Research Article

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Combating paraben pollution in surface waters with a variety of photocatalyzed systems: Looking for the most efficient technology

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Abstract: The constant presence of parabens in natural surface waters has raised a growing concern of the potential long-term toxic effects that parabens may have in wildlife, mainly as endocrine disruptors. The present report describes the results of a study in which different photocatalyzed systems, such as photo-Fenton, Fenton, UV-H₂O₂, UV-TiO₂ and UV-TiO₂-H₂O₂, were applied to the removal of these recalcitrant pollutants in some surface waters, including natural (e.g. rivers) and man-made (e.g. reservoirs and wastewater treatment plants). Degradation of four widely-used parabens (methyl-paraben, ethyl-paraben, propyl-paraben and butyl-paraben) was analyzed. Experimental results reveal that the most efficient method to combat these emerging pollutants was photo-Fenton. When this process was optimized, optimal removal efficiency was attained using doses of H₂O₂ and Fe(II) equal to 2.92·10⁻⁴ mol dm⁻³ and 1.85·10⁻⁵ mol dm⁻³, respectively. It is also worth noting that the removal rate of these contaminants is slower in natural waters. The results suggest that the photo-Fenton process is promising and maybe an adequate technology for the treatment of these persistent contaminants.

Keywords: Water Treatment; Surface-waters; Parabens pollution; photo-assisted Fenton; Remediation Systems.

1 Introduction

The detection of emerging contaminants (ECs) in the environment has been of increasing interest [1-2]. This group of pollutants includes personal care products, hormones, disinfectants, surfactant, and gasoline additives, among others [3]. One of the most important characteristics of ECs that makes them such critical threats to the environment is that many of them cannot be completely degraded through conventional treatments. Therefore, the development of new technologies is needed. Among emerging technologies, advanced oxidation processes (AOPs) provide a promising option for the treatment of ECs [4].

The impact on human and animal health of many substances that are present in the environment is not yet fully known [5]. Such is especially the case with parabens, a seemingly innocuous family of preservatives whose relationships with certain allergies [6], irritation of skin and eyes [7], a decrease of male fertility [8] and even breast cancer [9] have been reported over the past few years. Furthermore, parabens are among the most commonly found of the emerging pollutants, and their presence in ground- and surface water has been increasingly detected.

The most common parabens detected in natural waters are methyl-paraben (MP), ethyl-paraben (EP), propyl-paraben (PP) and butyl-paraben (BP). Currently, parabens are most commonly used as preservatives in the cosmetic industry [10], and they have also been used in pharmaceuticals, foodstuffs and other industrial products. Until the late 1990s, only a few studies had reported on the potentially harmful effects of parabens on both human health and the environment. Nowadays, however, the number of scientific studies warning about the effects of parabens on human health and the environment is increasing remarkably. The toxicity of parabens is closely related to their activity as hormone disruptors: for example, several recent studies have demonstrated relationships between breast cancer and the presence of

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parabens in tumour tissues [11-13]. Researchers studying the causes of breast cancer [12] confirmed that parabens are readily absorbed into the body.

The detection of parabens in human tissues from environmental exposures has also been recently reported [11]. Parabens have also been detected in human urine, in human milk, human serum, and human seminal fluid [14-21]. Parabens may be present in different types of water, including swimming pool water or seawater, albeit there are very few data on the presence of parabens in drinking water. In the United States, a study from four sources of treated drinking water reported that MP was undetectable [22]. On the contrary, in Spain, the presence of MP in tap water has been reported [23-24]; however, these authors did not investigate the presence of other parabens, such as EP, PP and BP. More recently, the presence of MP, PP and BP was found in tap water, although in this case, EP was undetectable [25].

The presence of parabens in inland waters can be largely attributed to discharges from sewage treatment plants and factories. Different areas of several rivers have been sampled, and large variations in the concentrations of parabens depending on the zone were demonstrated. Such concentrations have been linked to the presence of effluent discharge or industrial activities [25, 26-29].

