

Review

# Paraben Compounds—Part II: An Overview of Advanced Oxidation Processes for Their Degradation

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**Abstract:** Water scarcity represents a problem for billions of people and is expected to get worse in the future. To guarantee people's water needs, the use of "first-hand water" or the reuse of wastewater must be done. Wastewater treatment and reuse are favorable for this purpose, since first-hand water is scarce and the economic needs for the exploration of this type of water are increasing. In wastewater treatment, it is important to remove contaminants of emerging concern, as well as pathogenic agents. Parabens are used in daily products as preservatives and are detected in different water sources. These compounds are related to different human health problems due to their endocrine-disrupting behavior, as well as several problems in animals. Thus, their removal from water streams is essential to achieve safe reusable water. Advanced Oxidation Processes (AOPs) are considered very promising technologies for wastewater treatment and can be used as alternatives or as complements of the conventional wastewater treatments that are inefficient in the removal of such contaminants. Different AOP technologies such as ozonation, catalytic ozonation, photocatalytic ozonation, Fenton's, and photocatalysis, among others, have already been used for parabens abatement. This manuscript critically overviews several AOP technologies used in parabens abatement. These treatments were evaluated in terms of ecotoxicological assessment since the resulting by-products of parabens abatement can be more toxic than the parent compounds. The economic aspect was also analyzed to evaluate and compare the considered technologies.

**Keywords:** parabens; CEC; environmental pollution; AOP; wastewater treatment



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## 1. Introduction

Water scarcity is experienced by 1.1 billion people and about 2.7 billion people suffer from lack of water at least once a year [1]. It is expected that in 2025, about 1.8 billion people will be living in areas suffering from this problem [2].

To guarantee sustainability and all the needs for all forms of life, particularly in the areas affected by water scarcity, it is mandatory to ensure correct treatment and reuse of wastewater [3]. Effective wastewater treatment is not easy to obtain with the traditional treatments installed in the municipal wastewater treatment plants (WWTP) [4]. The exploitation of "first-hand water" could be a solution to overcome water scarcity, but this is expensive and such water is also scarce. In addition, the recovery of wastewater can be more economically viable than the exploration of "first-hand water"; even considering the economic aspects, the treatment of wastewater can present advantages [3].

Treated wastewater is mostly used in agricultural applications [2], since this activity requires high water consumption [3]. Additionally, the irrigation systems that are used in agriculture could lead to environmental, soil, and water pollution problems and can even present health risks due to the existence of contaminants and pathogenic microorganisms in treated water [2,3].

With this, claimed water from wastewater must have adequate quality to be reused, which sometimes is only possible when the wastewater is deputed with additional or complementary treatments to the traditional approaches [3].

Compounds that are continuously detected in water sources at low concentrations ( $\mu\text{g/L}$  or  $\text{ng/L}$ ) are called contaminants of emerging concern (CEC). This category includes several compounds such as endocrine disruptors (ED), pharmaceutical and personal care products (PPCP) [4], pesticides [3], illicit drugs, synthetic and natural hormones [2], and heavy metals [5], among others.

These pollutants enter and accumulate in water resources due to continuous effluents discharges [6,7] and the fact that existent WWTPs are not designed to remove these types of contaminants, mainly due to their recalcitrant character [8].

One group of compounds that are detected in different water sources are parabens [9]. They have already been detected in rivers [10], tap water [11], pool water [12], drinking water [13], and effluents [14].

Parabens are used in industries (cosmetic, food, and pharmaceutical) mainly due to their good preservative and anti-microbial properties but also due to their chemical stability, low toxicity, and low production costs [7,15,16]. These compounds are endocrine disruptors [17,18], which can present estrogenic [19] and antiandrogenic activity [20]. Furthermore, they are related to male infertility [17] and tumors [21], so parabens can negatively affect human health [17]. In animals, the use of parabens can have negative impacts, since endocrine disruptors compounds can cause feminization, imposex, abnormalities, and a decrease in fecundity of species [22].

Due to their continuous detection and negative impacts on different organisms, special measures must be taken to control and remove parabens from ecosystems. The use of advanced technologies in wastewater treatment can help to decrease the discharge of parabens and other CECs present in treated wastewater into rivers and other water resources. With this, advanced oxidation processes (AOPs) can present the most suitable solution since these technologies can efficiently promote the CECs abatement.

AOP technologies such as ozonation [23–25]; catalytic ozonation [26]; photocatalytic ozonation [27,28]; Fenton's process [29,30]; photo-Fenton [31]; photocatalysis with UV radiation [7,32], visible radiation [6,33], and solar radiation [34]; photolysis using UV radiation [35]; photoelectrocatalysis [36]; photo-sonochemical degradation [37]; or sonochemical oxidation [38,39] were already used for parabens abatement.

This paper overviews the application of AOPs in the removal of parabens from water mixtures. The effect on treated water ecotoxicology is considered, as well as the costs associated with the treatment.

## 2. Advanced Oxidation Processes

Advanced Oxidation Processes are technologies that can generate hydroxyl radicals that interact with the organic molecules and oxidize them into simpler substances [40]. This oxidation converts the pollutants into intermediate compounds or  $\text{CO}_2$  and  $\text{H}_2\text{O}$  when mineralization occurs [40].

The degradation mechanisms of AOPs can be hydrogen abstraction, electron transfer, or radical addition, and these technologies can eliminate complex compounds that cannot be removed by conventional approaches [40,41]. In WWTPs, AOPs can be used as preliminary processes in order to transform persistent and recalcitrant compounds into compounds that biological treatments can remove, or they can be applied as a final deputation step before the discharge of the effluent into water sources [42].

AOPs present several advantages, such as elimination of complex and persistent compounds [41], treatment of different effluents [42], toxicity reduction [43], increasing the effluent biodegradability [43], elimination of pathogenic agents, or achieve pollutants complete oxidation into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [44]. In addition, some AOP treatments can be important to decrease COD (chemical oxygen demand), BOD (biochemical oxygen demand), coloration, and turbidity, which are important parameters regarding effluent discharge

regulations. The main disadvantage of the use of these technologies is their expensive costs since they demand a significant amount of energy or reagents [41]. Moreover, in general, when real wastewater is considered, the AOP treatments can present efficiency problems, since the presence of carbonate or bicarbonate ions (or other scavenging compounds) can act as scavengers of hydroxyl radicals, which can negatively affect their reaction mechanism and decrease the pollutants removal [42,45].

Hydroxyl radical is the most common radical produced by AOPs and presents a high oxidative power and non-selective behavior. Furthermore, the generation of other oxidant species can occur during the use of AOPs, due to the existence of specific operational conditions. Examples of oxidizing radicals can be seen in Table 1 [42,46].

**Table 1.** Oxidant potential of different oxidizing species.

Oxidant Species	Oxidation Potential/[V]
Hydroxyl (OH)	2.80
Fluorine (F)	3.03
Ozone (O <sub>3</sub> )	2.07
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	2.01
Hydrogen Peroxide (H <sub>2</sub> O <sub>2</sub> )	1.77
Permanganate (MnO <sub>4</sub> <sup>2-</sup> )	1.77
Chlorine dioxide (ClO <sub>2</sub> )	1.57
Chlorine (Cl <sub>2</sub> )	1.36
Dichromate (Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> )	1.23
Oxygen (O <sub>2</sub> )	1.23

Other radicals such as ozonide (O<sup>3-</sup>), superoxide (O<sup>2-</sup>), or hydroperoxyl radical (HO<sup>2-</sup>) can also appear [40,47]. The radical's generation occurs in situ and can occur due to the existence of reagents, catalysts, or radiation [41].

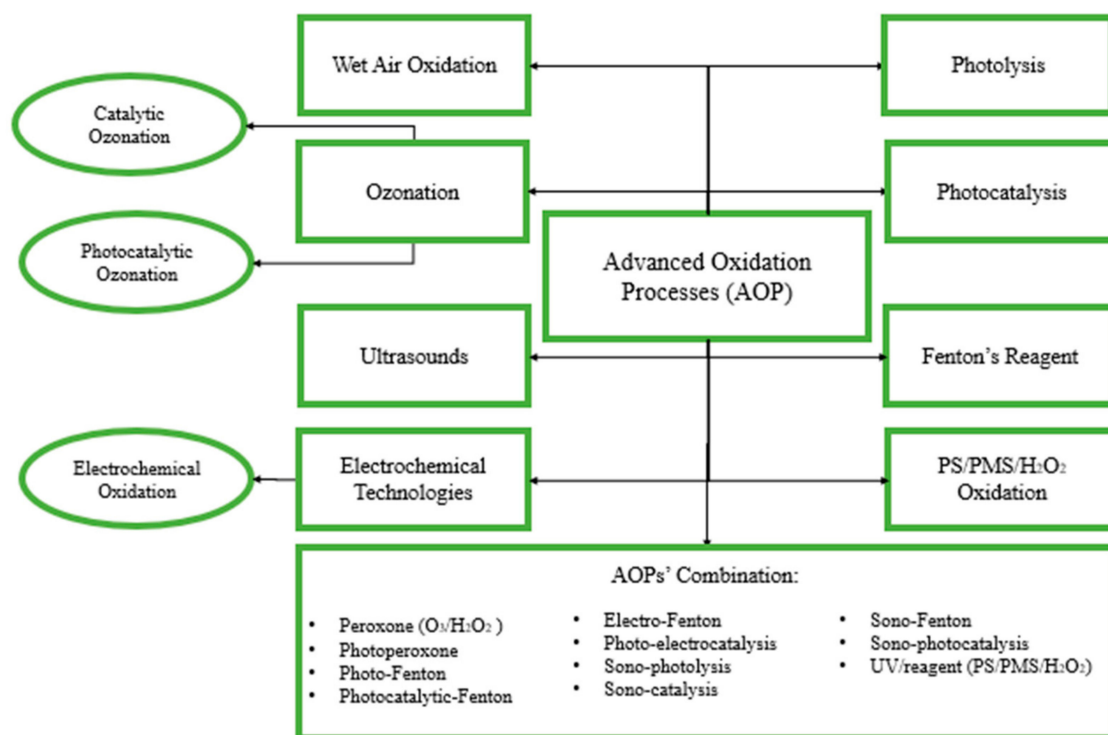
The group of AOPs is composed of several technologies, such as ozonation, photocatalysis, Fenton, wet air oxidation, radiation, oxidation by reagents, electrochemical oxidation, anodic oxidation, sonochemical methods, and others [41,46]. The combination and integration of several single techniques is also part of AOP, like photo-Fenton, photocatalytic ozonation, sono-Fenton, electro-Fenton, sono-photocatalysis, photo-ozonation, catalytic ozonation, and peroxone, among others [41–43]. Figure 1 presents a scheme summarizing some of the AOPs technologies reported in the literature.

Several studies are being carried out with the objective of lowering the operational costs, using new reactors [41], catalysts, reagents, and even radiation, particularly the use of solar radiation for being free, infinite, and considered as a “green-energy” [44].

### 2.1. Photolysis and Photocatalysis

Photolysis and photocatalysis are two technologies that use radiation for radicals generation, and they differ since photocatalysis also has a catalyst present, to increase the radical's formation rate.

Photolysis can be classified as direct or indirect photolysis, and it usually uses UV radiation from 200–400 nm. Direct photolysis allows the degradation of pollutants due to the photons generated by the irradiation source, and indirect photolysis (known also as photochemical degradation) causes the conversion of pollutants by the presence of radiation and different reagents that enhance the hydroxyl radicals' production [48]. Nowadays, UV radiation is already used for disinfection (inactivation of pathogenic organisms) purposes [49].



**Figure 1.** Scheme of examples of Advanced Oxidation Process (AOP) technologies.

Photocatalysis requires radiation to activate a catalyst, generally a heterogeneous semiconductor, and only this activation allows the radical's generation and the pollutants' elimination [50]. To activate the catalyst, the radiation source must emit photons with equal or higher energy than the catalyst's bandgap, which are absorbed into the catalyst and cause the excitation and migration of electrons from the valence band (VB) to the conduction band (CB). This electron migration generates electron-hole pairs ( $e^-/h^+$ ), which will interact with the pollutants present in the reactional medium or in the catalyst surface [44,47,51]. This interaction causes the generation of radicals, which react with the pollutants and promote their oxidation.

In photocatalysis, several catalysts, like  $TiO_2$ , ZnO, ZnS, or CdS, among others, have already been used [44,50]. Titanium dioxide ( $TiO_2$ ) is one of the most common catalysts, due to its low cost, high photo-activity, and chemical stability [52,53]. This catalyst can present three different crystallite phases: Anatase (the most wanted phase, since it is more stable at low temperatures and more photo-active), Rutile (more stable at high temperatures with lower band-gap energy), and Brookite phase (does not have catalytic properties and is rare) [54–56].

The costs related to photolysis or photocatalysis can be a drawback for its application, since the artificial UV light is expensive [57], and some semiconductor materials, like the  $TiO_2$  P25, requires this type of light, since this catalyst presents high band-gap energy, which can only be activated by UV [57]. Furthermore, the UV radiation represents only 3–5% of the solar spectrum which can make the use of solar light inefficient, despite the fact that it ensures new advantages as mentioned before [57–59]. The solar spectrum is mainly constituted by visible radiation (about 45%) [44], so the use of catalysts that can be activated by this type of radiation can reduce the operational costs of photocatalysis.

One possibility to decrease the catalyst's band-gap energy is doping the material with metals or non-metals elements due to the introduction of oxygen vacancies or impurity energy levels [59], although this makes the catalyst production more expensive. Cationic metals (such as Fe, Ag, Cu, Pd, Pt, and Au) can create an intermediate band between CB and VB, which will decrease the band-gap energy [44,60]. Non-metal doping (as C, N, F, S, ...) allows the use of solar radiation and can promote better electron trapping [44,61].

## 2.2. Ozone Based Technologies

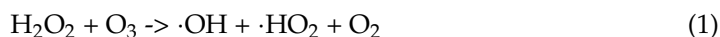
Ozonation uses a powerful oxidant, the ozone, to remove organic pollutants. This technology is pH-dependent, since it may involve two different pathways: direct reaction between the ozone and the pollutants (that occurs at pH < 7), or indirect reaction, by radical generation and interaction (at pH > 7) [41,49]. The use of ozonation at pH > 7 is desired, since the hydroxyl radical generation leads to a quicker reaction and generally to better removal of pollutants [41].

Ozone has a special preference for electron-rich molecules, like double and triple bonds, amines, or aromatic rings, and reacts the most with these molecules [49]. Ozonation can present different advantages, such as pollutant oxidation into H<sub>2</sub>O and CO<sub>2</sub>, quick reaction, easy ozone production, and oxidation of different and persistent molecules. However, as disadvantages, ozone is a corrosive, explosive, and toxic compound, its generation must occur in situ, it is expensive, and it is not efficient for the removal of saturated compounds. Furthermore, the ozonation system needs an O<sub>3</sub> destroyer for safety reasons, and this technology may not lead to high mineralization (COD and BOD removal rates are usually low) [46,62].

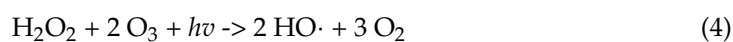
The combination of single ozonation with H<sub>2</sub>O<sub>2</sub>, UV radiation, or catalyst can enhance the radical generation, can increase the pollutants removal rate, and can also improve the mineralization efficiency [41,63]. Heterogeneous catalysts may initiate the hydroxyl radical generation and help in the initiation of ozone decomposition, enhancing the production of radicals [41].

Peroxone (H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>) improves the generation of hydroxyl radicals and can increase the pollutants oxidation efficiency, since the transformation of O<sub>3</sub> into ·OH, and the mass transference of ozone to the liquid phase is better [42]. H<sub>2</sub>O<sub>2</sub> interacts with O<sub>3</sub>, or vice versa, and produces ·OH or ·HO<sub>2</sub>. The existence of acidic pH can negatively affect the ·OH generation, so this technology is better when used at higher pH, since the H<sub>2</sub>O<sub>2</sub> usually reacts and is transformed into HO<sub>2</sub>, which in turn increases O<sub>3</sub> transformation into ·OH and OH<sup>-</sup> [42].

Equations (1)–(3) present the general reactions of peroxone technology [42]:



However, the use of H<sub>2</sub>O<sub>2</sub> in peroxone must be careful, since this compound can act as a scavenger of hydroxyl radical and decrease its generation, which could lead to a worse technology performance than single ozonation [41]. Regarding this process, some researchers have considered the optimum H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> ratio to be 0.5 mol/mol [49]. The use of UV with peroxone can increase the pollutants removal, due to higher generation of OH radicals, as presented in Equation (4) [42].



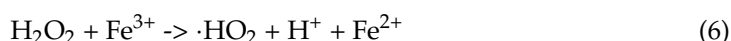
Catalytic ozonation combines the power of ozone with a catalyst. The presence of catalysts can initiate and enhance the decomposition of ozone molecules into oxidizing radicals, can allow a better absorption of ozone into the liquid phase [41], and, in general, can lead to lower ozone consumption, when compared to single ozonation [49].

Photocatalytic ozonation has a synergetic effect, since it combines the power of photocatalysis with ozone, allowing a higher production of radicals [64]. In this technology, the ozone molecule will react with the catalyst conduction band forming ozonide radicals (·O<sub>3</sub><sup>-</sup>), which will posteriorly generate ·OH radicals [65]. Other radicals such as oxygen atom radicals (·O) or superoxide radicals (·O<sub>2</sub><sup>-</sup>) can also be produced as intermediate radicals, interacting directly with the pollutants or forming hydroxyl radicals [66]. This technology can also prevent the recombination of generated electron-hole pairs [67].



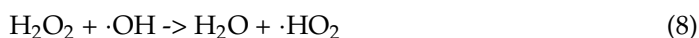
### 2.3. Fenton's Reagent

The traditional Fenton's reaction uses  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  as a catalyst for  $\cdot\text{OH}$  radical generation. During this process,  $\text{Fe}^{2+}$  is oxidized to  $\text{Fe}^{3+}$  and regenerated to  $\text{Fe}^{2+}$ , through the reaction of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{3+}$  [40]. The decomposition of  $\text{H}_2\text{O}_2$  is catalyzed by  $\text{Fe}^{2+}$ , forming the oxidative radicals that are going to attack the pollutants. However, the use of  $\text{Fe}^{2+}$  must be done with care, since it can react with the generated radicals, producing  $\text{Fe}^{3+}$ , and work as a scavenger of the reaction itself [46]. Furthermore, in Fenton's technology, the iron can be used in homogeneous or heterogeneous form [48]. Equations (5) and (6) present Fenton's process mechanism [40,41]:



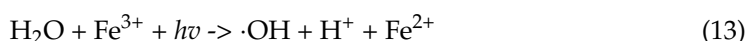
The Fenton's oxidation rate is higher at  $\text{pH} = 3$  since the hydroxyl radicals are more present at acidic  $\text{pH}$ , allowing a fast reaction [48]. This technology is effective but can present negative aspects related to the operational costs, due to the reagent's consumption and  $\text{pH}$  adjustments [46]. As disadvantages, it also presents difficult recovery and reuse of iron and limited operational  $\text{pH}$  range, which can restrict Fenton's applications and decrease its efficiency [68,69].

