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Solar lab and pilot scale photo-oxidation of ethylparaben using H_2O_2 and TiO_2 in aqueous solutions

Henry Zúñiga-Benítez[a,*], Gustavo A. Peñuela[b]

[a] Departamento de Recursos Naturales y Medio Ambiente, Universidad de Los Lagos, Camino a Chinquihue km 6 s/n, Puerto Montt, Chile
[b] Grupo GDCON, Facultad de Ingeniería, Sede de Investigación Universitaria (SIU), Universidad de Antioquia, Calle 70 # 52-21, Medellín, Colombia

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ABSTRACT

Ethylparaben (Eth-PB) is one of the most used parabens for preservation of many personal care products and food. However, a number of scientific studies have indicated that this compound could interfere with the endocrine or hormonal system of different living beings, which along with data about its presence in different water bodies generates the necessity of seeking alternatives to minimize the potential negative effect of this situation. In this way, removal of Eth-PB using heterogeneous photocatalysis with TiO_2, hydrogen peroxide and light radiation (solar spectrum: wavelength >290 nm) was assessed, considering the individual effects of different operational parameters like the catalyst and H_2O_2 dosages, the pH and the pollutant initial concentration. According to this, conditions that, under the experimental range, promote a higher paraben elimination were established. Tests were carried out at lab-scale using a photo-simulator equipped with a Xenon lamp, and at pilot scale (volume treated ~100 L) using a compound parabolic collector and direct solar light radiation. In both cases, more than a 80% of substrate elimination was reached in less than 6 h of reaction, demonstrating the effectiveness of the photocatalytic system to remove this kind of compounds. Additionally, a significant reduction of the total organic carbon present in the solutions, and an increment of the biodegradability of the samples were appreciated. Finally, some of the by-products generated during the contaminant removal were identified.

1. Introduction

Over the last years, different organic compounds have been classified as endocrine disrupting chemicals due to the fact that they can potentially interfere with the endocrine system of different species by affecting the balanced system of hormones. Parabens (alkyl and aryl esters of *p*-hydroxybenzoic acid), including ethylparaben (Eth-PB, 4-hydroxybenzoic acid ethyl ester), have been included in this group [1]. Accordingly, different *in vitro* and *in vivo* studies have confirmed that these compounds may have estrogenic activity and could be associated with some carcinogenic response [2,3]. But because they have a wide spectrum of anti-microbial activity, are highly stable at different pH, relatively safe to use and its low cost; are widely used as antimicrobial preservatives in the manufacture of different personal care products, beverages and food [1,4–6]. This has promoted its introduction to different environmental matrices, including water, air, dust, sediments and soil. In addition, some reports have indicated its presence in effluents from wastewater treatment plants and in drinking water, implying that conventional treatments are not sufficient to remove these pollutants, and consequently, they re-enter the aquatic environment [4,5].

In general, different authors have evaluated the potential use of diverse techniques for parabens removal such as ozonation, UV photolysis, ultrasound, Fenton, photo-Fenton, electrochemical oxidation, activated carbon adsorption and heterogeneous photocatalysis [7–10]. However, in many cases there is limited information regarding the scaling up, from the lab to pilot or full scale, of the developed methodologies.

In recent years, advanced oxidation process have been widely employed to degrade successfully various organic pollutants including some endocrine disruptors [8,11]. Among these techniques, the heterogeneous photocatalysis with TiO_2 has shown to be an effective method for wastewater treatment [6]. Eqs. (1)–(6) summarize some of the reactions that can occur during the process, where the presence of the semiconductor and the irradiation of light with energy higher than the catalyst band gap leads to a surface reaction in which electrons (e^-) are released from the solid valence band to the conduction band leaving

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[*] Corresponding author.
E-mail addresses: henry.zuniga@ulagos.cl, henry.zuniga@udea.edu.co (H. Zúñiga-Benítez).

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positive holes (h^+) (Eq. (1)). The pair e^-/h^+ can migrate towards the catalyst surface and react with pre-adsorbed compounds such as H_2O and/or OH^- groups forming hydroxyl radicals $^{\bullet}OH$ (Eqs. (2)–(3)), which are capable of oxidizing the organic matter (Eq. (4)). Likewise, other parallel reactions can take place and generate additional oxidative species like the superoxide radical, $O_2^{-\bullet}$. Additionally, organic pollutants also can be oxidized directly by the holes, as indicates Eq. (6) [6,12–14].

$$TiO_2 \xrightarrow{hv} e^- + h^+ \quad (1)$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH + H^+ \quad (2)$$

$$h^+ + OH^- \rightarrow {}^{\bullet}OH \quad (3)$$

$$\text{Pollutant} + {}^{\bullet}OH \rightarrow \text{Byproducts} \rightarrow\rightarrow\rightarrow CO_2 + H_2O \quad (4)$$

$$e^- + O_2 \rightarrow O_2^{-\bullet} \quad (5)$$

$$\text{Pollutant} + h^+ \rightarrow \text{Byproducts} \quad (6)$$

One of the undesirable reactions that can reduce the oxidative capacity of the heterogeneous photocatalytic systems is the e^-/h^+ pair recombination, for that the addition of external oxidants such as hydrogen peroxide could assist organic compounds photocatalytic degradation since the H_2O_2 is capable of react with e^-, generating additional radicals (Eq. (7)) [10,15].

$$H_2O_2 + e^- \rightarrow OH^- + {}^{\bullet}OH \quad (7)$$

On the other hand, several researchers have reported that the compound parabolic collectors (CPC) technology is suitable for application at pilot scale of different advanced oxidation processes that involve light radiation because this can be reflected and intensified towards the solution moving in the reactor tubes [16,17]. Moreover, some of the advantages of CPCs are their turbulent flow conditions, no vaporization of volatile compounds, no tracking, no overheating, the use of both direct and diffuse solar radiation, its low cost and weatherproof [17].