In summary, it can be stated that parabens are ubiquitous pollutants in surface waters. Since parabens were detected in wastewater treatment plants (WWTP) effluents, rivers and reservoirs, and even in drinking water, the implementation of more efficient degradation processes is a topic of current interest. Due to their cost efficiency and simplicity, AOPs appear to be excellent choices for the complete degradation of this kind of pollutant in aqueous media. Among them, chemical advanced oxidation processes are particularly useful for the removal of toxic or biologically non-degradable pollutants, such as aromatic compounds, dyes, pesticides, and volatile organic compounds present in wastewater [4, 30-34] and surface waters [34-36], although their widespread application is limited and depends on operation costs.

In particular, photo-assisted AOPs have been used for the removal of persistent pollutants from aqueous matrices. Among these photo-assisted AOPs, the photo-Fenton process constitutes an excellent choice due to its high effectiveness and relatively low cost. Furthermore, this kind of process makes it possible to achieve complete destruction of pollutants to harmless compounds, such as carbon dioxide and water [37]. All of these processes are based on the generation of reactive species (such as hydroxyl radical), which oxidize a wide variety of contaminants in a rapid and non-selective manner.

The basis of the photo-assisted Fenton process consists of hydrogen peroxide decomposition in acidic medium, catalyzed by iron (II) ions, giving rise to the strongly oxidizing $\cdot\text{OH}$ radical. This system consists of three steps:

1. Photolysis of hydrogen peroxide [38]:

2. The reaction of Fe(II) ions with hydrogen peroxide:

3. Reduction of Fe(III) ions to Fe(II) ions:

Therefore, the UV radiation accelerates the cycle Fe(II)-Fe(III)-Fe(II), thus facilitating the production of hydroxyl radicals. Hydroperoxyl radicals are also generated according to the following reaction:

Bossmann et al. [39] proposed that the ferric ion in the presence of UV radiation evolves to an excited state (Fe^{3+*}) that reacts faster with the hydrogen peroxide to form Fe^{2+} (Eq. (5)), or with organic compounds in its elemental state.

Analysis of the process described above suggests that the photo-Fenton process is adequate to be applied in water purification treatments since strongly oxidizing hydroxyl radicals are generated without the formation of potentially harmful chlorinated secondary oxidation products. This is an important advantage when compared with other traditional chemical oxidation processes that involve the use of chlorine or chlorine dioxide.

2 Materials

2.1 Chemicals

Methyl-paraben (CAS Number 99-76-3), ethyl-paraben (120-47-8), propyl-paraben (94-13-3), and butyl-paraben (94-26-8) were of the highest purity (>98%) and were purchased from Sigma (Spain). A stock solution of the four parabens

(5 mg dm⁻³) was created with high purity water (from a Millipore Milli-Q™ system). This initial concentration of parabens was selected in order to conform with a previous literature survey, which studied several experimental works that had the aim of removing parabens from WWTP influents or effluents [14]. The exact concentration of hydrogen peroxide (nominally 33% w/v, analytical grade, Sigma-Aldrich) was determined by a photometric method using Titanium (IV) oxysulfate-sulfuric acid solution (Fluka 89532) as reactant. FeSO₄·7 H₂O (99.9% analytical grade Sigma-Aldrich) was purchased from Merck (Spain), and the Fe²⁺ concentration was determined by permanganometry. TiO₂ (Degussa P25) was purchased from Degussa Portugal (AEROXIDE®-P25).

Surface water aqueous matrices were obtained from the Guadiana River (Badajoz, SW Spain) (type I), the reservoir of Peña del Águila (Villar del Rey, Badajoz, SW Spain) (type II), and secondary WWTP-Badajoz effluent (type III). Table 1 shows the physicochemical characterization of these surface -aqueous matrices.

2.2 Experimental

The reactor was filled with an aqueous solution containing the four parabens (5 mg dm⁻³). A total volume of 0.350 dm³ of the solution was used for all experiments, excepting Fenton (250 ml). Finally, in all cases, the reaction was stopped by addition of bisulfite at time intervals. In every experience involving UV radiation, the experiments were performed in a cylindrical glass and the reactor was equipped with an axial radiation source (Heraeus TNN 15/32 lamp, 15W, $\lambda = 254$ nm). The constant operating conditions for all the systems under study (based in our previous studies) were: [H₂O₂]=2.7·10⁻⁴ mol dm⁻³, [Fe²⁺]=2.7·10⁻⁵ mol dm⁻³ and [TiO₂]=3.83·10⁻⁴ mol dm⁻³.

