



Solar reclamation of wastewater effluent polluted with bisphenols, phthalates and parabens by photocatalytic treatment with TiO₂/Na₂S₂O₈ at pilot plant scale

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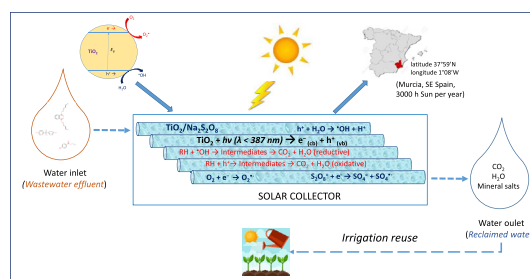
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HIGHLIGHTS

- Photocatalytic degradation of six endocrine disruptors in wastewater was assessed.
- Efficiency of three commercial samples of TiO₂ was compared.
- The conditions (catalyst load, electron acceptor and pH) were previously optimized.
- The mean rate constant for TiO₂ P25 was about 3 times higher than TiO₂ vlp 7000.
- TiO₂/Na₂S₂O₈/sunlight is an effective tool for removing endocrine disruptors.

GRAPHICAL ABSTRACT



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ABSTRACT

Investigations of anthropogenic contaminants in fresh- and wastewater have shown a wide variety of undesirable organic compounds such as Endocrine Disruptors (EDs). As a result, wastewater treatments using innovative technologies to remove those organic compounds are required. In this paper, the photodegradation of six EDs in wastewater at pilot plant scale is reported. The EDs were bisphenol A, bisphenol B, diamyl phthalate, butyl benzylphthalate, methylparaben and ethylparaben. Commercial TiO₂ nanopowders (P25, Alfa Aesar and Kronos vlp 7000) were used as photocatalysts. The operating variables (type and loading catalyst, effect of electron acceptor and pH) were previously optimized under laboratory conditions. The results show that the use of TiO₂ alongside an electron acceptor like Na₂S₂O₈ strongly enhances the degradation rate of the studied compounds compared with photolytic tests, especially P25. The oxidation rates of the EDs at pilot plant scale were calculated following the disappearance of the target compound as a function of fluence (H). The ED degradation followed a pseudo-first order kinetics in all cases. In our experimental conditions, the half-fluence (H₅₀) varied from 79 to 173 J cm⁻² (photolytic test), 10–117 J cm⁻² (TiO₂ vlp 7000) and 3–58 J cm⁻² (TiO₂ P25), for bisphenol B and butyl benzylphthalate, respectively. It is concluded that solar photocatalysis using the tandem TiO₂/Na₂S₂O₈ can be considered as an environmental-friendly tool for water detoxification and a sustainable

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technology for environmental remediation, especially in the Mediterranean Basin, where many places receive more than 3000 h of sunshine per year. Although the cost depends on the nature of the pollutant, the treatment cost was estimate to be about 150 € m^{-3} for photocatalytic treatment with TiO_2 P25.

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1. Introduction

Sewage effluents from homes and industries are a source of a diverse and multiple mixtures of chemicals that frequently enter the aquatic environment (Sibanda et al., 2015). Among others, preservatives used in foods, personal care products, pharmaceuticals, plasticizers included as additives in many products, pesticides or drugs of abuse have recently been detected in environmental water at different concentration levels, and this is an increasing cause for concern (Stuart et al., 2012; Robles-Molina et al., 2014; Gorga et al., 2015; Liang et al., 2015; Salgueiro-González et al., 2015; Garrido et al., 2016; Esteban et al., 2016). Many of them have been identified as endocrine disruptors (EDs), compounds that alter function(s) of the endocrine system and consequently cause adverse health effects in an intact organism, or its progeny, or sub-populations (IPCS, 2002). Humans and wildlife depend on the ability to reproduce and develop normally, which is not possible without a healthy endocrine system. Since the beginning of this century, numerous laboratory studies have added to our understanding of the impact of EDs on human and wildlife health (Diamanti-Kandarakis et al., 2009; EEA, 2012) and confirmed the scientific complexity of this issue. The European Union has introduced specific legislative requirements aimed at phasing out endocrine disruptors in water, industrial chemicals, plant protection products and biocides based on the Community Strategy EDs (EC, 2011). Several reports has provided a list of priority chemical substances based on scientific evidence concerning their ED capacity as well as production volume, persistence and potential exposure risks (Kortenkamp et al., 2011). More specially, bisphenols and phthalates used as plasticizers and paraben derivatives (personal care product additives) have been listed in Category 1, which is based on the endocrine disrupting activity of a substance in at least one species.

The reclamation of wastewaters for reuse is very important for ensuring water sustainability (i.e., supplying water for life in all its forms). The term “Reclaimed water” is refers to treated wastewater that has passed through an additional or complementary treatment process, when necessary, to reach the quality appropriate for its required use (Antoniades et al., 2010; Iglesias et al., 2010; Bernabeu et al., 2011; Prieto-Rodríguez et al., 2012). When “first-hand” water is expensive and/or scarce, reclaimed water has generated interest in many parts of the world due its economic advantage (Eludoyin, 2015). Among many other uses, irrigation is the highest water-consuming activity in many countries, and consequently, the first activity that should be considered in any reuse program, especially in countries of the Mediterranean Basin (Rodríguez-Liébaná et al., 2014). However, the presence of EDs in irrigation waters has certain risks for the subsurface environment, and is particularly as regard groundwater quality and drinking water safety (Ma et al., 2018). Therefore, low-cost, innovative and sustainable wastewater treatment technologies are necessary to avoid the discharge of EDs into natural aquatic ecosystems, as mentioned in the European Directive on water policy (EC, 2013).

Bearing in mind all the above, the development of solar photochemical technologies whereby sunlight is absorbed by a catalyst in order to change the structure of pollutants has aroused

much in recent years. Such methods constitute a relevant alternative to conventional biological and physical methods because they allow the removal of pollutants by mineralization rather than simply moving them from place to place (Ribeiro et al., 2015). Physical separation methods (membrane processes and activated carbon adsorption) are able to remove some EDs in water effluents, but the low efficiency when the membranes become saturated and the need to regenerated activated carbon limit the uses of these methods (Liang et al., 2015).

Among Advanced Oxidation Processes (AOPs), heterogeneous photocatalysis based on the generation of reactive oxygen species, mainly hydroxyl radical ($\cdot\text{OH}$) and other highly reactive radicals like superoxide anion (O_2^-) and hydroperoxide ($\cdot\text{OOH}$), has been extensively reviewed in the recent literature due to its efficiency in the abatement of different types of emerging organic pollutants (Gaya and Abdullah, 2008; Malato et al., 2009; Ahmed et al., 2011; Zhang et al., 2012; Ibhaddon and Fitzpatrick, 2013; Djurišić et al., 2014; Kanakaraju et al., 2014; Spasiano et al., 2015; Velegraki et al., 2015; Rani and Karthikeyan, 2016; Frontistis et al., 2017; Salimi et al., 2017; Vela et al., 2017; Reddy et al., 2018).