The purpose of this work was to study the use of TiO_2/H_2O_2 heterogeneous photocatalysis for Eth-PB removal in aqueous solutions considering the effects of operating parameters such as pH, catalyst, H_2O_2 and pollutant initial concentrations. Additionally, the conditions, under the evaluated experimental range, that promoted a higher substrate elimination were selected and tests were carried out at pilot scale using a CPC collector and direct solar light radiation. Besides, the variations of the total organic carbon and biodegradability of treated samples were evaluated; and some of the byproducts of the reaction were identified.

2. Experimental

2.1. Chemicals

Eth-PB containing more than 99% of pure compound was purchased from Alfa-Aesar. TiO_2 with a surface area of $50\,m^2\,g^{-1}$ (particle size ~20–30 nm), was obtained from Degussa AG (Degussa P-25). Hydrogen peroxide (35% w/w), isopropanol, acetonitrile and the chromatographic solvents were supplied by Merck. pH adjustment and control were carried out using concentrated solutions of HCl and NaOH, and sodium thiosulfate pentahydrate (Sigma Aldrich) was employed for quenching remaining H_2O_2 after sampling process.

2.2. Photocatalytic system

A Suntest CPS/CPS+ photosimulator (Atlas), equipped with a xenon lamp capable of emitting radiation of light in a spectrum similar to the sun (irradiance: $350 \pm 10\,W\,m^{-2}$, wavelength >290 nm), was used for photocatalytic experiments. Borosilicate glass flasks containing 200 mL of Eth-PB solution were used for light exposition. And in order to guarantee equilibrium between the pollutant and catalyst, TiO_2 was added to the solution after adjusting pH, and the resulting system was stirred in the dark for 30 min.

Degradation of Eth-PB at pilot scale was carried out in a solar CPC placed in the city of Medellín, Colombia (Latitude: 6°13′51″, Longitude 75°35′26″, Altitude 1495 m over sea level). The photoreactor consists of three modules, each with a working volume of 18 L and eight borosilicate glass tubes (Fig. 1). Water with the pollutant and the catalyst was recirculated at $1.6\,L\,s^{-1}$ from a storage tank (~100 L) through the glass tubes using a pumping system (Siemens).

2.3. Experimental design

Effects of solution initial pH and concentrations of TiO_2 and H_2O_2 on Eth-PB photo-treatment were evaluated using a face centered, central composite design, which allows to determine the conditions that conduct to a higher pollutant elimination. Results analysis was performed with a confidence level of 95% using Statgraphics Centurion XVI software. The extent of paraben removal after 30 min of treatment was selected as the experimental response. All the runs were conducted in triplicate and the standard deviations and coefficients of variation of the data were below 5%.

2.4. Analytical techniques

Samples of 1 mL were withdrawn during the reaction at different time intervals. An Acquity UPLC system (Waters Corporation) coupled to a triple quadrupole (TQD) mass spectrometer with orthogonal electrospray ionization (ESI) was employed to monitor pollutant concentration. Chromatographic separation was performed using an Acquity UPLC BEH C18 column (1.7 μm, 50 mm, 2.1 mm, Waters). Mobile phase consisted in a mix

Fig. 1. Solar CPC system employed in this study.
Source: GDCON Group Universidad de Antioquia.

of water/0.01% formic acid and methanol/0.01% formic acid. The organic phase fraction was maintained at 50% (isocratic mode). Ethylparaben-d4 (CDN isotopes) was used as internal standard. Analysis run time was 2.5 min, and the injection volume was 5 mL.

Degradation by-products were analyzed by GC–MS in an Agilent 7890A gas chromatograph coupled to an Agilent 5975C mass spectrometer using a programmed temperature-vaporizing injector (PTV). The column employed for chromatographic separation was an HP-5MS UI (30 m, 0.25 mm, 0.25 mm, Agilent Technologies).

2.5. Mineralization and biodegradability studies

Organic matter mineralization was evaluated analyzing the changes in the dissolved organic carbon (DOC) present in the solutions, using an Apollo 9000 series TOC analyzer (Teledyne Tekmar). Biodegradability index (biochemical oxygen demand (BOD_5)/chemical oxygen demand (COD) ratio) was determined according to the Standard Methods for the Examination of Water and Wastewater (2012) [18], methods 5220 D and 5210 D.

