the Micro-meritics Gemini VII 2390 by using N₂
adsorption at 77 K.

167

168	2.3.	Experimental	l set-up

169

Fig. 1b illustrates the scheme of the experimental set-up. A CPC solar reactor with a surface of 0.25 m², manufactured by Ecosystem, S.A., consisted of 2 borosilicate tubes and an irradiated volume of 2 L. The reactor was mounted on a fixed south-facing platform tilted 39° in Ciudad Real (Spain). It included a continuously stirred tank (volume= 1.5 L) and a centrifugal recirculation pump (flow rate: 30 L min⁻¹).

175

176 *2.4. Adsorption studies*

177

178 To analyze BPA adsorption on TiO₂ or TiO₂/graphene composites, different 179 experiments were conducted in the dark using the experimental reactor indicated above. 3.5 L of aqueous solution containing 10 mg L^{-1} BPA solution were prepared by 180 181 weighing and dissolving, by ultrasound mixing for 3 hours, the appropriate amount of BPA in deionized water. Then, the appropriate amount of catalyst (TiO₂ alone or 182 TiO_2 /graphene) was added to the solution to reach a concentration of 125 mg L⁻¹ TiO₂. 183 184 Solution pH can affect both the adsorbent electrical surface charge and the dissociation 185 of the adsorbate. The effect of pH on adsorption of BPA by TiO₂ or by TiO₂/graphene 186 was studied fixing the initial pH value of the solutions at 7.5 and 2.5. These pH values

187 were chosen taking into account the point of the zero charge (PZC) of TiO_2 (between 188 pH= 5.6 and 6.4 (Daneshvar et al., 2004). It is well-known that the surface charge of 189 TiO₂ depends on pH. At more acidic pH values, the TiO₂ surface is positively charged 190 and above TiO₂ PZC, the surface is negatively charged.

191

Samples were agitated at room temperature for a period of 2 h before being filtered
through 0.45 µm syringe filters to separate catalyst particles and to analyze the residual
concentrations of BPA.

195

196 2.5. Solar photocatalytic process

197

198 In a typical solar TiO₂ or TiO₂/graphene photocatalytic run, BPA was dissolved in 199 deionized water as indicated above. This BPA solution was then transferred into a 200 reservoir and the appropriate pre-weighted amount of TiO₂ or TiO₂/graphene catalyst 201 was added in it. The BPA solution was stirred in the dark for 30 minutes to attain 202 adsorption equilibrium between BPA and catalyst particles. The reactant mixture was 203 then pumped through the CPC and solar photocatalytic oxidation started. During the 204 experiments, samples were periodically withdrawn from the reactor and filtered through 205 0.45 µm syringe filters to separate catalyst particles from the liquid. Chemical analyses 206 for BPA, HO[•], Total Organic Carbon (TOC) and dissolved oxygen content were 207 performed.

208

To quantify the oxidation levels by HO[•], $O_2^{\bullet-}$ and 1O_2 , 1 M tert-butyl alcohol, 2 mM 1,4-benzoquinone and 2 mM sodium azide were used as scavenging agents, respectively.

212

All experiments were performed in triplicate, and the medium values were used. Before analysis, all filtered samples were immediately treated with excess Na_2SO_3 to prevent further oxidation (this procedure was performed to avoid overestimating degradation). All the experiments were conducted at room temperature and at natural pH of BPA solution (\cong 7.5).

218 219

220 2.6. Analysis

221

222 BPA concentration was determined using high-performance liquid chromatography 223 with UV detection (Agilent Technologies 1100 HPLC-UV) in the isocratic mode 224 immediately after sampling. An Eclipse XDB-C18 column (5 mm, 4.6×250 mm) was 225 used, and a 75:25 (v/v) methanol/(water with 1% acetic acid) mixture with an acidic pH 226 was used as the mobile phase (detection wavelength, λ = 225 nm; flow rate of 0.6 ml min⁻¹). The mineralization grade of the treated wastewater was determined using a TOC 227 analyzer (TOC-5050 Shimadzu, standard deviation $< 0.2 \text{ mg L}^{-1}$). Quantification of 228 229 hydroxyl radicals was carried out by fluorescence measurement using disodium salt of 230 terephthalic acid (NaTA) (Saran and Summer, 1999). Dissolved oxygen concentration 231 was measured using a Jenway 9200 DO₂ meter.