When semiconductor particles are irradiated with energy $h\nu \geq E_g$ a positive photohole (h^+) in the valence band and a photoelectron (e^-) in the conduction band are formed and subsequently either recombine and/or dissipate the input energy as heat. Simultaneously, spontaneous adsorption occurs (water and pollutant) and according to the redox potential of each adsorbate, an e^- transfer proceeds towards acceptor molecules ($A_{(\text{ads})} + e^- \rightarrow A^-_{(\text{ads})}$), whereas a positive h^+ is transferred to a donor molecule ($D_{(\text{ads})} + h^+ \rightarrow D^+_{(\text{ads})}$). The h^+ oxidizes either the pollutant directly or water to produce hydroxyl radical $\cdot\text{OH}$, whereas the e^- reduces the oxygen adsorbed on the photocatalyst surface (Malato et al., 2009; Ahmed et al., 2011). In the degradation of organic pollutants, the $\cdot\text{OH}$ generated from the oxidation of adsorbed water ($h^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+$) is the primary oxidant, and the presence of oxygen can prevent the recombination of the e^-/h^+ pairs. The $\cdot\text{OH}$ attacks organic compounds originating different intermediates depending on the nature of the parent compounds. Finally, those intermediates further react with $\cdot\text{OH}$ to produce CO_2 and H_2O (mineralization).

Transition metal chalcogenides are the most used heterogeneous photocatalysts because of their specific characteristics. Apart from chalcogenides, binary semiconductors (TiO_2 , ZnO , Fe_2O_3 , ZnS , CdS , etc.) have been widely used as photocatalysts due to their light absorption properties, electronic structure, charge transport characteristics, and excited-state lifetime. Among them, titanium dioxide (TiO_2) is the best known due to its properties that include high photoactivity, a non-toxic nature, low cost, commercial availability, the photochemical stability, possibility of doping and/or coating on a solid support (Ohtani et al., 2010; Herrmann, 2012). However, although TiO_2 is considered close to an ideal semiconductor, it has two main limitations: i) the rapid recombination of photogenerated e^-/h^+ pairs and ii) poor absorption of visible radiation.

In light of the above, the main purpose of this paper was to assess the proficiency of heterogeneous photocatalysis to degrade residual concentrations of several compounds (bisphenols,

phthalates and parabens) catalogued as EDs by the European Commission Institute for Environment and Health (EC, 2011) in sewage wastewater effluents. For this, two different commercial titania samples (P25 and Kronos vlp 7000) were used as semi-conductors in tandem with $\text{Na}_2\text{S}_2\text{O}_8$ as electron acceptor under natural sunlight at pilot-plant scale. Previously, influential parameters in the process such as catalyst type and loading, the effect of electron acceptor and pH were optimized in a photochemical reactor at lab scale.

2. Materials and methods

2.1. Endocrine disruptors, photocatalysts and reagents

The analytical standards of bisphenol A (BA), bisphenol B (BB), butyl benzylphthalate (BP), diamyl phthalate (DP), ethyl 4-hydroxybenzoate (EP) and methyl p-hydroxybenzoate (MP) with a purity >98% were purchased from ChemService Inc (West Chester, PA, USA). Their structures, uses and main physical-chemical characteristics are shown in Table 1 (Toxnet, 2017). Nanopowders of TiO_2 Aeroxide P25 (99.5%), TiO_2 Alfa Aesar (99.9%) and TiO_2 Kronos vlp 7000 (carbon doped Anatase, 87.5%) were supplied by Nippon Aerosil Co Ltd (Osaka, Japan), Alfa Aesar GmbH (Karlsruhe, Germany) and Kronos Titan GmbH (Leverkusen, Germany), respectively. All titania samples were previously characterized for DRS, XRD, FE-SEM, X-Ray EDX attached to SEM and BET surface according to the methodology published in a previous paper by Fenoll et al. (2016). Figs. S1 and S2 (Supplementary Data) show XRD patterns and SEM images with elemental microanalysis, respectively of the titania samples. Table S1 (Supplementary Data) shows the physical-chemical properties of the titania samples. Dichloromethane and acetone for residue analysis, sodium chloride and anhydrous sodium sulphate were purchased from Scharlab (Barcelona, Spain). Panreac Química (Barcelona, Spain) supplied sodium

persulfate (98%). Pure water was obtained from a Milli-RX purification system from Millipore (Bedford, MA, USA).



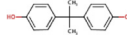
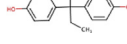
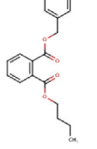
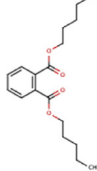
2.2. Wastewater effluent

The sewage wastewater effluent was obtained from a wastewater treatment plant (WWTP) that included the following steps: i) mechanical pre-treatment, ii) aerobic biological process as secondary treatment, and iii) disinfection with ultraviolet light. The WWTP is located in Las Torres de Cotillas (Murcia, SE of Spain) with an average capacity of $5000 \text{ m}^3 \text{ day}^{-1}$. The main physical-chemical properties of the wastewater effluent used in this study are shown in Table S2 (Supplementary Data).

2.3. Photocatalytic trials under lab-scale photoreactor

For the study, the design considered the catalyst load, electron acceptor concentration and the initial pH and as the main effects for an initial $300 \mu\text{g L}^{-1}$ spiking level of each ED. The aim of the experimental design was identify the operating conditions that maximized the overall mineralization of the EDs according to the Langmuir–Hinshelwood (H-L) model. For this purpose, three different concentrations (100 , 200 and 300 mg L^{-1}) of each TiO_2 sample (Alfa Aesar, P25 and vlp 7000) were evaluated. The slurries were maintained in complete darkness for 30 min prior to irradiation to ensure adsorption equilibrium (a period established based on the results of several experiments in the dark). The effect of $\text{Na}_2\text{S}_2\text{O}_8$ as electron acceptor was assessed at 100 , 250 and 400 mg L^{-1} . Finally, the appropriate concentration of $\text{TiO}_2/\text{Na}_2\text{S}_2\text{O}_8$ was assessed at three pH levels (5.5 , 7.0 and 8.5) to obtain the optimal operational conditions. In each case, the pH was adjusted using 1 M NaOH and 1 M HCl solutions. The photocatalytic and photolytic experiments were performed in a 2000 mL cylindrical glass (250 mm long, 100 mm diameter) photochemical reactor (SBS,

Table 1
Main physical-chemical characteristics, structures and uses of the compounds studied.