3. Results and discussion

3.1. Ethylparaben photocatalytic removal at lab-scale

3.1.1. Effect of solution initial pH

The effects of solution pH, catalyst and H_2O_2 initial concentrations on pollutant elimination were assessed considering the tests and levels reported in Table 1. In the same way, Fig. 2a represents the main effects plot for Eth-PB removal. From the figure, it can be noted that changes in the initial pH of the solution influence markedly the extent of pollutant removal after 30 min of photo-treatment. Initially, at pH values between 3 and ~7.5, an increment of this parameter implies a higher Eth-PB degradation. But, if the pH is higher, an inhibitory effect can be appreciated. This situation could be associated with the different electrostatic interactions between the pollutant and the catalyst surface that can occur during the reaction. TiO_2 Degussa P-25 has a point of zero charge (pzc) in the range 5.7–6.5 [19]. It means that at pH < pzc the catalyst surface is positively polarized, while at pH > pzc the TiO_2 charge is negative. For its part, the acid dissociation constant (pKa) of ethylparaben is 8.22 [5], implying that at pH conditions greater than this; the pollutant will be found primarily in its anionic form. Thus, at pH lower than 7.5, it is expected that almost all the Eth-PB is in its molecular form, while the catalyst surface is charged positively (pH < 6.5) or negative (pH between 6.5 and 7.5), which means that there is not a significant electrostatic interaction between these species. In this regard, results associated with the pH range 3–7.5 could be related to the fact that at higher pH values, there is a higher concentration of hydroxide anions (OH—), which promotes the generation of hydroxyl radicals (Eq. (3)) that eventually contributes to the contaminant oxidation [20]. In the opposite case, at a higher pH most of the paraben has a negative polarity, promoting a repulsive interaction Eth-PB-TiO_2 surface, which would probably be responsible for the decrease in the extent of substrate removal. Additionally, in an alkaline medium, H_2O_2 is highly unstable, conducting to its self-decomposition, which implies a reduction of a potential additional source of $^{\bullet}OH$ and, hence the pollutant removal rate [15].

3.1.2. Effect of TiO_2 initial concentration

According to Fig. 2a, the catalyst concentration plays an important role on pollutant photo-treatment. Initially, increasing this parameter from 0.2 to ~1.0 g L^{-1} leads to an increase in the extent of contaminant degradation (from ~62% to ~77% respectively). This situation is associated with the fact that when the concentration of the semiconductor increases, more photons may be absorbed, representing a higher number of active sites and a possible increment in the generation of $^{\bullet}OH$ radicals and other reactive species that eventually could contribute to the paraben removal [20,21]. However, at higher catalyst loads, aggregation of TiO_2 particles would imply a possible reduction and scattering of the light that penetrates to the solution, which is reflected in a decrease in the Eth-PB removal as the figure indicates [20–22].

3.1.3. Effect of H_2O_2 initial concentration

Similar to the results related to the influence of TiO_2 on substrate removal, Fig. 2a shows that variations in the initial concentration of H_2O_2 in the solution are associated with both positive and negative effects in terms of Eth-PB elimination. In the first case (H_2O_2 concentration between 50 and ~125 mg L^{-1}), presence of H_2O_2, could reduce the possibility of an electron–hole pair recombination, which would promote the generation of $^{\bullet}OH$ radicals as has been reported previously. H_2O_2 also can react with other species present in the solution to form additional reactive agents that would contribute to the contaminant degradation [22].

On the other hand, the excess of H_2O_2 (in this case concentrations >125 mg L^{-1}) may scavenge the $^{\bullet}OH$ free radicals present in the solution, reducing significantly the pollutant oxidation [15,22].

Table 1
Experimental design for pollutant removal using TiO_2/H_2O_2 heterogeneous photocatalysis (pollutant initial concentration: 1.0 mg L^{-1}, temperature: 35 ± 2 °C, irradiance: 350 W m^{-2}, irradiation time: 30 min).

Experiment	pH	TiO_2 concentration (g L^{-1})	H_2O_2 initial concentration (mg L^{-1})	Eth-PB removal (%)
1	9	1.5	50	65.9
2	3	1.5	150	68.8
3	9	0.85	100	80.4
4	6	0.85	100	75.6
5	6	0.2	100	67.5
6	3	1.5	50	60.7
7	6	0.85	100	78.4
8	9	1.5	150	69.2
9	3	0.2	150	59.8
10	6	1.5	100	65.2
11	9	0.2	150	63.6
12	6	0.85	50	71.5
13	3	0.2	50	35.6
14	3	0.85	100	63.4
15	6	0.85	100	76.8
16	6	0.85	150	72.4
17	9	0.2	50	55.2

