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

Photocatalytic degradation of a Bisphenol-A (BPA) aqueous solution was achieved using titanium dioxide (TiO_2) and graphene-based TiO_2 photocatalysts activated by solar light. First, a comparative study of the adsorption kinetics of BPA, in the presence of both catalysts, as a function of pH was performed. Then, the effect of the initial BPA concentration and catalyst loading was assessed and the optimal conditions for BPA degradation by means of heterogeneous solar photocatalysis were determined. It was observed that TiO_2 modified with 2 wt% graphene improved the photocatalytic efficiency in terms of BPA mineralization. The TiO_2 /graphene photocatalytic composite achieved a 16% increase in the photocatalytic mineralization of the BPA solution under solar light compared to un-doped TiO_2 . This enhancement of photocatalytic efficiency is a result of the increase of active sites for BPA adsorption, the more efficient harvesting of solar light, and the inhibition of electron-hole recombination. The dynamic behavior of hydroxyl radicals and dissolved oxygen in these systems was also discussed. Finally, the roles played by hydroxyl radical, $\text{HO}^\bullet$, superoxide radical anion, $\text{O}_2^{\bullet-}$, and singlet molecular oxygen, $^1\text{O}_2$, were studied in both TiO_2 and TiO_2 /graphene systems. It was found that $\text{O}_2^{\bullet-}$ were the main oxidative species in both systems.

Keywords: bisphenol-A; TiO_2 /graphene; oxidative species; solar light.

1. INTRODUCTION

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

It is well-known that Advanced Oxidation Processes (AOPs) are effective methods for treating organic pollutants in water. The efficacy of AOPs is based on the generation of highly reactive free radicals, especially hydroxyl radicals ($\text{HO}^\bullet$) or sulfate radicals ($\text{SO}_4^{\bullet-}$), which are capable of transforming bio-recalcitrant molecules into biodegradable products. Among AOPs, heterogeneous photocatalytic degradation reactions using semiconductor metallic oxides, such as TiO_2 , as photocatalysts to destruct persistent organic pollutants such as EDCs have been well studied (Esplugas et al., 2007; Durán et al., 2009; Xekoukoulotakis et al., 2011). Reactive oxygen species, mainly hydroxyl radical, superoxide radical anion, $\text{O}_2^{\bullet-}$, and singlet molecular oxygen, $^1\text{O}_2$, which can degrade a wide range of chemical contaminants in water, are generated during 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 energy can be used, alternatively to UV lamps, as a more sustainable option in order to reduce the energy and costs of the water treatment process. TiO_2 -assisted photocatalytic

degradation of several organic contaminants by solar light has been successfully used. This was found to be an economically viable process since solar energy is an abundant 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). TiO_2 has a wide band gap (anatase $E_{\text{bg}} = 3.2 \text{ eV}$ or $\lambda < 387 \text{ nm}$) and requires UV excitation (energy equal to or greater than the band-gap) to form electron-hole pairs. The conduction band electrons are able to reduce dissolved oxygen to generate superoxide radical, $\text{O}_2^{\bullet-}$, hydroperoxyl radicals, $\text{HO}_2^{\bullet}$, and through subsequent reduction reactions, hydrogen peroxide, H_2O_2 , and hydroxyl radical, $\text{HO}^{\bullet}$. The valence band holes, h^+ , are able to oxidize water to form $\text{HO}^{\bullet}$. The drawbacks of solar photocatalysis are that the UV radiation received by the earth is only around 5% of the entire solar energy spectrum and the photogenerated electron-hole pairs have fast recombination rates. In this sense, the efficiency of solar photocatalysis can be improved by doping TiO_2 composites with materials, such as graphene (Kumordzi et al., 2016), in order to expand the catalyst band-gap to the visible light region of the solar spectrum ($\lambda > 400 \text{ nm}$) and prevent electron-hole pair recombination (Fukahori et al., 2003; Bellobono et al., 2005; Ni et al., 2007; Fujishima et al., 2008). The use of graphene is of great scientific interest due to its excellent properties such as chemical inertness, stability in both acidic and basic mediums, its abundance and large surface area ($2630 \text{ m}^2/\text{g}$) (Upadhyay et al., 2014).