Moreover, the use of  $\text{H}_2\text{O}_2$  can present negative effects. In low amounts, it can decrease the efficiency of pollutants degradation due to insufficient radical's production, and in excessive quantities, it can form less reactive radicals, such as  $\text{HO}_2\cdot$ , and decompose itself into water and oxygen, reducing the technology performance, as presented in Equations (7)–(11) [62,70].



The advantages of Fenton's reaction are the use of environmentally friendly reagents, and the fact that the technology is easy to operate and implement, is efficient, and does not need energy to initiate the reaction. However, this technology also allows a quicker consumption of  $\text{Fe}^{2+}$  than its regeneration, has a limited operation  $\text{pH}$  range, and the complexation of iron species and the production of secondary sludge generally occur [71].

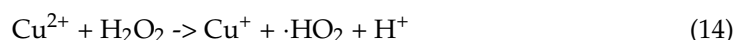
The use of photo-Fenton (UV and Fenton) could lead to lower reagent costs since the generation of radicals is enhanced, the reaction time is lower, and it requires less reagent compared to single Fenton's [48]. Photo-Fenton reactions are presented in Equations (12) and (13) [41]:

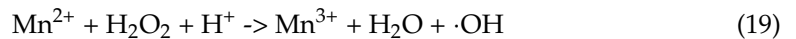
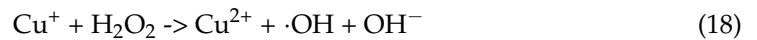
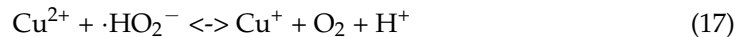


This technology also leads to a lower generation of secondary iron sludge, and to a faster iron regeneration [71]. The use of heterogeneous catalysts in Fenton's technology allows the occurrence of this reaction at higher  $\text{pH}$  [46].

Other methodologies can be used to overtake the traditional Fenton's drawbacks. The use of other metals (such as Cu, Mn, Cr, Ce, Co, Ru, or Al) instead of Iron (II) can be an option, and this substitution is widely known as Fenton-like processes [68,69,72].

Equations (14)–(20) present the Fenton's mechanism using  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  [69,72]:





Catalyst regeneration also occurs when  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  are used, due to the interaction with  $\text{H}_2\text{O}_2$ . The use of copper allows the existence of neutral and alkaline pH operations [69], which can be an advantage over the traditional Fenton's since this pH range would cause the precipitation of  $\text{Fe}^{3+}$  (in  $\text{Fe}(\text{OH})_3$  form) in the conventional Fenton [40]. Moreover, an increase in hydroxyl radical's generation can occur when magnetite substituents with transition metals are used [72].

However, Fenton-like processes also present disadvantages such as the existence of cytotoxic characteristics of metals, complex mechanisms, related high-costs, difficult anaerobic conditions, pH limitations, metal leaching, and loss of catalyst efficiency, depending on the type of metal used [72]. In general, metals do not allow good catalyst reuse and their reuse is only possible for a few cycles [72].

#### 2.4. Persulfate, Peroxymonosulfate, and Hydrogen Peroxide

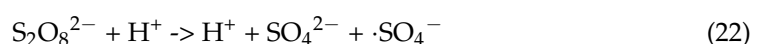
Oxidizing agents can be used in AOP, such as the persulfate anion ( $\text{S}_2\text{O}_8^{2-}$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), or peroxymonosulfate anion ( $\text{HSO}_5^-$ ), which are the most used oxidizing agents in wastewater treatment systems [73]. The objective is the same as other technologies, that is, the generation of hydroxyl and/or other radicals for the elimination of contaminants [42].

The persulfate anion is stable at ambient temperatures, is selective, and is a strong oxidant, which can work in a wide pH range, but it is cost-effective [74]. Its high solubility and longer lifetime allow it to decompose several organic pollutants [42].

Persulfate (PS) can produce  $\text{SO}_4^-$  radicals when activated by heat, UV light, bases, transition metals (catalysts), or ultrasound [42,73,74], and its reaction is shown in Equation (21) [42].

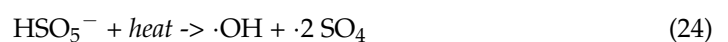


Persulfate can react in an acidic medium, enhancing the production of sulfate radicals as presented in Equation (22) [42].



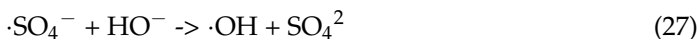
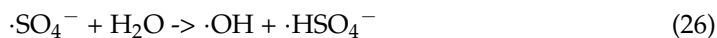
Usually, the performance of persulfate alone is low, so to achieve good efficiency, the presence of catalyst, heat, or radiation is desired [42]. The presence of catalyst enhances the sulfate radical's production. The use of  $\text{Fe}^{2+}$  is an option, since this metal can activate the PS for contaminants degradation, but this is not so efficient, probably due to the generation and accumulation of  $\text{Fe}^{3+}$  [42].

Peroxymonosulfate (PMS) is also a strong oxidant. It can be used in a wide pH range, and in the presence of light, heat, or catalysts, it is activated and can generate hydroxyl and sulfate radicals as presented in Equations (23) and (24), and in Equation (25) when exposed in an acidic medium [42], which may represent an advantage compared to the persulfate reaction.



Additionally, the sulfate radicals can be decomposed into more hydroxyl radicals in basic pH conditions, as shown in Equations (26) and (27) [42]. Furthermore, the radical's

production is favorable at basic pH regarding PS and PMS reactions, since this pH allows the formation of hydroxyl radicals, which are more reactive than the sulfate radicals formed in acidic media [42].



Hydrogen peroxide is a reagent with relatively high oxidative power that is used for radical's generation but may be inefficient when used alone since it cannot produce hydroxyl radicals by itself. It can also decompose into water and oxygen (as mentioned in Equations (28)–(30)), showing low performance in the removal of recalcitrant and refractory compounds [42].



The radicals generated by hydrogen peroxide are less reactive than  $\cdot\text{OH}$  radicals [45], and its oxidation potential is higher at low pH, so this reagent is favored when used in an acidic medium, and the combination of  $\text{H}_2\text{O}_2$  with other reagents or radiation can enhance its efficiency [42]. However, the presence of hydrogen peroxide must be carefully dosed, since high and low amounts can negatively affect its performance, as explained in Section 2.3. The optimum ratio of  $\text{H}_2\text{O}_2$  needs to be determined experimentally, and it is dependent on the experimental conditions [42,45,62] and effluent characteristics.

This reagent can only be used as an AOP technology when it is in the presence of radiation (UV, solar, etc.) or catalyst [42], and its good characteristics include good market availability, good thermal stability, infinite solubility in water, its ability to be stored in the operational site, and lack of mass transfer problems associated with gases [42,45].

The use of UV with  $\text{H}_2\text{O}_2$  reagent leads to the generation of two hydroxyl radicals (Equation (31)) which should enhance the removal performance [35,75,76] compared to a single  $\text{H}_2\text{O}_2$  reagent that cannot produce these types of radicals. Furthermore, organic and inorganic peroxy radicals can be generated using  $\text{H}_2\text{O}_2/\text{UV}$  in the presence of oxygen and other organic compounds [45]. However, this technology also shows disadvantages, since low-pressure UV lamps require high concentrations of  $\text{H}_2\text{O}_2$  for good OH generation, but the existence of  $\text{H}_2\text{O}_2$  at high concentrations can lead to a scavenging effect of hydroxyl radicals [49]. Therefore, the use of  $\text{H}_2\text{O}_2$  with UV radiation may not be recommended since it can have a high scavenging effect in secondary and tertiary wastewater treatments [49].



At alkaline pH, several studies report an interesting behavior of  $\text{H}_2\text{O}_2$  reagent, even when it is used alone. In fact, it has already obtained degradation efficiencies higher than 90% in 60 min regarding dibutylsulfide (DBS) degradation [77], higher DBS disappearance rate for single  $\text{H}_2\text{O}_2$  when compared to single ozone or  $\text{O}_3/\text{H}_2\text{O}_2$  system for  $\text{pH} < 12$  [77], and about 52% of 4-chloro-2 nitrophenol degradation at  $\text{pH} = 10$  [78], which showed better results than at  $\text{pH} < 10$ , with UV use, or in Fenton's (from  $\text{pH} = 6$  until  $\text{pH} = 10$ ) [78].

Regarding its use in real wastewater treatments,  $\text{H}_2\text{O}_2$  achieved COD reduction of about 35%, 29%, and 27% in 180 min for  $\text{pH} = 5, 7, \text{ and } 9$ , respectively, regarding the treatment of linear alkyl benzene industrial wastewater [79]. Furthermore, olive wastewater treatment allowed a maximum phenol degradation around 65%, 78%, and 81% and COD maximum abatement of about 20%, 25%, and 23% for  $\text{pH} = 9, 10, \text{ and } 11$ , respectively [80]. Other work for olive oil wastewater treatment led to a phenol degradation result of 65%, 74.4%, and 64.4% using single  $\text{H}_2\text{O}_2$ , while the UV/ $\text{H}_2\text{O}_2$  system achieved 66%, 59.2%, and 72.3% for  $\text{H}_2\text{O}_2$  concentrations of 0.11, 0.55, and 2 M in 150 min at  $\text{pH} = 9$ , which can show a bit better behavior in the single hydrogen peroxide system when compared to UV/ $\text{H}_2\text{O}_2$  [81].



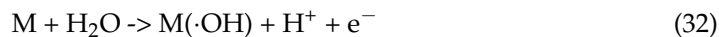
### 2.5. Electrochemical Oxidation

Electrochemical oxidation (EO) is the most used electrochemical technology for wastewater treatment [82]. In EO, an electric charge is produced between two electrodes (solid conductors) and is discharged in an electrolyte solution used as a medium [46]. One of the electrodes is positively charged (anode), while the other is negatively charged (cathode), and the oxidation of pollutants occurs in the anode, while the reduction occurs in the cathode [46]. This technology has the advantages of requiring less space, needing lower temperatures in the operation, and having a low by-product generation rate [83].

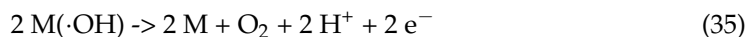
The organic compounds oxidation can occur by direct anodic oxidation (classified as “heterogeneous” when it occurs the direct electron transfer to the anode or classified as “homogeneous” when the oxidants are produced on anode surface from components of the electrolyte solution) or by chemical reaction with electrogenerated species ( $\cdot\text{OH}$  radicals or other oxidizing species). The first one leads to weak removal, while the second leads to high-performance removal [41,82,84].

The  $\cdot\text{OH}$  radicals generation starts with the oxidation of water in the anode, and only occurs at 2 V or above. Below this value, only direct oxidation can happen [46]. The indirect oxidation can also occur by the interaction of the pollutants with strong oxidants (such as chlorine), which must be generated during electrolysis by  $\text{Cl}^-$ -containing species present in the water matrix and/or in the electrolyte solution [41,82,85].

The occurrence of oxidative species is dependent on the anode oxygen-evolution-overpotential, in which the anodes can be classified as “active”, presenting low oxygen-overpotential, or as “non-active”, showing high oxygen-overpotential [41]. The “non-active” anodes produce hydroxyl radicals adsorbed on their surface as presented in Equation (32), allowing the direct oxidation of the pollutants with  $\text{M}(\cdot\text{OH})$ , while in the “active” anodes, the  $\text{M}(\cdot\text{OH})$  (M is the anode material) is chemisorbed and transformed into superoxide or a higher oxide (MO) as presented in Equation (33) [41,82].



MO can decompose into oxygen as presented in Equation (34) and  $\text{M}(\cdot\text{OH})$  can have side reactions as presented in Equations (35) and (36) [82].



A “non-active” anode can only act as an inert substrate and a sink for electron removal, and, consequently, it cannot participate in direct anodic oxidation or provide catalytic active sites for the adsorption of organic molecules from the reactional medium [82].

One important parameter is the anode material, since it can influence the selectivity and efficiency of this technology [82]. The most used and investigated electrodes are doped- $\text{SnO}_2$ ,  $\text{PbO}_2$ ,  $\text{RuO}_2$ ,  $\text{IrO}_2$ , boron-doped diamond (BDD), sub-stoichiometric and doped- $\text{TiO}_2$ , Pt, and dimensionally stable anodes (DSA) [41,49,86].

The BDD electrode presents the advantage of high stability even in strongly acidic media, low adsorption properties, inert surface, and high  $\text{O}_2$  evolution overvoltage, being the most preferable anode of electrochemical oxidation. The most responsible pathway for pollutants degradation using this electrode is by OH generation, and the BDD oxidation power is higher than for other anodes [49,82,87]. However, this material also presents disadvantages such as high cost and electrode instability during operation, and it is not easy to obtain BDD with large dimensions [88]. For wastewater treatment, only high voltages are used, since the use of low voltages can cause anode poisoning, because the direct anodic oxidation promotes by-products formation, which can be adsorbed into the anode [82].

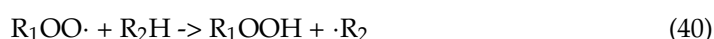
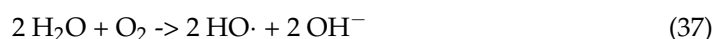
The advantages of the electrochemical AOP are that the removal of the pollutants and the mineralization occurs using the OH radical in situ. However, as disadvantages, in general, these technologies are associated with considerable electric costs, they need specific pH to obtain optimal conditions, the polluted solution must have good conductivity or it will need electrolytes to be added, and the catalyst is not usually recyclable or reused [89]. Other technologies are also part of the group of electrochemical AOPs, such as electrocoagulation, electrochemical reduction, electro-Fenton, electro-PS, electro-PMS, and electro-oxone, among others, as well as the integration of radiation with these processes [41,89,90].

### 2.6. Sonochemical Methods

Sonication or sonochemical methods, also known as sonolysis when it is used as a single technology, is an AOP technology where the  $\cdot\text{OH}$  radicals are generated from water pyrolysis due to the high intensity of acoustic cavity bubbles [40]. This technology, a type of hydrodynamic cavitation, is a cavitation method (i.e., a process involving the formation of micro-bubbles or cavities and quick collapse of bubbles to release energy), but until now, only ultrasound is used at the industrial level [46].

This process uses ultrasound frequencies (16 kHz–100 MHz) to produce a great amount of energy and promote substrate oxidation due to the formation and collapse of microbubbles from acoustical-wave-induced compression and rarefaction [46,49]. A violent implosion occurs after these microbubbles reach a critical resonance size, releasing high pressure and temperatures (>5000 K and >1000 atm), leading to highly reactive radical generation, due to the dissociation of water molecules into hydroxyl ions and hydroxyl radicals [46,49]. Furthermore, these radicals can react with the substrate, forming substrate radicals [46]. The oxidation of pollutants mainly occurs due to the action of the generated radicals but can also happen by thermal decomposition [49]. However, in this case, the chemical structure of the pollutant must also be considered.

Equations (37)–(40) present the general reactions of these sonochemical methods [46].



This technology presents as advantages a low interference from water matrix, low heat transfer required, and not needing chemicals. However, it has the disadvantage of using high amounts of energy and having low efficiency and mineralization, so this technology must be combined with other AOPs to overcome these problems, benefiting also from synergistic effects [40,46,49]. Therefore, other ultrasounds-based technologies such as sonophotolysis (UV + ultrasounds), sonocatalysis (catalyst + ultrasounds), sonophotocatalysis (UV + catalyst + ultrasounds), or even the presence of oxidation reagents with ultrasounds can present advantages compared to the single sonolysis [49].

## 3. AOP for Parabens Removal

After considering the characteristics of several AOPs technologies, this section overviews their application for paraben's abatement.

### 3.1. Photolysis and Photocatalysis

The use of radiation is known to increase the oxidizing radical's generation, but it is also needed when a semi-conductor catalyst is present, since it requires energy to be activated (i.e., to overpass the catalyst's bandgap). Although these technologies have disadvantages related to the application of UV radiation, the results of the reviewed studies show in general a good performance regarding the parabens abatement, with photocatalysis

showing better efficiency. Furthermore, overall, the parabens adsorption or their removal by photolysis presents poor results, although some experiments using photolysis have led to interesting removal outcomes. Some authors already report studies using solar radiation, although most studies use solar simulators.

In the literature, there are some studies using photolysis and particularly photocatalysis with different catalysts for parabens removal.

### 3.1.1. Parabens Abatement by Photolysis

Photolysis only uses radiation for contaminants degradation. UVA, UVC, and solar light (natural and simulated) have already been used in parabens abatement.

Regarding the parabens abatement, the photolysis performed by Gomes et al. [91] showed negligible results (lower than 4%), while the use of catalyst and radiation led to better results. Lin et al. [7] removed MP using photolysis with UV radiation, achieving less than 5% after 120 min in a pilot plant, while Lin et al. [32] removed 10% of BeP in a laboratory installation.

Gmurek et al. [35] used photolysis with UVC radiation, achieving 10% removal for MP, EP, PP, and BuP and about 60% degradation for BeP in 120 min for individual parabens and about 20% for MP and BuP, 30% for EP and PP in 120 min, and 80% for BuP in 20 min, when the parabens mixture was considered. Complete mixture removal was achieved at 480 min of UVC photolysis.

In general, several studies such as those of Gomes et al. [58], Lin et al. [7], Lin et al. [32], and Gomes et al. [91] present low performance when UVA photolysis was used in parabens abatement. Solar light studies by Gomes et al. [58] led to 16% of removal of MP, EP, and PP in 60 min, and the study by Vela et al. [3] led to 30% and 35% of MP and EP removal in 240 min using real wastewater effluent as water matrix, suggesting an interesting behavior of solar light by itself, although the study by Zúñiga-Benitez et al. [92] led to poor EP abatement.

The study by Gomes et al. [93] led to almost complete removal of PP and BuP using UV-Vis radiation, and the study by Álvarez et al. [94] achieved 80–99.8% of single degradation for MP, EP, or BuP in 120 min using UV (254 nm) radiation. Both studies performed good results regarding the parabens degradation, but the study by Gmurek et al. [35] using UVC radiation only led to about 20–30% mixture degradation for MP, EP, PP, and BuP removal in 120 min (BeP was 80% in 20 min), and the total removal was only achieved after 480 min.

