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1 **Photocatalytic degradation of bisphenol-A under UV-LED, blacklight and solar**
2 **irradiation**

3
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1 **Abstract**

2 This study aims at investigating the photocatalytic treatment of bisphenol-A (BPA)
3 under various irradiation sources in order to identify cleaner and more sustainable
4 technologies compared to conventional photocatalytic wastewater treatment systems.
5 For this purpose, parallel experimental runs were carried out in two batch-operated
6 slurry photoreactors under UVA irradiation provided by either a light-emitting diode
7 (UV-LED) or a UV blacklight lamp (UV-BL), as well as in a solar compound
8 parabolic collector (CPC) reactor under natural sunlight. The effect of key operating
9 parameters, such as the initial BPA and TiO₂ concentrations, water matrix, and
10 treatment time, on the efficiency of the three photocatalytic systems was evaluated.
11 The photocatalytic degradation of BPA was found to fit well with the pseudo-first-
12 order kinetic model. BPA removal rate increased with catalyst concentration and with
13 decreasing the initial concentration of BPA. The addition of humic acids was found to
14 be inhibitory for all photocatalytic systems. At the best conditions assayed (C₀= 2.5
15 mg/L, TiO₂= 250 mg/L), BPA was completely degraded within 20, 30, and 120 min
16 under UV-LED, solar, and UV-BL irradiation, respectively. The corresponding
17 reaction rates were 0.230, 0.151, and 0.025 min⁻¹, and TOC removal was 88, 67, and
18 33% after 90 min of treatment. In all cases, TiO₂/UV-LED achieved the highest
19 removal efficiency and it was found to be significantly more energy-efficient than the
20 TiO₂/UV-BL system. All in all, LED-driven photocatalysis was found to be
21 advantageous over conventional TiO₂/UV-BL systems in terms of performance and
22 sustainability, and an appropriate alternative to solar photocatalysis in areas where
23 sunlight is inadequate.

24

1 **Keywords:** EDCs; water purification; emerging contaminants; light-emitting diodes;
2 solar CPC; photocatalysis

3

4 **1 Introduction**

5 Bisphenol-A (BPA), a well-known endocrine disrupting compound (EDC), is an
6 alkylphenol used extensively in the synthesis of polycarbonate polymers and epoxy
7 resins (Deblonde et al., 2011). Due to its heat resistance and elasticity, BPA is found
8 in several products, such as food containers, metal cans, and baby bottles (Giulivo et
9 al., 2016; Rubin, 2011). Changes of the inner temperature and pH of BPA-containing
10 materials result in hydrolysis of the ester bonds of BPA, which subsequently lead to
11 BPA leaching into foods and beverages. Ingested BPA is thought to be absorbed by
12 the gastrointestinal tract and then excreted in urine (Giulivo et al., 2016). Existing
13 conventional wastewater treatment plants (WWTPs) are not typically designed for the
14 treatment of such persistent compounds (Belgiorno et al., 2007; Luo et al., 2014), and
15 therefore BPA escapes intact into the aquatic environment by means of the effluent
16 discharges of WWTPs. As a result, BPA has been extensively detected in influent and
17 effluent of WWTPs, groundwater, surface, and drinking water (Kasprzyk-Hordern et
18 al., 2009; Kleywegt et al., 2011; Loos et al., 2010). Exposure to BPA, even at trace
19 level concentrations, has been found to affect the reproductive system of humans (Li
20 et al., 2010; Meeker et al., 2010), and has been linked to growth, developmental, and
21 reproductive effects on aquatic invertebrates, fishes, amphibians, reptiles, birds, and
22 mammalian wildlife (Flint et al., 2012; Zhang et al., 2016). To this end, new, effective
23 and sustainable treatment methods are required to set a barrier to the release of
24 emerging microcontaminants, such as BPA, into the environment.

1 TiO₂-mediated photocatalysis has received considerable attention because of its
2 efficiency to eliminate EDCs in water and wastewater (Belgiorno et al., 2007;
3 Dalrymple et al., 2007). Photocatalytic oxidation is initiated upon ultraviolet (UV)
4 illumination of a catalyst, usually TiO₂. Highly reactive species, mainly hydroxyl
5 radicals ([•]OH), are then formed and attack organic pollutants, which are eventually
6 mineralised into CO₂ and inorganic anions (Herrmann, 1999; Malato et al., 2009).
7 Sunlight is a free and plentiful renewable energy that can be also used as an
8 irradiation source to increase process sustainability (Legrini et al., 1993). Solar
9 photocatalysis takes advantage of the near-UV band of the solar spectrum to excite
10 TiO₂ catalysts (Malato et al., 2009). In areas where sunlight is inadequate, artificial
11 irradiation is required for photon generation to supplement the efficiency of
12 traditionally employed conventional blacklight fluorescent (UV-BL) lamps (Tokode
13 et al., 2015). However UV-BL lamps suffer from several drawbacks, such as their low
14 energy efficiency, short lifespan and health and safety issues since they contain toxic
15 mercury gas (Jo and Tayade, 2014). As a consequence, UV-BL photocatalytic
16 applications suffer from high treatment costs and increased environmental impacts
17 (Chatzisyneon et al., 2013; Mahamuni and Adewuyi, 2010). To date, 128 countries
18 have signed the Minamata Convention on Mercury, which aims at the gradual phase-
19 out of mercury-containing products by 2020 (Matafonova and Batoev, 2018).
20 Therefore, sustainable mercury-free UV sources are sought to power photochemical
21 oxidation technologies. In this regard, UV light-emitting diodes (UV-LEDs) can be
22 used as eco-friendly alternatives to UV-BL lamps (Davididou et al., 2018). Key
23 features of LEDs include energy efficiency, extended lifetime, and toxic-free nature
24 (i.e. free of mercury and lead, and absence of gas fill) that can lower the cost and
25 improve process sustainability (Tokode et al., 2015).

1 Several studies have dealt with the photocatalytic degradation of BPA under
2 conventional UVA, vis-LED, and solar irradiation (Subagio et al., 2010; Tsai et al.,
3 2009; Zacharakis et al., 2013). (Saggiaro et al., 2014) compared the removal
4 efficiency of BPA under conventional UVA and solar irradiation in batch and
5 compound parabolic collector (CPC) reactors using TiO₂ P25 suspensions. The
6 authors reported enhanced photocatalytic performance in the solar CPC compared to
7 the batch reactor, ascribing it to the optimized optical design of CPC, which allows
8 the use of both direct and diffuse solar irradiation. The present study investigates the
9 photocatalytic degradation of BPA under UVA irradiation provided by either a UV-
10 LED, UV-BL or natural sunlight in parallel experimental runs. To the best of the
11 authors' knowledge, this is the first time that the efficiency of three different
12 photocatalytic systems is compared under similar experimental conditions (i.e.
13 catalyst concentration, substrate concentration, water matrix). Results of this work
14 will create important scientific knowledge on the kinetic rates of BPA degradation
15 under several irradiation sources and how these can be affected by altering basic
16 operating parameters. The lack of an environmentally friendly and low-cost
17 irradiation source with constant availability of light is the main technical barrier that
18 impedes the large-scale application of TiO₂-mediated photocatalytic water treatment.
19 Therefore, findings of this work can be used as a tool for researchers and water
20 industry to further scale-up the process by using the most suitable irradiation source
21 (or a combination of them) that will enable an effective and sustainable treatment of
22 water and wastewater. Moreover, to the best of the authors' knowledge, degradation
23 of BPA under UVA-LED irradiation in the presence of TiO₂ P25 suspensions has not
24 been reported in the literature yet.