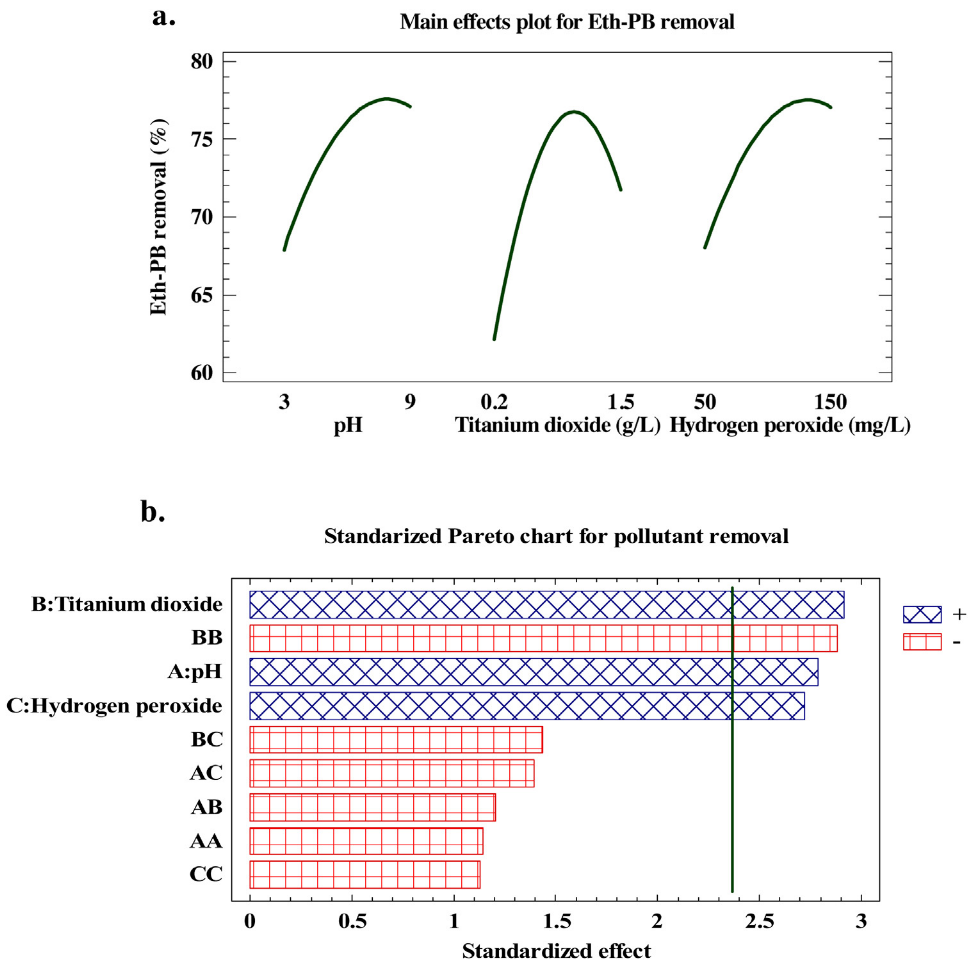


Fig. 2. a. Main effects plot and b. Pareto chart for pollutant removal (pollutant initial concentration: 1.0 mg L^{-1}, temperature: 35 ± 2 °C, irradiance: 350 W m^{-2}, irradiation time: 30 min).

3.1.4. Optimization of experimental conditions

Fig. 2b corresponds to the standardized Pareto chart for Eth-PB removal. This graphic allows to identify the variables and interactions between them that significantly affect the pollutant removal and promote a higher reaction rate. In this way, according to this graphic, factors and interactions that have a significant effect (standardized effect surpasses the chart reference line) on process are the TiO_2 initial concentration (B) and its quadratic coefficient (BB), the pH (A) and the H_2O_2 initial concentration (C). In general, the chart indicates that the pH and the initial concentrations of catalyst and H_2O_2 have a positive effect, while the square value BB represents a negative influence, which would be related to the fact that excess of TiO_2 could reduce the efficiency of the reaction, as was discussed previously.

Having into account the above, Eq. (8) represents a polynomial expression, determined using the statistical software, which relates the experimental results about the extent of paraben removal after 30 min of reaction and those significant factors and interactions (coefficient of determination, R^2, 89.3%).

$$\mathrm{Eth-PB}(\%) = 27.55 + 1.53A + 59.30B + 0.09C - 30.53B^2 \quad (8)$$

"A" corresponds to the solution initial pH, "B" is the semiconductor concentration (g L^{-1}) and "C" is the hydrogen peroxide concentration (mg L^{-1}).

Finally, according to the statistical analysis and Eq. (8), the conditions under the evaluated experimental range that favored a higher Eth-PB degradation are: pH: 7.3, TiO_2: 0.95 g L^{-1} and H_2O_2: 120.7 mg L^{-1}.

3.1.5. Ethylparaben removal under optimal conditions at lab-scale

Fig. 3 depicts the results of pollutant photo-treatment after 120 min of reaction under the selected optimal conditions. From the figure, it can be noted that the use of the photocatalytic system including TiO_2 and H_2O_2 leads to a ~97% of Eth-PB elimination, while that using the system TiO_2/light irradiation just a ~63% of removal was evidenced. These results confirm that the presence of H_2O_2 in this type of treatments improves notably the paraben elimination probably due to its capacity of inhibiting the e^-/h^+ pair recombination.

On the other hand, Fig. 3 also allows to compare the efficiency of different agents on the analyte removal. As can be appreciated, there is no a significant individual effect of adsorption, photolysis, hydrolysis and oxidation with H_2O_2 and H_2O_2/light irradiation on the pollutant final elimination. Therefore, the synergy of the TiO_2/H_2O_2/light combination is the main promoter of the decrease of the paraben presence in the solution, due probably to a higher generation of different oxidizing species including hydroxyl free radicals.

In order to evaluate the role of photogenerated electrons and holes on substrate removal, additional tests were done under the presence of isopropanol, which is considered as a good $^{\bullet}OH$ radicals scavenger [23,24]. Fig. 3 shows that the alcohol inhibits