In fact, Gmurek et al. [35] used a higher concentration of parabens (10 mg/L of MP, EP, PP, BuP, and BeP each and 10 mg/L of p-HBA), while Gomes et al. [93] only applied 10 mg/L of PP and BuP each (20 mg/L total). Moreover, Álvarez et al. [94] only used about 45.65 mg/L of MP, 49.85 mg/L of EP, and 58.29 mg/L of BuP. This should be responsible for the differences in the results, and, the presence of more compounds may make the degradation of each compound difficult.

In general, it seems that UVC must be preferred to UVA light when used alone to achieve better results. However, this implies higher energy costs, besides the danger associated with such strongly energetic radiation.

Table 2 presents several studies' results using photolysis in parabens abatement.

Table 2. Parabens removal by photolysis.

Pollutant	Test Conditions	Results and Conclusions	Reference
Bisphenol A, Bisphenol B, Diamylphthalate, Butylbenzylphthalate, MP, and EP	<ul style="list-style-type: none"> <li>• Sun radiation in a pilot plant.</li> <li>• 0.3 mg/L of each pollutant in real wastewater effluent.</li> </ul>	<ul style="list-style-type: none"> <li>• Degradation of about 30%, 35%, 55%, 50%, 30%, and 30% for MP, EP, BA, BB, BP, and DP, respectively, in 240 min.</li> </ul>	[3]
MP	<ul style="list-style-type: none"> <li>• UVA radiation</li> <li>• 10 mg/L of MP in deionized water.</li> </ul>	<ul style="list-style-type: none"> <li>• Degradation &lt;5% in 120 min.</li> </ul>	[7]
BeP	<ul style="list-style-type: none"> <li>• UVA radiation.</li> <li>• 10 mg/L of BeP in deionized water.</li> </ul>	<ul style="list-style-type: none"> <li>• Degradation of 10% in 120 min.</li> </ul>	[32]
MP, EP, PP, BuP, BeP, and p-HBA	<ul style="list-style-type: none"> <li>• 10 mg/L each paraben in distilled water.</li> <li>• UVC radiation.</li> </ul>	<ul style="list-style-type: none"> <li>• Individual parabens degradation of about 10% for MP, EP, PP, and BuP and about 60% for BeP in 2 min. About 95% for all in 120 min.</li> <li>• Mixture degradation of about 20%, 30%, 30%, and 20% in 120 min (2 h) for MP, EP, PP, and BuP and 80% BeP removal in 20 min. Total removal in 480 min.</li> </ul>	[35]
MP, EP, and PP	<ul style="list-style-type: none"> <li>• Parabens mixture solution of 1 mg/L each in ultrapure water.</li> <li>• UVA and Solar radiation.</li> </ul>	<ul style="list-style-type: none"> <li>• Degradation of 0% using UVA and 16% achieved by solar light in 60 min.</li> </ul>	[58]
MP, EP, PP, BuP, and BeP	<ul style="list-style-type: none"> <li>• Paraben mixture solution of 10 mg/L each in ultrapure water.</li> <li>• UVA radiation.</li> </ul>	<ul style="list-style-type: none"> <li>• Degradation: &lt; 4% in 180 min.</li> </ul>	[91]
EP	<ul style="list-style-type: none"> <li>• Solar radiation</li> <li>• Simulated solar radiation in the laboratory experiments</li> </ul>	<ul style="list-style-type: none"> <li>• Degradation of 0.46% at lab scale in 2 h.</li> <li>• At pilot scale was 1.5% and 2.72% in 2 h and 6 h.</li> </ul>	[92]
PP and BuP	<ul style="list-style-type: none"> <li>• PP and BuP in demineralized water or river water, at 10 mg/L each.</li> <li>• UV-Vis radiation.</li> </ul>	<ul style="list-style-type: none"> <li>• Deionized water: removal of 97–99% and 98–99% for PP and BuP, and the paraben mixture had 96–99% and 97–99% for PP and BuP, respectively, in 95 min.</li> <li>• River water: &gt;97% and &gt;99% for PP and BuP, while for the mixture of parabens was 90–99% and 92–99% for PP and BuP, respectively.</li> </ul>	[93]

Table 2. Cont.

Pollutant	Test Conditions	Results and Conclusions	Reference
MP, EP and BuP	<ul style="list-style-type: none"> <li>UV radiation (254 nm).</li> <li><math>0.3 \times 10^{-3}</math> mol/L single paraben solution.</li> </ul>	<ul style="list-style-type: none"> <li>Degradation of 77.2%, 88% and 96.3% in 90 min and 79.9%, 95.2% and 99.8% of MP, EP and BuP in 120 min.</li> <li>Water matrix: EP removal of 88%, 61.8% and 37.9% in 90 min for ultrapure water, tap water and wastewater, respectively.</li> </ul>	[94]
EP and BuP	<ul style="list-style-type: none"> <li>UVA radiation.</li> <li>6 mg/L paraben concentration.</li> </ul>	<ul style="list-style-type: none"> <li>Degradation: &lt;5% in 24 h.</li> </ul>	[95]

### 3.1.2. Parabens Abatement by Photocatalysis

The presence of catalysts should improve the degradation of parabens, particularly when UVA radiation is used since it seems that this kind of light poorly removes parabens when only light is applied. With this, it is expected to obtain better results when UVA photocatalysis is used.

Gomes et al. [91] used doped TiO<sub>2</sub> catalysts and pure TiO<sub>2</sub> to remove methylparaben (MP), ethylparaben (EP), propylparaben (PP), butylparaben (BuP), and benzylparaben (BeP) by UVA photocatalysis, reaching parabens degradation values higher than 15%. In fact, this was higher than the results obtained by the photolysis of the same mixture, which proves their good catalyst effect.

Lin et al. [7] removed MP using photocatalysis with UV radiation catalyzed with TiO<sub>2</sub> P25, reaching 94% degradation after 120 min, and Lin et al. [32] achieved 85% degradation of BeP. In both works, photocatalysis was clearly better than photolysis.

Vela et al. [3] used TiO<sub>2</sub> catalysts (P25 and Vlp-7000) for the degradation of six CECs, including MP and EP. Results showed that P25 is the most efficient catalyst, with degradations higher than 65%, and for which has the best dose of 200 mg/L and whose pH efficiency is in the order  $7 > 5.5 > 8.5$ . Moreover, the experiments using a pilot installation led to good results regarding the pollutants removal as well. Better degradation was achieved in the presence of catalyst as well.

Comparing these results to the photolysis results presented in Section 3.1.1, the presence of catalyst seems to show an obvious improvement in parabens abatement. The studies of Gomes et al. [91], Lin et al. [7], and Lin et al. [32] used UVA radiation, while Vela et al. [3] applied sunlight instead. The presence of UVA light (also present in the solar spectrum) is important, since this radiation is the only one able to activate the TiO<sub>2</sub> catalyst due to the high bandgap that is associated with this material. In fact, if its bandgap is reduced, then the more efficient use of visible radiation or solar light should be possible, which could decrease the operational costs of this technology. With this, several studies using doped TiO<sub>2</sub> catalyst or also other catalysts are also discussed.

Zúñiga-Benítez and Peñuela [92] used TiO<sub>2</sub> catalyst to remove EP through photocatalysis, using simulated solar radiation in laboratory experiments and sunlight for experiments at pilot scale. The use of catalyst under lab conditions led to 63.1% removal in 120 min reaction, with the application of 0.95 g/L of catalyst and initial EP concentration of 1 mg/L. Regarding the pilot-scale experiment, 45.88% degradation was achieved after 6 h, using the same experimental conditions, but a higher volume (100 L). The authors also used hydrogen peroxide with TiO<sub>2</sub>, resulting in a better EP removal performance using the best operational conditions, achieving 96.9% removal in 2 h and 81.38% in 6 h, for laboratory and pilot-scale experiments, respectively. Frontistis et al. [96] achieved better results, reaching almost total removal in 20 min using ZnO, while TiO<sub>2</sub> P25 led to about 90%

abatement in 30 min, using 1 mg/L of EP and 0.25 g/L of catalyst with a solar simulator as a radiation source. Although the experiments present several differences, these studies led to interesting results using solar radiation or solar simulated radiation, which should encourage more studies using these catalysts with the sun as a source of light. Furthermore, the study of Frontistis et al. [96] suggests a better performance of ZnO over the traditional titanium dioxide.

Several authors such as Gomes et al. [91], Kotzamanidi et al. [34], and Petala et al. [97] experimented with doped TiO<sub>2</sub> catalysts in parabens abatement. Kotzamanidi et al. [34] tested Al-TiO<sub>2</sub>, which had the best PP removal using a catalyst dose of 1 g/L with 95% abatement in 90 min, while Petala et al. [97] used N-TiO<sub>2</sub> getting EP abatement of 32% and 13% in 240 min for N-TiO<sub>2</sub> and TiO<sub>2</sub> with Vis radiation, while solar radiation was used for 10 min and achieved about 34% and 43% for TiO<sub>2</sub> and N-TiO<sub>2</sub>, respectively, for the best calcination temperature. In fact, the use of N-TiO<sub>2</sub> seems to enhance the parabens degradation under visible or solar radiation compared to pure TiO<sub>2</sub>. Although the experiment by Kotzamanidi et al. [34] achieved almost complete removal, the authors did not perform experiments with pure TiO<sub>2</sub>, and say that the presence of Al did not considerably change the band-gap energy. Moreover, for the best Al-TiO<sub>2</sub> (0.04 Al w%), the band-gap energy was about 3 eV, while the common TiO<sub>2</sub> catalyst usually has about 3.2 eV. This may suggest that Al it is not advantageous to make titanium dioxide more efficient under Vis or solar radiation.

Kotzamanidi et al. [34] used 1 g/L of catalyst and initial PP dose of 0.42 mg/L, and Petala et al. [97] used 0.5 g/L of catalyst and 0.3 mg/L of EP, while Gomes et al. [91] used 0.07 g/L of catalyst, 10 mg/L of each paraben (MP, EP, PP, BuP, and BeP), and UVA radiation. In Gomes et al.'s [91] study, they used a mixture with higher parabens concentrations and had lower catalyst concentration, but obtained removals of about 35–70%, 40–48%, 25–40%, 5–15%, and 1–10% for Pd, Ag, Pt, Au, and pure TiO<sub>2</sub>, respectively, after 180 min. In this work, the presence of metals enhanced the degradation when compared to bare TiO<sub>2</sub>, and Pd and Ag catalysts had better performance than the one obtained by Petala et al. [97] using Vis radiation. In fact, the use of these noble metals seems to enhance the photocatalytic activity of titanium dioxide, which the authors suggest may be related to the electron charge transfer from the CB to the metallic nanoparticles band, less electron-hole recombination, or higher hydroxyl radical's production. The authors did not determine the catalysts' band-gap energy, but studies have shown where the deposition of metals could lower the catalyst band-gap energy. However, the presence of noble metals should increase the catalysts' price, since these metals are usually expensive, so the N-TiO<sub>2</sub> may probably be more economically attractive, and it also showed good results under Vis and sunlight. Nevertheless, more tests using different concentrations and/or mixtures should be performed to confirm this theory.

Other catalysts have also been investigated for the same purpose. Fernandes et al. [6] tested single and mixture degradation of three parabens (MP, EP, and PP) using TiO<sub>2</sub> P25 and metal-free, graphite-like carbon nitride as catalysts with 417 nm radiation provided by LEDs. The GNC-500 catalyst had better performance, with about total removal in 20 min for single parabens and 99% removal for parabens mixture in 25 min. TiO<sub>2</sub> P25 only had total removal after 120 min for both experiments. Xiao et al. [33] removed single MP, EP, PP, and BuP by photocatalysis using I<sub>x</sub>-Bu<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> as a catalyst, leading to a higher PP removal of 94.5% for I<sub>0.7</sub>-Bu<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> in 60 min. The authors used >420 nm radiation, 1 g/L of catalyst, and 10 mg/L initial concentration of each paraben. In fact, this catalyst led to better abatement and had 2.51 eV, although not being the catalyst with lower band-gap energy (I<sub>1</sub>-Bu<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> with 2.41 eV that led to 91.2%). Furthermore, Petala et al. [98] achieved a better EP removal value of 97.6%, using CuO<sub>0.75</sub>/BiVO<sub>4</sub>, by photocatalysis in 60 min, when the catalyst dose was 0.5 g/L and the paraben concentration was 0.5 mg/L, using a solar simulator as a radiation source (>280 nm). Kumar et al. [99] used Fe<sub>3</sub>O<sub>4</sub>/BiVO<sub>4</sub> heterostructure (bandgap of Fe<sub>3</sub>O<sub>4</sub> of 2.57 eV and of BiVO<sub>4</sub> of 2.36 eV) for MP abatement, reaching 75% of degradation in 60 min, with 0.1 g/L of catalyst and



5 mg/L of MP using solar light. These studies suggest interesting results for different catalysts compared to the traditional semiconductors, which may be also an option in the application of photocatalysis. Moreover, some of these catalysts present lower bandgaps than the traditional TiO<sub>2</sub>, which may be mainly responsible for the good results using radiation such as solar, simulated solar, or Vis light. Thus, this can be an advantage for the use of natural light and simplify the industrial implementation powered by the sun.

The use of catalysts in powder form makes photocatalysis implementation and catalyst use difficult at an industrial level. This drawback can be overcome using powder catalyst immobilized in a support material, which can allow a good recovery and easy separation of the solid material from the reactional medium. With this, several supported and innovative catalysts have already been used, even for parabens degradation.

Gomes et al. [58] tested TiO<sub>2</sub> nanotubes (NT) arrays for photocatalytic degradation of parabens' mixture. In general, the catalyst presence improved the pollutants' degradation, but only 20% of removal was achieved in 60 min reaction, with 7 TiO<sub>2</sub>/NT plates and UVA. The maximum degradation was 25% when 14 plates were used. The usage of solar radiation enhanced the parabens mixture degradation compared to UVA, allowing a maximum parabens degradation of 80% using seven plates, although the operational installation was different. Furthermore, Sousa et al. [100] used photocatalysis catalyzed by nanostructures (titanate nanowires (TNW) and modified titanate nanowires with Mn) for MP removal in 90 min. The initial pollutant concentration was 10 mg/L, and the technology removed 62%, 50%, and 40% for Mn-doped TNW, Mn-adsorbed TNW, and single TNW, respectively, using UV-Vis (40–48% UV and 40–43% Vis). The use of these types of structures seems to allow good removal rates, combining also important advantages for industrial application. Gomes et al. [58] had 80% parabens mixture degradation using TiO<sub>2</sub>/NT, Zúñiga-Benítez and Peñuela [92] had 45.88% of EP degradation in 6 h using TiO<sub>2</sub>, Petala et al. [97] determined about 34% and 43% EP degradation for TiO<sub>2</sub> and N-TiO<sub>2</sub> in 10 min and achieved total removal in 60 min with N-TiO<sub>2</sub> catalyst, and Kumar et al. [99] used Fe<sub>3</sub>O<sub>4</sub>/BiVO<sub>4</sub> reaching 75% of MP degradation in 60 min. In all these studies, solar light was used as an energy source. Comparing these studies, the study of Gomes et al. [58] had better results than Zúñiga-Benítez and Peñuela [92] and Kumar et al. [99], and although total degradation was never achieved, contrary to what happened in Petala et al.'s [97] work, it should be noticed that in this study, it was used a parabens mixture, while in the others, only single parabens degradation was evaluated. Thus, the complexity of the reaction mixture highly influences the process efficiency.

Table 3 summarizes photocatalysis studies in parabens abatement.

**Table 3.** Parabens removal by photocatalysis.

Pollutant	Catalyst	Test Conditions	Results and Conclusions	Reference
Bisphenol A, Bisphenol B, Diamylphthalate, Butylbenzylphthalate, MP, and EP	TiO <sub>2</sub> P25 TiO <sub>2</sub> Vlp-7000	<ul style="list-style-type: none"> <li>Sun radiation in pilot plant.</li> <li>0.3 mg/L of each pollutant in real wastewater effluent.</li> <li>200 mg/L of catalyst</li> </ul>	<ul style="list-style-type: none"> <li>Degradation in 240 min of about 85%, 85%, 100%, 100%, 65%, and 75% for MP, EP, BA, BB, BP, and DP respectively, using TiO<sub>2</sub> P25, while for TiO<sub>2</sub> vlp-7000, the degradation was about 70%, 68% 100%, 100%, 40%, and 45%, respectively.</li> </ul>	[3]
MP, EP, and PP	Metal free graphite-like carbon nitride TiO <sub>2</sub> P25	<ul style="list-style-type: none"> <li>0.08 mM of each paraben in ultrapure, tap and river water.</li> <li>Catalyst dose of 1 g/L.</li> <li>417 nm radiation (LED).</li> </ul>	<ul style="list-style-type: none"> <li>For parabens mixture, the degradation was about 99% in 25 min for GNC-500 and about 94% for TiO<sub>2</sub> in 120 min.</li> </ul>	[6]

Table 3. Cont.