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/ $\text{K}_2\text{S}_2\text{O}_8$ and UV/ Na_2CO_3 processes was also studied (Sánchez-

Polo 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).

However, to the best of our knowledge, the application of graphene-TiO₂ composites irradiated by natural solar light for BPA degradation has not been studied yet. Therefore, further studies are required in this area to develop a more sustainable and cost efficient treatment technology. The aim of this work is to investigate BPA mineralization reactions by using solar photocatalytic oxidation in the presence of TiO₂ 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 various process parameters, such as initial concentrations of BPA and suspended photocatalysts as well as the type of the catalyst on mineralization reactions were evaluated. Afterwards, the dynamic behavior of HO• radicals and the profile of dissolved oxygen in both catalytic systems were determined. Finally, the roles played by different reactive oxidative species such as HO•, O₂•⁻ and ¹O₂, in both TiO₂ and TiO₂/graphene systems were evaluated using appropriate scavengers.

2. EXPERIMENTAL

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.

2.2. Photocatalyst preparation and characterization

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

Structural analyses of TiO₂ and TiO₂/graphene samples were determined by X-ray Diffraction (XRD) using a PHILIPS X'Pert MPD PW 3040 analyzer with a Cu KAlpha1 radiation. Ultraviolet-visible (UV-Vis) spectra were collected in a Cary 100 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 Brunauer-Emmett-Teller (BET) method using the Micro-meritics Gemini VII 2390 by using N₂ adsorption at 77 K.

2.3. Experimental set-up

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).

2.4. Adsorption studies

To analyze BPA adsorption on TiO₂ or TiO₂/graphene composites, different 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 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 TiO₂/graphene) was added to the solution to reach a concentration of 125 mg L⁻¹ TiO₂. Solution pH can affect both the adsorbent electrical surface charge and the dissociation of the adsorbate. The effect of pH on adsorption of BPA by TiO₂ or by TiO₂/graphene was studied fixing the initial pH value of the solutions at 7.5 and 2.5. These pH values

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

Samples were agitated at room temperature for a period of 2 h before being filtered through $0.45\ \mu\text{m}$ syringe filters to separate catalyst particles and to analyze the residual concentrations of BPA.

2.5. Solar photocatalytic process

In a typical solar TiO_2 or $\text{TiO}_2/\text{graphene}$ photocatalytic run, BPA was dissolved in deionized water as indicated above. This BPA solution was then transferred into a reservoir and the appropriate pre-weighted amount of TiO_2 or $\text{TiO}_2/\text{graphene}$ catalyst was added in it. The BPA solution was stirred in the dark for 30 minutes to attain adsorption equilibrium between BPA and catalyst particles. The reactant mixture was then pumped through the CPC and solar photocatalytic oxidation started. During the experiments, samples were periodically withdrawn from the reactor and filtered through $0.45\ \mu\text{m}$ syringe filters to separate catalyst particles from the liquid. Chemical analyses for BPA, $\text{HO}^\bullet$, Total Organic Carbon (TOC) and dissolved oxygen content were performed.

To quantify the oxidation levels by $\text{HO}^\bullet$, $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$, 1 M tert-butyl alcohol, 2 mM 1,4-benzoquinone and 2 mM sodium azide were used as scavenging agents, respectively.

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 ($\cong 7.5$).

2.6. Analysis

BPA concentration was determined using high-performance liquid chromatography with UV detection (Agilent Technologies 1100 HPLC-UV) in the isocratic mode immediately after sampling. An Eclipse XDB-C18 column (5 mm, 4.6×250 mm) was used, and a 75:25 (v/v) methanol/(water with 1% acetic acid) mixture with an acidic pH was used as the mobile phase (detection wavelength, $\lambda = 225$ nm; flow rate of 0.6 ml min^{-1}). The mineralization grade of the treated wastewater was determined using a TOC analyzer (TOC-5050 Shimadzu, standard deviation $< 0.2 \text{ mg L}^{-1}$). Quantification of hydroxyl radicals was carried out by fluorescence measurement using disodium salt of terephthalic acid (NaTA) (Saran and Summer, 1999). Dissolved oxygen concentration was measured using a Jenway 9200 DO_2 meter.