Compound CAS	Group Molecular formula	Use	Chemical structure	Molecular weight	Log K_{ow}	S_w^a
Methyl p-hydroxybenzoate 99-76-3 (MP)	Parabens $\text{C}_8\text{H}_8\text{O}_3$	Preservative: Used as a preservative in foods, cosmetics and pharmaceuticals		152.5	1.96	2500
Ethyl 4-hydroxybenzoate 120-47-8 (EP)	Parabens $\text{C}_9\text{H}_{10}\text{O}_3$	Preservative: Used as a preservative in pharmaceuticals, adhesives, and various cosmetic preparations (inhibits fungal and bacterial growth)		166.2	2.47	885
2,2-Bis(4-hydroxyphenyl)propan (Bisphenol A) 80-05-7 (BA)	Bisphenols $\text{C}_{15}\text{H}_{16}\text{O}_2$	Plasticizer: Used as a chemical intermediate, mainly for epoxy resins and polycarbonate resins		228.3	3.32	120
2,2-Bis(4-hydroxyphenyl)-n-butan (Bisphenol B) 77-40-7 (BB)	Bisphenols $\text{C}_{16}\text{H}_{18}\text{O}_2$	Plasticizer: Used as a chemical intermediate, mainly for epoxy resins and polycarbonate resins		242.3	4.13	ND
Butyl benzylphthalate 85-68-7 (BP)	Phthalate Esters $\text{C}_{19}\text{H}_{20}\text{O}_4$	Plasticizer: additives in polyvinyl chloride (PVC) products		312.4	4.73	0.30
Diamyl phthalate 131-18-0 (DP)	Phthalate Esters $\text{C}_{18}\text{H}_{26}\text{O}_4$	Plasticizer: additives in polyvinyl chloride (PVC) products		306.4	5.62	100

^a Water solubility (mg L^{-1}).

Barcelona, Spain) equipped with a magnetic stirring bar, and a set of two low pressure Philips mercury lamps with a nominal output power of 8 W each as photon source. The intensity of each lamp was approximately 10 mW cm^{-2} with major emission output at 366 nm (based on the manufacturer's data). Air was injected into the photoreactor every 15 min to maintain the O_2 concentration in the slurry at around $8\text{--}10 \text{ mg L}^{-1}$. A blank assay, without semiconductor and oxidant (photolytic test) was carried out. Each experiment was replicated three times. A drawing of the photochemical reactor and operational conditions used are shown in Fig. S3 (Supplementary Data).

2.4. Solar photocatalytic test

The trial was performed in a pilot plant located in Murcia, SE Spain under natural sunlight irradiation during June 2016. The solar pilot plant used in this experiment (Fig. S4, Supplementary Data) is based on compound parabolic collectors (CPC) technology as previously described by Vela et al. (2018a). Fig. 1 shows the scheme of the experimental setup. The values (W m^{-2}) of visible (VIS) plus near infrared (NIR) (400–1100 nm), UVA (315–400 nm), UVB

(280–315 nm) and UVC (200–280 nm) radiation were taken with a photoradiometer Delta Ohm HD 2102.2 (Caselle di Selvazzano, Italy) every 15 min (Fig. S5, Supplementary Data). The degradation rates (C_H/C_0) were calculated as a function of radiant fluence ($H = dE/dA$), i.e. amount of energy (photons) striking on the sample per area unit (J cm^{-2}) which was calculated bearing in mind the radiation accumulated with time (min).

2.5. Analytical determinations

After filtering the water samples, ED residues were isolated through a liquid-liquid (LL) extraction method by sonication with dichloromethane. After concentration and reconstitution, the extracts were injected into the GC/MS system composed of a Agilent (Waldbronn, Germany) HP 6890 GC coupled by transfer line to a 5973N mass spectrometer, as previously described (Vela et al., 2018b). The column (HP-5MSI, $30 \text{ m} \times 0.25 \text{ mm } \varnothing$, $0.25 \mu\text{m}$ film thickness) and GC-MS conditions used for the identification and quantitation of EDs according to their retention times, the identification of target and qualifier ions, and the determination of qualifier-to-target ratios are summarized in Fig. S6 (Supplementary

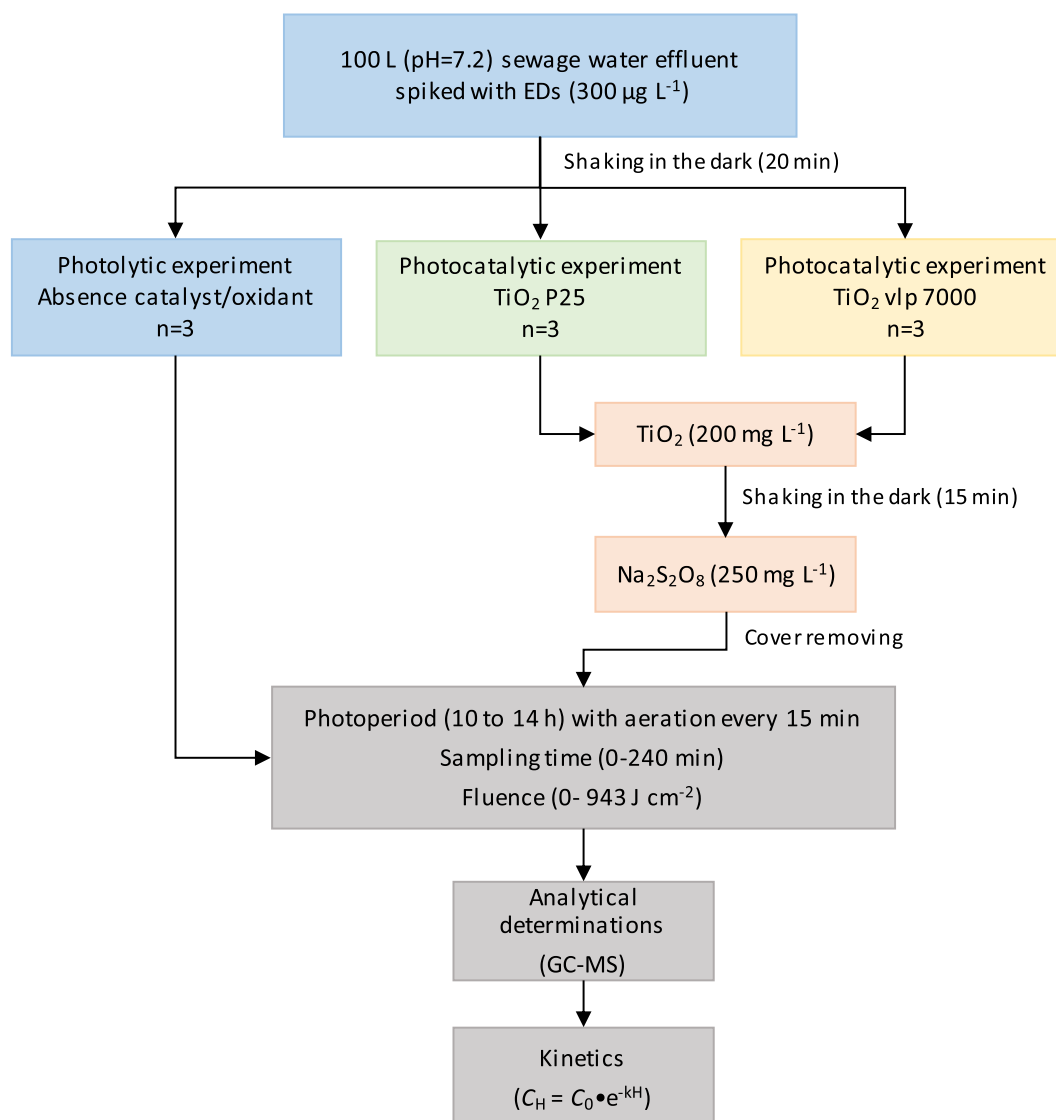


Fig. 1. Scheme for solar photocatalytic design at pilot plant scale.