Pollutant	Catalyst	Test Conditions	Results and Conclusions	Reference
MP	TiO <sub>2</sub> P25	<ul style="list-style-type: none"> <li>• UVA radiation.</li> <li>• 10 mg/L of MP in deionized water.</li> <li>• 2 g/L of catalyst.</li> </ul>	<ul style="list-style-type: none"> <li>• Degradation of 94% in 120 min.</li> </ul>	[7]
MP	Monolith-supported perovskite	<ul style="list-style-type: none"> <li>• UV radiation</li> <li>• 5 mg/L of MP solution in ultrapure water.</li> </ul>	<ul style="list-style-type: none"> <li>• Best degradation for BiFeO<sub>3</sub> of 82.8% under optimum conditions.</li> <li>• MP removal: 14.62%, 37.8%, 45.7%, 49.2%, and 54.5% for without catalyst, LaTi<sub>0.15</sub>Fe<sub>0.85</sub>O<sub>3</sub>, BiTi<sub>0.15</sub>Fe<sub>0.85</sub>O<sub>3</sub>, LaFeO<sub>3</sub>, and BiFeO<sub>3</sub>, respectively.</li> </ul>	[31]
BeP	TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>• UVA radiation.</li> <li>• 10 mg/L of BeP in deionized water</li> <li>• 2.5 g/L of catalyst.</li> </ul>	<ul style="list-style-type: none"> <li>• Removal of about 5% and 85% for adsorption (dark) and photocatalysis in 120 min.</li> </ul>	[32]
MP, EP, PP, and BuP	I-Bi <sub>4</sub> O <sub>5</sub> Br <sub>2</sub>	<ul style="list-style-type: none"> <li>• UV lamp with Vis radiation filter.</li> <li>• 1 g/L of catalyst</li> <li>• 10 mg/L of parabens.</li> </ul>	<ul style="list-style-type: none"> <li>• PP removal: 24.4%, 49.4%, 90.6%, 90.7%, 94.5%, 91.8%, and 91.2% for Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> and I<sub>x</sub>-Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> (x = 0.2, 0.4, 0.6, 0.7, 0.8, and 1), in 60 min.</li> </ul>	[33]
PP	Al-TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>• Solar simulator.</li> <li>• 420 µg/L PP solution in ultrapure water, secondary treated wastewater, and 50% diluted secondary treated wastewater.</li> <li>• Water matrix experiment using 500 mg/L of catalyst.</li> </ul>	<ul style="list-style-type: none"> <li>• PP removal: about 95%, 88%, 75%, 45%, and 22% for 1000, 1500, 500, 250, and 125 mg/L of catalyst, respectively, in 90 min.</li> <li>• Removal of about 75%, 30%, 28%, 23%, and 17% for ultrapure water, bottled water, river water, 50% wastewater, and 100% wastewater, respectively, in 90 min.</li> </ul>	[34]
MP, EP and PP	TiO <sub>2</sub> /NT	<ul style="list-style-type: none"> <li>• Parabens mixture solution of 1 mg/L each in ultrapure water.</li> <li>• UVA and Solar radiation.</li> </ul>	<ul style="list-style-type: none"> <li>• Maximum degradation (60 min) was 25% for UVA and 80% using solar light.</li> </ul>	[58]
MP, EP, PP, BuP, BeP	TiO <sub>2</sub> Ag-TiO <sub>2</sub> Au-TiO <sub>2</sub> Pd-TiO <sub>2</sub> Pt-TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>• Parabens mixture solution of 10 mg/L each in ultrapure water.</li> <li>• Catalyst dose of 70 mg/L (0.07 g/L).</li> <li>• UVA radiation.</li> </ul>	<ul style="list-style-type: none"> <li>• Degradation of parabens of &lt; 70%, &lt; 48%, &lt; 40%, &lt; 15%, and &lt; 10% for Pd, Ag, Pt, Au, and pure TiO<sub>2</sub>, respectively.</li> </ul>	[91]
EP	TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>• Solar radiation and similar for lab experiment.</li> <li>• 1 mg/L of paraben.</li> <li>• 0.95 g/L catalyst dose.</li> </ul>	<ul style="list-style-type: none"> <li>• EP removal was 63.1% for lab in 2 h, and about 17.94% and 45.88% at pilot scale, after 2 h and 6 h, respectively.</li> </ul>	[92]
EP and BuP	TiO <sub>2</sub> P25	<ul style="list-style-type: none"> <li>• UVA radiation.</li> <li>• 6 mg/L paraben concentration.</li> <li>• 2 g/L of catalyst.</li> </ul>	<ul style="list-style-type: none"> <li>• Best results at pH = 4 with 43.6% and 45.3% for EP and BuP, respectively, in 24 h.</li> </ul>	[95]

Table 3. Cont.

Pollutant	Catalyst	Test Conditions	Results and Conclusions	Reference
EP	ZnO TiO <sub>2</sub> P25	<ul style="list-style-type: none"> <li>Solar simulator (5% UVA and 0.1% UVB).</li> <li>EP solution of 1 mg/L in ultrapure water.</li> <li>250 mg/L of catalyst.</li> </ul>	<ul style="list-style-type: none"> <li>ZnO led to total removal in 20 min, while TiO<sub>2</sub> P25 led to about 90% removal in 30 min, respectively.</li> </ul>	[96]
EP	N-TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>Solar simulator</li> <li>Catalyst dose of 500 mg/L</li> <li>300 µg/L of EP.</li> </ul>	<ul style="list-style-type: none"> <li>At best conditions, the EP removal was about 13%, 32%, 34% and 43% for TiO<sub>2</sub>+Vis, N-TiO<sub>2</sub>+Vis, TiO<sub>2</sub>+Solar, and N-TiO<sub>2</sub>/Solar, respectively.</li> </ul>	[97]
EP	CuO <sub>x</sub> /BiVO <sub>4</sub>	<ul style="list-style-type: none"> <li>Solar simulator</li> <li>500 µg/L of EP</li> <li>500 mg/L of catalyst</li> </ul>	<ul style="list-style-type: none"> <li>97.6% removal was achieved in 60 min.</li> </ul>	[98]
MP and pesticide	Fe <sub>3</sub> O <sub>4</sub> /BiVO <sub>4</sub>	<ul style="list-style-type: none"> <li>0.1 g/L of catalyst.</li> <li>5 mg/L MP solution</li> <li>Solar radiation.</li> </ul>	<ul style="list-style-type: none"> <li>MP removal: 74.98% and 95.64% in 2 h for Fe<sub>3</sub>O<sub>4</sub>/BiVO<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>/BiVO<sub>4</sub>/biochar.</li> </ul>	[99]
MP	TNW Mn-TNW Mn/TNW	<ul style="list-style-type: none"> <li>40–48% UV and 40–43% Vis radiation.</li> <li>133.3 mg/L of catalyst.</li> <li>10 mg/L of MP in distilled water.</li> </ul>	<ul style="list-style-type: none"> <li>MP removal of 40% for TNW (titanate nanowires) and 62% and 50% for Mn-TNW (doped Mn) and TNW/Mn (adsorbed Mn), respectively, in 90 min.</li> </ul>	[100]
MP, EP, and PP	Fe ions	<ul style="list-style-type: none"> <li>350–410 nm radiation.</li> <li>5 mg/L of Fe for EP and PP, and 25 mg/L of Fe for MP.</li> </ul>	<ul style="list-style-type: none"> <li>Removal of EP and PP was 40% and 60% in 90 min.</li> <li>MP removal was about 35%.</li> </ul>	[101]

### 3.2. Ozone-Based Technologies

The treatment of parabens has been also investigated with the oxidant power of ozone to ensure the degradation of pollutants. Ozone-based techniques can bring different treatment perspectives and features, since the use of this molecule can allow good performance in the removal of different and persistent pollutants but can also bring problems related to ozone properties (explosive, toxic, and corrosive). Moreover, generally high production costs are necessary, the O<sub>3</sub> generation must be in situ, and there is usually a low efficiency of generation.

#### 3.2.1. Single Ozonation

The ozone molecule is known for being a powerful oxidant with very effective degradation results for organic molecules in wastewater treatment, despite having some drawbacks as poor mineralization. Besides wastewater treatment, this technology is also used for water disinfection.

Tay et al. [25] used ozonation to remove a mixture of five parabens. The authors achieved 99% parabens degradation in 12 min and 61% and 32% for COD and TOC removal in 3 h. As expected, while ozone was able to efficiently remove unsaturated molecules (such as the parabens), total mineralization was not possible to achieve. In fact, from the abatement of the parent molecules, saturated compounds were produced, which are refractory to further ozone oxidation. Furthermore, Gomes et al. [26] performed ozonation using the same mixture but with a concentration of 10 mg/L of each paraben, achieving total removal in 120 min. In fact, the results of ozonation should be analyzed as a function of transferred ozone dose (TOD), since this parameter allows one to understand

the amount of ozone transferred to the reactional medium and it represents an important parameter for the economic evaluation using ozone [102].

Cuerda-Correa et al. [23] treated a mixture of four parabens (MP, EP, PP, and BuP), achieving 82% removal in 20 min reaction. Asgari et al. [28] only achieved 47–52% removal for the best results. In fact, these results were obtained at pH = 9 and were higher than those reached for pH = 3 or pH = 5. This should be expected, since, in a basic medium, the generation of radicals is enhanced. This radical pathway is desired due to its higher performance when compared to direct ozone reaction at acidic pH [41]. Fernandes et al. [103] also removed 10 mg/L of parabens mixture, reaching a degradation higher than 97% in 120 min (a natural parabens solution has pH of 5 [104]), and Asgari et al. [28] achieved 36–42% for similar pH in 60 min, which is a concordant result. Furthermore, Gomes et al. [102] had total removal of 1 mg/L of each paraben (in mixture) in 15 min, which represents 10 times less than the concentration used by Asgari et al. [28] and Fernandes et al. [103].

In general, it seems that ozonation is able to eliminate parabens for whichever concentration is used. However, this does not imply that total mineralization was reached. In fact, ozone can react with unsaturated molecules, leading to low-molecular-weight by-products refractory to further ozonation. Thus, the results of the parent compounds degradation should be complemented with some information about COD or TOC removal as well as toxicological studies. This would be very important regarding the potential environmental impact of the treated water.

An overview of works dealing with single ozonation for parabens abatement is presented in Table 4.

**Table 4.** Parabens removal by single ozonation.

Pollutant	Test Conditions	Results and Conclusions	Reference
MP, EP, PP and BuP	<ul style="list-style-type: none"> <li>5 mg/L of each paraben in ultrapure water.</li> </ul>	<ul style="list-style-type: none"> <li>Degradation of about 82% in 20 min.</li> </ul>	[23]
MP, EP, PP, BuP, and BeP	<ul style="list-style-type: none"> <li>500 µM of parabens in deionized ultrapure water.</li> </ul>	<ul style="list-style-type: none"> <li>99% removal in 12 min.</li> </ul>	[25]
MP, EP, PP, BuP and BeP	<ul style="list-style-type: none"> <li>10 mg/L of each paraben in ultrapure water</li> </ul>	<ul style="list-style-type: none"> <li>Total paraben removal was achieved for TOD = 170 mg/L in 120 min.</li> </ul>	[26]
MP, EP, PP, BuP and BeP	<ul style="list-style-type: none"> <li>10 mg/L of each paraben</li> </ul>	<ul style="list-style-type: none"> <li>Parabens removal: 32–38% (pH = 3), 36–42% (pH = 5) and 47–52% (pH = 9) in 60 min.</li> </ul>	[28]
MP, EP and PP	<ul style="list-style-type: none"> <li>1 mg/L parabens mixture in ultrapure water.</li> </ul>	<ul style="list-style-type: none"> <li>Single ozone led to parabens total removal in 15 min with TOD of about 4.5 mg/L.</li> </ul>	[102]
MP, EP, PP, BuP and BeP	<ul style="list-style-type: none"> <li>10 mg/L of each paraben in ultrapure water.</li> </ul>	<ul style="list-style-type: none"> <li>&gt;97% removal for TOD of 46.2 mg/L in 120 min.</li> </ul>	[103]

### 3.2.2. Catalytic and Photocatalytic Ozonation

The performance of single ozonation can be enhanced using catalysts, radiation, and reagents, leading to higher degradation rates and reducing some disadvantages of this

technology. There are not many studies regarding the abatement of parabens by catalytic and photocatalytic ozonation. However, in general, the presence of catalysts and radiation plus catalyst seems to lead to better results.

Cuerda-Correa et al. [23] used photolytic and photocatalytic ozonation with  $\text{TiO}_2$  to remove four parabens. The results showed 95% and 100% removal for photocatalytic ozonation and photolytic ozonation in 20 min, respectively. In fact, these results were higher than for single ozonation (82% degradation) in the same study. Furthermore, the same occurred in the study of Asgari et al. [28], who used  $\text{ZnO}$  as photocatalyst and had 47–52% degradation (pH = 9) in 60 min for single ozonation, while photolytic and photocatalytic ozonation led to 53–65% and 96–98% degradation, respectively. This behavior was also verified by Gomes et al. [26], who studied the degradation of a mixture of five parabens by ozonation and catalytic ozonation. The presence of catalyst required a lower ozone dose compared to single ozonation. Moreover, a treated solution with lower toxicity was achieved by the catalytic process. These results prove a clear improvement of ozonation when coupled with radiation and/or catalyst. However, in the study of Cuerda-Correa et al. [23], the catalyst did not improve the parabens degradation, which can be related to the generation of radicals (OH or ozonide) or even to a negative interaction between the ozone and the catalyst. The same was reported in the study by Gomes et al. [102], in which they used photocatalytic and catalytic ozonation for the degradation of a parabens mixture in different water matrices using  $\text{TiO}_2/\text{NT}$  and carried out toxicity assessment analysis using *Allivibrio fischeri* bacteria and *Lepidium sativum* seeds. The presence of catalyst only decreased the solutions' toxicity since the luminescence inhibition for *A. fischeri* was lower and the germination index for *L. sativum* was higher when the ozone was used with the catalyst.

In addition, Gomes et al. [102] used UVA and sun as light sources. When sunlight was used, the objective was quickly achieved, but more ozone was consumed, while the use of UVA seemed to slightly enhance parabens degradation, although the difference was not as significant. Total parabens removal was achieved for  $\text{TOD} = 4.5 \text{ mg/L}$  and  $\text{TOD} = 8.5 \text{ mg/L}$  for UVA and sunlight, respectively, using an initial concentration of  $1 \text{ mg/L}$ .

Gomes et al. [26] required  $\text{TOD} = 70 \text{ mg/L}$  ( $\text{Pt-TiO}_2$ ) for the removal of  $10 \text{ mg/L}$  of each paraben (MP, EP, PP, BuP, and BeP) using catalytic ozonation, while the study of Gomes et al. [27] needed about  $40 \text{ mg/L}$  of  $\text{TOD}$  ( $\text{Ag-TiO}_2$ ) using photocatalytic ozonation for the same paraben's mixture and concentration. Both studies reached total removal of parabens. Furthermore, in the study of Gomes et al. [26], about  $94 \text{ mg/L}$  of  $\text{TOD}$  were necessary for catalytic ozonation using  $\text{Ag-TiO}_2$ , while in Gomes et al.'s [27] study, the presence of UVA led to a lower  $\text{TOD}$  of  $40 \text{ mg/L}$  using the same catalyst [27]. Moreover, in Gomes et al.'s [26] experiment, the best catalysts were Pd and  $\text{Pt-TiO}_2$  in the catalytic experiments, while in the photocatalytic experiments of Gomes et al. [27], this was not verified, since the best catalysts were Ag and  $\text{Pt-TiO}_2$  [27]. The catalyst's performance and behavior can be influenced by the photogenerated electrons and the generation of radicals. In fact, the authors suggest that the  $\text{Au-TiO}_2$  had low performance in photocatalytic ozonation due to a higher retention of photogenerated electrons related to its higher electronegativity, which could lower the generation of ozonide radicals, and, therefore, the generation of hydroxyl radicals [27]. Furthermore,  $\text{Ag-TiO}_2$  has lower electronegativity, so its good performance could also be related to this fact, and this can explain why the presence of UVA did not have any effect on  $\text{Au-TiO}_2$  [27]. In addition, in the study of Gomes et al. [27],  $\text{TiO}_2$  also did not have any improvement when UVA was added, which could be related to poor photoactivity of the catalyst due to its high band-gap, while in the other doped catalysts, the results were better than the pure  $\text{TiO}_2$  and without UVA, which means that UVA had a positive influence on them, maybe to their lower band-gap and high photoactivity [26,27].

Fernandes et al. [103] had almost total removal using  $10 \text{ mg/L}$  for different synthesis methods of  $\text{N-TiO}_2$  reaching  $\text{TOD}$  of  $30\text{--}44 \text{ mg/L}$ , and about  $26\text{--}45 \text{ mg/L}$ , for the different methods, using photocatalytic ozonation. These results were better than the ones provided

by Gomes et al. [27], who used a catalyst doped with noble metals (best results for Ag-TiO<sub>2</sub> with TOD = 40 mg/L). This may suggest a good behavior of non-metal doping for photocatalytic ozonation, which may be interesting due to the costs associated with noble metals.

Table 5 overviews works dealing with ozone-based technologies for parabens removal.

**Table 5.** Parabens removal by catalytic and photocatalytic ozonation.

Pollutant	AOP	Catalyst	Test Conditions	Results and Conclusions	Reference
MP, EP, PP, and BuP	Photolytic ozonation Photocatalytic ozonation Other ozone techniques	TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>5 mg/L of each paraben in ultrapure water.</li> <li>UV radiation.</li> </ul>	<ul style="list-style-type: none"> <li>Degradation of about 65%, 70%, 91%, 94%, 95%, 100%, and 100% for O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub>/Fe<sup>2+</sup>, O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/UV/TiO<sub>2</sub>, O<sub>3</sub>/UV/H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub>, and O<sub>3</sub>/UV, respectively in 20 min.</li> </ul>	[23]
MP, EP, PP, BuP, and BeP	Catalytic ozonation	TiO <sub>2</sub> Au-TiO <sub>2</sub> Ag-TiO <sub>2</sub> Pd-TiO <sub>2</sub> Pt-TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>10 mg/L of each paraben in ultrapure water.</li> <li>70 mg/L of catalyst.</li> </ul>	<ul style="list-style-type: none"> <li>TOD = 70 mg/L for 0.5%Pt-TiO<sub>2</sub> and TiO<sub>2</sub>, and TOD = 80 mg/L for 0.5%Pd-TiO<sub>2</sub> in 120 min.</li> </ul>	[26]
MP, EP, PP, BuP and BeP	Photocatalytic Ozonation	TiO <sub>2</sub> Ag-TiO <sub>2</sub> Au-TiO <sub>2</sub> Pd-TiO <sub>2</sub> Pt-TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>10 mg/L of each paraben in ultrapure water.</li> <li>70 mg/L of catalyst dose.</li> <li>UVA radiation.</li> </ul>	<ul style="list-style-type: none"> <li>Photocatalytic ozonation led to total paraben degradation.</li> <li>Catalysts efficiency: Ag (TOD = 40 mg/L) &lt; Pt (TOD = 58 mg/L) &gt; Pd (TOD = 64 mg/L) TiO<sub>2</sub> (TOD = 70 mg/L) &gt; 0.5%Au-TiO<sub>2</sub> (TOD = 84 mg/L).</li> </ul>	[27]
MP, EP, PP, BuP and BeP	Photolytic Ozonation Photocatalytic Ozonation	ZnO	<ul style="list-style-type: none"> <li>10 mg/L paraben solution.</li> <li>UV radiation.</li> </ul>	<ul style="list-style-type: none"> <li>Photocatalytic ozonation removed 96–98% (pH = 9) and 74–80% (pH = 3), while photolytic ozonation obtained 50–53% (pH = 3) and 53–65% (pH = 9).</li> <li>MP degradation: 34.5% and 98% (15 min), and 65% and 100% (45 min) for O<sub>3</sub> + UV and O<sub>3</sub> + UV + ZnO, respectively.</li> </ul>	[28]
MP, EP, and PP	Photocatalytic ozonation	TiO <sub>2</sub> /NT	<ul style="list-style-type: none"> <li>1 mg/L parabens mixture in ultrapure water.</li> <li>UVA and Solar radiation.</li> </ul>	<ul style="list-style-type: none"> <li>Photocatalytic ozonation led to total removal with UVA using about TOD = 4.5 mg/L and solar radiation about TOD = 8.5 mg/L (10 min).</li> </ul>	[102]
MP, EP, PP, BuP, and BeP	Photocatalytic ozonation	N-TiO <sub>2</sub> TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>10 mg/L of each paraben.</li> <li>70 mg/L of catalyst dose.</li> <li>UVA radiation.</li> </ul>	<ul style="list-style-type: none"> <li>Almost total removal achieved for TOD between about 30 and 44 mg/L, and about 26 and 45 mg/L, for different catalyst synthesis methods.</li> </ul>	[103]
MP, EP, PP, BuP, and BeP	Photocatalytic ozonation	N-TiO <sub>2</sub>	<ul style="list-style-type: none"> <li>10 mg/L of each paraben in ultrapure water.</li> <li>70–140 mg/L of catalyst dose.</li> <li>UVA radiation</li> </ul>	<ul style="list-style-type: none"> <li>Total removal was achieved for TOD of about 44–60 mg/L for 70 mg/L of catalyst, while for 140 mg/L of catalyst, TOD was about 62 mg/L.</li> <li>In 120 min, total removal of MP and EP was practically achieved using TOD of about 44, 48, and 62 mg/L for river, wastewater, and ultrapure water, respectively.</li> </ul>	[104]



### 3.3. Fenton's Process

There are not many studies regarding the paraben's abatement using Fenton's process. The most conventional Fenton's oxidation uses  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  for the elimination of organic molecules through the generation of oxidative radicals. The presence of iron allows the continuous generation of hydroxyl radicals that are the most wanted radicals for pollutants removal.