1 For this purpose, photocatalytic experiments were performed both in batch and CPC
2 reactors in the presence of TiO₂ catalyst. The degradation of BPA was studied with
3 consideration to the potential application of photocatalysis as a final polishing step
4 after secondary treatment in domestic wastewater or drinking water treatment plants.
5 The effect of key operating parameters, such as initial substrate and catalyst
6 concentration, treatment time, and water matrix on photocatalytic performance was
7 evaluated. Furthermore, the three photocatalytic systems were compared in terms of
8 their technical and economic benefits.

9 **2 Materials and Methods**

10 **2.1 Materials**

11 Bisphenol-A (BPA; $\geq 99\%$ purity, CAS No. 80-05-7) was purchased from Sigma-
12 Aldrich. Leonardite humic acid (HA) IHSS standard was used. HA stock solution was
13 prepared by dissolving a prescribed amount of HA in 0.1 M NaOH and further
14 diluting it in ultra-pure water (UPW; 18.2 M Ω .cm at 25 °C, ELGA LabWater).
15 Aeroxide TiO₂ P25 (anatase:rutile 80:20, 21 nm primary particle size, 50 \pm 15 m²/g
16 BET surface area), supplied by Evonik Industries, was used as the catalyst.

17

18 **2.2 Photocatalytic experiments**

19 Experiments under artificial irradiation were performed in batch-operated, slurry
20 photoreactors at lab-scale. For LED-driven photocatalysis, an indium gallium nitride
21 (InGaN) UVA emitter (UV-LED; $\lambda = 365$ nm, LZ4-00U600, LED Engin) was
22 employed providing continuous irradiation. The UVA emitter was mounted onto a
23 heat sink (588-SV-LED-176E, Ohmite S Series) to prevent radiant flux decrease due
24 to temperature rise on the diode's surface. The LED assembly was placed above the

1 reactor and a quartz protective plate was placed between them (Figure 1a). The
2 second irradiation source was a UV low-pressure blacklight fluorescent lamp (UV-
3 BL; PLS G23, Casell Lighting), emitting predominantly at $\lambda = 365$ nm. UV-BL was
4 housed in a quartz tube and, for the sake of comparison, positioned on top of the
5 reactor at the same height as the LED assembly (i.e. 8 cm distance between irradiation
6 source and surface of reactant mixture at the beginning of each experiment) (Figure
7 1b). Both set-ups were covered with aluminium shields to prevent light diffusion out
8 of the reactors and minimise penetration of ambient light. The reactors (250 mL
9 Schott Duran beakers, diameter 7 cm, height 9 cm) provided an illuminated area of
10 38.5 cm^2 . The quartz glasses were UV transparent and used to protect the lamps from
11 water spills. UV-LED and UV-BL irradiation sources were driven by electrical power
12 of 11 W and were connected in series to a DC power supply.

13

14 Figure 1. Schematics of (a) UV-LED, (b) UV-BL, and (c) solar CPC reactors.

15

16 In a typical run, 150 mL of BPA solution was introduced in the photoreactor and a
17 prescribed amount of catalyst was added. The obtained slurry solution was
18 continuously stirred magnetically at 500 rpm to promote uniform dispersion of
19 catalyst powder and dissolved oxygen. At the beginning of each experiment, the
20 solution was stirred in the dark for 30 min to ensure complete adsorption-desorption
21 equilibrium of BPA on the catalyst surface. After adsorption, the UV light source was
22 switched on (taken as $t = 0$), initiating the photocatalytic redox reactions. Samples
23 were withdrawn at regular time intervals and filtered through $0.45 \mu\text{m}$ polyvinylidene
24 fluoride (PVDF) syringe filters (CM Scientific Ltd) to remove catalyst particles and

1 further analysed in terms of their organic content. All experiments were conducted at
2 the inherent pH of BPA solution (~ 6.4), which remained constant during
3 photocatalytic treatment.

4 The photocatalytic experiments under solar irradiation were carried out in a
5 compound parabolic collector (CPC) with 0.25 m^2 total illuminated surface area
6 (Figure 1c), manufactured by Ecosystem S.A. The CPC reactor consisted of 2
7 borosilicate tubes providing an irradiated volume of 2 L, solar reflectors (anodised
8 aluminium with a concentration factor of 1), a continuously stirred tank (1.5 L), a
9 centrifugal recirculation pump (flow rate = 30 L/min), connecting tubes, and valves.
10 The CPC reactor was mounted on a fixed south-facing platform 39° tilted, which was
11 installed in Ciudad Real (Spain). A radiometer (Ecosystem, ACADUS 85), 45° tilted,
12 was used to provide the global (direct + diffuse) UV (200 - 400 nm) radiation data.
13 The light intensity of solar irradiation during the photocatalytic experiments ranged
14 from 25 to 30 W/m^2 . At the beginning of each experiment, the BPA-polluted water
15 matrix and the catalyst were added into the continuously stirred tank and pumped
16 through the covered reactor for 30 min. This step was applied to ensure adequate
17 mixing and complete equilibration of adsorption-desorption of BPA onto catalyst
18 surface. The reactor was then uncovered initiating the photocatalytic redox reactions
19 (taken as $t = 0$). Samples were withdrawn at predetermined times, filtered and
20 analysed, as previously described.

21

22 **2.3 Analytical techniques**

23 BPA concentration in the filtered water samples was measured by a high performance
24 liquid chromatography (HPLC) system (S200 Pump, S225 Autosampler, Perkin

1 Elmer) coupled with a diode array detector (S200 EP, Perkin Elmer). Separation was
2 performed on a reverse phase C18 analytical column (Luna Phenomenex 5u, 250 x
3 4.6 mm) in isocratic elution mode (flow rate = 1 mL/min). The mobile phase
4 consisted of 35:65 (v/v) UPW:acetonitrile (Frontistis et al., 2011). The injection
5 volume was 40 μ L and the detection wavelength was set at 225 nm.

6 Mineralisation efficiency was determined by measuring the residual organic
7 concentration by a TOC analyser (Shimadzu TOC-V_{CPH}) in the non-purgeable organic
8 carbon (NPOC) mode.

9 Light intensity and spectral distribution of UV-LED and UV-BL light sources were
10 acquired by a Labsphere spectral irradiance receiver head (E1000) with a concentrator
11 area of 1 cm². The distance between the receiver head and the irradiation source was
12 set at 8 cm, which was equal to the distance between UV-LED or UV-BL and the
13 surface of the reactant mixture. More information about the analysis can be found in
14 (Tsonev et al., 2015). The spectral irradiance of UV-LED relatively to that of UV-BL
15 can be seen in Figure 2. The light intensities of UV-LED and UV-BL were estimated
16 to be 1005 and 22.49 W/m², respectively.

17
18 Figure 2. The relative spectral irradiance of UV-LED and UV-BL irradiation sources
19 and the action spectra of TiO₂ P25 catalyst (in grey).