Data).

The dissolved organic carbon (DOC) content was measured using a Multi N/C 3100 TOC Analyzer (Analytic Jena AG, Jena, Germany) equipped with an NDIR detector (950 °C) after passing the samples through a nylon filter (0.45 mm). An Agilent 7900 ICP-MS with standard nickel cones, a MicroMist glass concentric nebulizer, and Ultra High Matrix Introduction (UHMI) system was used for Ti^{4+} determination. To assess the toxicity of EDs during photocatalytic degradation the luminescent marine bacteria *Vibrio fischeri* was used. The luminescence was determined by means of a MICROTOX M500 analyzer (Orbit Technologies Pvt. Ltd., India) following the method of bioluminescence inhibition (UNE-EN-ISO 11348-3).

2.6. Statistical analysis

The experimental data were fitted using the statistical software SigmaPlot version 13 (Systat, Software Inc., San Jose, CA). The incidence of the studied variables was evaluated by analysis of variance (ANOVA) using the IBM-SPSS Statistics version 24 software (Armonk, NY) followed by Tukey's significant difference post-hoc test ($p < 0.05$).

3. Results and discussion

3.1. Photocatalytic activity test under lab-conditions

The photocatalyst load is an important variable for optimizing the photocatalytic treatment process, since efficiency can decrease if the load is too low or too high. The amount of TiO_2 in which all the particles are completely illuminated (higher limit) depends on the geometry and working conditions of the photoreactor. According to Herrmann (1999), the degradation rate of the pollutant is proportional to the radiant flux (ϕ) for $\phi < 25 \text{ mW cm}^{-2}$. For this reason, we have considered that in our case, the photon flux (10 mW cm^{-2}) used is proportional to the degradation rate of the EDs.

The preliminary experiments demonstrated that the catalyst type and loading affects the process (Fig. S7, Graph A, Supplementary Material). The rate constants (mean \pm SD) calculated for the photolytic experiment according to a pseudo-first order kinetics ranged from 0.006 ± 0.005 to $0.012 \pm 0.003 \text{ min}^{-1}$ for EP and BP, respectively. In all cases, the degradation rates were significantly lower ($p < 0.05$) in photolysis than in the experiments using photocatalysts. The efficiency of the process was in the order: TiO_2 P25 \gg TiO_2 vlp 7000 $>$ TiO_2 Alfa Aesar, for all the studied compounds. The mean values of the rate constants calculated for the six compounds were $0.053 \pm 0.002 \text{ min}^{-1}$ (TiO_2 P25), $0.017 \pm 0.001 \text{ min}^{-1}$ (TiO_2 vlp 7000) and $0.013 \pm 0.001 \text{ min}^{-1}$ (TiO_2 Alfa Aesar). For three TiO_2 samples, the optimal catalyst load was 200 mg L^{-1} with mean values ($n = 6$) of $0.058 \pm 0.007 \text{ min}^{-1}$ (TiO_2 P25), $0.018 \pm 0.007 \text{ min}^{-1}$ (TiO_2 vlp 7000), and $0.015 \pm 0.003 \text{ min}^{-1}$ (TiO_2 Alfa Aesar). In some cases, further increase in catalyst loading (300 mg L^{-1}) significantly ($p < 0.05$) reduced the degradation rates possibly due to the reversibility of sorption/interaction between catalyst and EDs and/or a screening effect. The absorptivity and dispersion coefficient linked to the catalyst load and the availability of radiation are key factors in the distribution of the photons inside the photoreactor (Satuf et al., 2005). A decrease in the photodegradation efficiency may also result from particle agglomeration, which reduces the active sites on the TiO_2 catalysts exposed to UV illumination (Vela et al., 2017). Therefore, the catalyst load used for subsequent experiments was 200 mg L^{-1} , and TiO_2 Alfa Aesar was discarded for further experiments due to its lower efficiency. Regarding to the compounds studied, the efficiency of the process was in the order: bisphenols $>$ parabens $>$ phthalates for all TiO_2

samples ($p < 0.05$). The mean values ($n = 3$) of the rate constants for a catalyst load of 200 mg L^{-1} ranged from $0.050 \pm 0.002 \text{ min}^{-1}$ for DP to $0.071 \pm 0.006 \text{ min}^{-1}$ for BA (TiO_2 P25) and $0.012 \pm 0.006 \text{ min}^{-1}$ for DP to $0.028 \pm 0.005 \text{ min}^{-1}$ for BA (TiO_2 vlp 7000).

Regarding the effect of the oxidant (electron acceptor) on the degradation rate, three assays were performed using three different concentrations of $\text{Na}_2\text{S}_2\text{O}_8$ (100 , 250 and 400 mg L^{-1}), while maintaining TiO_2 (P25 and vlp 7000) loading at a fixed mass (200 mg L^{-1}). As can be seen in Fig. S7, Graph B (Supplementary Material), significant differences ($p < 0.05$) were observed for all EDs when the concentration of $\text{Na}_2\text{S}_2\text{O}_8$ was increased from 100 to 250 – 400 mg L^{-1} for both (TiO_2 P25 and TiO_2 vlp 7000). Bearing in mind the obtained results, the mean rate constants ($n = 6$) obtained after addition of 100 , 250 and 400 mg L^{-1} of $\text{Na}_2\text{S}_2\text{O}_8$ were $0.066 \pm 0.02 \text{ min}^{-1}$, $0.081 \pm 0.018 \text{ min}^{-1}$ and $0.082 \pm 0.018 \text{ min}^{-1}$ (TiO_2 P25) and $0.030 \pm 0.018 \text{ min}^{-1}$, $0.039 \pm 0.025 \text{ min}^{-1}$ and $0.039 \pm 0.024 \text{ min}^{-1}$ (TiO_2 vlp 7000). In the case of TiO_2 vlp 7000, these differences were less marked for parabens and phthalates as can be seen in Fig. S7, Graph B (Supplementary Material). Because no significant differences ($p < 0.05$) were observed between 250 and 400 mg L^{-1} , the optimum level selected for further experiments at pilot plant scale was 250 mg L^{-1} . As widely referenced in the scientific literature, the recombination of electron (e^-) and holes (h^+) is one of the main restrictions to the efficacy of heterogeneous photocatalysis (Ohtani, 2013). For many pollutants, the addition of electron acceptors to slurries improves their photodegradation rates because they can trap the photogenerated electrons (e_{CB}^-), consequently decreasing the e^-/h^+ recombination (Vela et al., 2017). However, the beneficial effect of persulfate cannot only be attributed to this. Persulfate can be activated by heat and/or ultraviolet light, to form stronger oxidizing free radical SO_4^- ($E_0 = 2.6 \text{ V}$) than persulfate. Persulfate forms two sulphate radicals through scission of the peroxide bond resulting from absorption of heat energy or ultraviolet light [$\text{S}_2\text{O}_8^{2-} + \text{heat/hv (UV)} \rightarrow 2 \text{SO}_4^-$ ($k = 1.0 \times 10^{-7} \text{ s}^{-1}$ (25°C) to $5.7 \times 10^{-5} \text{ s}^{-1}$ (70°C)) and hydroxyl radicals ($\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^- + \cdot\text{OH} + \text{H}^+$) (Matzek and Carter, 2016).