Gmurek et al. [30] used Fenton for the degradation of a mixture of parabens (10 mg/L). In this experiment, the initial pH was 6, and after the addition of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ , the pH decreased to 3, which is generally the optimal condition for this reaction, due to a better generation of oxidizing radicals. This reaction led to the complete removal of parabens. Zúñiga-Benítez et al. [105] used Fenton's reagent to remove 3-benzophenone and methylparaben. Several conditions were tested, and the MP removal was between 45.39% and 89.96% after 30 min. Using Fenton's reagent and light, the removal was 98% for the best operational conditions, while the use of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  only removed 35%, which shows a clear improvement when UV radiation was applied to the Fenton's process.

Dominguez et al. [106] treated 150 mL mixture with 5 mg/L of each paraben (MP, EP, PP, and BuP). An experimental design was applied in which the initial concentration of the reagents ( $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ ) were variable. Best performance achieved 95.8%, 97.7%, 98.0%, and 98.6% of MP, EP, PP, and BuP removal for concentrations of  $2.70 \times 10^{-4}$  mol/L and  $2.70 \times 10^{-5}$  mol/L for  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ , respectively.

In general, the studies suggest a good performance of Fenton's over parabens abatement, since high removal rates were generally reported. Table 6 presents an overview of the use of Fenton's technology regarding parabens removal.

**Table 6.** Parabens removal by Fenton's process.

Pollutant	AOP	Iron Source	Test Conditions	Results and Conclusions	Reference
MP, EP, PP, BuP, and BeP	Fenton	Iron (II) sulfate heptahydrated	<ul style="list-style-type: none"> <li>Parabens mixture in ultrapure water at 10 mg/L each.</li> <li>120 min reaction and initial pH = 6.</li> </ul>	<ul style="list-style-type: none"> <li>Fenton's process led to total parabens abatement in 120 min.</li> </ul>	[30]
3-Benzophenone and MP	Fenton	Iron (II) chloride tetrahydrate	<ul style="list-style-type: none"> <li>300–800 nm radiation.</li> <li>1 mg/L of pollutants and pH = 3.</li> </ul>	<ul style="list-style-type: none"> <li>MP removal in 120 min using best parameters: about 98%, 35%, 15%, 2%, 0% and 0% for light + <math>\text{Fe}^{2+}</math> + <math>\text{H}_2\text{O}_2</math>, <math>\text{Fe}^{2+}</math> + <math>\text{H}_2\text{O}_2</math>, <math>\text{Fe}^{2+}</math> + light, light + <math>\text{H}_2\text{O}_2</math>, <math>\text{H}_2\text{O}_2</math> and photolysis, respectively.</li> </ul>	[105]
MP, EP, PP, and BuP	Fenton	Iron (II) sulfate heptahydrated	<ul style="list-style-type: none"> <li>Parabens mixture using MilliQ water with 5 mg/L each.</li> </ul>	<ul style="list-style-type: none"> <li>Using <math>2.70 \times 10^{-4}</math> mol/L of <math>\text{H}_2\text{O}_2</math> and <math>2.70 \times 10^{-5}</math> mol/L of <math>\text{Fe}^{2+}</math>, the removal efficiency was 95.8%, 97.7%, 98.0%, and 98.6% being the higher values obtained.</li> <li>32.8%, 37.9%, 39.5% and 41.5% degradation for same parabens order was achieved using <math>0.46 \times 10^{-4}</math> mol/L of <math>\text{H}_2\text{O}_2</math> and <math>0.46 \times 10^{-5}</math> mol/L of <math>\text{Fe}^{2+}</math>.</li> </ul>	[106]

### 3.4. PS, PMS, and H<sub>2</sub>O<sub>2</sub> Oxidation

PS and PMS anions are widely used oxidizing reagents. In fact, these agents are applied as other compounds in their molecular form (such as sodium persulfate (SPS) or potassium peroxymonosulfate), in which their dissociation into the anions and their interaction with light, heat, or catalysts generates sulfate radicals that will promote the pollutant's oxidation. However, the efficiency of persulfate anions alone is not as good, and the presence of other materials is required to enhance the generation of sulfate radicals, so, in general, and as presented in the referred studies, the use of these agents is accompanied by the presence of radiation and/or catalyst. Furthermore, the basic pH is favorable when these anions are used, since at this pH it is possible to form OH radicals that are more reactive than the  $\cdot\text{SO}_4^{2-}$  radicals.

Hydrogen peroxide is another widely used reagent for the generation of oxidizing radicals, and, at low or high amounts, its efficiency can be negatively affected due to low pollutants oxidation or scavenging behavior of hydroxyl radicals. This reagent is mainly used in the presence of other materials considered as an AOP technology, and its presence can enhance the technology's efficiency, particularly with the use of UV radiation, which allows the generation of hydroxyl radicals.

Gmurek et al. [35] used hydrogen peroxide for the degradation of a mixture of five parabens and p-HBA. The individual parabens using UVC/H<sub>2</sub>O<sub>2</sub> technology occurred in about 6 min, and the mixture of parabens was totally removed in 30 min.

Dhaka et al. [73] tested ethylparaben conversion using radiation and three different reagents (persulfate, peroxymonosulfate, and hydrogen peroxide). In 90 min, EP removal was about 97%, 98.1%, 81.3% and 36% for UV/H<sub>2</sub>O<sub>2</sub>, UV/PS, UV/PMS, and UVC photolysis, respectively. Furthermore, Dhaka et al. [74] removed about 98.9% and 34% of methylparaben using UV/PS and UVC at the same time. These results are very similar and prove the good performance of persulfate anion when coupled with UVC light. Compared to photolysis results, the existence of oxidizing agent seems to significantly increase the oxidation of the parabens compounds, which may be related to a higher generation of oxidizing radicals. Moreover, the use of UV/PMS was less effective than UV/PS in the study of Dhaka et al. [73], which is not expected, since PMS can generate hydroxyl and sulfate radicals and PS can only produce sulfate radicals [42]. Total removal of PP using UV/PS oxidation was obtained by Ioannidi et al. [107], which used UVA radiation and simulated solar light, but only 12% was achieved using Vis radiation. However, these results suggest a good performance of these technologies regarding the parabens abatement for different radiation sources, which may be an advantage for this purpose.

The presence of a catalyst may also enhance this degradation. Yang et al. [108] removed BuP by peroxymonosulfate oxidation with Mn-Fe oxycarbide catalyst, achieving the highest removal of 99% on 180 min, while Bekris et al. [109] used graphene-based catalysts with PS to remove 1 mg/L of PP, achieving 95% degradation for the best catalyst in 20 min. Moreover, the use of SPS alone was tested, reaching 10% degradation in 120 min, which shows the poor performance of this agent when used alone. Matthaïou et al. [110] used 1 g/L of SPS and different iron materials as a catalyst for the removal of 0.4 mg/L of PP, achieving the best degradation, 90%, in 90 min. Comparing these studies shows that the presence of catalyst led to almost total removal in general, which shows a good degradation performance when a catalyst material is present, and the study by Bekris et al. [109] also presented a poor performance for SPS when used alone, which is the expected behavior. Moreover, these performances were also obtained for different types of catalysts, which may suggest that it is possible to use a wide range of different catalytic materials.

Table 7 presents the use of reagents for parabens abatement.

Table 7. Parabens degradation by PS, PMS or H<sub>2</sub>O<sub>2</sub> oxidation.

Pollutant	AOP	PS/PMS/H <sub>2</sub> O <sub>2</sub> Source	Test Conditions	Results and Conclusions	Reference
MP, EP, PP, BuP, BeP, and p-HBA	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O <sub>2</sub> (30%)	<ul style="list-style-type: none"> <li>10 mg/L each paraben in distilled water.</li> <li>UVA and UVC radiation.</li> </ul>	<ul style="list-style-type: none"> <li>Individual parabens degradation by UVC of 10–60% in 120 min, while the use of UVA and 0.5 M H<sub>2</sub>O<sub>2</sub> allowed total parabens removal in 6 min.</li> <li>Degradation of parabens mixture of 30% in 2 h (8 h for total removal) by UVA/H<sub>2</sub>O<sub>2</sub>, while UVC/H<sub>2</sub>O<sub>2</sub> removes 100% in 30 min.</li> </ul>	[35]
EP	UV/H <sub>2</sub> O <sub>2</sub> UV/PS UV/PMS	H <sub>2</sub> O <sub>2</sub> (30%) Sodium persulfate Potassium monopersulfate	<ul style="list-style-type: none"> <li>UVC radiation</li> <li>30 µM of EP and 1 mM of oxidizing agent.</li> </ul>	<ul style="list-style-type: none"> <li>In 90 min, EP removal was 97%, 98.1%, 81.3%, and about 36% for UV/H<sub>2</sub>O<sub>2</sub>, UV/PS, UV/PMS, and UV.</li> </ul>	[73]
MP	UV/PS	Sodium persulfate	<ul style="list-style-type: none"> <li>UVC radiation</li> <li>32.8 µM of MP and 1 mM of persulfate.</li> </ul>	<ul style="list-style-type: none"> <li>MP removal: 98.9% for UV/persulfate and about 34% for UV in 90 min.</li> </ul>	[74]
PP	UV/PS	Sodium persulfate	<ul style="list-style-type: none"> <li>UVA radiation and Solar simulator</li> <li>PP solution in ultrapure water, real effluent, and bottled water.</li> <li>200 µg/L of PP and 250 mg/L of SPS</li> </ul>	<ul style="list-style-type: none"> <li>PP removal was about 100%, 98% and 5% for bottled, ultrapure water, and wastewater, in 60 min.</li> <li>UVA and Solar simulate light led to total PP removal, while the SPS (dark), photolysis, and Vis radiation + SPS removed about 9%, 0%, and 12%, respectively, in 60 min.</li> </ul>	[107]
BuP	PMS oxidation	Potassium monopersulfate	<ul style="list-style-type: none"> <li>Aqueous solutions and Mn-Fe oxycarbide.</li> </ul>	<ul style="list-style-type: none"> <li>0%, 49%, 91%, 96%, 99%, and 99% removal were achieved in 180 min for no material, mMFS, mMFC-2, mMFC-8, mMFC-4, and mMFC-6, respectively.</li> <li>mMFC-6/PMS removed 73% and 81% of BuP for real wastewater.</li> </ul>	[108]
PP	PS oxidation	Sodium persulfate	<ul style="list-style-type: none"> <li>Oxidation using several catalysts (PureG+ graphene, UltraG+ graphene, Elicarb graphene and Graphene oxide (GO)) and sodium persulfate.</li> </ul>	<ul style="list-style-type: none"> <li>For 1 mg/L PP, 500 mg/L catalyst dose, and 20 mg/L of SPS, the degradation results were: 95% for PureG+ and UltraG+, 70% for GO and Elicarb was less than 10%, in 20 min.</li> <li>SPS alone led to 10% removal in 2 h, while catalyst led to removals of about 10–95%.</li> </ul>	[109]
PP	PS oxidation	Sodium persulfate	<ul style="list-style-type: none"> <li>Iron materials were used for sodium persulfate activation.</li> <li>0.4 mg/L of PP in ultrapure water.</li> <li>1 g/L of SPS and 50 mg/L of catalysts.</li> </ul>	<ul style="list-style-type: none"> <li>PP removal was about 90% for S1, S2, and S3 catalyst in 90 min and was 50–55% for S4 and S5 catalyst.</li> </ul>	[110]

### 3.5. Electrochemical Technologies

Electrochemical methods are also part of advanced oxidation processes and are widely used for degradation of pollutants. The use of these technologies on an industrial scale can be difficult, due to high costs, since one of the most used anodes is the boron-doped diamond (BDD), which is a very expensive material.

Martins et al. [36] used photo-electrocatalysis for PP removal using TiO<sub>2</sub> nanotubes as a catalyst. At pH = 3, total removal was achieved in only 30 min. The authors also showed that the presence of WO<sub>3</sub> in TiO<sub>2</sub> nanotubes enhances the photo-activity by 20%. Frontistis et al. [85] used electrochemical oxidation with BDD anode and achieved total EP removal in about 15 min for 200 µg/L of EP and 30 min when 600 µg/L was used as the initial concentration.

Dionisio et al. [111], Steter et al. [112], and Dionisio et al. [113] removed 100 mg/L of methylparaben using electrochemical oxidation with BDD [111,112] and DSA-Cl<sub>2</sub> [113]. Dionisio et al. [111] had 100% removal in 20 min for electrochemical oxidation and photo-electrocatalysis with UVC radiation, while photochemical degradation led to 20% removal in almost 500 min reaction. When 3 g/L of Na<sub>2</sub>SO<sub>4</sub> was used as an electrolyte solution, the efficiency decreased, since total removal was achieved for photo-electrocatalysis in about 240 min, for electrocatalysis in 300 min, and the photochemical oxidation led to less than 10% in almost 500 min. This clearly shows the influence of electrolyte solution on the technology's performance. Moreover, it seems that NaCl presents a good behavior for these experiments. Dionisio et al. [113] used 0.15 mol/L of NaCl as electrolyte solution, which also had 100% MP removal, but it was obtained in 40 min for electrocatalysis and photo-electrocatalysis, which did not show improvement when UVC radiation was added to the degradation process. UVC photolysis was also tested, but only 17% of MP was removed in 120 min. In the studies by Dionisio et al. [111,113], the presence of radiation was not able to increase the electrochemical experiments' efficiency, but when compared to single radiation, the high performance of the electrochemical route was noticed [113]. Steter et al. [112] used BDD as an anode and 0.05 mol/L of K<sub>2</sub>SO<sub>4</sub> as an electrolyte solution but only achieved 34.65% of MP removal in 20 min for the best conditions. In fact, compared to the study of Dionisio et al. [111], the choice of electrolyte solution may explain the difference in the obtained results. With this, it is possible to notice that NaCl and Na<sub>2</sub>SO<sub>4</sub> are good choices at a first sight, and the use of K<sub>2</sub>SO<sub>4</sub> should not be considered due to low performance.

The removal of BuP by electrochemical technologies was also investigated. Pueyo et al. [114] used electrochemical oxidation, using different materials as anode and stainless-steel as cathode, to remove 0.5 mg/L of BuP in an electrolyte solution of 0.1 M of Na<sub>2</sub>SO<sub>4</sub>. BDD anode allowed a BuP removal of 100% in 15 min, while stainless steel and platinum only achieved 40% and 18% degradation, respectively. Gomes et al. [115] also removed BuP in river water with this technology, but using platinum or glassy carbon anodes, for different electrolyte solution (KCl, H<sub>2</sub>SO<sub>4</sub> and K<sub>4</sub>P<sub>2</sub>O<sub>7</sub>). In this condition, 95% of BuP was degraded in 180 min in the presence of 0.1 M of K<sub>4</sub>P<sub>2</sub>O<sub>7</sub> as electrolyte and 40 µM of CTAC on glassy carbon. The study by Pueyo et al. [114] proved the good performance of BDD over platinum and stainless-steel anodes. This should be expected, since one of the good characteristics of BDD is its good working performance, but the disadvantages such as its high cost can make it difficult to implement electrochemical experiments with this anode. Furthermore, the study of Gomes et al. [115] suggested an easy degradation of the target compound when used in a real water matrix, which is a positive sign for real application purposes.

As well as electrochemical oxidation or photoelectrocatalysis methodologies, electro-Fenton and photo-electro Fenton were also used in parabens abatement. Steter et al. [88] removed MP, EP, and PP by photo-electro Fenton with BDD or RuO<sub>2</sub> anode. Regarding the BDD anode, a removal of 65% (360 min), 100% (360 min), and 100% (180 min) was achieved for H<sub>2</sub>O<sub>2</sub>, electro-Fenton, and photoelectron-Fenton with solar radiation. Furthermore, the authors studied the influence of the water matrix in the paraben's abatement. When real wastewater was tested, BDD led to total removal in 150 min, while the RuO<sub>2</sub> anode led to a removal higher than 95% in 180 min, using solar light photoelectron-Fenton. This study

proved the good efficiency of electro-Fenton and Photo-electro Fenton, since the removal rate was higher when Fenton's reagent was used compared to single  $H_2O_2$ , and the same conclusion was reached when radiation was added. These results can be explained by an improvement in the generation of hydroxyl radicals. Furthermore, this study also showed high degradation results when real wastewater was used which may suggest a good efficiency for these experimental conditions when applied to real treatment approaches. Rosales et al. [116] tested the MP abatement for electro-Fenton and anodic oxidation, using BDD/Nb anode, and graphite felt (GF) or Nb as cathode. Results showed that anodic oxidation led to about 60% removal for Ru and GF cathodes, while the electro-Fenton using the same cathodes led to about 78% and 98% removal, respectively, in which the electro-Fenton process led to higher performance when compared to anodic oxidation. The results are related to the different technologies' mechanisms.

Table 8 presents the use of electrochemical technologies in parabens removal.