- 234 3. RESULTS AND DISCUSSION
- 235 *3.1. Characterization Results*
- 236 Surface area and porosity measurement

237 The specific surface area, pore volume, and the pore size of the samples are summarized 238 in Table 1. The BET surface area of the TiO₂ increased (10 %) with graphene 239 incorporation, indicating that the physical adsorptivity of the nanocomposite was 240 improved. This is presumably due to the high theoretical specific surface area (2600 241 m^2/g) of reduced graphene oxide (Akhavan and Ghaderi, 2009). The pore size 242 distribution was also estimated using the Barrett-Joyner-Halenda (BJH) method (Lellala 243 et al., 2016) from the desorption branch of the isotherm. It can be seen that compared to 244 the pure TiO₂, the pore volume of TiO₂/graphene was increased, which is vital to 245 improve the adsorption capacity of the nanocomposite and to increase the efficiency of 246 separation of electron-hole pairs (Saha et al., 2012). In addition, the values showed 247 average pore diameter characteristic of mesoporous materials, which is important for 248 photocatalytic applications.

249

250 UV-Vis diffusive reflectance spectroscopy

The TiO_2 absorption capacity can be studied by UV-Vis diffusive reflectance spectroscopy. Fig. 2 shows that both pure TiO_2 and TiO_2 /graphene have high absorption capacities in the UV region. However, only TiO_2 /graphene composite exhibited a broad adsorption spectra in the visible region. That shows the possibility of visible light photocatalyst by TiO_2 /graphene composite.

257 X-Ray diffraction (XRD)

258 X-Ray diffraction (XRD) was used to examine the crystalline structure of TiO₂ and 259 TiO₂/graphene 2 wt%. Figs. 3a and 3b show XRD patterns obtained for TiO₂ and 260 TiO₂/graphene, respectively. As it is shown, TiO₂/graphene exhibited a similar XRD 261 pattern to pure TiO₂. Anatase and rutile crystalline phases were observed in both 262 composites. Peaks associated only with TiO₂ were observed and no peak was assigned 263 to GO. This indicates that GO was reduced to graphene during the hydrothermal 264 treatment. Graphene did not affect the crystalline structure of TiO₂. The XRD patterns 265 of the samples revealed the crystalline structure of the anatase TiO₂ phase due to the 266 presence of a distinct diffraction peak at 2θ of 25.2° that correspond to the {011} crystal 267 plane. This peak and their corresponding reflections agree with ICSD collection code n° 268 96946 for anatase. The peak diffraction of the rutile TiO_2 phase was observed at 20 of 269 27.4° corresponding to the {110} crystal plane (ICSD collection code n° 76172). The 270 proportion anatase: rutile and the maximum intensities of the peaks of anatase and rutile 271 phases in the diffractograms were almost the same in both samples (anatase: rutile: 272 87:13 for TiO₂ and 86:14 for TiO₂/graphene; maximum intensities: 509 and 76 counts, 273 respectively, for TiO₂ and 524 and 87 counts, respectively, for TiO₂/graphene). It is well 274 known that the intensity of the diffracted peak from a given crystalline structure of the 275 element (i.e., anatase or rutile phase) is proportional to the amount of the structural 276 element present in the crystal sample. The TiO₂ modified with graphene did not suffer 277 modifications in its crystalline structure. It is well-known that anatase form has a 278 photocatalytic activity greater than rutile (Wang and Yu, 2013) which indicates that 279 anatase can generate more oxidative species than rutile and besides the recombination 280 rate of holes and electrons is lower in the anatase phase than in the rutile phase.

Figs. 3c-f present the TEM images of TiO₂/graphene-2 wt% nanocomposite. It can be seen clearly the spherical TiO₂ nanoparticles and the graphene oxide sheets, which is covered with TiO₂ nanoparticles. Intraparticle aggregation formed a mesoporous structure, which was previously confirmed by nitrogen adsorption–desorption analysis. The average diameter of TiO₂ nanoparticles was about 10–30 nm, which is in agreement with the mean crystal size value of 19 nm estimated by the Scherrer equation (Patterson, 1939) based on (200) peak from the X-ray diffractogram.