On the other hand, the pH of the solution determines the electric charge on the catalyst surface, and consequently, the type of compounds that can be adsorbed by the semiconductor. As can be observed in Fig. S8 (Supplementary Material), the efficiency of the process was in the order $\text{pH } 7.0 > \text{pH } 5.5 > \text{pH } 8.5$ for all EDs. Highest significant differences ($p > 0.05$) were found in the experiment with TiO_2 vlp 7000, especially in the case of bisphenols. With this catalyst, the mean values ($n = 3$) of rate constants ranged from $0.032 \pm 0.006 \text{ min}^{-1}$ to $0.065 \pm 0.004 \text{ min}^{-1}$ for BA and $0.040 \pm 0.003 \text{ min}^{-1}$ to $0.068 \pm 0.005 \text{ min}^{-1}$ for BB. These results show that the highest degradation took place in all cases at neutral pH values, indicating that the process was favoured by the predominance of cationic or neutral species in the mineralization process. For this reason, neutral pH was considered the optimum level for further experiments at pilot plant scale. The pKa of the EDs and the point of zero charge (PZC) of the photocatalyst markedly influence their photodegradation rates. The PZC (the pH at which the surface exhibits a neutral net electrical charge) of titania is quite insensitive to the crystallographic structure (anatase versus rutile) and the experimental method used. The PZC for TiO_2 vary from 4.7 to 7 depending on the production method. Concretely, the PZC of TiO_2 P25 is about 6.3 (Kosmulski, 2016), which means that at pH values > 6.3 the catalyst surface will be negatively charged and positively charged below this value. According to Malato et al. (2009), when pH vary from 3 to 10, the predominant specie is $-\text{TiOH}$ (80%), while $-\text{TiO}^- \geq 20\%$ if $\text{pH} > 10$ and $-\text{TiOH}_2^+ \geq 20\%$ when $\text{pH} < 3$. At pH below its pKa value, an organic compound exists as neutral state. Above this pKa value, organic compounds attain a

negative charge, which can significantly influence their photocatalytic degradation. At pH 8.5, the surface of the catalyst is negatively charged and EDs present a negative charge because of their values of pKa (8.5–10.1). As consequence, repulsion is favoured. At pH below 8.5, the compounds are mainly in the neutral form. Therefore, an apparent first order kinetics suggest a catalytic reaction with associative (non-dissociative) adsorptions of the reactants.

3.2. Evolution of ED concentrations during solar photocatalytic experiment

Fig. 2 shows the change of ED concentrations (C_H/C_0) as a function of total fluence (H) during the photolytic and photocatalytic experiments at fixed TiO_2 (P25 and Kronos vlp 7000) load (200 mg L^{-1}) in tandem with $\text{Na}_2\text{S}_2\text{O}_8$ (250 mg L^{-1}) at pilot plant scale under natural sunlight.

The initial concentrations observed at the beginning of the experiments varied from 0.27 mg L^{-1} to 0.33 mg L^{-1} for BP and MP,

respectively. Under natural irradiation (photolytic test), the EDs degraded very slowly compared with the reaction rates obtained using photocatalysts. As depicted in Fig. 2, TiO_2 P25 showed higher degradation rates than TiO_2 vlp 7000 for all the studied compounds. At the end of photolytic experiment (240 min , equivalent to approximately 100 J cm^{-2}), the percentage remaining (mean \pm RSD) varied from $48 \pm 5\%$ (BB) to $70 \pm 6\%$ (BP). In the photocatalytic experiments, the remaining percentages were significantly ($p < 0.05$) lower ($58 \pm 6\%$ and $0.004 \pm 0.001\%$ for BP and BB, respectively in the case of TiO_2 vlp 7000 and 34 ± 5 and $0.002 \pm 0.001\%$ for the same compounds in the TiO_2 P25 slurry). For both systems, the behaviour of the three groups was very similar (bisphenols > parabens > phthalates).

The evolution of dissolved organic carbon (DOC) during the photolytic and photocatalytic experiments is shown in Fig. 3. The mean initial value after addition of the EDs was $17.3 \pm 4.5 \text{ mg L}^{-1}$, $19.6 \pm 3.8 \text{ mg L}^{-1}$ and $18.4 \pm 4.3 \text{ mg L}^{-1}$ for photolysis, TiO_2 vlp 7000 and TiO_2 P25, respectively. At the end of the photoperiod, the concentrations were 10.3 ± 7.5 (60%), 7.1 ± 6.1 (36%) and 3.2 ± 8.1