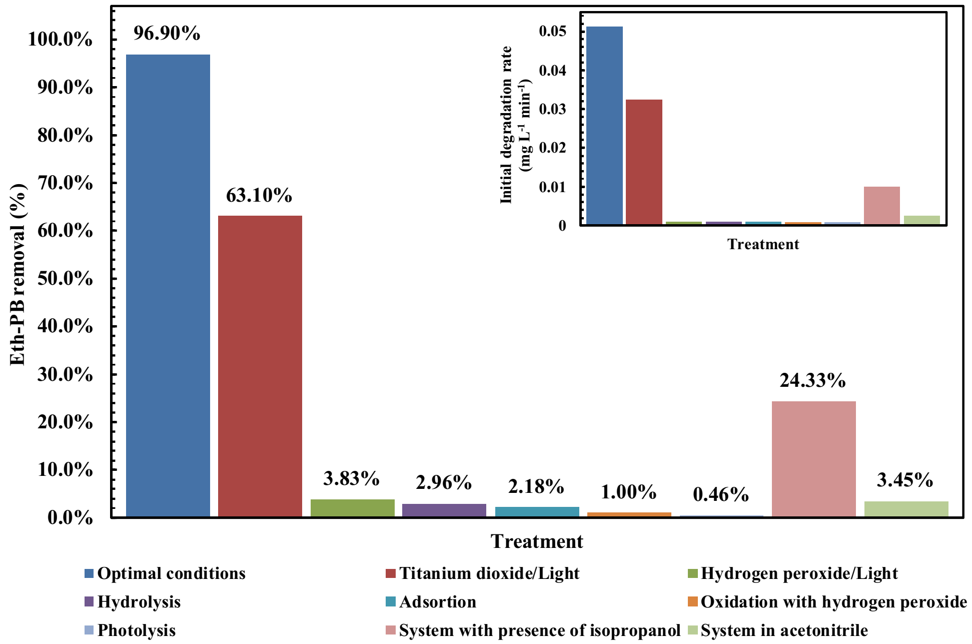


Fig. 3. Pollutant photocatalytical oxidation using different treatments at lab scale. Inset graph: Pollutant initial degradation rate after 1 min of reaction (pollutant initial concentration: 1.0 mg L^{-1}, pH: 7.3, TiO_2: 0.95 g L^{-1}, H_2O_2: 120.7 mg L^{-1}, temperature: 35 ± 2 °C, irradiance: 350 W m^{-2}, isopropanol: 100 mg L^{-1}, irradiation time: 120 min).

considerably the treatment efficiency, indicating that radical species play an important role in the process. Additionally, the use of a no aqueous reaction medium allows to clarify the influence of both $^{\bullet}OH$ and h^+ on the photo-treatment because in aqueous systems, there is a higher possibility of radicals generation due to the H_2O molecules oxidation (Eq. (2)) [21,23]. In this way, the results of some experiments carried out using acetonitrile as solvent show a marked reduction of the substrate elimination (~3.5% of removal after 120 min of reaction), which would imply that Eth-PB photocatalytical elimination is mainly a result of the molecule oxidation by the photogenerated $^{\bullet}OH$ radicals.

3.1.6. Effect of ethylparaben initial concentration

Effect of pollutant initial concentration (C_0) on the process was evaluated varying this parameter in the range 0.5–4.0 mg L^{-1}. Accordingly, Fig. 4 indicates that after 120 min of reaction more than 80% of Eth-PB was eliminated regardless the initial concentration. In general, heterogeneous photocatalytic reactions can be described using the Langmuir–Hinshelwood (LH) kinetic model represented by Eq. (9) [20,25].

$$r_0 = -\frac{dC}{dt} = k_{LH}\theta = k_{LH}\left(\frac{K_{LH}C_{eq}}{1 + K_{LH}C_{eq}}\right) \tag{9}$$

r_0 corresponds to the initial reaction rate, C_{eq} is the pollutant concentration in equilibrium, K_{LH} is the pollutant adsorption constant onto the catalyst surface and k_{LH} is the intrinsic reaction rate constant.

However, when the extent of adsorption and/or substrate concentration is small, $C_{eq} \approx C_0$ and the term $K_{LH}C_{eq}$ can be neglected with respect to 1, converting the expression 9 to a pseudo first-order kinetic equation (Eq. (10)) [20,25,26]:

$$r_0 = -\frac{dC}{dt} = k_{LH}\left(\frac{K_{LH}C_{eq}}{1 + K_{LH}C_{eq}}\right) \approx k_{LH}K_{LH}C_0 \Leftrightarrow r_0 = k_{app}C_0 \therefore k_{app} = k_{LH}K_{LH} \tag{10}$$

k_{app} is an apparent rate constant.