20

21 **2.4 Energy consumption**

22 The energy consumption of UV-LED and UV-BL light sources was estimated using
23 figures-of-merit, developed to evaluate the energy efficiency of electric-energy-driven
24 advanced oxidation processes. (Bolton et al., 2001) introduced the concept of the

1 electric energy per order, E_{EO} , defined as the energy required for 90% degradation of
2 a pollutant per cubic meter of contaminated water. The E_{EO} (kWh/m³/order) for a
3 batch-operated photoreactor is calculated by equation (1):

$$4 \quad E_{EO} = \frac{P \times t \times 1000}{V \times 60 \times \log\left(\frac{C_i}{C_f}\right)} \quad (1)$$

5 where P (kW) is the power of the irradiation source, t (min) is the irradiation time, V
6 (L) is the volume of the treated effluent, and C_i and C_f (mg/L) are the initial and the
7 final pollutant concentrations.

8

9 **2.5 UV energy requirement**

10 The UV energy requirement of each photocatalytic system is calculated by equation
11 (2):

$$12 \quad Q_{UV,n+1} = Q_{UV} + \Delta t_n \cdot \overline{UV}_{G,n+1} \cdot \frac{A_i}{V_T}; \quad \Delta t_n = t_{n+1} - t_n \quad (2)$$

13 where Q_{UV} (kJ/L) is the accumulated UV energy per unit of volume, $\overline{UV}_{G,n+1}$ (W/m²)
14 is the average solar UV radiation ($\lambda < 400$ nm) measured between t_{n+1} and t_n , A_i
15 (m²) is the illuminated area, and V_T (L) is the total volume of the reactor. The
16 calculation of Q_{UV} for the solar CPC reactor was based on the average light intensity
17 measured (i.e. 27.5 W/m²).

18

1 **3 Results and Discussion**

2 **3.1 Effect of initial BPA concentration**

3 To assess the effect of the initial concentration of BPA on photocatalytic
4 performance, different initial BPA concentrations (2.5 – 10 mg/L) were applied in the
5 presence of 125 mg/L TiO₂. As can be seen in Table 1 and the inset graphs of Figure
6 3, reaction rates decrease with increasing initial concentrations. For instance, a 4-fold
7 increase of BPA concentration (i.e. from 2.5 to 10 mg/L) results in a 3-fold decrease
8 of the reaction rate (i.e. from 0.021 to 0.007 min⁻¹) during UV-BL photocatalytic
9 treatment. The fact that reaction rate changes proportionally less than the initial
10 concentration of BPA implies a shift from first- to zero-order kinetics [although the
11 pseudo-first-order kinetic model was found to describe well the photocatalytic
12 degradation of BPA]. The plot of the normalised BPA concentration against
13 irradiation time resulted in straight lines with the coefficient of linear regression of
14 data fitting, r^2 , ranging from 0.90 to 1.00 (Table 1). From the slopes of the resulting
15 lines, the values of the pseudo-first-order kinetic constant, k , were computed.

16 The increase of initial BPA concentration resulted in decreased removal efficiencies.
17 In detail, when the initial concentration of BPA increased from 2.5 to 10 mg/L, the
18 degradation rate decreased from 99.9 to 79.7% ($k = 0.179 - 0.036 \text{ min}^{-1}$) under UV-
19 LED irradiation, and from 66.8 to 29.5% ($k = 0.021 - 0.007 \text{ min}^{-1}$) under UV-BL
20 irradiation (Figures 3a and 3b). Similarly, the gradual increase of initial BPA
21 concentration (up to 10 mg/L) decreased its removal efficiency from 99.9 to 72.9% (k
22 = 0.132 – 0.035 min⁻¹) in the CPC reactor (Figure 3c). It is generally accepted that
23 increase in the initial organic concentration, at a fixed set of photocatalytic conditions,
24 lowers the ratio of oxidant species to substrate molecules and further results in
25 decreased degradation yields (Dimitrakopoulou et al., 2012), thus explaining the

1 findings presented above. According to the results, TiO₂/UV-LED and TiO₂/solar
2 systems could degrade up to 8 and 7.2 mg/L BPA within 45 min of treatment,
3 whereas the respective removal for TiO₂/UV-BL system was limited to 2.9 mg/L.

4

5 Figure 3. Effect of initial BPA concentration on photocatalytic degradation under (a)
6 UV-LED, (b) UV-BL, and (c) solar irradiation. Inset graphs: relationship between
7 reaction rate constant and initial BPA concentration (TiO₂ = 125 mg/L).

8

9 Table 1. Removal percentages (R), pseudo-first-order kinetic constants (*k*), and
10 coefficients of linear regression of data fitting (*r*²) for the photocatalytic degradation
11 of BPA under UV-LED, UV-BL, and solar irradiation.

12

13 **3.2 Effect of catalyst concentration**

14 Control experiments (i.e. photolysis and catalysis in the dark) were performed to
15 assess the effect of the presence of the catalyst on process efficiency. As can be seen
16 in Figure 4, BPA degradation is negligible after 45 min for both photolysis and
17 catalysis in the dark in TiO₂/UV-LED and TiO₂/UV-BL systems, proving that
18 photocatalysis is the main mechanism for BPA removal. The maximum UV
19 absorbance of BPA appears at 199 and 276 nm, therefore BPA cannot be photolyzed
20 by either UV-LED or UV-BL, which both emit predominantly at 365 nm.
21 Furthermore, existence of UV light ($\lambda < 380$ nm) is a prerequisite for the activation of
22 TiO₂ catalyst, thus explaining the stability of BPA during catalysis in the dark. In the
23 case of solar photolysis and catalysis in the dark, BPA degradation of about 20% was

1 observed after 45 min of treatment. In the CPC reactor, the borosilicate glass has a
2 cut-off around 285 nm (Malato et al., 2009), however BPA is still photolyzed under
3 solar irradiation at $\lambda \geq 285$ nm since this range falls within the absorbance spectrum of
4 BPA. The experiments in the CPC reactor were performed outdoors and the
5 penetration of ambient light during catalysis in the dark was higher than in the batch
6 reactors, which were placed indoors; a fact that explains the difference in BPA
7 removal between the three systems as can be seen in Figure 4.

8 The effect of catalyst concentration on process efficiency was then investigated by
9 applying various catalyst concentrations (100 – 500 mg/L) in order to remove 5 mg/L
10 initial BPA concentration. In Figure 4, it is shown that increase of catalyst
11 concentration from 100 to 250 mg/L improves significantly the removal of BPA in
12 TiO₂/UV-LED and TiO₂/solar systems. For instance, the increase of TiO₂ from 100 to
13 250 mg/L enhances BPA degradation by 21% and doubles the reaction rate (i.e. from
14 0.040 to 0.080 min⁻¹) in the CPC reactor (Figure 4c, Table 1). However, in TiO₂/UV-
15 BL system, a 4-fold increase of TiO₂ (i.e. from 125 to 500 mg/L) increases the
16 reaction rate only by 1.5 times (i.e. from 0.013 to 0.018 min⁻¹), resulting finally in
17 64.8% BPA removal after 45 min of treatment [a percentage still much lower than
18 those obtained by TiO₂/UV-LED and TiO₂/solar systems at the half TiO₂
19 concentration (i.e. 250 mg/L)]. In general, increase of TiO₂ concentration up to a
20 point, where all catalyst particles are totally irradiated, enhances removal efficiency
21 by offering more active sites for photocatalytic oxidation (Kaneco et al., 2004).
22 However, this dependence is less profound in the case of TiO₂/UV-BL system, which
23 can be attributed to the lower light intensity emitted by the UV-BL lamp.