**Table 8.** Parabens degradation by electrochemical technologies.

Pollutant	AOP	Material	Test Conditions	Results and Conclusions	Reference
PP	Photo-Electrocatalysis	TiO <sub>2</sub> /NT WO <sub>3</sub> -TiO <sub>2</sub> /NT	<ul style="list-style-type: none"> <li>TiO<sub>2</sub>/NT as working electrode.</li> <li>50 mg/L PP in electrolyte solution of 0.1 mol/L of Na<sub>2</sub>SO<sub>4</sub> in ultrapure water.</li> </ul>	<ul style="list-style-type: none"> <li>100% removal in 30 min at pH = 3.</li> <li>The presence of WO<sub>3</sub> improves the photo-activity by 20%.</li> </ul>	[36]
MP, EP, PP, BuP, and BeP	Electrochemical oxidation	Ti/Pt anode	<ul style="list-style-type: none"> <li>Mixture of parabens at 10 mg/L each.</li> <li>Ti/Pt used as anode and stainless steel as cathode.</li> </ul>	<ul style="list-style-type: none"> <li>The best result was 125 A/m<sup>2</sup> and 3 g/L NaCl achieving total parabens removal in 10 min.</li> </ul>	[83]
EP	Electrochemical Oxidation	BDD anode	<ul style="list-style-type: none"> <li>BDD anode and stainless-steel cathode</li> <li>200–600 µg/L of EP in electrolyte solution of 0.1 M.</li> </ul>	<ul style="list-style-type: none"> <li>Total removal achieved for all experiments within 15–30 min.</li> </ul>	[85]
MP, EP, PP, and BuP	Electrolysis	BDD anode	<ul style="list-style-type: none"> <li>BDD as anode and stainless steel as cathode</li> </ul>	<ul style="list-style-type: none"> <li>Best results of 100% degradation. The next best results were 98.3, 97.7, 100, and 100 for MP, EP, PP, and BuP, respectively.</li> <li>Degradation: 24.4–100% (MP), 25.9–100% (EP), 28.4–100% (PP), and 34.3–100% (BuP).</li> </ul>	[87]
MP, EP and PP	Photoelectro-Fenton	BDD anode RuO <sub>2</sub> anode	<ul style="list-style-type: none"> <li>Electrolyte solution of 5 mM of Na<sub>2</sub>SO<sub>4</sub> in simulated water matrix (SWM) or real wastewater (RWW).</li> <li>Parabens solution with 0.3 mM each.</li> <li>Solar radiation</li> <li>BDD or RuO<sub>2</sub> plate as anode, PTFE air diffusion as cathode.</li> </ul>	<ul style="list-style-type: none"> <li>Electrolysis using BDD with H<sub>2</sub>O<sub>2</sub> led to 65% removal in 360 min, electro-Fenton led to 100% removal in 360 min, and 100% achieved by solar photo electro-Fenton (SPEF) in 180 min.</li> <li>Using BDD in SWM and RWW, total removal was achieved in 180 and 150 min, respectively, and the RuO<sub>2</sub>, SPEF SWM, and RWW at 10 mA/cm<sup>2</sup>, the removal rate was &gt; 95% (240 min) and &gt; 95% (180 min).</li> </ul>	[88]

Table 8. Cont.

Pollutant	AOP	Material	Test Conditions	Results and Conclusions	Reference
MP	Electrolysis Photo-electrolysis	BDD anode	<ul style="list-style-type: none"> <li>BDD used as anode and stainless steel as cathode.</li> <li>UVC radiation.</li> <li>100 mg/L of MP.</li> <li>3.7 g/L of NaCl electrolyte solution.</li> </ul>	<ul style="list-style-type: none"> <li>Total MP removal for electrocatalysis and photoelectrocatalysis in 20 min, and about 20% removal in almost 500 min for photochemical process.</li> </ul>	[111]
MP	Electrochemical oxidation	BDD anode	<ul style="list-style-type: none"> <li>100 mg/L of MP in 0.05 mol/L of K<sub>2</sub>SO<sub>4</sub> electrolyte solution.</li> <li>BDD thin film used as anode, Ti as cathode, and the reference electrode was Ag/AgCl.</li> </ul>	<ul style="list-style-type: none"> <li>MP removal was 30.12, 34.65, 31.61, 30.07, and 19.85 for 1.35, 2.70, 5.44, 10.8, and 21.6 mA/cm<sup>2</sup> in 120 min.</li> </ul>	[112]
MP	Electrochemical oxidation Photo-electrolysis	DSA-Cl <sub>2</sub> of Ti/Ru <sub>0.3</sub> Ti <sub>0.7</sub> O <sub>2</sub> anode	<ul style="list-style-type: none"> <li>Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> used as anode and Ti plate used as cathode.</li> <li>100 mg/L of MP in 0.15 mol/L NaCl solution.</li> <li>UVC radiation.</li> </ul>	<ul style="list-style-type: none"> <li>Total removal in 80 and 40 min for 5 and 10 mA/cm<sup>2</sup>, respectively.</li> <li>Photo electrocatalysis led to 31, 78, and 100% removal for 1, 2.5, and 5 mA/cm<sup>2</sup>, respectively. Photolysis led to 17% removal in 2 h.</li> </ul>	[113]
BuP	Electrochemical Oxidation	BDD Stainless-steel Platinum	<ul style="list-style-type: none"> <li>BDD, stainless-steel, and platinum as anode and stainless-steel as cathode.</li> <li>0.5 mg/L of BuP in electrolyte solution of 0.1 M of Na<sub>2</sub>SO<sub>4</sub>.</li> </ul>	<ul style="list-style-type: none"> <li>BuP total removal achieved by BDD in 15 min, while for the stainless-steel and platinum anode, the degradation was 40% and 18% respectively.</li> </ul>	[114]
BuP	Electrochemical Oxidation	Platinum Glassy carbon	<ul style="list-style-type: none"> <li>Platinum foil or glassy carbon as working electrode, the counter electrode was platinum wire and Ag/AgCl electrode in 3 M KCl solution was used as reference electrode.</li> <li>Electrolyte solutions: 0.1 M KCl, H<sub>2</sub>SO<sub>4</sub>, or K<sub>4</sub>P<sub>2</sub>O<sub>7</sub>.</li> </ul>	<ul style="list-style-type: none"> <li>Using a real water sample from river, electrolysis led to 95% BuP removal in 2.5 h.</li> </ul>	[115]
MP	Electro-Fenton Anodic Oxidation	BDD anode	<ul style="list-style-type: none"> <li>BDD as anode and graphite felt (GF) or Ru as cathode.</li> <li>150 mg/L MP solution in 10 mM Na<sub>2</sub>SO<sub>4</sub> electrolyte solution.</li> </ul>	<ul style="list-style-type: none"> <li>MP removal of 60% using GF and Ru in anodic oxidation.</li> <li>Electro-Fenton using Ru and GF led to about 78% and 98% removal in 60 min.</li> </ul>	[116]
MP	Dielectric barrier discharge induced non-thermal plasma	ZnO-rGO nanosheets	<ul style="list-style-type: none"> <li>MP concentration of 20 mg/L.</li> <li>ZnO/GO = 10:1.</li> </ul>	<ul style="list-style-type: none"> <li>Best MP removal of 99%, 55%, and 8% in 15 min for NTP with ZnO-rGO, single NTP, and catalyst alone.</li> </ul>	[117]

### 3.6. Sono-Based Technologies

Ultrasound can generate oxidizing radicals from water pyrolysis due to the creation and collapse of microbubbles. This technology can present good advantages but has the



disadvantages of high amount of energy needed, low mineralization, and low efficiency, which can make this technology infeasible with difficult implementation at industrial scale.

Daghrir et al. [37] used photosonochemical degradation for BuP abatement (20 mg/L). The experiments led to a removal of 61.3%, 60.02%, and 87.96% for single UV light, ultrasound, and the combination of both in 120 min. Furthermore, for different experimental conditions (BuP concentration = 10 mg/L, US/UV experiment, 40 W, pH = 7) a removal of 99.2% was achieved. Nikolau et al. [38] removed about 92% of MP using the best operational parameters of T = 20 °C, pH = 6, power density of 60 W/L and the presence of biochar. This result was similar to the conclusions obtained by Sasi et al. [118], which showed 99% MP removal using an ultrasound frequency of 350 and 620 kHz, or a power density of 40.25 and 22.75 W/mL.

Ultrasound was also tested in the presence of a catalyst. Zanas et al. [119] studied sonocatalysis for MP removal using bimetallic Co-Fe carbon xerogel as a catalyst. Adsorption into catalyst was 29.2% of MP in 60 min, and sonocatalysis led to 54.6% removal in 60 min for a power density of 25 W/L, but almost full removal was obtained in 45–60 min, when the power density was increased to 52 W/L.

In general, the removal of parabens was achieved, and high parabens degradation was reported. Nevertheless, the drawbacks associated with sonochemical processes as the high energy requirement or poor mineralization may affect their choice and their use in pollutants degradation at full-scale. In fact, other AOPs with better performances and lower energy requirements can be used in wastewater treatments.

An overview of parabens degradation by sono-based technologies is presented in Table 9.

**Table 9.** Parabens degradation using sono-based technologies.

Pollutant	AOP	Catalyst	Test Conditions	Results and Conclusions	Reference
BuP	Photosonochemical	(no catalyst)	<ul style="list-style-type: none"> <li>BuP concentration of 20 mg/L.</li> <li>120 min reaction.</li> </ul>	<ul style="list-style-type: none"> <li>BuP removal: 61.3%, 60.02%, and 87.96% for UV, US (best value), and US/UV (best value).</li> <li>99.2% best removal for optimized conditions.</li> </ul>	[37]
PP	Sonochemical	(no catalyst)	<ul style="list-style-type: none"> <li>1 mg/L of PP in ultrapure water (UPW), bottled water (BW), ground water (GW), and wastewater (WW).</li> <li>125 mg/L of biochar (BC)</li> </ul>	<ul style="list-style-type: none"> <li>In 60 min, degradation was about 42%, 55%, 55%, and 78% for WW, GW, BW, and UPW, respectively, using 20 W/L and BC.</li> </ul>	[38]
MP	Sonochemical	(No catalyst)	<ul style="list-style-type: none"> <li>1.52 mg/L of MP</li> <li>MP removal in 1 h</li> <li>22.75 W/mL for different frequencies (200, 350, 620 and 1000 kHz).</li> </ul>	<ul style="list-style-type: none"> <li>Degradation: 350 (about 99% removal) &gt; 620 (99%) &gt; 1000 (95%) &gt; 200 kHz (85%).</li> <li>Power density: 40.25 (100% in 1 h) &gt; 22.75 (100%) &gt; 7 W/mL (80%).</li> </ul>	[118]
MP	Sonocatalysis	Bimetallic Co-Fe carbon xerogel	<ul style="list-style-type: none"> <li>20 kHz ultrasound coupled with catalyst (25 mg/L).</li> <li>Power density of 25 and 52 W/L.</li> </ul>	<ul style="list-style-type: none"> <li>Ultrasound removes 10% and 64% in 60 min for 25 W/L and 52 W/L, respectively.</li> <li>Sonocatalysis led to removal of 54.6% in 60 min for 25W/L and led to almost total degradation within 45–60 min for 52 W/L.</li> </ul>	[119]

#### 4. Toxicological Studies of Parabens Abatement

As proven by the previous sections, the advanced oxidation processes can promote the total abatement of parabens (single or mixture), but some studies reveal that in some conditions, the total parabens removal cannot be achieved. Moreover, also the formation of by-products during these processes can interfere with the initial toxicity or even increase the toxic character of the treated solution [24,30,75]. In this way, it is important to consider the impact of treatments in target species, such as aquatic species, since the resulting by-products can be more toxic than the parent compounds [120]. With this, the toxicological study must be a parameter of consideration in the design and application of AOP technologies for wastewater treatment, since although the target substances may be eliminated, the solution toxicity can increase, causing negative impacts if discharged into the environment.

Table 9 presents toxicity studies of initial and treated solutions of single or mixtures of parabens, using different AOP technologies. In general, all the treated samples had less toxicity compared to the initial ones, concluding that photolysis, photocatalysis, and ozone-based technologies can help in reducing toxicity.

Gomes et al. [102] tested the abatement of MP, EP, and PP mixture at 1 mg/L each, by photocatalytic and catalytic ozonation, using TiO<sub>2</sub>/NT. For catalytic ozonation, the light inhibition (LI) of *A. fischeri* decreased about 57%, while *L. sativum* had a germination index (GI) increase of 90%, while for single ozonation, the toxicity of *A. fischeri* decreased by 46% and occurred a GI increase of 79% for *L. sativum* seeds. For both species, the toxicity decreased when the treatments were applied.

Gomes et al. [121] treated 10 mg/L of each paraben in a five parabens mixture using photolysis and photocatalytic ozonation, and the toxicity was evaluated using *V. fischeri*, *C. fluminea*, and *L. sativum*. Regarding the *V. fischeri*, the treatment reduced the initial LI of 96% to 43% for the best catalyst, while *C. fluminea*'s total mortality was reduced to zero mortality in 72 h, except for 1%Pd-TiO<sub>2</sub> catalyst, which led to a mortality of 29%. *L. sativum* had an initial GI of 42% and the best results showed a GI of 112%. Furthermore, Gomes et al. [26] removed a mixture of five parabens at 10 mg/L each by ozonation and catalytic ozonation using several doped TiO<sub>2</sub> catalysts. Toxicity decreased for all the treated samples, achieving a maximum of 53.7% of inhibition decrease for *V. fischeri*, 79% mortality decrease for *C. fluminea*, and an increase of 50% for *L. sativum*, while Gomes et al. [27] tested the same but using ozonation, photolysis, photolytic ozonation, and photocatalytic ozonation, achieving a maximum decrease for photocatalytic ozonation of 60% for *V. fischeri*, 100% for *C. fluminea* (no mortality observed), and an increase of 70%, achieving a maximum of 112% for *L. sativum*. Moreover, Gomes et al. [91] used photocatalysis with different TiO<sub>2</sub> catalysts for the degradation of a mixture of five parabens, reaching the best results of decrease from 100% to 21% (79% decrease) in mortality of *C. fluminea* and an increase from 40% to 70% (30% increase) for *L. sativum*, while *V. fischeri* showed 80% inhibition after treatment.

Comparing these studies, Gomes et al. [121] had a higher *V. fischeri* LI decrease of 53%, which was similar to the results obtained by Gomes et al. [26] (53.7%) and Gomes et al. [27] (60%) for the same species. This represents an important behavior for the treatment technologies regarding toxicity removal, and the difference obtained by photocatalytic ozonation in Gomes et al. [121] and Gomes et al. [26] was similar to the ones obtained by catalytic ozonation of Gomes et al. [121] but better than the results obtained for photocatalysis performed by Gomes et al. [91], which showed about 80% light inhibition after treatment, which represent the worst result of these studies.

Moreover, photolytic ozonation seems to be worse than photocatalytic ozonation, which may suggest a good behavior of catalysts presence regarding the toxicity elimination. This may also suggest that the presence of catalyst can be an interesting advantage in wastewater treatment, since it can lower the treatment costs (when compared to single ozone) [27] and can also enhance the toxicity decrease. For *C. fluminea* total mortality, this was reduced to zero in almost all experiments in 72 h in the study of Gomes et al. [121], which was concordant with the results of Gomes et al. [27], but Gomes et al. [26] obtained

mortality of 29% and 21% for single ozonation and catalytic ozonation with TiO<sub>2</sub>. Photocatalysis showed the worst results once again, with the worst clam mortality of 55% [91]. These studies show a better behavior of photocatalytic ozonation and photolytic ozonation than catalytic ozonation and photocatalysis when doped TiO<sub>2</sub> catalysts were used, which showed even worse results. In fact, this is interesting, since the use of ozone should easily generate intermediaries from parabens' abatement that can be more toxic than the parent compounds. However, these contaminants may have been completely degraded without affecting the toxicity. Furthermore, the behavior of photocatalytic ozonation regarding this species is similar to the one observed for *A. fischeri*. For *L. sativum*, Gomes et al. [121] achieved the best GI of 112%, Gomes et al. [26] of 90%, Gomes et al. [91] of 70%, and best GI of 112% for Gomes et al. [27] study, which presents similar results and behaviors than the observed for the other species.

Fernandes et al. [103] treated the same solution than Gomes et al. [26,27,91,121] but used catalytic ozonation with N-TiO<sub>2</sub> and single ozone. The authors achieved better results of 30%, 30%, and 20% for *C. fluminea* mortality using ozonation, catalytic ozonation with TiO<sub>2</sub>, and catalytic ozonation with N-TiO<sub>2</sub>, respectively, while the initial mortality was 84% in 48 h. Regarding *L. sativum*, it showed an initial GI of 41.8% and had GI of 74.6%, 108.6%, and 123.4% for O<sub>3</sub>, O<sub>3</sub> + TiO<sub>2</sub>, and O<sub>3</sub> + N-TiO<sub>2</sub>. The toxicity evaluation using *A. fischeri* showed an initial LI of 95.6% and LI of 70%, 73.9%, and 63% for O<sub>3</sub>, O<sub>3</sub> + TiO<sub>2</sub>, and O<sub>3</sub> + N-TiO<sub>2</sub>. In fact, compared to Gomes et al. [26], the results obtained by Fernandes et al. [103] were the worst, which may indicate a weak performance of N-TiO<sub>2</sub> for toxicity decreased when compared to TiO<sub>2</sub> doped with noble metals.

Velegraki et al. [75] used photocatalysis for MP removal, and the toxicity was evaluated using *Artemia franciscana nauplii*. In this study, the formation of more toxic intermediaries occurred when the MP removal was about 39%, in which an increase of 10% in toxicity was observed. However, after the complete MP removal, the intermediaries were also removed, and the solution's toxicity was similar to the initial one. Furthermore, Orak et al. [31] used cress seeds for toxicity evaluation of an MP solution that was treated with photo-Fenton-like reaction (using best operational conditions). In fact, the observed inhibition was about 1% for the treated water and about 30% for the initial MP solution.

Gmurek et al. [30] used several AOPs for the degradation of a mixture of MP, EP, PP, BuP, and BeP at 10 mg/L each. Considering the treatments, regarding *A. fischeri*, the worst result was achieved for photocatalysis using several catalysts that had LI higher than 80%, and the best results occurred for ozone with Au-TiO<sub>2</sub> with a LI of 31.4%. For *L. sativum*, the worst GI was obtained by 43% for photocatalysis with TiO<sub>2</sub> and the best was 112% for O<sub>3</sub> with UVA radiation and Ag-TiO<sub>2</sub>. Furthermore, the toxicity of *C. fluminea* was worst for UVA with Pt-TiO<sub>2</sub>, with 55%, and the best occurred for photocatalytic ozonation, in which all the catalysts led to 0% mortality.

A review of several toxicity studies is presented in Table 10.

Table 10. Toxicity studies of parabens.