- 289
- 290 *3.2 Bisphenol-A adsorption kinetics*
- 291

TiO₂ and TiO₂/graphene particles consist of different adsorption sites which will define the adsorption ability of each catalyst. Two models were tested to analyze BPA adsorption: a) Lagergren model, a pseudo-first-order adsorption rate equation (Lagergren, 1898) and b) Ho and McKay model, pseudo-second-order adsorption rate equation (Ho and McKay, 1999).

297

298 The Lagergren equation can be represented by the following equation:

299

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \tag{1}$$

301 where Q_e and Q_t are the values of BPA mass adsorbed per unit mass of adsorbent at 302 equilibrium and time *t* (mg g⁻¹), respectively, and k_1 is the pseudo-first-order rate 303 constant (min⁻¹). The integration of Eq (1) gives the following equation:

305
$$\log(Q_e - Q_t) = \log(Q_e) - \frac{k_1}{2.303}t$$
 (2)

307 Plot of log $(Q_e - Q_t)$ versus t would yield a straight line if the adsorption follows a 308 pseudo-first order kinetic behaviour. This model is based on the assumption that the 309 adsorption rate depends on the number of adsorption sites on the adsorbent surface 310 (Lagergren, 1898). Figs. 4a and 4b show the kinetics of adsorption of BPA on the TiO₂ 311 and TiO₂/graphene surface, respectively, at both pH values, 2.5 and 7.5. We can see that 312 the pseudo-first-order kinetics for both systems, TiO₂ and TiO₂/graphene, was found to be suitable only for an initial interaction time (up to 60 min) and not for the 120 min of 313 314 total contact time.

The pseudo-second order kinetic model (Ho and McKay model), given by Eq (3) is based on the assumption that the adsorption rate is determined by the square of the number of vacant adsorption sites on the adsorbent surface (Ho and McKay, 1999).

318

319
$$\frac{dQ_t}{dt} = k_2 (Q_e - Q_t)^2$$
(3)

320

where Q_e and Q_t are the values of BPA mass adsorbed per unit mass of adsorbent at equilibrium and time t (mg g⁻¹), respectively, and k_2 is the pseudo-second-order rate constant (g min⁻¹ mg⁻¹). The integration of Eq (3) gives the following expression:

325
$$\frac{t}{Q_t} = \frac{1}{k_2(Q_e)^2} + \frac{1}{Q_e}t$$
 (4)

327 Figs. 4c and 4d show the plot of t/Q_t versus t for the adsorption of BPA by TiO₂ and 328 TiO₂/graphene catalysts, respectively, for the two studied pH values, 2.5 and 7.5. As it 329 can be seen, the data fit well to a pseudo-second-order rate kinetics at both pH values 330 for the whole contact time. As shown in Table 2, it can be concluded that: (i) the k_2 331 values are higher for BPA adsorption on TiO₂/graphene than in pure TiO₂; (ii) in both systems, k_2 values depend on the medium pH being higher at pH 7.5 since it takes a 332 shorter time to reach equilibrium (values of $k_2(BPA-TiO_2) = 0.0007$ and 0.0037 g min⁻¹ 333 mg⁻¹ at pH 2.5 and 7.5, respectively, and k_2 (BPA-TiO₂/graphene)= 0.0029 and 0.0043 g 334 min⁻¹ mg⁻¹ at pH 2.5 and 7.5, respectively. This may be explained by the abatement of 335 336 hydrogen ions after the increase of pH, which reduces the chance of competition 337 between hydrogen ions and the BPA molecules. Due to the natural negative charge of 338 TiO_2 at pH > PZC and the natural negative charge of GO over this whole pH range, it 339 would be possible for hydrogen ions to be adsorbed by TiO_2 and TiO_2 /graphene through 340 electrostatic interactions. On the other hand, at pH < 4.5, catalyst particles 341 agglomeration could reduce the BPA adsorption as well as photon absorption (Muruganandham and Swaminathan, 2004); (iii) the adsorption capacity, Q_e , of BPA by 342 TiO_2 /graphene catalyst is higher than that by pure TiO_2 being approximately 31 and 18 343 mg g^{-1} , respectively. 344

345

When adsorption data follow a pseudo-second-order kinetics, the rate limiting step may be chemical adsorption. The excellent adsorption ability may be attributed to π - π stacking interaction and hydrogen bond between BPA and graphene in agreement with other authors (Shen et al., 2014; Jin et al., 2015). Taking into account these adsorption

results and the natural pH of BPA solution (\cong 7.5), this value of pH was chosen as optimal pH for all the photocatalytic experiments.