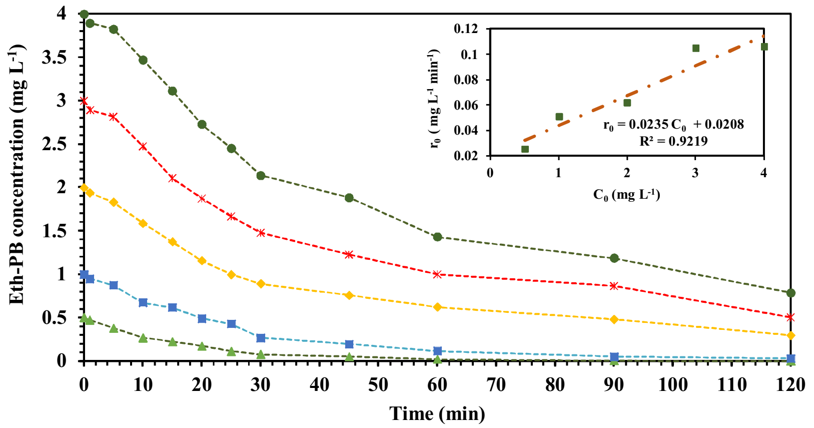


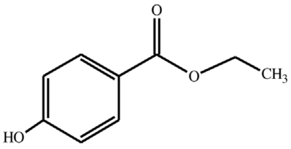
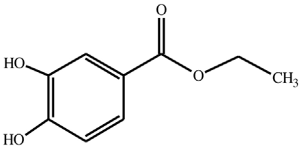
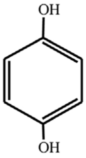
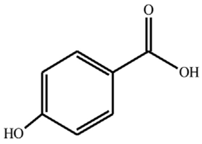
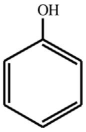
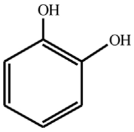
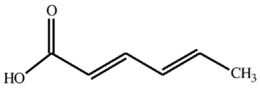
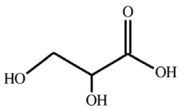
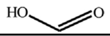
Fig. 4. Effect of pollutant initial concentration on Eth-PB removal using heterogeneous photocatalysis. Inset graph: Relation between substrate initial concentration and initial degradation rate (pollutant initial concentration: 1.0 mg L^{-1}, pH: 7.3, TiO_2: 0.95 g L^{-1}, H_2O_2: 120.7 mg L^{-1}, temperature: 35 ± 2 °C, irradiance: 350 W m^{-2}).

Inset graph in Fig. 4 shows the relationship between the analyte initial concentration and r_0 (computed as $\Delta C/\Delta t$ over the first min of reaction). From the figure, it can be concluded that higher Eth-PB initial concentrations lead to an increase in the initial degradation rate, and model represented by Eq. (10) describes the experimental data correctly ($R^2 \sim 92.2\%$). In this way, substrate photo-oxidation under the evaluated conditions satisfies a first-order kinetic with an associated apparent rate constant equals to $\sim 0.0235\,\text{min}^{-1}$.

3.2. Byproducts identification

Considering the previously defined optimal conditions for Eth-PB removal using heterogeneous photocatalysis with TiO_2/H_2O_2, eight reaction intermediates were identified using gas chromatography coupled with mass spectrometry: Ethyl 3,4-dihydroxybenzoate (A), hydroquinone (B), 4-hydroxybenzoic acid (C), phenol (D), 1,2-Benzenediol (E), sorbic acid (F), 2,3-dihydroxypropanoic acid

Table 2
Identified intermediates during photocatalytic degradation of ethylparaben.

Compound	Molecular structure	Main fragments (m/z)	Retention time (min)
Ethylparaben (Eth-PB)		121, 166, 138, 65	17.20
Ethyl 3,4-dihydroxybenzoate (A)		137, 182, 154, 109	19.00
Hydroquinone (B)		110, 81, 55	11.00
4-hydroxybenzoic acid (C)		121, 138, 93, 65	13.90
Phenol (D)		94, 66, 65, 39	9.50
1,2-Benzenediol (E)		110, 64, 63, 81	9.00
Sorbic acid (F)		97, 112, 67	9.60
2,3-dihydroxypropanoic acid (G)		75, 47, 45	8.10
Formic acid (H)		29, 46, 45	5.30

(G) and formic acid (H). Thus, Table 2 shows the molecular structure of each identified byproduct, its chromatographic retention time and the main fragments used for its identification.

In general, hydroxylation has been found to be a significant reaction in the removal of parabens using different advanced oxidation processes [6,27]. In this way, identified byproducts allow to infer that oxidation of ethylparaben using heterogeneous photocatalysis starts with a hydroxylation reaction in which an —OH group is added to the aromatic ring of the substrate forming ethyl 3,4-dihydroxybenzoate (A). Subsequently, generated oxidation processes would lead to the breaking of the bond between the benzene ring and the carbonyl group of the molecules, promoting the generation of byproducts B, D and E. For its part, 4-hydroxybenzoic acid (C) has been reported as a typical intermediate of alkyl-parabens advanced oxidation, whose formation is due to the •OH radical attack on the aliphatic chain present in the structure of the contaminant [6,27]. Additionally, it has been reported that presence of the isomers hydroquinone (B) and 1,2-Benzenediol (E) can also be result of the photocatalytic oxidation of phenol (D) [27].

On the other hand, the presence of different oxidizing species in the solution would promote the generation of compounds F, G and H after the opening of the aromatic ring.

Finally, the organic matter will potentially be transformed into carbon dioxide and water due to the breaking down of the benzene ring and subsequent mineralization [6]. Fig. 5 shows a schematic representation of byproducts generation during the ethylparaben degradation using heterogeneous photocatalysis with TiO_2 and H_2O_2.

3.3. Ethylparaben photocatalytic removal at pilot scale

Different tests were conducted at pilot scale using direct sunlight and the CPC collector previously described. The experiments were carried out under the same conditions used at laboratory scale during 6 h (between 10:00 and 16:00). Solutions containing 1 mg L^{-1} of Eth-PB were prepared in drinking water and the average radiation intensity during the experiments was ~395 W m^{-2}.

The results of each evaluated treatment are depicted by Fig. 6. From figure, it can be seen that under the defined optimal conditions more than a 80% of Eth-PB is removed in 6 h, while the conventional TiO_2/light technology conducts to a ~45.9% of contaminant elimination in the same time, results that are related to the fact that H_2O_2 presence would enhance the efficiency of the photocatalytic oxidation, as was mentioned in previous sections.