2.3 Analytical

MP, EP, PP and BP were determined by HPLC using a Waters HPLC chromatograph, equipped with a photodiode Array 996 detector and a Phenomenex-Pak C-18 column (5 μ m, 150 mm x 3.9 mm). Well-defined peaks were obtained at 2.2, 2.8, 4.2 and 6.8 min for MP, EP, PP and BP, respectively. The mobile phase was a 60:40 methanol:water mixture (10⁻² mol dm⁻³ orthophosphoric acid) in isocratic operation mode.

Table 1: Characterization of the different used surface-water aqueous matrices. Guadiana River (Badajoz, SW Spain), type I, reservoir of Peña del Águila (Villar del Rey, Badajoz, SW Spain), type II, and secondary WWTP-Badajoz effluent, type III.

	Surface Water		
	Type I	Type II	Type III
pH	8.1	7.0	8.3
Conductivity, μ S/cm	415.0	126.2	550
Hardness, mg CaCO ₃ /L	180.0	38.0	236.0
Alcalinity, mg/L	84.0	24.0	222.0
Ammonium, mg/L	0.05	0.02	5.8
COD, mg/L	27.5	18.0	37.0
TOC, mg/L	8.0	6.7	13.0

2.4 Design of experiments (DoE)

The removal efficiency of parabens after 30 minutes was considered as the response variable (Y). The operating levels of the statistical design of experiments (DoE) for the photo-Fenton process were: [H₂O₂]₀ codified values (-1, +1) corresponds to (4.31·10⁻⁵ mol dm⁻³, 2.51·10⁻⁴ mol dm⁻³), respectively; in the case of [Fe²⁺]₀ these codified values were (4.31·10⁻⁶ mol dm⁻³, 2.5·10⁻⁵ mol dm⁻³) respectively.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Preliminary experiments

The generation of hydroxyl radicals in Fenton processes is strongly influenced by several factors, including pH and initial concentrations of the reagents (namely, H₂O₂ and Fe²⁺). Due to the scarce solubility of iron hydroxides, the pH range to be used in Fenton processes is restricted to values of 4.5 and below. Furthermore, according to the experience of the authors, optimum results are attained in terms of removal efficiency of this kind of compounds by using a [H₂O₂]₀ : [Fe²⁺]₀ ratio equal to 10 [40-41]. However, the selection of an adequate initial concentration of hydrogen peroxide is far from easy. Hence, in order to optimize the initial H₂O₂ concentration, a set of preliminary experiments were performed with [H₂O₂]₀ ranging from 1.25·10⁻⁵ mol dm⁻³ to 2.50·10⁻⁴ mol dm⁻³.

Figure 1: MP removal efficiency (%) vs. time as at different initial concentrations of hydrogen peroxide. $[MP]_0 = 5 \text{ mg dm}^{-3}$, $[H_2O_2]_0 : [Fe^{2+}]_0 = 10$. $T = 25^\circ \text{C}$.

The results of the preliminary trials with MP are shown in Figure 1. According to these results, it can be concluded that, as a rule, the removal efficiencies after 60 min of treatment are relatively low (at most, 54.9, 58.0 and 67.0%) for MP, EP and PP, respectively. For BP, on the contrary, up to 76.9% of removal is attained even using low initial concentrations of H_2O_2 . For higher initial concentrations of this reagent, namely 1.25 and $2.50 \cdot 10^{-5} \text{ mol dm}^{-3}$, complete abatement of the parabens is achieved after 45–60 minutes of treatment. It is worth noting that above a given concentration of hydrogen peroxide no remarkable effect is observed in terms of removal efficiency of the pollutants with an increase in hydrogen peroxide concentration. This saturating effect is in good agreement with the fact that H_2O_2 may serve as a radical scavenger as suggested by Eq. (4) and the formation of hydroperoxyl radicals ($HO_2\cdot$), a chemical species with a lower oxidation potential than $HO\cdot$.