352

- 353 *3.3 Degradation of BPA by solar TiO₂ process*
 - 354

The degradation reaction of BPA solutions using a solar/TiO₂ photocatalytic system was investigated to find out the optimal values for the initial concentrations of BPA and TiO₂ being 2.5 mg L⁻¹ and 250 mg L⁻¹ the selected values, respectively (Figs. S1-S4, Supplementary Material).

359

360 3.4 Degradation of Bisphenol-A by solar graphene-based TiO₂ process

361

362 To evaluate the performance of the catalytic activity of the TiO₂/graphene catalyst, the degradation of 2.5 mg L⁻¹ BPA aqueous solution using 250 mg L⁻¹ TiO₂/graphene 363 364 catalyst (1, 2 and 3 wt% graphene concentrations with respect to TiO₂) under natural 365 solar light was tested. The initial pH was 7.5 in all experiments. The solar power was around 25-30 W/m², and the average temperature was around 26°C in all experiments. 366 367 Fig. 5a shows an enhancement in the mineralization efficacy of the BPA solution with 368 the TiO_2 /graphene catalyst compared to TiO_2 alone. The percentage of TOC removal 369 increased when TiO₂ was modified with amounts of graphene up to 2 wt%. Fig. 5b 370 exhibits that the incorporation of graphene enhances their photoactivity for BPA 371 mineralization. As can be observed, as the weight percentage of graphene increased from 0 to 2% at a fixed catalyst concentration of TiO_2 (250 mg L⁻¹) the pseudo-first-372 order kinetic rate constant increased from 0.0128 to 0.0149 min⁻¹, respectively, which 373

indicates about 16% improvement over that of pure TiO₂ catalyst. This improvement on 374 375 the performance of TiO₂/graphene could be due to the following: (a) the increase of 376 catalytic surface active sites for the adsorption of BPA, as was discussed in the previous 377 section, resulting in a more efficient photocatalytic process, (b) a good assembly and 378 interfacial coupling between TiO₂ and graphene sheets, as observed by TEM images 379 (Figs. 3c-f), could promote charge migration between both phases and increase the 380 catalyst efficiency, (c) graphene when combined with TiO₂ reduced charge 381 recombination, facilitating the electron-hole separation and the availability of photo-382 generated e⁻ for the photocatalytic reaction, and (d) the introduction of graphene 383 allowed a more efficient utilization of the solar spectrum (Malekshoar et al., 2014). It 384 may note that when 3 wt% of graphene was used, the mineralization efficiency was 385 lower possibly because the photoactivity of the catalyst decreased due to an increase in 386 catalyst agglomerate size and a decrease in light penetration.

387

388 3.5 HO[•] and dissolved O_2 behavior in solar/TiO₂ and solar/TiO₂/graphene

389

390 Figs. 6a and 6b show the behavior of hydroxyl radical and dissolved oxygen, 391 respectively, along BPA degradation reactions by means of the solar/TiO₂ process and 392 for different initial concentrations of the organic pollutant. The initial concentration of BPA varied between 2.5 and 10 mg L^{-1} in the presence of 125 mg L^{-1} TiO₂. The solar 393 power in these experiments was around 25-30 W/m^2 , and the average temperature was 394 395 26°C. The reaction time was 120 min in all experiments. As it can be seen, when an initial concentration of BPA below 5 mg L^{-1} was used, the concentration of HO[•] rapidly 396 397 increased reaching a maximum value at around 6-10 min and then it remained constant.

Above 5 mg L⁻¹ BPA, the increase of the hydroxyl concentration was much lower reaching values of approximately 2000 and 500 nmol L⁻¹ for 7.5 and 10 mg L⁻¹ BPA, respectively. The greater concentration of HO[•] (\cong 13500 nmol L⁻¹) was obtained using the smaller concentration of BPA, 2.5 mg L⁻¹, being higher both the BPA and TOC removal in this case due to the higher TiO₂ photocatalytic efficiency, as indicated above.

