




## Article

# Parabens and Methylisothiazolinone (MIT): Preservatives with Different Behaviors When Subjected to Ozone and Ultraviolet Light Treatments

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**Abstract:** The influence that contaminants exert on the degradation of other substances commonly found in the same water bodies drives this study, which aims to investigate the simultaneous degradation of preservatives such as parabens and methylisothiazolinone (MIT). Mixtures of five parabens, MIT solutions, and mixtures of all five parabens plus MIT (each at 5 mg/L) were treated using 254 nm UV light, ozone treatments, and simultaneous ozone and UV light treatments at three different pH levels (3, 5, and 9). Regardless of pH, UV light is inefficient in degrading parabens, whereas MIT is efficiently degraded under this radiation. On the other hand, ozone treatments rapidly degrade the paraben mixture at any pH, with a basic pH resulting in faster degradation due to the predominance of the indirect mechanism. MIT, due to its structural characteristics, reacts minimally with ozone, and the process is enhanced at basic pH when hydroxyl radicals are involved. The simultaneous treatment with ozone and UV light proves to be the fastest method for eliminating both parabens and MIT at any pH. However, when treating joint mixtures of parabens and MIT, behaviors change notably, particularly for processes involving UV light due to the interfering effect of MIT. Both parabens and MIT require more time to degrade, except at an acidic pH. Only MIT reduces its ozone treatment time when treated alongside parabens due to the distinct degradation mechanisms that each type of contaminant has in the presence of ozone.

**Keywords:** parabens; methylisothiazolinone (MIT); pH effect; UV light; ozonation



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## 1. Introduction

In recent years, studies on the control and monitoring of water pollution in the environment have undergone certain variations. New developments and advances in analytical techniques have made it possible to investigate compounds that, though they appear in extremely low concentrations in water ( $\mu\text{g/L}$ ), show potential levels of toxicity [1,2]. The focus has shifted from the most frequent, toxic, persistent, and hazardous pollutants to other pollutants that, although present in lower concentrations, show increasing accumulations in the environment and are already beginning to pose concerning toxicity problems [3,4]. It is essential to continue working in this direction and to study these pollutants along with their effects in greater depth [4]. It is for this very reason that numerous studies are being carried out to promote the prioritization of potentially toxic pollutants, and thus achieve their inclusion in the new legislation regulating their discharge [5].

Among these emerging contaminants are pharmaceuticals, pesticides, and personal care products [6,7]. The significant growth of the cosmetic industry in recent years has increased both the quantity and variety of compounds appearing in wastewater, which

has led to growing public concern. An increasing number of studies are focusing on this type of water with the aim of developing effective methods to treat it and prevent or avoid problems arising from the presence of toxic pollutants in the environment [8].

Preservatives, particularly parabens, are among these contaminants of concern due to their extensive use and toxicity; they are a group of chemicals that are used as preservatives in cosmetics and other products and that have been shown to be harmful to the environment. Parabens are esters of 4-parahydroxybenzoic acid (PHBA) and are antimicrobial preservatives used in cosmetics, pharmaceuticals, and prepared foods [9–11]. The high toxicity levels of these compounds are related to their potential endocrine disrupting properties, which pose a serious threat to the environment. Recently, several authorities have stressed the urgency of regulating the use of these substances and the need to look for alternative preservatives that do not have these negative environmental effects [12].

Certain isothiazolinone derivatives, among which methylisothiazolinone (MIT) is one of the most often used, may serve as an alternative to parabens as preservatives [13–15]. However, even though MIT's toxicity seems to be lower than that of parabens, and it appears that this substitution on the market makes environmental sense [16], some studies have demonstrated the toxic effect of MIT on *Daphnia magna* [17]. It is, therefore, evident that all these preservatives must be adequately degraded before their presence in water can harm the environment. However, these compounds share the common characteristic of being resistant to degradation by conventional treatments. They can inhibit the proper functioning of activated sludge in biological treatment plants, so they cannot be removed. As a result, these compounds are detected in most wastewater treatment plant fluids [18]. The properties of these pollutants highlight the need to look for alternative processes to achieve their effective removal from the environment. In this context, advanced oxidation processes (AOPs), which have a high oxidizing capacity through the generation of highly reactive species such as hydroxyl radicals, stand out as a viable solution [19,20].