Taking into consideration these results, an experimental design was planned using an initial H_2O_2 concentration of $1.25 \cdot 10^{-5} \text{ mol dm}^{-3}$ as the central point (0) and $2.50 \cdot 10^{-5} \text{ mol dm}^{-3}$ as the factorial point (+1).

3.2 Parabens abatement by several AOPs

The oxidation of the four pollutants, simultaneously in ultrapure water, was first performed with Fenton's

reagent (H_2O_2/Fe^{2+}) and with the following AOPs that employ UV radiation: UV/ H_2O_2 , UV/ Fe^{2+}/H_2O_2 (photo-Fenton system), UV/ TiO_2 and UV/ TiO_2/H_2O_2 . In order to perform a comparison of all of the AOPs here studied, the experimental conditions indicated in Section 3.1 were considered as optimal and consistently used in all cases.

The removal efficiencies for MP by all of the examined AOPs are shown in Figure 2. Similar results were obtained for EP, PP and BP (data not shown). It can be readily concluded that the photo-Fenton (UV/ Fe^{2+}/H_2O_2) ternary system yields the most effective process. The other ternary system (i.e., UV/ TiO_2/H_2O_2) also exhibits removal efficiencies that are larger than those of the binary systems, i.e., Fenton (Fe^{2+}/H_2O_2), UV/ H_2O_2 and UV/ TiO_2 , but in this case, the efficiencies are more similar to those of the binary systems. The sequence shown in Figure 2 suggests that, in combination with H_2O_2 , Fe^{2+} is somewhat more efficient than TiO_2 . The synergistic effect observed for the photo-Fenton system is consistent with results obtained in the 1990s [42–44] and more recently by Serna-Galvis et al. [45]. Figure 2 confirms that UV radiation accelerates the Fenton process, thus improving the degradation of the parabens. A reasonable explanation for this result is the fact that during the reaction, Fe^{2+} oxidizes to Fe^{3+} (Eq. (2)) and that the regeneration of the ferrous ions occurs in a process that is mediated by UV radiation (Eq. (3)), thus facilitating the production of hydroxyl radicals (Eq. (4) and Eq. (5)).

Figure 2: Methylparaben removal efficiency (%) for the different AOPs. $[MP]_0 = 5 \text{ mg dm}^{-3}$, $[H_2O_2]_0 = 2.7 \cdot 10^{-4} \text{ mol dm}^{-3}$, $[Fe^{2+}] = 2.7 \cdot 10^{-5} \text{ mol dm}^{-3}$, $[TiO_2]_0 = 0.38 \cdot 10^{-3} \text{ mol dm}^{-3}$, $T = 25^\circ \text{C}$. UV radiation source = Heraeus TNN 15/32 (15W).

Moreover, the Fenton system is more effective than UV/H₂O₂ because the hydroxyl radicals generated in this latter system by the photocatalytic degradation of H₂O₂ (Eq. (1)) are consumed during the reaction [46]. In the Fenton system, the rate of degradation of the contaminant increases, since the reaction of hydroxyl radical generation may still occur in the medium by the reduction of ferric ions to ferrous ions (Eq. (5)) in the presence of H₂O₂. Furthermore, titania catalyzes the reaction of the organic contaminant by photodegradation due to the intrinsic nature of its electrical structure [47] so that it facilitates the $\cdot\text{OH}$ radical generation. However, the presence of H₂O₂ exerts an important influence on the photodegradation process of the organic compounds, because H₂O₂ acts as a powerful oxidant, generating large amounts of $\cdot\text{OH}$ radicals [48]. In the UV/TiO₂ process, the contribution of radical oxidation is very low, like that of the photooxidation process. However, in the UV/H₂O₂ process, oxidation by free radicals (especially $\cdot\text{OH}$) is much more remarkable due to the presence of H₂O₂ [49].

These results allow us to conclude that the photo-Fenton system is clearly the most effective process for the destruction of these pollutants. Therefore, this system was studied in more detail.