404

405 Fig. 6b shows measurements of dissolved oxygen concentration during the solar/TiO₂ 406 process at different initial BPA concentrations. It can be observed that the behaviour of 407 dissolved oxygen was similar in all experiments although its concentration was lower 408 when the initial BPA concentration was increased. In the first reaction stage, dissolved 409 oxygen was decreased by reacting with the photo-excited electrons in the conduction band (Eq. (5)), thus generating superoxide radical anion, O_2^{\bullet} . During this time period, 410 411 solution TOC decreased (see Fig. S2, Supplementary Material). In a second reaction 412 phase, after 90 min, when TOC remained constant, possibly due to the formation of 413 recalcitrant intermediates, hard to be degraded, the concentration of dissolved O_2 was 414 slightly increased according to reactions (6)-(8).

415

416
$$O_2 + e_{CB}^- \to O_2^{\bullet-} \tag{5}$$

417

418
$$O_2^{\bullet-} + H^+ \leftrightarrow HO_2^{\bullet} \tag{6}$$

$$420 \qquad \qquad 2HO_2^{\bullet} \to O_2 + H_2O_2 \tag{7}$$

$$H_2 O + 4h^+ \to \frac{1}{2}O_2 + 2H^+$$
 (8)

423

422

Figs. 6c and 6d show the behavior of hydroxyl radical and dissolved oxygen during 424 BPA treatment by the solar/TiO₂ process in the presence of different initial TiO₂ 425 concentrations of TiO₂ (between 100 and 500 mg L^{-1}). For the sake of comparison, 426 results during BPA treatment by means of the solar/TiO₂/graphene (250 mg L^{-1} 427 428 TiO₂/2wt% of graphene) system are also shown in these figures. The initial concentration of BPA was fixed at 5 mg L^{-1} . The solar power in these experiments was 429 around 25-30 W/m^2 , and the average temperature was 26°C. The reaction time was 120 430 431 min in all experiments. It can be seen that, in the solar/TiO₂ process, the increase of TiO₂ loading from 100 to 250 mg L^{-1} led to the increase in HO[•] generation due to the 432 433 increase of active sites on the catalyst surface and consequently to the increase in the 434 photocatalytic yield and percentage of BPA and TOC removal, as indicated above. It can be also seen the reduction in the production of HO[•] when the initial concentration of 435 TiO_2 was 500 mg L⁻¹, justifying the degradation results indicated above. Also, Fig. 6c 436 shows the behavior of HO[•] when TiO_2 /graphene (250 mg L⁻¹ TiO₂ with 2 wt% of 437 graphene) irradiated by solar light was used. In this case, the concentration of HO[•] 438 439 showed a similar tendency and it was slightly higher than under the same conditions in the presence of pure TiO_2 catalyst. This could be attributed to the consumption of HO[•] 440 by reaction with superoxide radical, O_2^{\bullet} , to form singlet molecular oxygen, in the 441 442 solar/TiO₂ process as given in Eq. (9):

444
$$O_2^{\bullet-} + HO^{\bullet} \to {}^1O_2 + OH^-$$
 (9)

446 With respect to the dissolved oxygen, Fig. 6d showed a similar behavior of O₂ in the 447 BPA solution although its values were slightly higher when the initial TiO₂ loading 448 increased in the solar/TiO₂ treatment process. This could be attributed to higher rates of 449 recombination of electrons and holes, which decreased the availability of 450 photogenerated electrons, e_{CB}, to react with oxygen. However, as can be also seen in Fig. 6d, when TiO_2 was modified with graphene (250 mg L⁻¹ TiO₂ and 2 wt% of 451 452 graphene) a more pronounced decrease of dissolved oxygen was observed, possibly due 453 to a higher amount of e_{CB} on the catalyst surface which consumed more O_2 forming 454 superoxide radical and therefore inhibiting the hole/electron recombination. Thus, the 455 photocatalytic efficacy was higher in the solar TiO₂/graphene treatment process as 456 indicated above.