24
25

1 Figure 4. Control experiments and effect of catalyst concentration on photocatalytic
2 degradation under (a) UV-LED, (b) UV-BL, and (c) solar irradiation ($C_0 = 5 \text{ mg/L}$).

3

4 **3.3 Mineralisation efficiency**

5 The aim of photocatalytic oxidation is to destroy both parent compounds, and
6 transformation products (TPs) formed during treatment. To this end, additional
7 experiments were performed at the best-assayed conditions (i.e. $C_0 = 2.5 \text{ mg/L}$, TiO_2
8 $= 250 \text{ mg/L}$) to assess the mineralisation efficiency of the three photocatalytic
9 systems. As can be seen in Figure 5, the mineralisation of BPA proceeds slower than
10 BPA degradation, which is attributed to the fact that mineralisation includes a
11 sequence of reactions for the oxidation of BPA and its TPs to CO_2 and H_2O , thus
12 taking longer than the partial oxidation of BPA. In detail, 99.9% of BPA is degraded
13 within 20, 30, and 120 min under UV-LED, solar, and UV-BL irradiation, while the
14 respective TOC removals after 90 min of treatment are 88, 67, and 33%.

15

16 Figure 5. BPA and TOC removal under UV-LED, UV-BL, and solar irradiation ($C_0 =$
17 2.5 mg/L , $\text{TiO}_2 = 250 \text{ mg/L}$).

18

19 (Kondrakov et al., 2014) reported that the TiO_2 -mediated photocatalytic oxidation of
20 BPA is driven by photogenerated holes and hydroxyl radicals leading to the formation
21 of seven TPs according to the mechanism illustrated in Figure 6. Briefly, BPA
22 oxidation proceeds via hydroxylation yielding hydroxylated and oxidized TPs that are
23 transformed into aliphatic alcohols, carboxylic acids, and aldehydes via ring-opening

1 and further oxidation reactions, before their complete mineralisation (Kondrakov et
2 al., 2014; Repousi et al., 2017).

3
4 Figure 6. Mechanism of BPA degradation by TiO₂-mediated photocatalysis, adopted
5 from (Kondrakov et al., 2014).

6

7 **3.4 Effect of water matrix**

8 Humic acids (HA) solution was used in order to resemble more realistic water and
9 wastewater treatment conditions. HA typically found in surface waters, may interfere
10 with the reactive oxygen species produced during photocatalytic oxidation reactions,
11 and, thus affect the degradation yields. The concentration of HA in surface waters
12 typically varies from 2 to 10 mg/L (Alrousan et al., 2009). Taking this into account, 5
13 and 8 mg/L HA were added to the reactant mixture to examine the effect of water
14 matrix on the photocatalytic removal of BPA. Noticeably, and as shown in Figure 7,
15 the addition of HA has a detrimental effect on photocatalytic performance under both
16 UV-LED and UV-BL irradiation. Removal efficiency substantially decreases with the
17 increasing concentration of HA. For example, when the reactant mixture is spiked
18 with 8 mg/L HA, BPA removal is suppressed by 77 and 67% under UV-LED and
19 UV-BL irradiation, respectively (Figure 7a). The retardation effect of HA on process
20 efficiency can be ascribed to: (i) the competitive adsorption of HA onto the active
21 sites of TiO₂ that slows down oxidation either via hydroxyl radical ($\cdot\text{OH}$) attack or
22 through direct electron transfer between photogenerated holes (h_{vb}^+) and target
23 molecules (Selli et al., 1999), and (ii) the reduced light penetration in the solution
24 (Antonopoulou et al., 2015).

1 Additional experiments were performed at 2.5 mg/L BPA in the presence of 250 mg/L
2 TiO₂ in the CPC reactor. Likewise, the increase in HA concentration from 5 to 8 mg/L
3 resulted in a gradual decrease of BPA degradation rate, as shown in Figure 7b. These
4 results indicate that the retardation degree of photocatalytic oxidation depends
5 strongly on the complexity of the water matrix. Reaction rate decreases with
6 increasing complexity, therefore, degradation in real water samples (e.g. wastewater,
7 surface water) is expected to be slower due to the presence of constituents that can act
8 as hydroxyl radical scavengers (Zacharakis et al., 2013).

9
10 Figure 7. Photocatalytic removal of BPA in the presence of different concentrations of
11 HA under (a) UV-LED and UV-BL and (b) solar irradiation ((a) C₀ = 5 mg/L, TiO₂ =
12 125 mg/L, (b) C₀ = 2.5 mg/L, TiO₂ = 250 mg/L).

13

14 **3.5 Comparison of the three photocatalytic systems**

15 It was observed that the LED-driven photocatalytic system achieved the highest
16 oxidation reaction rates (Table 1) under all experimental conditions assayed, due to
17 the increased light intensity provided by the UV-LED. Although UV-LED and UV-
18 BL light sources are both driven by the same electrical power of 11 W and emit
19 irradiation predominantly at 365 nm, their light intensities vary significantly. The
20 intensity of UV-LED light is 1005 W/m², whereas the light intensity of UV-BL is
21 only 22.49 W/m². This difference stems from the directionalities of the two light
22 sources; UV-LED produces a directional beam of light so there is no leak of UV light
23 outside the reactor, UV-BL lamp, to the contrary, emits light in all directions,
24 therefore, a fraction of the photons is lost. However, the higher light intensity

1 provided by the UV-LED does not lead to the analogous improvement of the reaction
2 rates. In fact, the k values obtained during LED-photocatalysis are only 4 – 9 times
3 higher than UV-BL, thus suggesting the lower photonic efficiency of the TiO₂/UV-
4 LED system. This can be explained by the dependency of the reaction rate to light
5 intensity: (i) at low light intensities, the rate of photocatalytic reaction increases
6 linearly with the light intensity, (ii) at intermediate light intensities, reaction rate
7 increases with the square foot of the light intensity because separation of electron-hole
8 pairs competes with recombination, and (iii) at high light intensities, reaction rate
9 becomes independent of the light intensity and mass transfer is the main limitation
10 (Herrmann, 1999; Ollis et al., 1991). Therefore, the right balance should be set
11 between removal efficiency of pollutants and energy requirements of the process in
12 order to obtain sustainable and cost-efficient photocatalytic systems. Scaling-up LED-
13 driven photocatalysis can increase the photonic efficiency of the process because the
14 high rate of energy transfer provided by the UV-LED makes the system ideal for the
15 treatment of large volumes of wastewater.