3. RESULTS AND DISCUSSION

3.1. Characterization Results

Surface area and porosity measurement

The specific surface area, pore volume, and the pore size of the samples are summarized in Table 1. The BET surface area of the TiO₂ increased (10 %) with graphene incorporation, indicating that the physical adsorptivity of the nanocomposite was improved. This is presumably due to the high theoretical specific surface area (2600 m²/g) of reduced graphene oxide (Akhavan and Ghaderi, 2009). The pore size distribution was also estimated using the Barrett-Joyner-Halenda (BJH) method (Lellala et al., 2016) from the desorption branch of the isotherm. It can be seen that compared to the pure TiO₂, the pore volume of TiO₂/graphene was increased, which is vital to improve the adsorption capacity of the nanocomposite and to increase the efficiency of separation of electron-hole pairs (Saha et al., 2012). In addition, the values showed average pore diameter characteristic of mesoporous materials, which is important for photocatalytic applications.

UV-Vis diffusive reflectance spectroscopy

The TiO₂ absorption capacity can be studied by UV-Vis diffusive reflectance spectroscopy. Fig. 2 shows that both pure TiO₂ and TiO₂/graphene have high absorption capacities in the UV region. However, only TiO₂/graphene composite exhibited a broad adsorption spectra in the visible region. That shows the possibility of visible light photocatalyst by TiO₂/graphene composite.

X-Ray diffraction (XRD)

X-Ray diffraction (XRD) was used to examine the crystalline structure of TiO_2 and $\text{TiO}_2/\text{graphene}$ 2 wt%. Figs. 3a and 3b show XRD patterns obtained for TiO_2 and $\text{TiO}_2/\text{graphene}$, respectively. As it is shown, $\text{TiO}_2/\text{graphene}$ exhibited a similar XRD pattern to pure TiO_2 . Anatase and rutile crystalline phases were observed in both composites. Peaks associated only with TiO_2 were observed and no peak was assigned to GO. This indicates that GO was reduced to graphene during the hydrothermal treatment. Graphene did not affect the crystalline structure of TiO_2 . The XRD patterns of the samples revealed the crystalline structure of the anatase TiO_2 phase due to the presence of a distinct diffraction peak at 2θ of 25.2° that correspond to the $\{011\}$ crystal plane. This peak and their corresponding reflections agree with ICSD collection code n° 96946 for anatase. The peak diffraction of the rutile TiO_2 phase was observed at 2θ of 27.4° corresponding to the $\{110\}$ crystal plane (ICSD collection code n° 76172). The proportion anatase: rutile and the maximum intensities of the peaks of anatase and rutile phases in the diffractograms were almost the same in both samples (anatase: rutile: 87:13 for TiO_2 and 86:14 for $\text{TiO}_2/\text{graphene}$; maximum intensities: 509 and 76 counts, respectively, for TiO_2 and 524 and 87 counts, respectively, for $\text{TiO}_2/\text{graphene}$). It is well known that the intensity of the diffracted peak from a given crystalline structure of the element (i.e., anatase or rutile phase) is proportional to the amount of the structural element present in the crystal sample. The TiO_2 modified with graphene did not suffer modifications in its crystalline structure. It is well-known that anatase form has a photocatalytic activity greater than rutile (Wang and Yu, 2013) which indicates that anatase can generate more oxidative species than rutile and besides the recombination 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.

3.2 Bisphenol-A adsorption kinetics

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).

The Lagergren equation can be represented by the following equation:

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

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_1 is the pseudo-first-order rate constant (min⁻¹). The integration of Eq (1) gives the following equation:

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

306

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 TiO_2
 311 and $\text{TiO}_2/\text{graphene}$ surface, respectively, at both pH values, 2.5 and 7.5. We can see that
 312 the pseudo-first-order kinetics for both systems, TiO_2 and $\text{TiO}_2/\text{graphene}$, was found to
 313 be suitable only for an initial interaction time (up to 60 min) and not for the 120 min of
 314 total contact time.