457

458 3.5 Role of different oxidative intermediate species

459

460 The contributions of various oxidative intermediate species to the degradation of BPA 461 using both solar/TiO₂ and solar/TiO₂/graphene processes were also examined. To 462 quantify the oxidation levels by free radical reactions, the scavenging of intermediate 463 active species was accomplished with 1 M concentration of tert-butyl alcohol (HO[•] and HO_2^{\bullet} quencher), 2 mM 1,4-benzoquinone ($O_2^{\bullet-}$ quencher) and 2mM sodium azide (1O_2 464 465 quencher) (Li et al., 2009; Monteagudo et al., 2011). Several additional experiments 466 under solar/TiO₂ and solar/TiO₂/graphene process were carried out at the optimal 467 conditions in the presence or absence of these scavengers. In these reactions, various 468 oxidative intermediate species could be generated, such as the hydroxyl radical (HO[•]),

hydroperoxyl (HO₂ $^{\bullet}$), singlet oxygen (¹O₂), and the superoxide radical anion (O₂ $^{\bullet-}$). The 469 470 roles of these species are shown in Figs. 7a and 7b. As shown, the presence of some 471 scavenging agents inhibited the degradation reaction (the %BPA removal decreased as 472 compared with the scavenger-free reaction). This indicates the participation of these species in the reaction. Superoxide radical anion, O2[•], was found to be the primary 473 species contributing to the degradation of BPA in both solar/TiO2 and 474 475 solar/TiO₂/graphene systems since p-benzoquinone was the most significant scavenging 476 agent. In the case of TiO₂/graphene treatment system, this may be due to the formation 477 of a heterojunction interface in the TiO_2 /graphene composites, where there is a space-478 charge separation region, graphene nanosheets can accept photogenerated electrons 479 from the TiO₂ conduction band. This reduced the electron-hole pair recombination, and 480 subsequently the oxygen molecules adsorbed on the catalyst surface act as electron scavengers and combine with e_{CB} to form O_2^{\bullet} , according to reaction (5) indicated 481 above. $O_2^{\bullet-}$ is in an acid-base equilibrium (Eq. (6)) but these species predominated over 482 HO_2^{\bullet} since the medium pH was around 7 (pKa (HO_2^{\bullet}) = 4.8 ±0.1) (Bielski et al., 1985). 483

484

From Fig. 7, it can be also concluded that singlet molecular oxygen, ${}^{1}O_{2}$, played a role in the degradation of BPA, but it was more significant in the pure TiO₂ rather than in the TiO₂/graphene treatment system. ${}^{1}O_{2}$ is formed by O₂^{•-} oxidation by holes, h⁺, according to Eq. (10):

489

$${}^{\bullet}O_2^- + h^+ \to {}^{1}O_2$$
 (10)

490 In the case of solar/TiO₂ treatment reaction, the role played by hydroxyl radical, HO[•], 491 was less significant than that played by singlet oxygen. This could be attributed to the 492 participation of HO[•] radicals instead of h^+ in Eq. (10) as given in Eq (9) (Daimon et al., 493 2008), thus decreasing the availability of hydroxyl radicals for the degradation reaction. 494 However, the role of HO[•] was more significant than that played by ${}^{1}O_{2}$ in the 495 degradation of BPA under the solar TiO₂/graphene process possibly due to the higher 496 availability of h⁺ as indicated above. In this case, the contribution of HO[•] to the ${}^{1}O_{2}$ 497 formation was less significant in comparison with the oxidation by h⁺.

498

499 **4.** Conclusions

500

501 The solar photocatalytic degradation and mineralization of a BPA aqueous solution in 502 the presence of TiO_2 /graphene composites was compared to that of pure TiO_2 503 photocatalyst. The TiO₂/graphene catalyst was prepared by a simple hydrothermal 504 treatment method. The results showed that there was an improvement in both the 505 reaction rate and the mineralization degree when TiO₂ was modified with graphene. 506 This higher efficiency could be attributed to the increase of the active sites for 507 adsorption of BPA, to the more effective use of solar spectrum, to the inhibition of 508 electron-hole recombination and the increase of catalyst efficiency by the charge 509 migration between TiO₂ and graphene. Experimental results showed that 20 and 120 min of 25-30 W m⁻² solar irradiation were required to degrade 2.5 mg L^{-1} Bisphenol-A 510 and 84% solution TOC, respectively, when 250 mg L⁻¹ TiO₂/graphene-2 wt% was used. 511 Superoxide radical, O_2^{\bullet} , was found to be the primary species contributing to the 512 513 degradation of BPA in both solar/TiO₂ and solar/TiO₂/graphene systems. In the case of 514 solar/TiO₂ reaction, hydroxyl radicals, HO[•], played a less important role than that of singlet oxygen, due to the participation of HO^{\bullet} radicals instead of h^{+} in the reaction with 515 O_2^{\bullet} to form singlet oxygen. It can be concluded that this solar photocatalytic 516