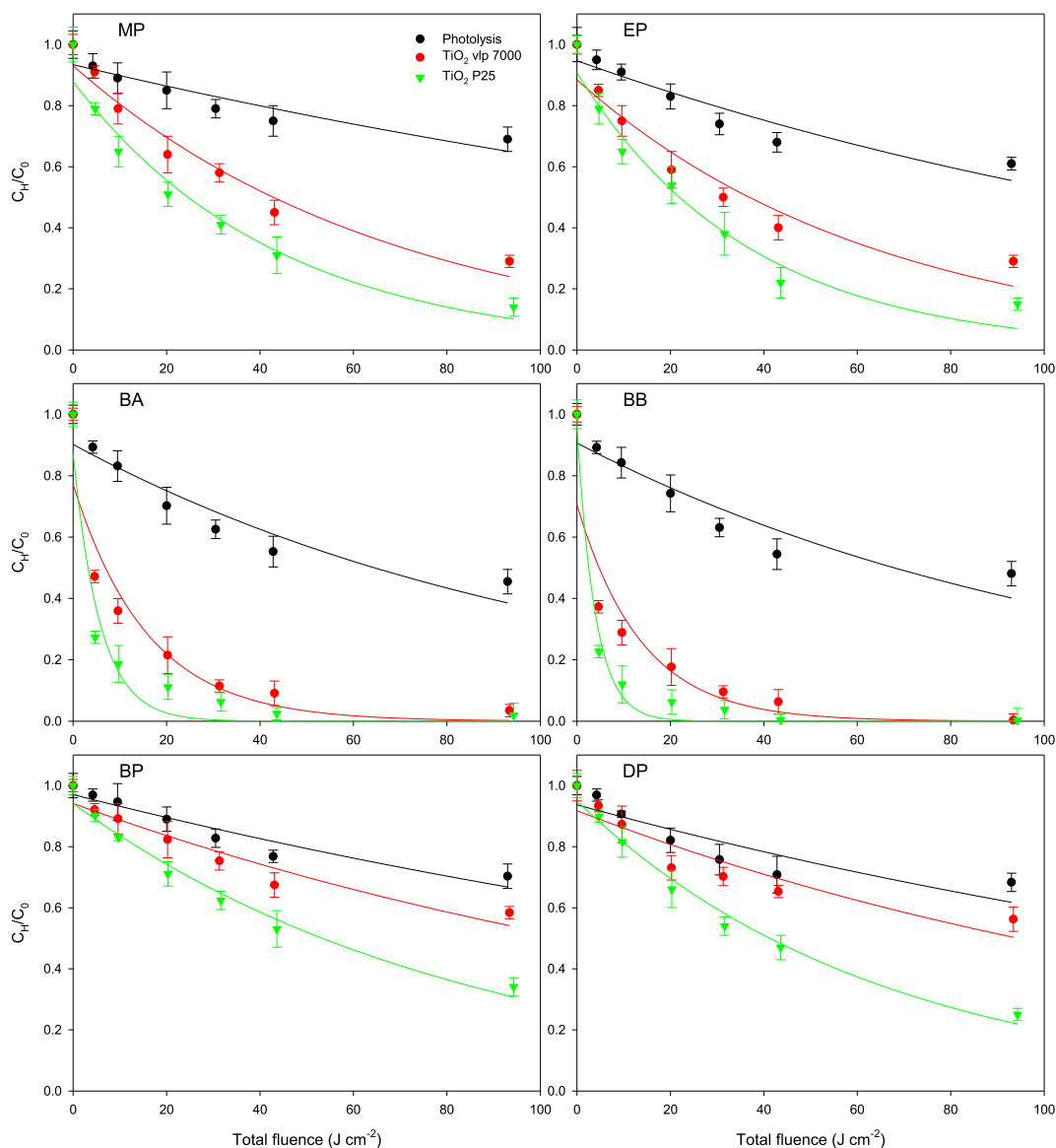


Fig. 2. Change of EDs concentrations as a function of total fluence during photolytic and photocatalytic experiments at fixed TiO_2 load (200 mg L^{-1}) in tandem with $\text{Na}_2\text{S}_2\text{O}_8$ (250 mg L^{-1}) at pilot plant scale. Error bars denote standard deviation.

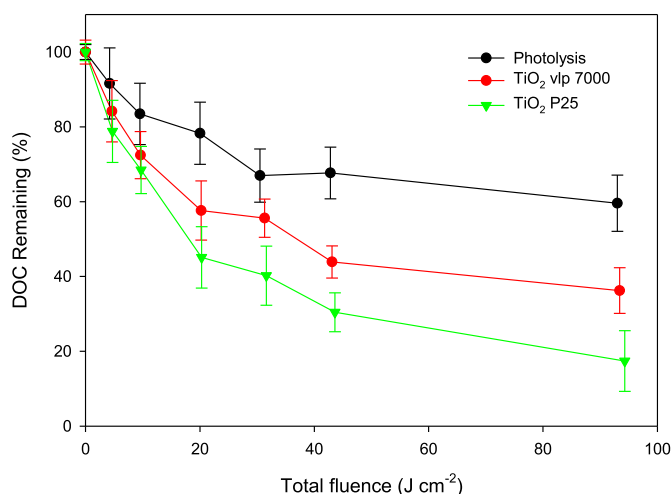


Fig. 3. Evolution of dissolved organic carbon (DOC) during the photolytic and photocatalytic experiments under natural sunlight irradiation. Error bars denote standard deviation.

(17%) for photolysis, TiO₂ vlp 7000 and TiO₂ P25, respectively. The fluence required for 50% of initial DOC to disappear was 57 and 31 J cm⁻² for TiO₂ vlp 7000 and TiO₂ P25, respectively. As can be observed mineralization was not complete after 240 min (≈ 100 J cm⁻²) possibly due to the generation of some hydroxylated and dealkylated intermediates originated during the photo-experiment and the presence of residual concentrations of parabens (MP and EP) and phthalates (BP and DP).

A slight drop in pH (0.4 units) was observed as photodegradation progressed, probably related to the presence of S₂O₈²⁻ because H⁺ was generated in solution (SO₄²⁻ + H₂O → SO₄⁻ + OH + H⁺). Parallel to the decrease observed in DOC, the electrical conductivity (EC) slightly increased up to 4.4 dS m⁻¹, due to mineralization and the evolution of some inorganic ions like SO₄²⁻.

On the other hand, the presence of inorganic ions and DOC plays a key role in the photocatalytic efficiency. In our case, the wastewater effluent contained a high concentration of ions like Cl⁻ (464 mg L⁻¹), SO₄²⁻ (485 mg L⁻¹), Ca²⁺ (263 mg L⁻¹) and Na⁺ (694 mg L⁻¹) and DOC (11 mg L⁻¹). Some dissolved ions may affect the photodegradation rate of different pollutants depending on the pH of the solution due to their strong adsorption to the catalyst surface and their ability to act as scavengers of h⁺/OH during photocatalysis (Ahmed et al., 2011). However, as also mentioned by Zhang et al. (2012), only a weak impact on the part of the ions was observed during the removal of different EDs from secondary effluent since the presence of DOC (mainly macromolecules with molecular weights larger than 4.5 kDa like humic and fulvic acids) plays a more prominent role than inorganic ions in inhibiting photocatalytic removal. The concentration of Ti⁴⁺ dissolved after 240 min ranged from 1.2 ± 0.5 μg L⁻¹ to 5.4 ± 1.9 μg L⁻¹ for TiO₂ P25 and TiO₂ vlp 7000, respectively. Both values were well to the tolerance level set for *Vibrio fischeri* (Heinlaan et al., 2008).

Fig. 4 shows how the inhibition of *Vibrio fischeri* progressed during the photolytic and photocatalytic experiments. As can be observed, toxicity decreased from 67 ± 7% (initial value) to 48 ± 8% (photolysis), 29 ± 5% (TiO₂ vlp 7000) and 19 ± 5% (TiO₂ P25) at the end of the treatments. A slight increase was observed of about 10 J cm⁻² (30 min) in the case of TiO₂ P25, which could be related to the generation of some intermediates during the early reaction stages that would be more toxic than the parent compounds. At the end of the treatments, especially in the case of TiO₂ P25, toxicity had fallen to acceptable values.

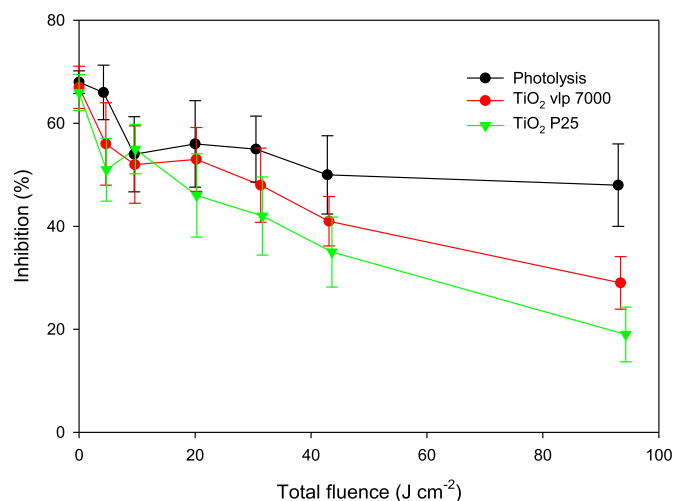


Fig. 4. Evolution of toxicity to *Vibrio fischeri* during the photolytic and photocatalytic experiments under solar irradiation. Error bars denote standard deviation.