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

318

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

320

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

324

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

326

327 Figs. 4c and 4d show the plot of t/Q_t versus t for the adsorption of BPA by TiO_2 and
328 $\text{TiO}_2/\text{graphene}$ 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 $\text{TiO}_2/\text{graphene}$ than in pure TiO_2 ; (ii) in both
332 systems, k_2 values depend on the medium pH being higher at pH 7.5 since it takes a
333 shorter time to reach equilibrium (values of $k_2(\text{BPA-TiO}_2) = 0.0007$ and $0.0037 \text{ g min}^{-1}$
334 mg^{-1} at pH 2.5 and 7.5, respectively, and $k_2(\text{BPA-TiO}_2/\text{graphene}) = 0.0029$ and 0.0043 g
335 $\text{min}^{-1} \text{ mg}^{-1}$ at pH 2.5 and 7.5, respectively. This may be explained by the abatement of
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 $\text{pH} > \text{PZC}$ 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 $\text{TiO}_2/\text{graphene}$ through
340 electrostatic interactions. On the other hand, at $\text{pH} < 4.5$, catalyst particles
341 agglomeration could reduce the BPA adsorption as well as photon absorption
342 (Muruganandham and Swaminathan, 2004); (iii) the adsorption capacity, Q_e , of BPA by
343 $\text{TiO}_2/\text{graphene}$ catalyst is higher than that by pure TiO_2 being approximately 31 and 18
344 mg g^{-1} , respectively.

345

346 When adsorption data follow a pseudo-second-order kinetics, the rate limiting step may
347 be chemical adsorption. The excellent adsorption ability may be attributed to π - π
348 stacking interaction and hydrogen bond between BPA and graphene in agreement with
349 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.

3.3 Degradation of BPA by solar TiO₂ process

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).

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

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 catalyst (1, 2 and 3 wt% graphene concentrations with respect to TiO₂) under natural 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. Fig. 5a shows an enhancement in the mineralization efficacy of the BPA solution with the TiO₂/graphene catalyst compared to TiO₂ alone. The percentage of TOC removal increased when TiO₂ was modified with amounts of graphene up to 2 wt%. Fig. 5b exhibits that the incorporation of graphene enhances their photoactivity for BPA mineralization. As can be observed, as the weight percentage of graphene increased from 0 to 2% at a fixed catalyst concentration of TiO₂ (250 mg L⁻¹) the pseudo-first-order kinetic rate constant increased from 0.0128 to 0.0149 min⁻¹, respectively, which

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

3.5 HO• and dissolved O₂ behavior in solar/TiO₂ and solar/TiO₂/graphene

Figs. 6a and 6b show the behavior of hydroxyl radical and dissolved oxygen, respectively, along BPA degradation reactions by means of the solar/TiO₂ process and 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 power in these experiments was around 25-30 W/m², and the average temperature was 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 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• (≅ 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.

Fig. 6b shows measurements of dissolved oxygen concentration during the solar/TiO₂ process at different initial BPA concentrations. It can be observed that the behaviour of dissolved oxygen was similar in all experiments although its concentration was lower when the initial BPA concentration was increased. In the first reaction stage, dissolved oxygen was decreased by reacting with the photo-excited electrons in the conduction band (Eq. (5)), thus generating superoxide radical anion, O₂^{•-}. During this time period, solution TOC decreased (see Fig. S2, Supplementary Material). In a second reaction phase, after 90 min, when TOC remained constant, possibly due to the formation of recalcitrant intermediates, hard to be degraded, the concentration of dissolved O₂ was slightly increased according to reactions (6)-(8).

Figs. 6c and 6d show the behavior of hydroxyl radical and dissolved oxygen during BPA treatment by the solar/TiO₂ process in the presence of different initial TiO₂ concentrations of TiO₂ (between 100 and 500 mg L⁻¹). For the sake of comparison, results during BPA treatment by means of the solar/TiO₂/graphene (250 mg L⁻¹ 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 around 25-30 W/m², and the average temperature was 26°C. The reaction time was 120 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 increase of active sites on the catalyst surface and consequently to the increase in the 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 TiO₂ was 500 mg L⁻¹, justifying the degradation results indicated above. Also, Fig. 6c shows the behavior of HO• when TiO₂/graphene (250 mg L⁻¹ TiO₂ with 2 wt% of graphene) irradiated by solar light was used. In this case, the concentration of HO• showed a similar tendency and it was slightly higher than under the same conditions in the presence of pure TiO₂ catalyst. This could be attributed to the consumption of HO• by reaction with superoxide radical, O₂•⁻, to form singlet molecular oxygen, in the solar/TiO₂ process as given in Eq. (9):