16 The consumption of electric energy, E_{EO} , in TiO₂/UV-LED system was found to be
17 significantly lower compared to TiO₂/UV-BL (Figure 8), also suggesting the high
18 sustainability of LED-photocatalysis. For instance, at the best-assayed conditions, E_{EO}
19 has been estimated at 7.171 kWh/m³/order for TiO₂/UV-LED system and 43.067
20 kWh/m³/order for TiO₂/UV-BL. This 6-fold difference in E_{EO} values translates into
21 higher treatment cost for the TiO₂/UV-BL system, as well as increased environmental
22 impact due to augmented CO₂ emissions and fossil depletion (Chatzisyneon et al.,
23 2013). (Shie et al., 2008) and (Shie and Pai, 2010) also found that the photocatalytic
24 degradation of indoor air pollutants (e.g. toluene, formaldehyde) under UV-LED
25 irradiation is a process substantially more energy-efficient than using conventional

1 UV irradiation sources. At this point, it should be also mentioned that the use of
2 conventional UV lamps further increases the environmental impact of the process due
3 to the hazards related to the presence of mercury.

4
5 Figure 8. Electric energy per order (E_{EO}) of TiO₂/UV-LED and TiO₂/UV-BL systems
6 for the photocatalytic degradation of various initial concentrations of BPA (TiO₂ =
7 125 mg/L).

8
9 Comparing the three treatment systems, TiO₂/solar delivers the second highest
10 removal efficiency following TiO₂/UV-LED (Table 1), which is due to the fact that
11 TiO₂ is activated by solar light at $\lambda < 380$ nm, which accounts for only about 5% of
12 the solar spectrum. Solar photocatalysis results in higher degradation rates than
13 TiO₂/UV-BL system, which can be explained by the higher intensity of sunlight (i.e.
14 25 - 30 W/m² at $\lambda < 400$ nm) than UV-BL (i.e. 22.5 W/m²), as well as the optimised
15 geometry of CPC reactors.

16 The geometry of the photocatalytic reactors affects significantly process efficiency
17 and this can be seen by the UV energy requirement, Q_{uv} , of the three systems. The
18 Q_{uv} , at the best-assayed conditions, for the removal of 99% of BPA was estimated at
19 30.9 kJ/L, 4.2 kJ/L, and 3.54 kJ/L for TiO₂/UV-LED, TiO₂/UV-BL, and TiO₂/solar
20 system, respectively. TiO₂/solar system requires the lowest UV energy under the
21 studied conditions. Similar results have been reported by (Saggioro et al., 2014) and
22 (Haranaka-Funai et al., 2017), who compared the photocatalytic performance of CPC
23 and batch-operated reactors in the presence of TiO₂ suspensions. Solar CPC reactors
24 have been already optimised and provide a high optical efficiency that allows the use

1 of direct and diffuse radiation (Saggiaro et al., 2014). Meanwhile, LED photocatalysis
2 is an emerging technology and the optimisation of LED reactors is still under
3 investigation.

4 Overall, high degradation rates combined with significant advantages regarding
5 process economy and environmental safety, make the TiO₂/solar photocatalytic
6 system ideal for water treatment applications in sun-rich areas. For areas with
7 inadequate sunlight, the use of LEDs as irradiation source was found to be an
8 appropriate alternative to conventional UV-BL lamps, leading to photocatalytic
9 systems of increased performance, energy efficiency and environmental sustainability.

10

11 **4 Conclusions**

12 The degradation of bisphenol-A (BPA), a well-known endocrine disruptor, was
13 investigated in three photocatalytic systems under various UVA irradiation sources,
14 namely UV-LED, UV-BL lamp, and natural sunlight. The effect of key operating
15 parameters, such as initial BPA, catalyst concentration, treatment time, and water
16 matrix, on the photocatalytic performance of the three systems was assessed. LED-
17 driven photocatalysis yielded the highest reaction rates, followed by TiO₂/solar, and
18 TiO₂/UV-BL systems, under all experimental conditions assayed. UV energy
19 requirements of the three systems was found to descend in the order: TiO₂/solar <
20 TiO₂/UV-BL < TiO₂/UV-LED, indicating the low photonic efficiency of the UV-LED
21 system and, thus, highlighting the need for optimised LED photocatalytic reactors.

22 All in all, photocatalysis powered by either sunlight, a renewable energy, or LEDs, an
23 energy efficient and environmentally friendly light source, features significant
24 advantages regarding the overall sustainability of the process. The increased

1 performance and environmental safety of LED-photocatalysis make the process ideal
2 for the removal of emerging micropollutants in areas where solar photocatalysis might
3 not be feasible due to inadequate sunlight. LEDs could be also used as a backup
4 irradiation source in solar photocatalytic systems during less sunny days or periods
5 with increased influent loads (e.g. touristic periods). To this end, future work should
6 focus on the evaluation of process efficiency in real secondary wastewater matrices
7 with emerging micropollutants present at environmentally relevant concentrations.
8 Also, economic and environmental impact assessment of LED-photocatalysis is
9 necessary in order to establish the suitability of the process as a tertiary treatment step
10 in WWTPs before further scale-up.

11

12 **Acknowledgements**

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14 gratefully acknowledged. The authors would also like to thank Dr John Fakidis from
15 Li-Fi R&D Centre at the University of Edinburgh for the measurements of the
16 spectral irradiance of UV-LED and UV-BL.

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12 **List of Tables**

13 Table 1. Removal percentages (R), pseudo-first-order kinetic constants (k), and
14 coefficients of linear regression of data fitting (r^2) for the photocatalytic degradation
15 of BPA under UV-LED, UV-BL, and solar irradiation.

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6 Table 1.

Operating parameter	Irradiation source	mg/L	R, %	Pseudo-first-order reaction model	
				k , min ⁻¹	r^2
C_0^a	UV-LED	2.5	99.9	0.179	1.00
		5	95.9	0.058	1.00
		7.5	90.6	0.047	0.98
		10	79.7	0.036	0.99
	UV-BL	2.5	66.8	0.021	0.98
		5	45.6	0.013	0.97
		7.5	36.0	0.011	0.99
		10	29.5	0.007	0.98
	Solar	2.5	99.9	0.132	0.95
		5	84.0	0.047	0.93
		7.5	81.5	0.037	0.90
		10	72.9	0.035	0.98
TiO_2^b	UV-LED	100	97.9	0.068	0.99
		125	95.9	0.057	1.00
		250	99.0	0.101	1.00
	UV-BL	125	45.6	0.013	0.97
		250	57.5	0.016	0.97
		500	64.8	0.018	0.99
	Solar	100	79.0	0.040	0.99
		125	84.0	0.047	0.93
		250	99.9	0.080	0.97
Best-assayed operating conditions ^c	UV-LED		99.9	0.230	0.99
	UV-BL		75.6	0.025	0.98
	Solar		99.9	0.151	0.98

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^aTiO₂ = 125 mg/L, irradiation time = 45 min;

1 ^bC₀ = 5 mg/L, irradiation time = 45 min;
2 ^cC₀ = 2.5 mg/L, TiO₂ = 250 mg/L, irradiation time = 45 min.

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7 Figure 1. Schematics of (a) UV-LED, (b) UV-BL, and (c) solar CPC reactors.

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9 and the action spectra of TiO₂ P25 catalyst (in grey).