3.3 Photo-Fenton Experimental Design

Two operational variables (namely, A: $[H_2O_2]_0$ and B: $[Fe^{2+}]_0$), their mutual interaction (AB), and their respective quadratic effects (A^2 and B^2) are considered in the ANOVA test. A nonlinear equation regression was performed (Eq. (6)) for each paraben compound.

$$Y(\%) = b_0 + a \cdot [H_2O_2]_0 + b \cdot [Fe^{2+}]_0 + c \cdot ([H_2O_2]_0)^2 + d \cdot [H_2O_2]_0 \cdot [Fe^{2+}]_0 + e \cdot ([Fe^{2+}]_0)^2 \quad (6)$$

Table 2 shows the fitting coefficients obtained for the removal of the different parabens. The positive influences of $[H_2O_2]_0$ and $[Fe^{2+}]$ are due to the fact that these variables positively impact the generation of $\cdot\text{OH}$ radicals. The value of the correlation factor (R^2) reaches 0.959, which is consistent with adequate modelling of the process.

Table 3 lists the values of $[H_2O_2]_0$ and $[Fe^{2+}]_0$ that optimize the removal of each contaminant separately. It can be clearly appreciated that, for all parabens, with respect to $[Fe^{2+}]_0$ an optimum for the separate removal has been found in the range of coded values comprised between 0.683 and 0.776 (excepting for propyl-paraben, 1.410). This corresponds to initial concentrations of $2.17 \cdot 10^{-5}$ - $2.27 \cdot 10^{-5} \text{ mol dm}^{-3}$. However, for $[H_2O_2]_0$, no optimum is predicted in this range. Nevertheless, the initial concentration of hydrogen peroxide should not

be excessively increased due to the aforesaid scavenging effect. Table 3 also shows the coded and natural values of $[H_2O_2]_0$ and $[Fe^{2+}]_0$ that optimize the removal of all contaminants simultaneously [50]. Operating under these conditions (i.e., $[H_2O_2]_0 = 2.92 \cdot 10^{-4} \text{ mol dm}^{-3}$ and $[Fe^{2+}]_0 = 1.85 \cdot 10^{-5} \text{ mol dm}^{-3}$), total removal of the four compounds should be obtained.

3.3.1 Graphical analysis

A model was developed according to five factors, which correspond to Eq. (6). The so-called Pareto plot (Figure 5) may be considered as a plot of the results of the ANOVA test. Grey bars represent negative factors, and white bars correspond to positive factors.

The main effect plots allow us to conclude that $[H_2O_2]_0$ represents a positive influence in this range of study. This fact is consistent with an increase in the formation of $\cdot OH$ radicals. With respect to $[Fe^{2+}]_0$, in all cases except for PP, the curve shows a maximum. This suggests that the presence of ferrous ions favours the oxidation process due to the catalytic role of Fe^{2+} , but only up to a coded value around 0.5–0.7. Larger coded values exert a negative effect on the removal of all compounds except for PP.

Table 2: Fitting coefficients of eqn (6) obtained for each compound. Reaction time=30 min. Target variable = paraben removal percentage (%).

Compound	b_0	a	b	c	d	e
Methyl-paraben	62.1	21.9	7.1	-1.13	-6.8	-10.8
Ethyl-paraben	67.9	22.4	5.32	-2.27	-0.58	-10.1
Propyl-paraben	72	20.9	13	-5.4	-5.02	-1.85
Butyl-paraben	80	18.9	5.03	-4.27	-4.45	-8.29

Table 3: Optimal conditions. Coded and natural values. Reaction time=30 min. Target variable = paraben removal percentage.

	Separate optimization				
	Coded		Natural		
	Optimum Removal (%)	$[H_2O_2]_0$	$[Fe^{2+}]_0$	$[H_2O_2]_0$	$[Fe^{2+}]_0$
Methyl-paraben	97.25	1.414	0.776	$2.93 \cdot 10^{-4}$	$2.27 \cdot 10^{-5}$
Ethyl-paraben	100.00	1.414	0.726	$2.93 \cdot 10^{-4}$	$2.22 \cdot 10^{-5}$
Propyl-paraben	100.00	1.414	1.410	$2.93 \cdot 10^{-4}$	$2.92 \cdot 10^{-5}$
Butyl-paraben	100.00	1.414	0.683	$2.93 \cdot 10^{-4}$	$2.17 \cdot 10^{-5}$
			Joint	optimization	
	100.00	1.395	0.363	$2.92 \cdot 10^{-4}$	$1.85 \cdot 10^{-5}$

Figure 3 displays these results regarding BP degradation. The response surface is remarkably convex along with the whole operational range. Both variables (namely, $[H_2O_2]_0$ and $[Fe^{2+}]_0$) affect the compound removal in a similar manner but only for $[Fe^{2+}]_0$ can an optimum be determined.