445

446 With respect to the dissolved oxygen, Fig. 6d showed a similar behavior of O_2 in the
447 BPA solution although its values were slightly higher when the initial TiO_2 loading
448 increased in the solar/ TiO_2 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
451 Fig. 6d, when TiO_2 was modified with graphene (250 mg L^{-1} TiO_2 and 2 wt% of
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 TiO_2 /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/ TiO_2 and solar/ TiO_2 /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 ($HO^\bullet$ and
464 $HO_2^\bullet$ quencher), 2 mM 1,4-benzoquinone ($O_2^{\bullet-}$ quencher) and 2mM sodium azide (1O_2
465 quencher) (Li et al., 2009; Monteagudo et al., 2011). Several additional experiments
466 under solar/ TiO_2 and solar/ TiO_2 /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 ($HO^\bullet$),

hydroperoxyl ($\text{HO}_2^\bullet$), singlet oxygen ($^1\text{O}_2$), and the superoxide radical anion ($\text{O}_2^{\bullet-}$). The roles of these species are shown in Figs. 7a and 7b. As shown, the presence of some scavenging agents inhibited the degradation reaction (the %BPA removal decreased as compared with the scavenger-free reaction). This indicates the participation of these species in the reaction. Superoxide radical anion, $\text{O}_2^{\bullet-}$, was found to be the primary species contributing to the degradation of BPA in both solar/ TiO_2 and solar/ TiO_2 /graphene systems since p-benzoquinone was the most significant scavenging agent. In the case of TiO_2 /graphene treatment system, this may be due to the formation of a heterojunction interface in the TiO_2 /graphene composites, where there is a space-charge separation region, graphene nanosheets can accept photogenerated electrons from the TiO_2 conduction band. This reduced the electron-hole pair recombination, and subsequently the oxygen molecules adsorbed on the catalyst surface act as electron scavengers and combine with e^-_{CB} to form $\text{O}_2^{\bullet-}$, according to reaction (5) indicated above. $\text{O}_2^{\bullet-}$ is in an acid-base equilibrium (Eq. (6)) but these species predominated over $\text{HO}_2^\bullet$ since the medium pH was around 7 ($\text{pK}_a(\text{HO}_2^\bullet) = 4.8 \pm 0.1$) (Bielski et al., 1985).

From Fig. 7, it can be also concluded that singlet molecular oxygen, $^1\text{O}_2$, played a role in the degradation of BPA, but it was more significant in the pure TiO_2 rather than in the TiO_2 /graphene treatment system. $^1\text{O}_2$ is formed by $\text{O}_2^{\bullet-}$ oxidation by holes, h^+ , according to Eq. (10):

In the case of solar/ TiO_2 treatment reaction, the role played by hydroxyl radical, $\text{HO}^\bullet$, was less significant than that played by singlet oxygen. This could be attributed to the participation of $\text{HO}^\bullet$ radicals instead of h^+ in Eq. (10) as given in Eq (9) (Daimon et al.,

2008), thus decreasing the availability of hydroxyl radicals for the degradation reaction. However, the role of $\text{HO}^\bullet$ was more significant than that played by $^1\text{O}_2$ in the degradation of BPA under the solar TiO_2 /graphene process possibly due to the higher availability of h^+ as indicated above. In this case, the contribution of $\text{HO}^\bullet$ to the $^1\text{O}_2$ formation was less significant in comparison with the oxidation by h^+ .

4. Conclusions

The solar photocatalytic degradation and mineralization of a BPA aqueous solution in the presence of TiO_2 /graphene composites was compared to that of pure TiO_2 photocatalyst. The TiO_2 /graphene catalyst was prepared by a simple hydrothermal treatment method. The results showed that there was an improvement in both the reaction rate and the mineralization degree when TiO_2 was modified with graphene. This higher efficiency could be attributed to the increase of the active sites for adsorption of BPA, to the more effective use of solar spectrum, to the inhibition of electron-hole recombination and the increase of catalyst efficiency by the charge migration between TiO_2 and graphene. Experimental results showed that 20 and 120 min of $25\text{--}30\text{ W m}^{-2}$ solar irradiation were required to degrade 2.5 mg L^{-1} Bisphenol-A and 84% solution TOC, respectively, when 250 mg L^{-1} TiO_2 /graphene-2 wt% was used. Superoxide radical, $\text{O}_2^{\bullet-}$, was found to be the primary species contributing to the degradation of BPA in both solar/ TiO_2 and solar/ TiO_2 /graphene systems. In the case of solar/ TiO_2 reaction, hydroxyl radicals, $\text{HO}^\bullet$, played a less important role than that of singlet oxygen, due to the participation of $\text{HO}^\bullet$ radicals instead of h^+ in the reaction with $\text{O}_2^{\bullet-}$ to form singlet oxygen. It can be concluded that this solar photocatalytic