10 Figure 3. Effect of initial BPA concentration on photocatalytic degradation under (a)
11 UV-LED, (b) UV-BL, and (c) solar irradiation. Inset graphs: relationship between
12 reaction rate constant and initial BPA concentration (TiO₂ = 125 mg/L).

13 Figure 4. Control experiments and effect of catalyst concentration on photocatalytic
14 degradation under (a) UV-LED, (b) UV-BL, and (c) solar irradiation (C₀ = 5 mg/L).

15 Figure 5. BPA and TOC removal under UV-LED, UV-BL, and solar irradiation (C₀ =
16 2.5 mg/L, TiO₂ = 250 mg/L).

17 Figure 6. Mechanism of BPA degradation by TiO₂-mediated photocatalysis, adopted
18 from (Kondrakov et al., 2014).

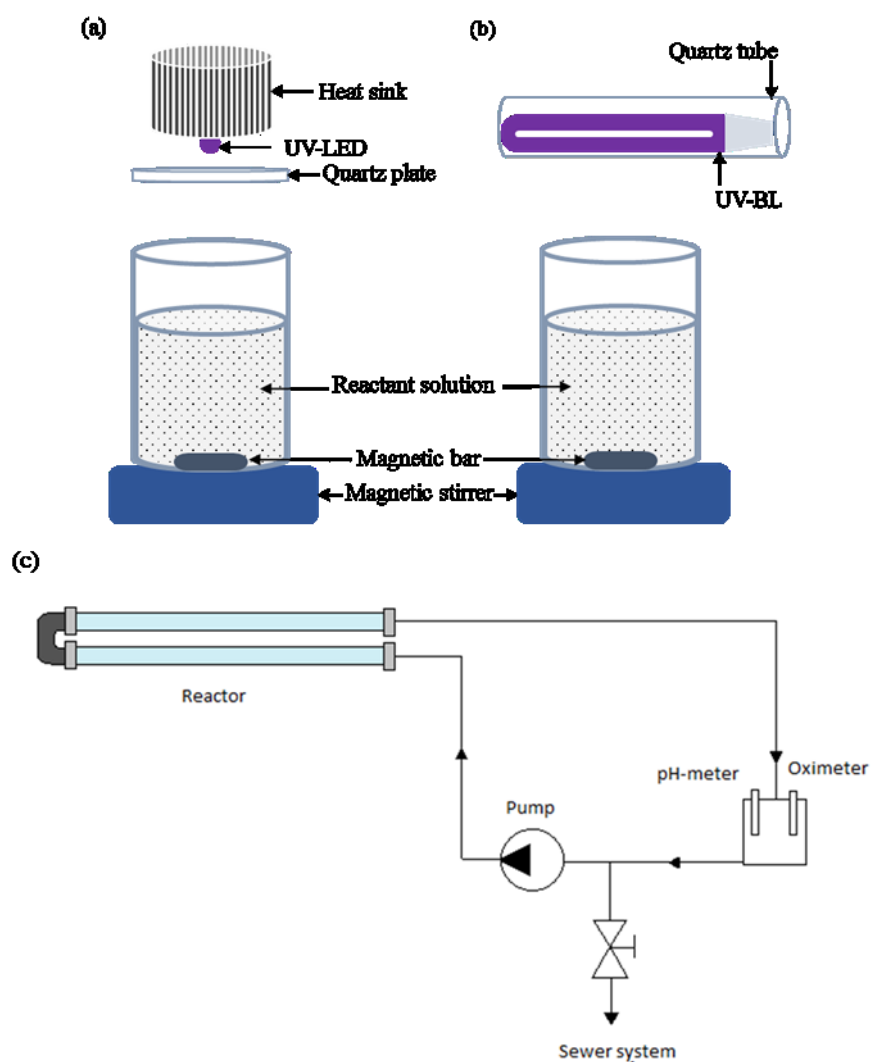
19 Figure 7. Photocatalytic removal of BPA in the presence of different concentrations of
20 HA under (a) UV-LED and UV-BL and (b) solar irradiation ((a) C₀ = 5 mg/L, TiO₂ =
21 125 mg/L, (b) C₀ = 2.5 mg/L, TiO₂ = 250 mg/L).

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2 for the photocatalytic degradation of different initial concentrations of BPA ($\text{TiO}_2 =$
3 125 mg/L).

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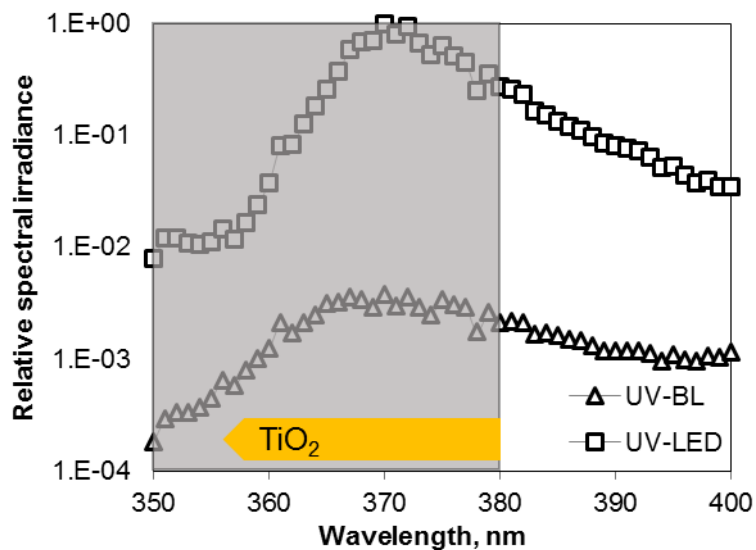
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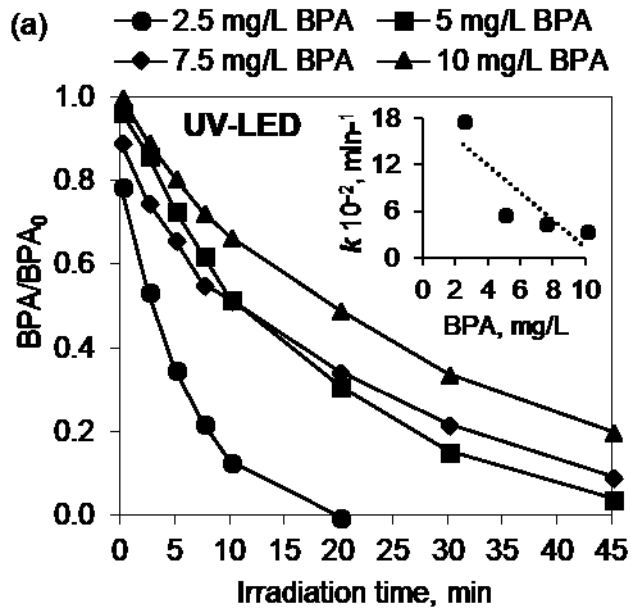
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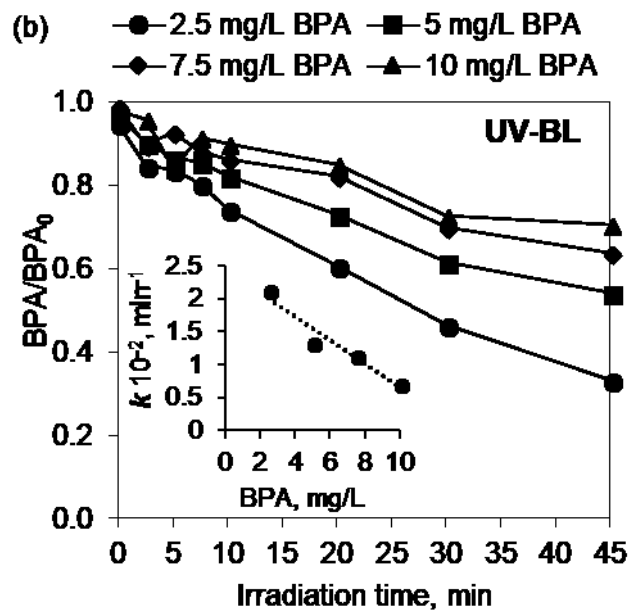
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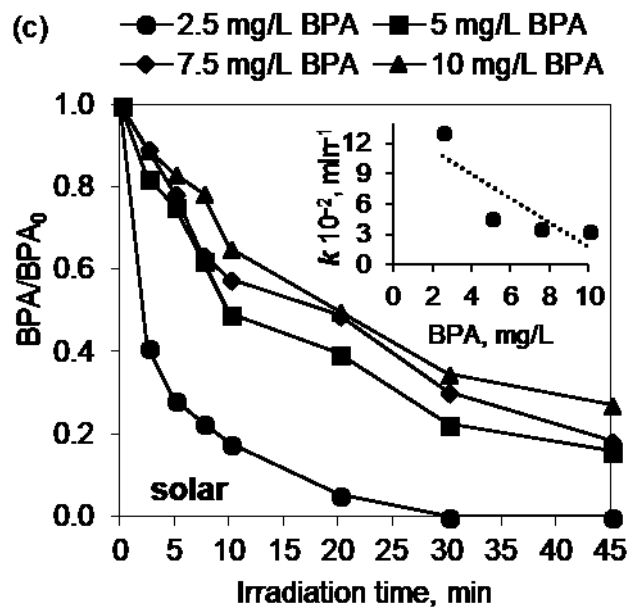
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 3 UV-LED, (b) UV-BL, and (c) solar irradiation. Inset graphs: relationship between
 4 reaction rate constant and initial BPA concentration ($\text{TiO}_2 = 125 \text{ mg/L}$).