3.4 Influence of the aqueous matrix on the photo-Fenton system

With regard to the influence of the aqueous matrix, three different aqueous surface waters type I (Guadiana River), type II (Peña del Águila reservoir) and type III (Badajoz-WWTP effluent) were tested. Experiments were carried out at the previously determined optimal conditions for the Photo-Fenton process. Figure 4 shows the evolution of the EP removal vs. time in the four aqueous matrices (including Milli-Q ultrapure water). Similar results were obtained for MP, PP and BP. As can be seen, the removal efficiency follows the trend ultrapure water $\approx$ river water $>$ WWTP effluent $\approx$ reservoir water. It can be stated that the removal is faster when ultrapure water is used, followed by river water and WWTP effluent. The removal of the parabens from reservoir water is very slow in all cases.

The removal rate of pollutants in different aqueous matrices by Fenton process -- or its derivatives -- has been investigated in recent years, and some controversies have arisen. For instance, Derbalah et al. [51] reported that the degradation of fenitrothion in river water by Fenton and photo-Fenton processes was slightly faster than in pure water and attributed this fact to the presence of Fe^{2+} and Fe^{3+} in natural water, which caused a higher rate of $\cdot OH$ radicals generation. Similarly, Moncayo-Lasso et al. [52] attribute the faster mineralization of dihydroxy-benzene

Figure 3: Response surface and contour plot for the removal of BP by photo-Fenton system. Influence of initial concentration of hydrogen peroxide and ferrous salt. $T=25\text{ }^{\circ}\text{C}$. $[\text{BP}]_0=5\text{ mg dm}^{-3}$

Figure 4: Ethyl-paraben removal in different aqueous matrices by the photo-Fenton process in optimal conditions $[\text{EP}]_0=5\text{ mg dm}^{-3}$, $[\text{H}_2\text{O}_2]_0=2.92\cdot 10^{-4}\text{ M}$ and $[\text{Fe}^{2+}]_0=1.85\cdot 10^{-5}\text{ M}$, $T=25\text{ }^{\circ}\text{C}$, Heraeus TNN 15/32 lamp, 15W, $\lambda=254\text{ nm}$.

by a photo-Fenton process in river-water compared to ultrapure water to the concurrence of three facts, namely i) the formation of photoactive intermediaries that contribute to mineralization by photoassisted electron transfers; ii) the presence of Fe^{3+} ions in river waters, that results in the generation of singlet oxygen, H_2O_2 and $\cdot\text{OH}$ radicals that attack the dihydroxy-benzene compounds, and iii) the presence of humic acids that, at adequate pH (3-5) can form complexes with the Fe^{3+} , increasing the amount of photoactive Fe^{3+} and therefore the efficiency of the process. Also, Jacobs et al. [53] reported that the

presence of fulvic acids in river waters accelerates the degradation rate of caffeine approximately threefold.

However, more recently, Veloutsou et al. [54] reported a delay in the mineralization rate of atenolol and metoprolol in river waters by the photo-Fenton process with respect to an ultrapure aqueous matrix. An increase in the total consumption of H_2O_2 was reported, too. These authors indicate that hydroxyl radicals and other oxidizing species are neutralized by attacking other organic molecules naturally present in river waters. Also, $\cdot\text{OH}$ radicals may be involved in reactions with inorganic ions such as

Table 4: Optimal conditions reported for the removal of different pollutants by photo-Fenton processes.