On the other hand, Fig. 6 also indicates that even during long periods of irradiation the sole sunlight action is not able to promote the pollutant elimination. Additionally, in a similar way to the laboratory scale experiments, oxidation with H_2O_2 or H_2O_2/light, hydrolysis and substrate adsorption onto the TiO_2 surface and the walls of the solar reactor were no significant.

However, comparing the results of Eth-PB removal at laboratory and pilot scale after 2 h of photo-treatment (Fig. 3 y 6), it is evident that there is a decrease of the extent of pollutant elimination using the CPC collector. This situation could be associated with different aspects, including the effect of the water matrix. For example, the presence of different anions has been reported as a factor that could affect the performance of some advanced oxidation process [28–30]. In this regard, the analysis of the drinking water employed to prepare the pollutant solutions showed a notable presence (higher than the Eth-PB initial concentration) of chloride, nitrate, sulfate and carbonate (Table 3), species that have been classified by different authors as hydroxyl radicals scavengers, situation that could limit the efficiency of the photocatalytical system [29–31]. In addition, the fact that the CPC pilot plant has not a temperature control could promote the H_2O_2 decomposition due to increments

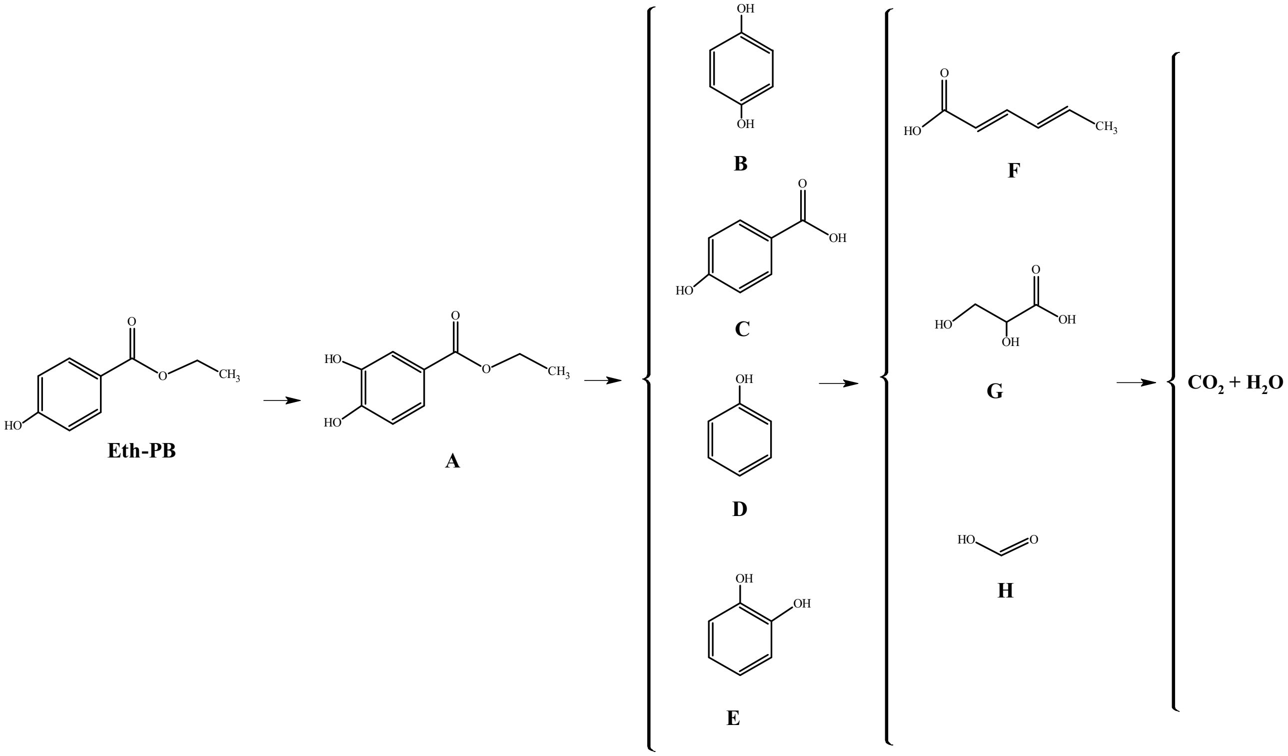
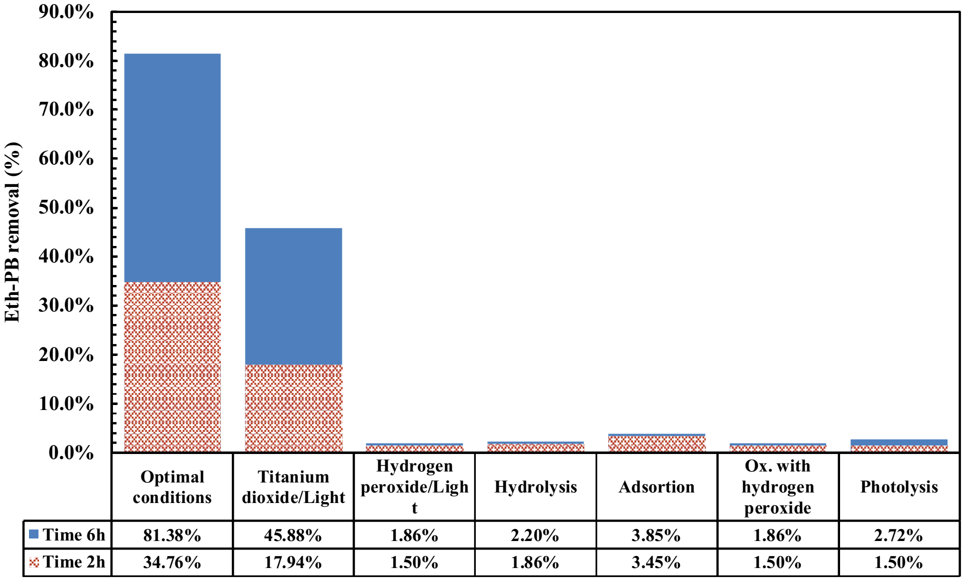


Fig. 5. Plausible pathway for the ethylparaben degradation using heterogeneous photocatalysis with TiO_2 and H_2O_2.