3.3. Kinetics during solar photocatalytic experiment

The pseudo-first order kinetic model (Liu et al., 2014) is usually used for describing the photodegradation rate of pollutants in heterogeneous photocatalysis for semiconductor systems at low substrate concentration (Eq (1)):

$$-dC/dt = k_{app}C \rightarrow C_t = C_0 e^{-k_{app} \cdot t} \text{ or } \ln(C_0/C_t) = k_{app} \cdot t \quad (1)$$

where k_{app} (time⁻¹) is the apparent reaction rate constant, t the reaction time, C_0 the initial concentration of pollutant and C_t is the residual concentration of pollutant at time t .

In our case, we used fluence (H) units (the radiant energy received by a surface per unit area) because time units depend on the geometry of the photoreactor. Fluence units are transferrable between different studies (Eq (2)):

$$C_H = C_0 \cdot e^{-k_{app} \cdot H} \text{ or } \ln(C_0/C_H) = k_{app} \cdot H \quad (2)$$

The fluence required for x percent of pollutant to disappear from the water due to degradation processes alone was calculated according to the following equation (Eq (3)):

$$H_x = \ln(100/(100-x))/k_{app} \quad (3)$$

Table 2 lists the fitting parameters calculated for the degradation of each ED in both photolytic and photocatalytic systems. All compounds followed an apparent first-order degradation curve, with R² ranging from 0.779 (DP in photolytic assay) to 0.986 (DP in photocatalytic assay using TiO₂ P25). The standard error of the estimate ($S_{y/x}$) was lower than 0.22 in the most unfavourable case (BA using TiO₂ P25). The lowest degradation was observed for all compounds in the photolytic assay. According to the rate constants calculated (cm² J⁻¹) significant differences ($p < 0.05$) existed in photocatalytic efficiency. The highest degradation rate was observed in all cases with TiO₂ P25. The rate constant (as mean value for all EDs) for TiO₂ P25 was about 3 orders of magnitude higher than for TiO₂ vlp 7000 ($K_{P25} \approx 2.8 \times K_{vlp7000}$). The mean rate constants ($n = 6$) ranged from 0.084 ± 0.104 to 0.030 ± 0.030 for TiO₂ P25/Na₂S₂O₈ and TiO₂ vlp 7000/Na₂S₂O₈, respectively. In both cases, the degradation rate was in the order: BB > BA > EP > MP > DP > MP. The mean rate constant values ($n = 2$) for parabens (MP and EP), bisphenols (BA and BB) and phthalates (BP and DP) in the TiO₂ P25/Na₂S₂O₈ system were

Table 2

Kinetic parameters (n = 3) calculated for the photolytic and photocatalytic degradation of EDs under natural sunlight irradiation according to the pseudo-first order model.

ED	R ²	C _H /C ₀	k _{app} (cm ² J ⁻¹)	S _{y/x}	H _{50/90} (J cm ⁻²)
Photolysis					
MP	0.8642**	0.9341***	0.0039**	0.04	178/590
EP	0.8875**	0.9468***	0.0057**	0.06	122/404
BA	0.8919**	0.9017***	0.0091**	0.08	76/253
BB	0.8690**	0.9064***	0.0088**	0.09	79/262
BP	0.9166***	0.9704***	0.0040***	0.04	173/576
DP	0.7789**	0.9371***	0.0045*	0.07	154/512
TiO ₂ vlp 7000/Na ₂ S ₂ O ₈					
MP	0.9626***	0.9306***	0.0145***	0.07	48/159
EP	0.9173***	0.8845***	0.0155**	0.10	45/149
BA	0.9074***	0.7721**	0.0629**	0.16	11/37
BB	0.9071***	0.7060**	0.0728**	0.19	10/32
BP	0.9273***	0.9416***	0.0059**	0.05	117/390
DP	0.8532**	0.9179***	0.0064**	0.08	108/360
TiO ₂ P25/Na ₂ S ₂ O ₈					
MP	0.9706***	0.8791***	0.0229***	0.08	30/101
EP	0.9421***	0.9079***	0.0272***	0.12	25/85
BA	0.8223**	0.8722**	0.1741*	0.21	4/13
BB	0.9098***	0.9511**	0.2538**	0.16	3/9
BP	0.9802***	0.9415***	0.0119***	0.05	58/193
DP	0.9856***	0.9496***	0.0155***	0.05	45/149

H: Fluence; S_{y/x}: Standard error of estimate; * (p < 0.05); ** (p < 0.01); *** (p < 0.001).

0.025 ± 0.030, 0.214 ± 0.056 and 0.014 ± 0.003, respectively, while for vlp 7000/Na₂S₂O₈ the corresponding values were 0.015 ± 0.001 (parabens), 0.068 ± 0.007 (bisphenols) and 0.0062 ± 0.0004 (phthalates). Bearing in mind the mean rate constants for all compounds (n = 6), the H₅₀ P25/H₅₀ vlp 7000 ratio was about 0.5.

TiO₂ P25 is cheap, photostable in solution and nontoxic, although its main drawback is its inability to absorb visible light (Gupta and Tripathi, 2011). It is important to remark that only 2.5% of the radiation measured during the experiment corresponds to UV radiation (2.33% UVA, 0.15% UVB and 0.02% UVC). The rest (97.5%) is VIS plus NIR radiation. To overcome this problem, different strategies using the visible light to activate TiO₂ for environmental applications have been developed (Pelaez et al., 2012; Fagan et al., 2016). Among other, TiO₂ doping has been used to decrease the band gap or introduce intra-band gap states, increasing the absorption of visible light. TiO₂ P25 is a semiconductor with a wide band-gap energy of 3.2 eV (λ < 390 nm). The band gap of the TiO₂ can be narrowed by doping the titanium with carbon. Due to this, carbon doped TiO₂ (Kronos vlp 7000) can use not only UV radiation, but also part of the visible light spectrum with a wavelength of >400 nm due to a lower band-gap energy of 2.4 eV (λ < 535 nm). The new energy states produced in the TiO₂ band gap due to substitution of oxygen by carbon atoms are responsible for the visible light absorption (Goldstein and BeharRabani, 2008). The presence of rutile in P25 may explain its higher activity compared with vlp 7000. As referenced by Hurun et al. (2003), rutile absorbs photons, generating electron/hole pairs because its smaller band gap transfers electrons to the anatase phase. Consequently, recombination decreases and holes can move to the particle surface to react.

A review of the scientific literature shows BA to be one of the most studied EDs due to extensive human exposure as a result of it being commonly used as raw material in many industrial processes (e.g., the preparation of epoxy and polycarbonated resins). Therefore, the efficiency of different TiO₂ samples has been extensively reviewed for the photocatalytic removal of BA in aqueous media (Reddy et al., 2018). However, revisions on the other EDs studied are scarce. Thus, Velegraki et al. (2015) obtained similar results to our findings using various commercial TiO₂ nanopowders (Aeroxide P-

25, Kronos Vlp 7000 and Kronos Vlp 7001) in a solar simulator photoreactor equipped with a xenon lamp. In this study, TiO₂ Aeroxide P25 was determined as optimum catalytic material for photocatalytic degradation of MP, even at low catalyst loading. Song et al. (2016) demonstrated the higher efficiency of diethyl phthalate removal using UV/H₂O₂ than UV/TiO₂ treatments. Some noble metals such as Ag and Pd supported on TiO₂, show a reduction higher than 50% of the initial parabens (methyl-, ethyl-, propyl-, butyl- and benzylparaben) concentration was achieved after 180 min of reaction (Gomes et al., 2017). Moreover, the positive effect of N-doped TiO₂ catalysts on the degradation of EP has been demonstrated using a solar simulator (Petala et al., 2015).