Pollutant	Organism	AOP	Results	Reference
Bisphenol A, Bisphenol B, Diamylphthalate, Butylbenzylphthalate, Methylparaben, and Ethylparaben	<ul style="list-style-type: none"> <li><i>Vibrio fischeri</i></li> </ul>	<ul style="list-style-type: none"> <li>Photolysis</li> <li>Photocatalysis</li> </ul>	<ul style="list-style-type: none"> <li>Mixture of 0.3 mg/L of each pollutant in effluent from a WWTP.</li> <li><i>V. fischeri</i> showed initial toxicity of 67% and showed LI values of 48%, 19%, and 29% for photolysis, TiO<sub>2</sub> P25, and TiO<sub>2</sub> vlp-7000, respectively.</li> </ul>	[3]
MP, EP, PP, BuP and BeP	<ul style="list-style-type: none"> <li><i>Vibrio fischeri</i></li> <li><i>Corbicula fluminea</i></li> <li><i>Lepidium sativum</i></li> </ul>	<ul style="list-style-type: none"> <li>Ozonation</li> <li>Catalytic Ozonation</li> </ul>	<ul style="list-style-type: none"> <li>Mixture of 10 mg/L each paraben in ultrapure water.</li> <li><i>V. fischeri</i> had initial inhibition of 95.1% and final inhibition of 53.6%, 41.4% and 48.2% for ozonation, TiO<sub>2</sub> and 0.5%Ag-TiO<sub>2</sub>.</li> <li><i>C. fluminea</i> had initial lethal mortality in 72 h, while for treated samples, the mortality was 29% and 21% for ozonation and TiO<sub>2</sub>.</li> <li><i>L. sativum</i> showed an initial germination index (GI) of 40%, while the GI was 90% for Pd and Pt-TiO<sub>2</sub>, and 65% for TiO<sub>2</sub>.</li> </ul>	[26]
MP, EP, PP, BuP, and BeP	<ul style="list-style-type: none"> <li><i>Vibrio fischeri</i></li> <li><i>Corbicula fluminea</i></li> <li><i>Lepidium sativum</i></li> </ul>	<ul style="list-style-type: none"> <li>Photolysis</li> <li>Ozonation</li> <li>Photolytic Ozonation</li> <li>Photocatalytic Ozonation</li> </ul>	<ul style="list-style-type: none"> <li>Mixture of 10 mg/L each paraben in ultrapure water.</li> <li><i>V. fischeri</i> had initial light inhibition (LI) of 96%. Photolytic ozonation showed LI of 60% while photocatalytic ozonation for Au-TiO<sub>2</sub>, Pd-TiO<sub>2</sub>, Ag-TiO<sub>2</sub>, Pt-TiO<sub>2</sub>, and TiO<sub>2</sub> had LI of 55%, 44%, 43%, 61%, and 36%, respectively.</li> <li><i>C. fluminea</i> showed full mortality for the initial sample. All the treated samples using photolytic ozonation or photocatalytic ozonation did not show any mortality in 72 h.</li> <li><i>L. sativum</i> showed an initial GI of 42% and photolytic ozonation had GI of 93%. Photocatalytic ozonation showed GI of 107%, 108%, 112%, 107%, and 90% for Au-TiO<sub>2</sub>, Pd-TiO<sub>2</sub>, Ag-TiO<sub>2</sub>, Pt-TiO<sub>2</sub>, and TiO<sub>2</sub>, respectively.</li> </ul>	[27]
MP, EP, PP, BuP, and BeP	<ul style="list-style-type: none"> <li><i>V. fischeri</i></li> <li><i>C. fluminea</i></li> </ul>	<ul style="list-style-type: none"> <li>Fenton</li> </ul>	<ul style="list-style-type: none"> <li>Initial paraben mixture of 10 mg/L each paraben.</li> <li>The EC<sub>50</sub> regarding <i>C. fluminea</i> mortality in 72h ([Fe<sup>2+</sup>] = 0.18 mM and [H<sub>2</sub>O<sub>2</sub>] = 8.8 mM) in MilliQ water was 40.43% for untreated samples and 80.87% for treated samples (1 h).</li> <li>For <i>V. fischeri</i>, the EC<sub>50</sub> using MilliQ water was 0.16%, 49.97% for 0 and 2 min, respectively, while after 5 min the value inhibits 50% of LI. Regarding the use of river water, values were 0.39%, 21.28%, and 39.96% for 0, 5, and 60 min.</li> </ul>	[29]

Table 10. Cont.

Pollutant	Organism	AOP	Results	Reference
MP, EP, PP, BuP, and BeP	<ul style="list-style-type: none"> <li><i>fischeri</i></li> <li><i>fluminea</i></li> <li><i>L. sativum</i></li> </ul>	<ul style="list-style-type: none"> <li>Fenton</li> <li>UVA/TiO<sub>2</sub></li> <li>UVA/doped-TiO<sub>2</sub></li> <li>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub></li> <li>O<sub>3</sub>/UVA</li> <li>O<sub>3</sub>/TiO<sub>2</sub></li> <li>O<sub>3</sub>/doped-TiO<sub>2</sub></li> <li>O<sub>3</sub>/UVA/TiO<sub>2</sub></li> <li>O<sub>3</sub>/UVA/doped-TiO<sub>2</sub></li> </ul>	<ul style="list-style-type: none"> <li>Initial paraben mixture of 10 mg/L each paraben in ultrapure water.</li> <li>Fenton led to 37% mortality of <i>C. fluminea</i>.</li> <li>The use of UVA and all catalysts led to &gt; 80% <i>A. fischeri</i> LI. 55%, 29%, and 21% mortality for <i>C. fluminea</i> was achieved for UVA/Pt-TiO<sub>2</sub>, UVA/Pd-TiO<sub>2</sub> and UVA/Ag-TiO<sub>2</sub>, respectively. The <i>L. sativum</i> GI was 43%, 57%, 70%, 61%, and 44% for UVA with TiO<sub>2</sub>, Pt-TiO<sub>2</sub>, Pd-TiO<sub>2</sub>, Ag-TiO<sub>2</sub>, and Au-TiO<sub>2</sub>, respectively.</li> <li>The use of ozone with H<sub>2</sub>O<sub>2</sub>, UVA, TiO<sub>2</sub>, and doped TiO<sub>2</sub> (Pt, Pd, Ag, and Au) led a LI of 57.1%, 59.9%, 26.5%, 32.9%, 33.7%, 35.2%, and 31.4%, respectively, while for <i>C. fluminea</i> mortality, the values were 29%, 0%, 21%, 0%, 15%, 0%, and 0% for the same order. Regarding the GI, values were 93%, 71%, 86%, 90%, 80%, and 71% for O<sub>3</sub>/UVA, O<sub>3</sub>/TiO<sub>2</sub>, O<sub>3</sub>/Pt-TiO<sub>2</sub>, O<sub>3</sub>/Pd-TiO<sub>2</sub>, O<sub>3</sub>/Ag-TiO<sub>2</sub>, and O<sub>3</sub>/Au-TiO<sub>2</sub>, respectively.</li> <li>For O<sub>3</sub> with UVA and catalysts, LI values were 36.3%, 61.4%, 44.2%, 43.4%, and 55.4% for TiO<sub>2</sub>, Pt-TiO<sub>2</sub>, Pd-TiO<sub>2</sub>, Ag-TiO<sub>2</sub>, and Au-TiO<sub>2</sub>, respectively, while the mortality was 0% for all the catalysts. GI was 90%, 107%, 108%, 112%, and 107% for the same order.</li> </ul>	[30]
MP	<ul style="list-style-type: none"> <li>Cress seeds</li> </ul>	<ul style="list-style-type: none"> <li>Photo-Fenton like</li> </ul>	<ul style="list-style-type: none"> <li>Inhibition of 30% and 1% was achieved for 5 mg/L of MP and treated water, respectively, using cress seeds.</li> </ul>	[31]
MP	<ul style="list-style-type: none"> <li><i>Artemia franciscana nauplii</i></li> </ul>	<ul style="list-style-type: none"> <li>Photocatalysis</li> </ul>	<ul style="list-style-type: none"> <li>MP initial concentration of 0.1 g/L.</li> <li>Initial solution had a low toxicity. Intermediaries were formed reaching at higher toxicity of 10% immobilization at 39% MP removal.</li> <li>At 100% MP elimination, toxicity is practically the same as the initial solution. Intermediaries were removed.</li> </ul>	[75]
MP, EP, PP, BuP and BeP	<ul style="list-style-type: none"> <li><i>Vibrio fischeri</i></li> <li><i>Corbicula fluminea</i></li> <li><i>Lepidium sativum</i></li> </ul>	<ul style="list-style-type: none"> <li>Photolysis</li> <li>Photocatalysis</li> </ul>	<ul style="list-style-type: none"> <li>Mixture of 10 mg/L each paraben in ultrapure water.</li> <li><i>V. fischeri</i> showed 80% inhibition after treatment.</li> <li><i>C. fluminea</i> decrease from 100% (initial) to 55%, 21% and 29% for 0.5%Pt-TiO<sub>2</sub> 0.5%, Ag-TiO<sub>2</sub> 0.5% and Pd-TiO<sub>2</sub>, respectively. Photolysis, TiO<sub>2</sub> and 0.5%Au-TiO<sub>2</sub> had practically the same results as the initial sample.</li> <li><i>L. sativum</i> had initial GI of 40%, while Ag, Pt, and Pd catalysts showed GI of 61%, 57%, and 70%, respectively. Photolysis, TiO<sub>2</sub>, and 0.5%Au-TiO<sub>2</sub> had similar results to the initial.</li> </ul>	[91]

Table 10. Cont.

Pollutant	Organism	AOP	Results	Reference
PP and BuP	<ul style="list-style-type: none"> <li><i>Ceriodaphnia dubia</i></li> </ul>	<ul style="list-style-type: none"> <li>Photolysis</li> </ul>	<ul style="list-style-type: none"> <li>Untreated samples present acute toxicity 53.3% and 100% for single PP and BuP, respectively, and 84% for the mixture of PP + BuP.</li> <li>Photolysis led to a decrease in toxicity for 33.3% and 76.6% for single PP and BuP at half the time of reaction, and at the end of treatment, toxicity was residually 3.3% and 8.3% for the same parabens. Regarding the mixture of parabens, at half the time, toxicity was 72% and at the end was 4%.</li> </ul>	[93]
MP, EP, and PP	<ul style="list-style-type: none"> <li><i>Aliivibrio fischeri</i></li> <li><i>Lepidium sativum</i></li> </ul>	<ul style="list-style-type: none"> <li>Ozonation</li> <li>Photocatalytic Ozonation</li> </ul>	<ul style="list-style-type: none"> <li>Mixture of 1 mg/L each paraben in ultrapure water or in municipal wastewater (MWW).</li> <li><i>A. fischeri</i> exhibited a LI of 41% for MWW and 100% for MWW parabens mixture, while the treated MWW parabens mixture had LI of 54% and 43% for ozonation and photocatalytic ozonation.</li> <li><i>L. sativum</i> showed an initial GI of 70% and 7% for MWW and MWW parabens mixture, respectively. Treated samples had values of 86% and 97% for ozonation and photocatalytic ozonation, respectively.</li> </ul>	[102]
MP, EP, PP, BuP, and BeP	<ul style="list-style-type: none"> <li><i>V. fischeri</i></li> <li><i>C. fluminea</i></li> <li><i>L. sativum</i></li> </ul>	<ul style="list-style-type: none"> <li>Ozonation</li> <li>Catalytic Ozonation</li> </ul>	<ul style="list-style-type: none"> <li>10 mg/L of parabens in ultrapure water.</li> <li><i>C. fluminea</i> mortality (48 h) were 84%, 30%, 30%, and 20% for initial solution, O<sub>3</sub>, O<sub>3</sub> + TiO<sub>2</sub> and O<sub>3</sub> + 2.5%N-TiO<sub>2</sub>, using best results.</li> <li><i>L. sativum</i> GI presented values of 41.8%, 74.6%, 108.6%, and 123.4% for initial solution, O<sub>3</sub>, O<sub>3</sub> + TiO<sub>2</sub> and O<sub>3</sub> + 5%N-TiO<sub>2</sub>.</li> <li><i>A. fischeri</i> had LI of 95.6%, 70%, 73.9%, and 63% for initial solution, O<sub>3</sub>, O<sub>3</sub> + TiO<sub>2</sub> and O<sub>3</sub> + 10%N-TiO<sub>2</sub> for the best results.</li> </ul>	[103]
MP, EP, PP, BuP, and BeP	<ul style="list-style-type: none"> <li><i>L. sativum</i></li> </ul>	<ul style="list-style-type: none"> <li>Photocatalytic ozonation</li> </ul>	<ul style="list-style-type: none"> <li>10 mg/L of parabens in river and wastewater.</li> <li>Initial GI of 67% and 75% for river and wastewater, and after 120 min, treatment was 146% and 139%, respectively.</li> </ul>	[104]
MP, EP, PP, BuP, and BeP	<ul style="list-style-type: none"> <li><i>Raphidocelis subcapitata</i></li> <li><i>Lemna minor</i></li> <li><i>Daphnia Magna</i></li> <li><i>Corbicula fluminea</i></li> <li><i>Lepidium sativum</i></li> </ul>	<ul style="list-style-type: none"> <li>Ozonation</li> <li>Catalytic Ozonation</li> </ul>	<ul style="list-style-type: none"> <li>Mixture of 0.62, 5, and 10 mg/L of each paraben in ultrapure water.</li> <li>For 10 mg/L solution, the <i>D. magna</i> immobilization, <i>C. fluminea</i> mortality, <i>R. subcapitata</i> yield inhibition, <i>L. sativum</i> GI and <i>L. minor</i> yield inhibition was 100%, 100%, 84%, 49%, and 52% respectively, while for 5 mg/L each paraben was 95%, 47%, 83%, 68%, and 30%, and for 0.62 mg/L each, these parameters were 0%, 0%, 13%, 100%, and -50%.</li> </ul>	[120]



Table 10. Cont.

Pollutant	Organism	AOP	Results	Reference
MP, EP, PP, BuP, and BeP	<ul style="list-style-type: none"> <li><i>Vibrio fischeri</i></li> <li><i>Corbicula fluminea</i></li> <li><i>Lepidium sativum</i></li> </ul>	<ul style="list-style-type: none"> <li>Photolysis</li> <li>Photocatalytic Ozonation</li> </ul>	<ul style="list-style-type: none"> <li>Mixture of 10 mg/L each paraben in ultrapure water.</li> <li><i>V. fischeri</i> exhibited initial inhibition of 96%, while the best (0.5%Ag-TiO<sub>2</sub>) and worst (1%Pd-TiO<sub>2</sub>) catalyst had 43% and 72% inhibition, respectively.</li> <li><i>C. fluminea</i> had 100% mortality in 72 h for the initial mixture and 29% mortality for 1%Pd-TiO<sub>2</sub>. All the other samples treated with the other catalysts had 0% of mortality.</li> <li><i>L. sativum</i> showed an initial GI of 42%, with best results of 112% (0.5%Ag-TiO<sub>2</sub> and 0.1%Pt-TiO<sub>2</sub>) and worst results of 80% (1% Ag-TiO<sub>2</sub>).</li> </ul>	[121]
MP, PP, BuP, BeP and 4-benzophenone	<ul style="list-style-type: none"> <li><i>Daphnia Magna</i></li> <li><i>Ptmephales promelas</i></li> <li><i>Tetrahymena thermophila</i></li> <li><i>Vibrio fischeri</i></li> <li><i>Photobacterium leognathi</i></li> <li><i>Oryzias latipes</i></li> </ul>	(non-applicable)	<ul style="list-style-type: none"> <li>Acute toxicity evaluated for wastewaters effluents and influents samples.</li> <li>Hazard quotients were 0.5 (medium risk) for all species regarding MP, &gt;0.5 for all species regarding PP up to a maximum of 3.32, and &lt;0.5 to a maximum of 0.58 for <i>V. fischeri</i> regarding BuP. When HQ is &gt;0.5, the WWTPs must be periodically monitored, and the values of wastewaters are &gt;1.0, which shows risks for water organisms.</li> <li>The EC<sub>50</sub> (50% effect concentration) and LC<sub>50</sub> (50% lethal concentration) were used.</li> <li>EC<sub>50</sub>-LC<sub>50</sub> were 5.3, 7.3, 7.3, 2.8, 4.3, and 3.1 mg/L for <i>D. magna</i>, <i>P. promelas</i>, <i>T. thermophila</i>, <i>V. fischeri</i>, <i>P. leognathi</i>, and <i>O. latipes</i>, respectively, regarding BuP. For PP, the values were 12.3, 9.7, 12.6, 2.6, 25, and 4.9 mg/L for the same order of species, while for MP, EC<sub>50</sub>-LC<sub>50</sub> values were 24.6, 58, 10, 35, and 63 mg/L for <i>D. magna</i>, <i>T. thermophila</i>, <i>V. fischeri</i>, <i>P. leognathi</i>, and <i>O. latipes</i>.</li> </ul>	[122]

## 5. Treatment Costs

Besides the efficiency of the paraben's abatement, it is important to evaluate the impact of AOPs in terms of economic aspect since these kinds of processes are mainly associated with high operational costs.

All the presented costs pertain to different paradigms, so the values themselves are affected by several issues such as the location of the study, quantity treated, effluent characteristics, energy price, types of equipment, treatment time, etc.

In this work, the kWh values were converted, considering the price of industrial electricity referred by Gomes et al. [123] of 0.1276 €/kWh, and dollars (\$) were converted to Euros (€), considering \$1 = €0.84. It should be noted that a complete economic analysis must consider maintenance and costs related to operators, among other factors, such as contingencies, cost of raw materials, utilities, etc. [124]. Furthermore, if it involves the treatment of effluents, it should be noted that the choice of technologies must include reactor design, maintenance costs, and other operating costs [27].

Vela et al. [3] removed 90% of a mixture of methylparaben, ethylparaben, bisphenol A, bisphenol B, diamylphthalate, and butyl-benzylphthalate by photocatalysis with ZnO,

TiO<sub>2</sub> P25, and TiO<sub>2</sub> Vlp 7000. The treatment costs were 103 €/m<sup>3</sup>, 149 €/m<sup>3</sup>, and 285 €/m<sup>3</sup>, respectively, considering the facility and project contingency, engineering project, consumables, service, and overhead cost. For the use of ZnO and P25, the treatment related only to parabens costs about 30 €/m<sup>3</sup> and 84 €/m<sup>3</sup>, respectively. This value is slightly more expensive than other values reported in Table 11, but this estimation may be more accurate since it already considers some important project (estimation) costs, and it is regarding a pilot-scale installation.