Recent studies have also shown that the simultaneous application of oxidants such as  $H_2O_2$  or Fenton reagent, with cavitation processes, increases the generation of a peroxyl radical—OOH, a hydroxyl radical—OH favoring the degradation processes [21] and disinfection processes [22].

There have been some previous studies on the degradation of parabens and MIT through the application of advanced oxidation processes. Parabens have been degraded through photocatalysis [23,24], the photo-Fenton process [25,26], or ozonation [27]. MIT degradation has been studied through UV photolysis [28], UV light combined with hydrogen peroxide [29], UV light and persulfate [30], photocatalysis [31], or ozone oxidation [32]. However, to our knowledge, the simultaneous treatment of both preservatives, which usually appear in the same waters, has only been studied once with very interesting results. This study was carried out by means of a photo-Fenton process, showing different behaviors for both types of contaminants, with a strong influence of MIT in the degradation of parabens, demonstrating that treatment with Fenton-type processes is clearly inhibited by the presence of MIT [16].

Among the known AOPs, ozonation ( $O_3$ ) is a treatment capable of oxidizing contaminants that are very resilient to other degradation methods due to its ability to generate highly oxidizing species, especially when combined with UV light or other oxidants such as peroxydisulfate [32,33]. Specifically, ozone and the combination of ozone with UV are among the most applied treatments at the level of water regeneration both in industry and in tertiary treatments [34], and therefore, although studies have been performed separately, it is interesting to carry them out together to see the possible inhibitory or competing effect that MIT could have, and to see if there is any variation in behavior, in degradation, etc.

Ozone treatments have two possible oxidation mechanisms: direct oxidation of the ozone molecule on the contaminant molecule and indirect oxidation through the generation of hydroxyl radicals ( $\bullet OH$ ) [35]. The redox potentials of ozone and hydroxyl radicals are 2.07 V and 2.8 V, respectively. Furthermore,  $\bullet OH$  reacts in a less selective manner with all contaminants, with high reaction constants ranging from  $10^9$  to  $10^{10} M^{-1}s^{-1}$  [36], often

leading it to seek out the synergistic effect of ozone with other compounds or with radiation capable of increasing the proportion of hydroxyl radicals generated [37]. This difference in reactivity is also responsible for the strong pH dependence observed in ozone treatments. At an acidic pH the molecular attack of ozone on pollutant molecules predominates, whereas at basic pH the decomposition of ozone into more reactive species such as hydroxyl radicals is favored. These differences in the predominance of one mechanism over the other explain why pollutants tend to degrade at a faster rate when present in basic environments.

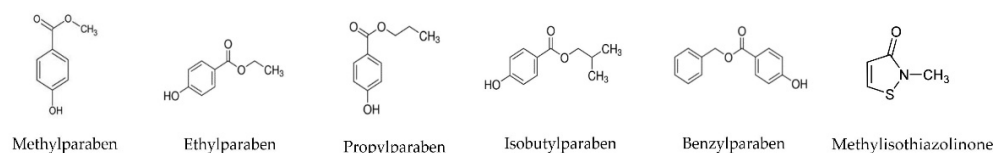
On the other hand, the degradation mechanisms of MIT may appear to be more complex. MIT suffers direct photolysis when irradiated with 254 nm UV light; however, in the presence of hydrogen peroxide oxidation with the hydroxyl radicals, it becomes predominant. Previous studies employing a combination of UV-C radiation and hydrogen peroxide have shown that the contribution of photolysis to MIT degradation is less than 10%, while the contribution of oxidation with hydroxyl radical is more than 90%. The  $\bullet\text{OH}$  radicals formed undergo complex chain reactions with dissolved oxygen and  $\text{OH}^-$  ions present in the solution to form  $\text{O}_2^{\bullet-}$ ,  $\text{H}_2\text{O}_2$ , and other reactive species [28].