Target pollutant	Initial Concentration	Optimal $[H_2O_2]_0/[Fe^{2+}]_0$	Optimal pH	Removal efficiency (%)	pH range	T (°C)	Reference
λ -cyhalothrin	10 ppm	12.83	n.a.	100	2-5	n.a.	[59]
6 common pharmaceuticals	5 ppm each	15	5	50	3-7	30-35	[60]
Carmoisine	20 ppm	20	3.5	95	2-6	25	[37]
Sucralose	15 ppm	17	3	96	2-7	38	[49]
Azure-B	30 ppm	13.2	2.2	100	1.5-2.7	25	[61]

chloride, nitrate, sulphate or phosphate. Nevertheless, the total disappearance of the initial compounds was also achieved after 10 min of illumination in river water as it is the case in the present study.

Likewise, Benítez et al. [55] reported a higher removal rate in ultrapure water when compared to other surface-water matrices. These authors asserted that the dissolved organic matter that naturally occurs in real water matrices may deplete at least part of the oxidizing species and, hence, the total amount of oxidizing agents available for the degradation of the target pollutants decreases. Obviously, in the case of ultrapure water, the emitted radiation and the oxidizing agents generated *in situ* are almost totally devoted to the degradation of the pollutants, which results in higher removal rates. The detrimental effect of the presence of non-dissolved organic matter in the aqueous media has also been reported by Polo-Lopez et al. [56] when investigating the removal of phytopathogen fungi spores in natural effluents.

On the other hand, Neamtu et al. [57] indicated that the presence of inorganic anions dissolved in the real water matrices could exert a coordination effect over the Fe^{2+} and, mostly, Fe^{3+} ions that are involved in the photo-Fenton process. For instance, the presence of chloride ion in real waters favours the formation of thermodynamically stable Fe^{3+} complexes as, for instance, $FeCl_2^+$ or $FeCl_2^+$. Furthermore, sulphate ions may also form complexes such as $Fe[(SO_4)_2]^+$. Consequently, the regeneration of Fe^{2+} ions is handicapped and the process efficiency decreases markedly. In addition, Fe^{2+} and Fe^{3+} ions may also form stable complexes with certain organic compounds that naturally occur in real waters, which also contribute to lower the amount of oxidizing species available to react with the pollutant. The same conclusion was reached by De Luna et al. [58] when investigating the degradation of dimethyl sulfoxide by different Fenton processes.

Finally, but not less important, it must be taken into consideration that the presence of organic matter in real water matrices may hinder the penetration of light due to

increased turbidity. Table 4 summarizes the operational conditions that lead to optimum removal of different pollutants using the photo-Fenton process. It is worth noting that the experimental conditions that resulted in an optimized removal of the target molecules are, as a rule, similar to those reported in this work (i.e., $[H_2O_2]_0$ to $[Fe^{2+}]_0$ ratio equal to 15.8 and pH = 3.5).

4 Conclusions

Removal rates of parabens (methyl-paraben (MP), ethyl-paraben (EP), propyl-paraben (PP), and butyl-paraben (BP)) in ultrapure water using different photocatalyzed processes (photo-Fenton, Fenton, UV- H_2O_2 , UV- TiO_2 and UV- TiO_2 - H_2O_2) have been studied.

- 1) The photo-Fenton process is the most efficient photocatalyzed technology to remove these contaminants.
- 2) With regard to the influence of experimental conditions on the photo-Fenton system, $[H_2O_2]_0$ is the variable that most strongly influences the removal of parabens, followed by $[Fe^{2+}]_0$. After 30 minutes, the removal of these pollutants reached 100%.
- 3) Total removal of parabens is achieved using initial concentrations of H_2O_2 and Fe^{2+} equal to $2.92 \cdot 10^{-4}$ and $1.85 \cdot 10^{-4}$ mol dm⁻³, respectively.
- 4) Experimental confirmation of these results in other surface aqueous matrices (river water, reservoir water and WWTP effluent) was carried out. The removal efficiency of photo-Fenton process in ultrapure water and river water reaches 100%, decreasing to approximately 80% for WWTP effluent and reservoir water. In all cases, the removal rate of parabens was slower when natural waters were used.

Conflicts of interest: There are no conflicts to declare.

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