Most of the titania based photocatalysts are able to achieve the complete removal of BA without forming any toxic intermediates. In contrast, in the case of other photocatalysts, complete mineralization is difficult to realize although the removal of BA can proceed rapidly (Reddy et al., 2018). However, other experimental results have indicated that the degradation efficiency in the presence of ZnO under artificial UV irradiation is higher than that of TiO₂ for BA (An et al., 2018) and EP (Frontistis et al., 2017). In addition, in a previous study, we found significantly (p < 0.05) higher photoactivity of ZnO than TiO₂ P25 for the removal of the six studied EDs in wastewater effluent under sunlight (Vela et al., 2018b).

3.4. Economic assessment for water treatment

In addition to the experimental and modelling work, it is very convenient the achievement of economic studies, which could present this innovative technology as a cost-competitive one. Different methods can be used to estimate the costs of implementing for water treatment but all of them including the total installed costs (facility cost, project contingency, engineering project and replacement costs) and operating costs (personnel, maintenance, electricity and materials and services). Thus, the yearly economic impact can be evaluated (Giménez et al., 2015).

Following this premise, a comparison of the treatment cost for both TiO₂ systems (P25 and vlp 7000) with regard to the effectivity of the ZnO system evaluated in a previous paper (Vela et al., 2018b) under similar experimental conditions is showed in Table 3.

Bearing in mind that the Region of Murcia (SE of Spain) receives about 3000 h of sunlight per year on average and that the useful time of the pilot plant (UT) is fixed in 480 min day⁻¹, the treatment capacity (TC) of our system was calculated according to the following equation:

$$TC = UT \cdot V \cdot 365 / DT_{90} \text{ m}^3 \text{ year}^{-1} \quad (4)$$

where V is the volume of water treated (100 L) and DT₉₀ is the amount of time (min) required for 90% of the initial pollutant concentration to disappear corresponding to the more recalcitrant compound (BP in all cases). The data were obtained in the summer season. DT₉₀ values shown in Table 3 correspond to a fluence of 132 (ZnO), 193 (TiO₂ P25) and 390 J cm⁻² (TiO₂ vlp 7000). This remark is important because in summer it is expected a high photon flux compared to winter. Thus, results can be transferred to other studies.

Considering a period of work of 365 days per year (8 h day⁻¹) the treatment cost was estimate to be 103, 149 and 285 € m⁻³ for photocatalytic treatment with ZnO, TiO₂ P25 and TiO₂ vlp 7000, respectively. However, if only 240 days of use is considered bearing in mind the inclement weather the cost is noticeably higher (144, 209 and 406 € m⁻³). The significant differences found between the treatments are due to the high reaction times to reach 90% degradation of the ED more persistent (BP). If only bisphenols and parabens are considered, the cost is considerably reduced (18 and 24 €

Table 3
Economic assessment for water photocatalytic treatment with ZnO and TiO₂ (P25 and vlp 7000).

Costs ^a		Photocatalytic Treatment			
		ZnO	TiO ₂ P25	TiO ₂ vlp 7000	
I	Facility + Project Contingency (€/year)^b	32,694.21	3269.42	3269.42	3269.42
II	Engineering project (€/year)	(10% I)	326.94	326.94	326.94
III	Operation and maintenance (€/year)	(2.5% I + II)	89.91	89.91	89.91
IV	Consumables (€/year)	Unit price	129.20	87.43	43.76
	Na ₂ S ₂ O ₈	10 €	310.09	265.77	140.02
	ZnO	30 €			
	TiO ₂ P25	38 €			
	TiO ₂ vlp 7000	40 €			
	Total reagents		439.29	353.20	183.78
V	Service (€/year)	Unit price	64.60		
	Rinse water (€/L)	0.0025	648.24		
	Electricity (€/kW h ⁻¹)	0.12			
	Total service		712.84	691.95	670.12
	Total I + II + III + IV + V		4838.41	4731.42	4540.17
VI	Overheads (€/year)	(10% I + II + III + IV + V)	483.84	473.14	454.20
	Total (I + II + III + IV + V + VI)		5322.25	5204.56	4994.18
	DT ₉₀ (min)		339	501	1001
	TC (m ³ /year)		51.68	34.97	17.50
	Treatment cost (€/m³)^c		102.98 (143.85)	148.83 (209.22)	285.34 (406.01)

^a Personnel cost are not included.

^b The facility cost (building and civil works, solar collector, deposits, measurement equipment, industrial benefit, etc.) has been calculated on the basis of a 10 years period.

^c In parentheses is the treatment cost considering only a period of work 240 of days per year.

m⁻³ for bisphenols and 30 and 84 € m⁻³ for parabens) for ZnO and TiO₂ P25 treatments, respectively, attributed to their lower DT₉₀ in both cases. It is important to remark the significant differences in the hours of sunlight per year received by the different European countries (Fig. S9, Supplementary Material). For example, Scotland has less than 1200 h year⁻¹ (i.e., below 3.3 h per day on average). Therefore, the number of annual treatments must be considerably reduced. Finally, the cost of these treatments should be compared with other physical-chemical, electrochemical, photo-Fenton, etc. treatments to obtain precise conclusions.

4. Conclusions

Water is the most important resource on Earth for maintaining all aspects of human life. Freshwater makes up less than 1% of the world total water resources, and is becoming scarce in many areas. Therefore, an important reason for reclaiming water is that water resources are limited. In addition, the discharge of different synthetic compounds able to alter certain functions of the endocrine system (EDs) from sewage wastewater effluents has polluted many environmental waters in the last decades.

The wastewater treatments (preliminary, primary and secondary) commonly carried out in WWTP are not effective enough in many cases to remove recalcitrant compounds that are very resistant to biodegradation. Consequently, advanced treatment methods other than those used in conventional treatment are required.

Photolysis only marginally contributes to the degradation process, which implies that degradation is due to the interactions between the catalyst/oxidant and photons. In this context, the use of TiO₂ (mainly P25) in tandem with Na₂S₂O₈ to avoid recombination e⁻/h⁺ pairs under sunlight radiation may be proposed as an attractive tool to remove or at least considerably reduce the initial amounts of bisphenols, phthalates and parabens present in wastewater effluent before its release into the environment or reuse for agricultural purposes. Moreover, thanks to ultrafiltration technology, more than 90% of the TiO₂ can be recovered for reuse in further photocatalytic processes.

Therefore, the use of heterogeneous solar photocatalysis can be considered as a suitable technology for removing many EDs from

wastewater effluents, especially in some areas of the Mediterranean Basin such as south-eastern Spain where shortages of irrigation water is a major problem but more than 3000 h of sunlight per year is common. In addition, the treatment can be considered economically sustainable although the cost depends in a great way on the nature of the pollutant present in the wastewater effluent.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2018.08.069>.

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