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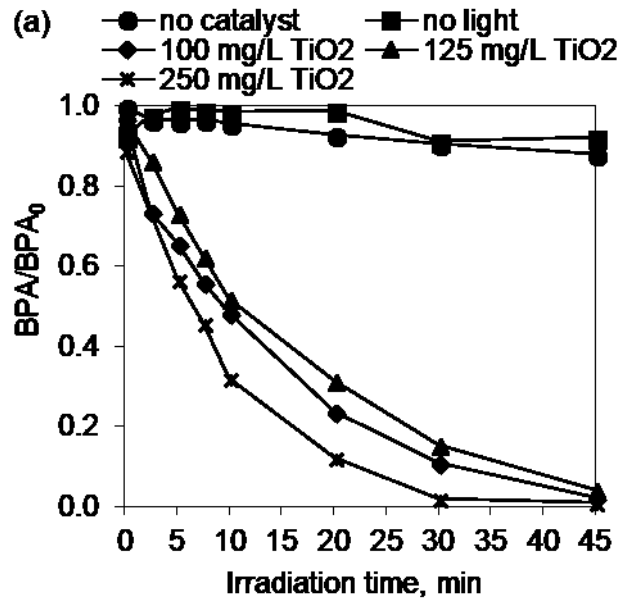
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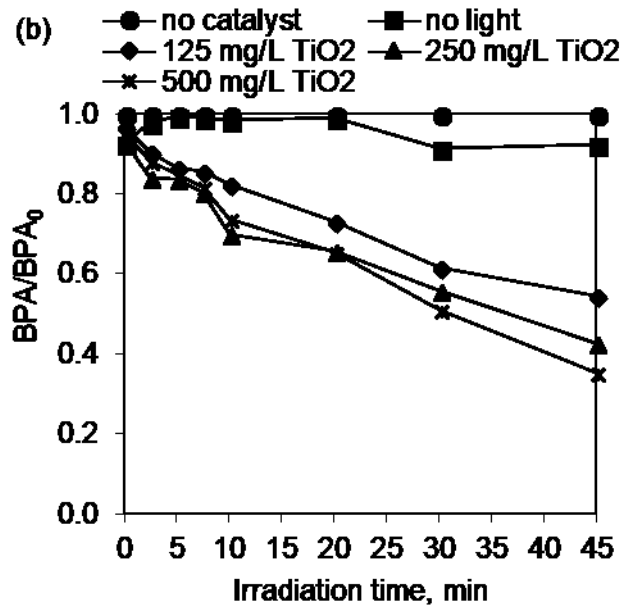
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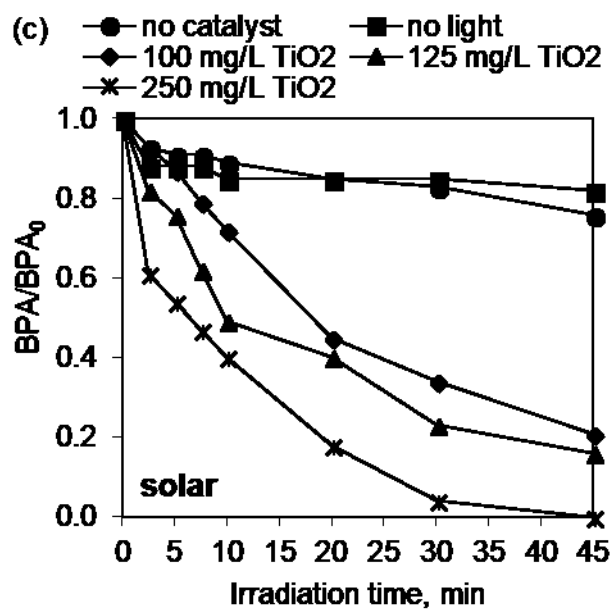
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2 Figure 4. Control experiments and effect of catalyst concentration on photocatalytic
 3 degradation under (a) UV-LED, (b) UV-BL, and (c) solar irradiation ($C_0 = 5 \text{ mg/L}$).