	Optimal conditions	Titanium dioxide/Light	Hydrogen peroxide/Light	Hydrolysis	Adsortion	Ox. with hydrogen peroxide	Photolysis
■ Time 6h	81.38%	45.88%	1.86%	2.20%	3.85%	1.86%	2.72%
▨ Time 2h	34.76%	17.94%	1.50%	1.86%	3.45%	1.50%	1.50%

Fig. 6. Pollutant photocatalytical oxidation using different treatments at pilot scale (pollutant initial concentration: 1.0 mg L^{-1}, pH: 7.3, TiO_2: 0.95 g L^{-1}, H_2O_2: 120.7 mg L^{-1}, average irradiance: 395 W m^{-2}, volume: 100 L).

Table 3
Different anions presence on the water matrix.

Anion	Chloride	Nitrate	Sulfate	Carbonate
Concentration (mg L^{-1})	5.250	2.578	6.180	22.32

in this factor associated with the sunlight irradiation, reducing the possibility of a higher •OH free radicals generation [32].

3.4. Biodegradability and mineralization studies

Fig. 7 shows the variation of the solution dissolved organic carbon (DOC) and the samples biodegradability (BOD_5/COD index) during the Eth-PB photo-treatment at lab and pilot scale. From the figure, it can be noted that in both cases, more than a 82% of DOC is removed after 360 min, which is evidence that the heterogeneous photocatalysis with TiO_2/H_2O_2, under our experimental conditions, is able to promote the pollutant mineralization (transformation in CO_2 and water).

On the other hand, evaluation of solution biodegradability indicates that the photocatalytic system enhances significantly the solution BOD_5/COD ratio. In addition, under the laboratory conditions this parameter was higher than 0.4 after 300 min of reaction, which would imply that the contaminated water could be treated using biological techniques [33].

4. Conclusions

Heterogeneous photocatalytic treatment of the endocrine disrupting chemical, ethylparaben was evaluated considering the effect of the solution initial pH and the catalyst and H_2O_2 concentrations. Experiments were carried out at lab and pilot scale, reaching in both cases a pollutant removal higher than 80%. In general, experimental results allow to conclude that hydroxyl free radicals are the main specie responsible for pollutant oxidation and

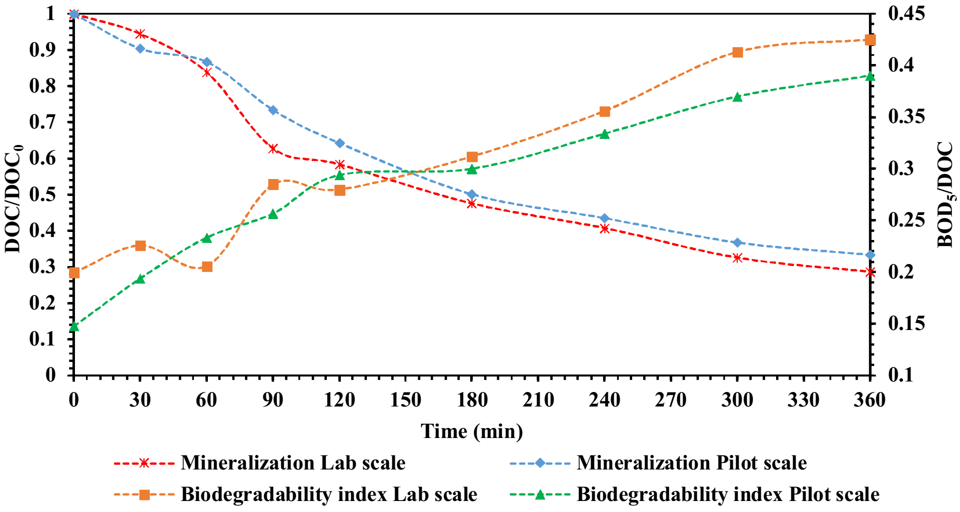


Fig. 7. DOC/DOC_0 and BOD_5/COD evolution during pollutant photocatalytic degradation (pollutant initial concentration: 50.0 mg L^{-1}, pH: 7.3, TiO_2: 0.95 g L^{-1}, H_2O_2: 120.7 mg L^{-1}, irradiance: 350 W m^{-2}).

that the presence of H_2O_2 contributes positively to enhance the conventional system efficiency.

On the other hand, hydroxylation of the paraben molecule seems to be one of the most important stages during the organic matter oxidation. Solution DOC decreased significantly during 360 min of photo-treatment and BOD_5/COD index was increased notably. Based on these aspects TiO_2/H_2O_2 photocatalysis could be considered as an efficient method for ethylparaben removal in water.

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