- 517 TiO₂/graphene oxidation system can be a potential alternative to degrade wastewater
- 518 containing emerging contaminants, such as bisphenol-A.
- 519

520 **5. ACKNOWLEDGMENTS**

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685

687	Figure captions:				
688 689	Figure 1 : a) Structure and properties of Bisphenol-A; b) Schematic illustration of the				
690	experimental set-up.				
691					
692	Figure 2: Normalized UV-vis diffuse reflectance spectra (DRS) of TiO_2 and				
693	TiO ₂ /graphene-2 wt% composite.				
694					
695	Figure 3: a) XRD pattern of TiO ₂ ; b) XRD pattern of TiO ₂ /graphene; c,d) TEM images				
696	of TiO_2 /graphene nanocomposite; e) TEM images of graphene sheets; f) TEM images				
697	of TiO ₂ spheres.				
698					
699	Figure 4 : a) Pseudo-first-order kinetics for the adsorption of BPA on TiO ₂ surface; b)				
700	Pseudo-first-order kinetics for the adsorption of BPA on TiO_2 /graphene surface; c)				
701	Pseudo-second-order kinetics for the adsorption of BPA on TiO_2 surface; d) Pseudo-				
702	second-order kinetics for the adsorption of BPA on TiO_2 /graphene surface.				
703					
704	Figure 5: a) Mineralization degree of BPA solutions under the TiO ₂ /graphene				
705	photocatalyst with 1, 2 and 3 wt% of graphene. b) Effect of weight percentage of				
706	graphene in the TiO_2 /graphene composite on the pseudo-first-order kinetic rate constant.				
707	Experimental conditions: [BPA]: 2.5 mg L ⁻¹ ; [TiO ₂]: 250 mg L ⁻¹ ; solar power: 25-30				
708	W/m ² ; average temperature: 26°C; reaction time: 120 min.				
709					
710	Figure 6: Evolution of the concentration of hydroxyl radicals and dissolved oxygen				
711	along the BPA degradation reaction. a-b) solar/TiO2 process: Influence of the initial				

712 BPA concentration, $[TiO_2]$: 125 mg L⁻¹; c-d) solar/TiO₂ and solar/TiO₂/graphene

713 processes: Effect of TiO₂ loading, [BPA]: 5 mg L^{-1} . Solar power: 25-30 W/m²; average

714 temperature: 26°C; reaction time: 120 min.

- 715
- 716 **Figure 7:** Roles played by different intermediate oxidative species in the degradation of
- 717 BPA solutions under a) solar TiO₂ process; b) solar TiO₂/graphene process.
- 718 Experimental conditions: [BPA]: 2.5 mg L^{-1} ; [TiO₂/graphene]: 250 mg $L^{-1}/2$ %wt; solar
- 719 power: 25-30 W/m²; average temperature: 26°C; reaction time: 120 min.

720

721

Table 1. N₂ adsorption-desorption characteristics of pure TiO₂ P25 and TiO₂/graphene-2 wt% composites

Sample	Surface area ^a (m ² g ⁻¹)	Pore volumen ^b (cm ³ g ⁻¹)	Average pore size ^c (nm)
TiO ₂ P25	50.56	0.27	19.99
TiO ₂ /graphene	55.41	0.46	28.84

^a BET specific surface area was calculated from the linear part of the corresponding
 BET plot.
 ^b BJH desorption cumulative pore volume between 1.7 and 300 nm diameters.

^c Average pore diameter was estimated from the BJH formula

734
735 Table 2. Kinetic parameters for the adsorption of BPA by TiO₂ or by

736 TiO₂/graphene

	Pseudo-	second-order		
TiO ₂			TiO ₂ /graphene	
	pH 2.5	рН 7.5	pH 2.5	рН 7.5
Q_e (mg/g)	18.149	18.248	31.056	31.056
k_2 (g min ⁻¹ mg ⁻¹)	0.0007	0.0037	0.0029	0.0043













a)



d)



e)



- Figure 3





Figure 4



a)



y = -0.0119x - 0.0411 R² = 0.9972

775

b)

 $R^2 = 0.9898$









Figure 7