**Table 11.** Associated costs for different parabens removal technologies.

Treatment	Contaminant	Associated Costs	Observations	Reference
Photocatalysis w/ZnO	MP, EP, Bisphenol A, Bisphenol B, Diamylphthalate and Butyl-benzylphthalate	103 €/m <sup>3</sup>	<ul style="list-style-type: none"> <li>Regarding Murcia, Spain</li> <li>Considering treatment (3000 h/year of sun; 8 h/day, 365 days/year), consumable, service, and other costs related to the project.</li> <li>90% contaminants removal.</li> <li>For parabens (MP and EP) the value is 30 €/m<sup>3</sup></li> </ul>	[3]
Photocatalysis w/TiO <sub>2</sub> P25	MP, EP, Bisphenol A, Bisphenol B, Diamylphthalate and Butyl-benzylphthalate	149 €/m <sup>3</sup>	<ul style="list-style-type: none"> <li>Regarding Murcia, Spain</li> <li>Considering treatment (3000 h/year of sun; 8 h/day, 365 days/year), consumable, service and other costs related to the project.</li> <li>90% contaminants removal.</li> <li>For parabens (MP and EP) the value is 84 €/m<sup>3</sup></li> </ul>	[3]
Photocatalysis w/TiO <sub>2</sub> vlp 7000	MP, EP, Bisphenol A, Bisphenol B, Diamylphthalate and Butyl-benzylphthalate	285 €/m <sup>3</sup>	<ul style="list-style-type: none"> <li>Regarding Murcia, Spain</li> <li>Considering treatment (3000 h/year of sun; 8 h/day, 365 days/year), consumable, service, and other costs related to the project.</li> <li>90% contaminants removal</li> </ul>	[3]
UVC	MP, EP, PP, BuP, BeP and p-HBA	7 €/gEDC	<ul style="list-style-type: none"> <li>100% contaminant removal in 8 h</li> <li>Regarding a mixture of parabens and p-HBA</li> </ul>	[35]
UVC/H <sub>2</sub> O <sub>2</sub>	MP, EP, PP, BuP, BeP and p-HBA	0.5 €/gEDC	<ul style="list-style-type: none"> <li>100% contaminant removal in 0.5 h</li> <li>Regarding a mixture of parabens and p-HBA</li> </ul>	[35]
UV/H <sub>2</sub> O <sub>2</sub>	EP	5.93 €/m <sup>3</sup>	<ul style="list-style-type: none"> <li>The total cost is 7.06 \$/m<sup>3</sup>.</li> <li>Regarding EP degradation with initial concentration of 30 µM, reagent initial concentration of 1 mM, pH = 6.5, and reaction time of 90 min.</li> </ul>	[73]
UV/PS	EP	5.26 €/m <sup>3</sup>	<ul style="list-style-type: none"> <li>The total cost is 6.26 \$/m<sup>3</sup>.</li> <li>Regarding EP degradation with initial concentration of 30 µM, reagent initial concentration of 1 mM, pH = 6.5, and reaction time of 90 min.</li> </ul>	[73]
UV/PMS	EP	12.28 €/m <sup>3</sup>	<ul style="list-style-type: none"> <li>The total cost is 14.62 \$/m<sup>3</sup>.</li> <li>Regarding EP degradation with initial concentration of 30 µM, reagent initial concentration of 1 mM, pH = 6.5, and reaction time of 90 min.</li> </ul>	[73]

Table 11. Cont.

Treatment	Contaminant	Associated Costs	Observations	Reference
UV/PS	MP	6.92 €/m <sup>3</sup>	<ul style="list-style-type: none"> <li>The total cost is 54.2 kWh/m<sup>3</sup>.</li> <li>Regarding MP degradation with initial concentration of 32.8 µM, initial persulfate concentration of 1 mM, pH = 6.5, and reaction time of 90 min.</li> </ul>	[74]
Electrocatalysis	MP	0.19–4.59 €/kg	<ul style="list-style-type: none"> <li>Regarding MP removal (100 mg/L in 0.05 mol/l of K<sub>2</sub>SO<sub>4</sub> electrolyte solution) by electrochemical oxidation using BDD anode.</li> <li>MP removal between 19.85 and 34.65%.</li> <li>Values were 1.49, 3.28, 7.01, 15.61, and 36.0 kWh/kg for 1.35, 2.70, 5.44, 10.8, and 21.6 mA/cm<sup>2</sup>.</li> </ul>	[112]
Electrocatalysis	MP	0.03–0.92 €/m <sup>3</sup>	<ul style="list-style-type: none"> <li>Regarding MP removal (100 mg/L in 0.05 mol/l of K<sub>2</sub>SO<sub>4</sub> electrolyte solution) by electrochemical oxidation using BDD anode.</li> <li>MP removal between 19.85 and 34.65%.</li> <li>Values were 0.26, 0.54, 1.21, 2.75, and 7.24 kWh/m<sup>3</sup> for 1.35, 2.70, 5.44, 10.8, and 21.6 mA/cm<sup>2</sup>.</li> </ul>	[112]
DBD plasma with ZnO-rGO nanosheets	MP	0.01–0.14 €/g	<ul style="list-style-type: none"> <li>The cost is 0.119 \$/g for MP initial concentration of 2 mg/L, 0.024 \$/g for 10 mg/L and 0.012 \$/g for 20 mg/L.</li> <li>Regarding P = 20 W, t = 15 min, V = 200 mL, ZnO-rGO dose = 0.015 g/L and pH = 7</li> </ul>	[117]
Photocatalysis	MP	84 €/g	<ul style="list-style-type: none"> <li>TiO<sub>2</sub> dose = 2 g/L, initial concentration = 10 mg/L, pH = 6, V = 25 mL, and P = 125 W</li> <li>Regarding MP degradation, the price is 100 \$/g.</li> </ul>	[117]
Photocatalysis	EP	166.25–443.33 €/g	<ul style="list-style-type: none"> <li>Price is 263.889, 197.917, and 527.778 \$/g for initial concentration of 0.3 mg/L (t = 60 min), 0.6 mg/L (t = 90 min) and 0.15 mg/L (t = 60 min), respectively and P = 100 W and V = 120 mL.</li> </ul>	[97,117]
Ultrasonic	MP	570–1050 €/g	<ul style="list-style-type: none"> <li>Initial concentration of 1.52 mg/L at pH = 4.6.</li> <li>Price is 678.571, 1417.910, and 1250 \$/g for P = 7 W/mL (t = 90 min), P = 22.75 W/mL (t = 60 min), and P = 40.25 W/mL (t = 30 min), respectively.</li> </ul>	[117,118]
Ozonation w/Vulcanic rocks	MP, EP, PP, BeP, and BuP	0.08 €/m <sup>3</sup>	<ul style="list-style-type: none"> <li>10 mg/L mixture of MP, EP, PP, BeP, and BuP in ultrapure water</li> <li>Associated treatment costs</li> <li>Total contaminants removal</li> <li>Value is 0.66 kWh/m<sup>3</sup></li> </ul>	[125]

Table 11. Cont.

Treatment	Contaminant	Associated Costs	Observations	Reference
Ozonation	MP, EP, PP, BeP, and BuP	0.26 €/m <sup>3</sup>	<ul style="list-style-type: none"> <li>10 mg/L mixture of MP, EP, PP, BeP, and BuP in ultrapure water</li> <li>Associated treatment costs in 120 min</li> <li>Value is 2.04 kWh/m<sup>3</sup></li> </ul>	[125]
O <sub>3</sub> + UVA	MP, EP, PP, BeP, and BuP	1.91 €/m <sup>3</sup>	<ul style="list-style-type: none"> <li>10 mg/L mixture of MP, EP, PP, BeP, and BuP in ultrapure water</li> <li>Associated treatment costs in 90 min</li> <li>Value is 15 kWh/m<sup>3</sup></li> </ul>	[125]
O <sub>3</sub> + TiO <sub>2</sub>	MP, EP, PP, BeP, and BuP	0.11 €/m <sup>3</sup>	<ul style="list-style-type: none"> <li>10 mg/L mixture of MP, EP, PP, BeP, and BuP in ultrapure water</li> <li>Associated treatment costs in 120 min</li> <li>Value is 0.84 kWh/m<sup>3</sup></li> </ul>	[125]
O <sub>3</sub> + TiO <sub>2</sub> + UVA	MP, EP, PP, BeP, and BuP	1.20 €/m <sup>3</sup>	<ul style="list-style-type: none"> <li>10 mg/L mixture of MP, EP, PP, BeP, and BuP in ultrapure water</li> <li>Associated treatment costs in 60 min</li> <li>Value is 9.4 kWh/m<sup>3</sup></li> </ul>	[125]

Gomes et al. [27] estimated the degradation costs of a mixture of MP, EP, PP, BeP, and BuP by photocatalytic ozonation with UVA, catalytic ozonation, photolytic ozonation with UVA, and single ozonation, estimating an expense of 2.04 kWh/m<sup>3</sup> (0.26 €/m<sup>3</sup>), 15 kWh/m<sup>3</sup> (1.91 €/m<sup>3</sup>), 0.84 kWh/m<sup>3</sup> (0.11 €/m<sup>3</sup>), and 9.4 kWh/m<sup>3</sup> (1.20 €/m<sup>3</sup>) for these techniques, respectively. In this study, the use of TiO<sub>2</sub> catalyst seems to decrease the associated treatment costs. Dhaka et al. [73] used different reagents with UV radiation for EP abatement, achieving a value of 7.06 \$/m<sup>3</sup> (5.93 €/m<sup>3</sup>), 6.26 \$/m<sup>3</sup> (5.26 €/m<sup>3</sup>), and 14.62 \$/m<sup>3</sup> (12.28 €/m<sup>3</sup>) for UV/H<sub>2</sub>O<sub>2</sub>, UV/PS, and UV/PMS, respectively, and Dhaka et al. [74] removed MP by UV/PS, estimating costs of 54.2 kWh/m<sup>3</sup> (6.92 €/m<sup>3</sup>). These technologies are more expensive than the ones studied by Gomes et al. [27], and this can be related to the costs related to the reagents and with radiation. Furthermore, in Gomes et al.'s [27] study, the presence of catalyst and radiation seems to decrease the technologies' costs, and the use of single UVA with ozone is cheaper than catalyst with ozone and then UVA with catalyst and ozone. Catalytic ozonation was the most expensive treatment process, but this was not verified when photocatalytic ozonation was used. Moreover, this study suggests that the use of UVA makes the treatment more expensive but reduces the time of treatment, which can lead to smaller equipment and cheaper investment costs. When volcanic rocks are considered as the catalyst, the technology price decreases to 0.08 €/m<sup>3</sup>, which may indicate a significant decrease in operational costs when low-price catalysts are used and when UV radiation is not considered.

Furthermore, Nian et al. [117] calculated the costs of Lin et al. [7] photocatalysis with TiO<sub>2</sub> for MP removal, achieving treatment costs of 100 \$/g (84 €/g), and Sasi et al. [118] used sonochemical oxidation for methylparaben abatement. The cost is dependent on the chosen power density, but the cost varied from 197.92 \$/g to 527.78 \$/g (570–1050 €/g). These studies report high expensive technologies, which present a huge disadvantage in using these treatments applied at industrial scale.

Steter et al. [112] achieved an MP removal comprised between 19.85% and 34.65%, using electrocatalysis with a BDD anode. The cost is related to the energy consumption, which is dependent on current density and was estimated to be between about 1.49 kWh/kg and 36 kWh/kg (0.19–4.59 €/kg) and 0.26 kWh/m<sup>3</sup> and 7.24 kWh/m<sup>3</sup> (0.03–0.92 €/m<sup>3</sup>). In fact, the real price for this technology is more expensive, since the costs with the BDD, the other electrodes, the electrolyte solution, which needs to be replaced several times (the costs related to reagents), etc. are not considered. Furthermore, these energy costs are only

related to single MP removal, and if more parabens (in mixture) are considered, the price will normally increase.

Table 11 shows some associated costs of different advanced oxidation processes in the abatement of parabens mixtures as a pollutant.

Considering the presented studies regarding the treatment costs, a solid comparison and analysis can only be completed if several parameters are considered. In this case, this is difficult to do, since these parameters are different from study and study and due to the fact that not the same parameters are considered by all the studies. However, the state of the art was analyzed based on several studies from literature, and this should motivate more investigation in this subject.

Moreover, from doing an ad hoc analysis, it seems that the technologies using different oxidizing agents are more expensive than others using catalysts or radiation, which can be expected since the use of reagents should enhance the operational costs because these agents cannot be recovered. The use of sonolysis and some photocatalytic degradation treatments seems to be also expensive, but other reported works using ozonation, catalytic ozonation, and photocatalytic ozonation with  $\text{TiO}_2$  show low values associated. In general, it seems that the use of catalysts reduces the operational costs, but the use of UV radiation and the catalyst increases the related costs as well. Therefore, a balance between the operational costs, toxicity abatement, and pollutants removal performance should be considered to choose the technology for wastewater treatment. Furthermore, the values reported by Vela et al. [3] exhibit values from a study at a pilot scale regarding a real treatment plant, and it already considers some important project variables, parameters, and costs that must be taken in economic analysis. Compared to the studies at the laboratory scale, higher values were reached, and these values should be closer to real values at the industrial scale.

To understand the real values related to these technologies, extensive in-depth studies at a real scale for the same effluent and the same operational conditions should be done using the different AOP technologies.

## 6. Future Perspectives

The elimination of parabens and other CECs has been studied using different AOP technologies over the years by different authors. However, much research must be done before these can be easily implemented with low costs and in an environmentally friendly manner.

In general, and regarding the treatment of parabens, it seems that the use of catalysts should be preferred to the use of radiation or reagents alone. Furthermore, to lower the catalyst cost, it is important to guarantee that these can be used several times and can be recovered, regenerated, and reused. The use of radiation and catalyst should be considered depending on the technique to be applied, since some technologies, such as photocatalysis, need radiation to work. If the catalyst can be activated by solar radiation, the costs related to these technologies should be lower and attractive for industrial implementation. The common catalyst that is reported ( $\text{TiO}_2$ ) cannot be activated by this type of radiation or by visible radiation, but it is already known that this can be possible with catalyst doping. Furthermore, another thing to turn the industrial application closer is the use of immobilized catalysts, since the most used ones are present in powder form, and this can make industrial application difficult, since the powder will need more separation and recovery units, which can be traduced into more equipment, energy, labor, or resuming more operational and investment costs.

During the use of different AOPs, it is noticed that the poor mineralization and the increase in toxicity can occur due to the generation of more (toxic) by-products (or, in other words, the lack of complete oxidation into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ). This parameter should always be considered since it is possible to remove the wanted target compounds while, on the other hand, generating more toxic compounds that, when released into the environment, could have a worse impact than the initial pollutant's solution.

Moreover, in the AOP treatment designs, the associated costs (investment and operational costs) are another important evaluation parameter for the choice of the technology to be used. In fact, one major disadvantage of this group of advanced treatments is the associated high costs, especially related to energy and reagents consumption; this problem needs to be overcome in order to make these technologies feasible. Furthermore, in some of the countries already affected by water scarcity, the costs may be the biggest obstacle for advanced wastewater treatment technologies.

With this, there are many parameters that need to be considered and optimized for the implementation of these technologies on an industrial scale, but it is important that in the near future, the implementation of easily operational, efficient, low-cost, and environmentally friendly AOPs technologies be applied for real wastewater treatment.

So, for future perspectives, it is important to

- Produce high-performance catalysts with lower costs;
- Dope and support catalyst to allow their reuse and the use of other types of radiation, such as solar radiation;
- Produce cheaper and more eco-friendly radiation sources;
- Test different types of reactors and operational parameters;
- Test different AOP technologies for the same effluent on a real scale;
- Study in depth the toxicological effects in different species and impacts in the environment;
- Study in depth the operational economics for different technologies.

Based on the reviewed works, regarding parabens' treatment (which may not be applied to other CECs or real wastewater solutions due to the diversity of compounds presented in wastewaters from different places), authors appear to be focused on photocatalysis and ozone-based solutions. In fact, some disadvantages of other technologies such as the generation of iron sludge in Fenton's process, the high energy needed and low efficiency in sonochemical methods, the high costs and difficult reuse of specific materials (electrodes) that can be related to the use of electrochemical oxidation, the high amount of reagent needed in the use of oxidizing agents, or the needed severe conditions in wet air oxidation may be responsible for the lack of improvement in these technologies. Although photocatalysis and ozone-based technologies present disadvantages, the solution to overcome these problems can be easily explored, which, together with its operational simplicity and high efficiency, can be the reason why these technologies are the subject of several studies by different authors. For example, the poor mineralization of ozonolysis can be diminished by using catalysts. Furthermore, it is important to consider that the use of combined AOPs or the use of AOP technology followed by secondary treatment or other combination can have a synergetic effect. For example, if the wastewater solution is very blurred, the use of photocatalysis will require a pretreatment of coagulation and flocculation (for example) to make the wastewater less blurred and so the radiation can penetrate it. Furthermore, for the poor mineralization of ozonolysis, or even to complete the mineralization of catalytic ozonation or photocatalytic ozonation, a secondary treatment technology can probably be used after this treatment. These are only a few hypotheses of problems that can be related to the photocatalysis or ozone technologies use and their possible solutions.

However, none of these technologies should be removed from consideration until some research for the treatment of a specific wastewater is carried out. In fact, the choice of technology depends on several parameters already mentioned, and others, such as the volume/flow of wastewater to treat, wastewater composition, and wastewater properties (pH, COD, BOD, turbidity, etc.). It is also important to note that AOPs can/should be implemented considering other treatment technologies that are already common in WWTPs (as preliminary, primary, and secondary treatments) to take advantage of their synergetic effect, increasing the treatment station efficiency (as an entire treatment) and possibly reducing costs in project and operational treatments.



## 7. Conclusions

Different AOP technologies are discussed in this work for parabens degradation from water. These compounds' detection in the environment is related to effluents discharge and weak parabens elimination in WWTPs. The correct parabens' removal is possible using advanced oxidation processes, so the parabens abatement by different AOP technologies (such as ozone-based technologies, photolysis and photocatalysis, oxidizing agents, Fenton' process, sonochemical technologies, and electrochemical technologies) is reviewed in this work. Literature does not have so many references for the use of some AOP, regarding parabens abatement, which can be related to the technology's characteristics. Furthermore, some of these technologies may be infeasible for industrial application due to some related disadvantages, for example, high operational costs or low efficiencies.

The impact of treated solutions was revealed with an overview of different ecotoxicity tests. This type of experiment is important to choose the technology to use in the treatment of wastewater, since the AOPs interfere with and change the solutions' toxicity, which can make it more dangerous to the environment than the initial solution. Among the technology performance and removal efficiency, the operational costs are another characteristic to consider in the choice of treatment technologies, so with this in mind, several costs presented in the literature were reviewed.

Finally, regarding the parabens removal from wastewater with different technologies, the results are encouraging for efficient use, but there are still opportunities improvement that must be investigated. However, it is important to remember that these results are only for a specific pollutants mixture solution (mainly parabens in most cases), so their behavior for treatment of other CEC compounds or other toxic pollutants must also be analyzed. On the other hand, since these compounds enter wastewater with a diverse composition including several compounds, it will be interesting to study further steps before the real application can be achieved, such as the use and analysis of these technologies' efficiency and characteristics for the treatment of real wastewater stream.

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