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

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Figure captions:

Figure 1: a) Structure and properties of Bisphenol-A; b) Schematic illustration of the experimental set-up.

Figure 2: Normalized UV–vis diffuse reflectance spectra (DRS) of TiO_2 and $\text{TiO}_2/\text{graphene}$ -2 wt% composite.

Figure 3: a) XRD pattern of TiO_2 ; b) XRD pattern of $\text{TiO}_2/\text{graphene}$; c,d) TEM images of $\text{TiO}_2/\text{graphene}$ nanocomposite; e) TEM images of graphene sheets; f) TEM images of TiO_2 spheres.

Figure 4: a) Pseudo-first-order kinetics for the adsorption of BPA on TiO_2 surface; b) Pseudo-first-order kinetics for the adsorption of BPA on $\text{TiO}_2/\text{graphene}$ surface; c) Pseudo-second-order kinetics for the adsorption of BPA on TiO_2 surface; d) Pseudo-second-order kinetics for the adsorption of BPA on $\text{TiO}_2/\text{graphene}$ surface.

Figure 5: a) Mineralization degree of BPA solutions under the $\text{TiO}_2/\text{graphene}$ photocatalyst with 1, 2 and 3 wt% of graphene. b) Effect of weight percentage of graphene in the $\text{TiO}_2/\text{graphene}$ composite on the pseudo-first-order kinetic rate constant. Experimental conditions: $[\text{BPA}]$: 2.5 mg L^{-1} ; $[\text{TiO}_2]$: 250 mg L^{-1} ; solar power: 25-30 W/m^2 ; average temperature: 26°C ; reaction time: 120 min.

Figure 6: Evolution of the concentration of hydroxyl radicals and dissolved oxygen along the BPA degradation reaction. a-b) solar/ TiO_2 process: Influence of the initial BPA concentration, $[\text{TiO}_2]$: 125 mg L^{-1} ; c-d) solar/ TiO_2 and solar/ $\text{TiO}_2/\text{graphene}$

processes: Effect of TiO_2 loading, $[\text{BPA}]$: 5 mg L^{-1} . Solar power: $25\text{-}30 \text{ W/m}^2$; average temperature: 26°C ; reaction time: 120 min.

Figure 7: Roles played by different intermediate oxidative species in the degradation of BPA solutions under a) solar TiO_2 process; b) solar $\text{TiO}_2/\text{graphene}$ process. Experimental conditions: $[\text{BPA}]$: 2.5 mg L^{-1} ; $[\text{TiO}_2/\text{graphene}]$: $250 \text{ mg L}^{-1}/2 \text{ \%wt}$; solar power: $25\text{-}30 \text{ W/m}^2$; average temperature: 26°C ; reaction time: 120 min.

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

Table 2. Kinetic parameters for the adsorption of BPA by TiO₂ or by TiO₂/graphene

Pseudo-second-order				
TiO ₂			TiO ₂ /graphene	
	pH 2.5	pH 7.5	pH 2.5	pH 7.5
<i>Q_e</i> (mg/g)	18.149	18.248	31.056	31.056
<i>k₂</i> (g min ⁻¹ mg ⁻¹)	0.0007	0.0037	0.0029	0.0043

Linear formula: $(\text{CH}_3)_2\text{C}(\text{C}_6\text{H}_4\text{OH})_2$

Molecular weight: $228.29 \text{ g mol}^{-1}$

Water solubility: 120 mg L^{-1} (25°C)

a)

b)

Figure 1

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759 **Figure 2**

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a)

b)

c)

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e)

f)

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766 **Figure 3**

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a)

b)

c)

d)

Figure 4

a)

b)

Figure 5

Figure 6

a)

b)

782 **Figure 7**