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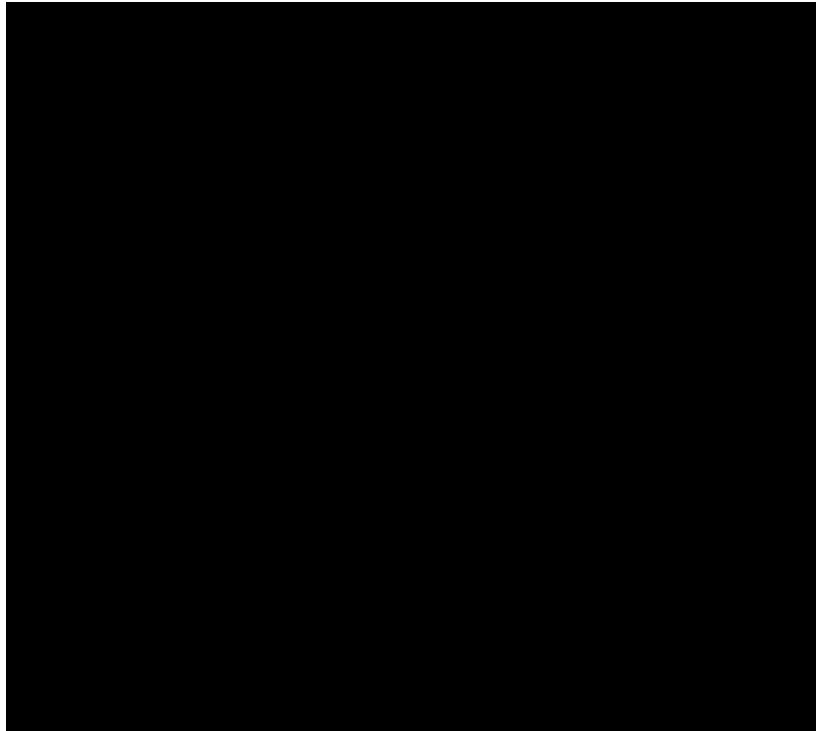
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2 Figure 5. BPA and TOC removal under UV-LED, UV-BL, and solar irradiation ($C_0 =$
3 2.5 mg/L, $TiO_2 = 250$ mg/L).

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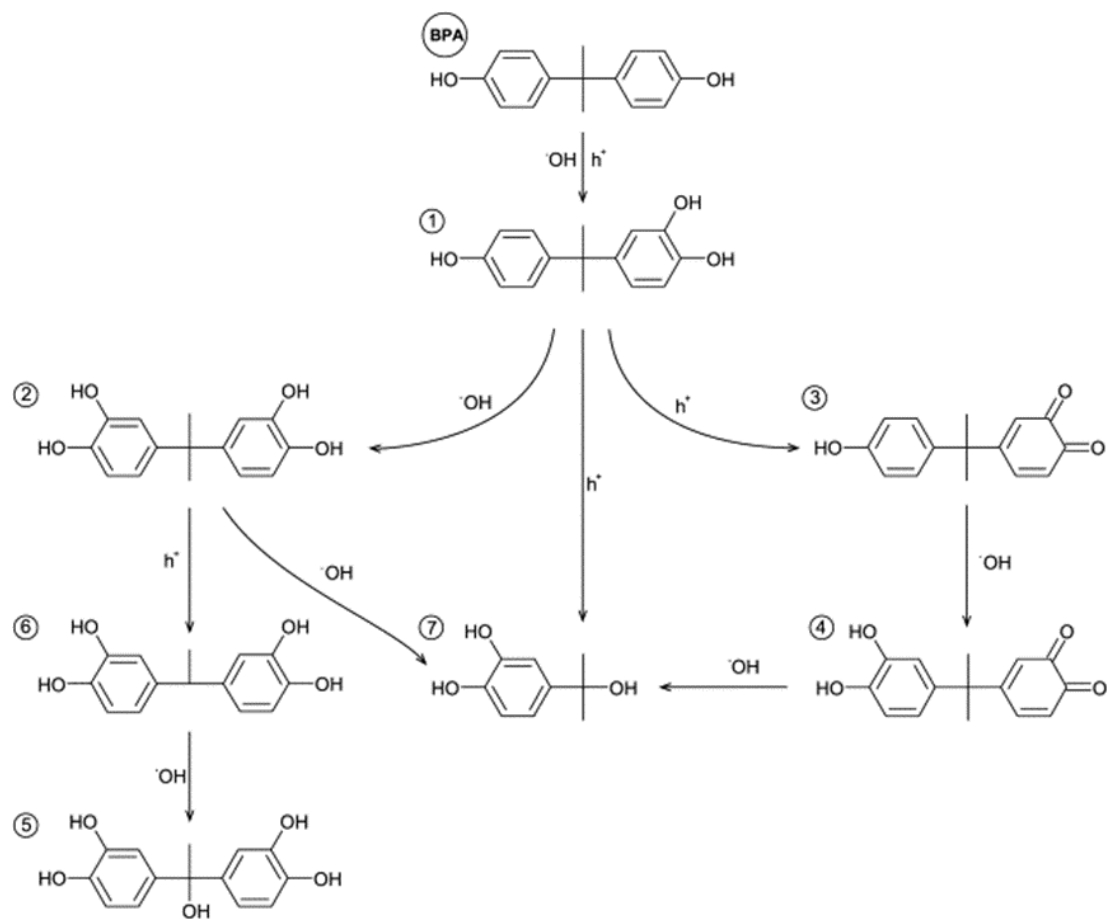
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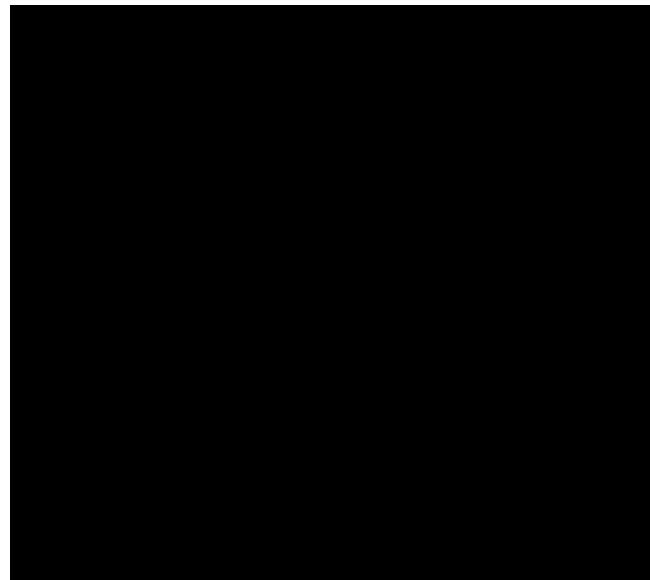
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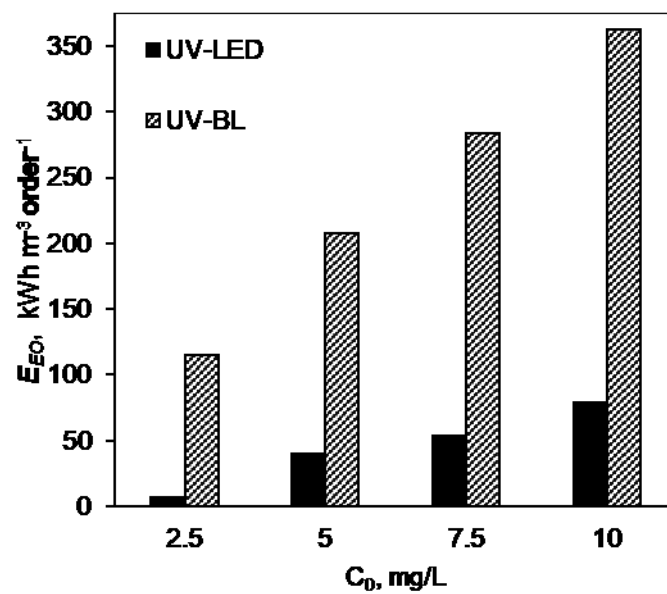
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