Based on this analysis, the objective of this study is to investigate the degradation of parabens, MIT, and mixtures of both using UVC (254 nm) light treatment, ozone treatment, or a combination of both processes. These technologies require large amounts of energy, but fortunately today, this energy can also be generated by renewable sources, making these treatments green methods. The different behavior of both types of contaminants when treated separately and when treated as a combined mixture of both compounds will be compared.

## 2. Materials and Methods

### 2.1. Reagents

Ultrapure water (Milli-Q) produced by a Millipore (Burlington, MA, USA) distillation system was used to prepare all the solutions. High purity pollutants (>98%): benzylparaben (BP), methylparaben (MP), ethylparaben (EP), propylparaben (PP), isobutylparaben (IP) and 2-Methyl-4-isothiazolin-3-one (MIT), were obtained from Sigma-Aldrich (St. Louis, MO, USA) and used as received (Scheme 1).



**Scheme 1.** Scheme of the contaminants employed as target pollutants in this work: 5 parabens and MIT.

The water used in all solutions was Milli-Q grade. To control the pH of the solutions, 0.1 M sodium hydroxide solutions or 0.1 M sulfuric acid solutions were used. These solutions were provided by Panreac with purities above 98% and 96%, respectively.

### 2.2. Target Solution

The target solution consists of a mixture of contaminants with an initial concentration of 5 mg/L for each, resulting in 5 mg/L of each paraben studied (25 mg/L total for the parabens) and 5 mg/L of MIT. In this study, three different target solutions were used. One solution was a mixture of the five parabens, another solution was the MIT solution, and the third target solution was a mixture of the five parabens and MIT.

### 2.3. Experimental Set-Up

The ozonation tests were performed in a 1 L capacity cylindrical glass reactor, which has been described elsewhere [38]. Ozone was supplied by a generator (Ozogas, Barcelona, Spain, T.R.C.E. 4000) capable of producing 8 g/h when fed with oxygen. The ozone production was adjusted to the desired experimental conditions, with a production range

between 0.2 and 1 g/h. The ozone dosage in the reactor was selected based on previous studies conducted by the research group using the laboratory ozonizer [39]. A dosage of 0.2 g/h of ozone was chosen as the most suitable value for the degradation of a mixture of phenolic compounds in that previous study. By using this ozone dosage, the researchers aimed to ensure efficient degradation of the paraben mixture, considering the similarities in the chemical properties of phenolic compounds and parabens.

An enclosed glass reactor (8 cm in diameter and 25 cm in height) was used for the irradiations. Different outlets enabled batch or continuous operation, gas bubbling, and sampling. The light source was a 15 W low-pressure mercury lamp (Heraeus Noblelight, Cambridge, UK) that was set up axially inside the reactor and shielded by a quartz envelope. It produced virtually monochromatic irradiation at a wavelength of 254 nm. Water was continuously recirculated through an outer jacket that acted as the system's refrigeration unit. The 500 mL of the solution to be treated was placed into the reactor for each experiment. The process was maintained and stirred magnetically.

The system was cooled with water. In all cases, the reactor was loaded with 250 mL of solution, and the gas flow rate was set to 10 NL/min.

The pH of each solution was adjusted to the desired experimental value (pH = 3 or 9) by adding either sodium hydroxide or sulfuric acid. To analyze the evolution of the contaminants in the solution, samples were periodically taken from the reactor and transferred to the UPLC (Ultra-Performance Liquid Chromatography) for analysis. All experiments were repeated twice to check reproducibility.

#### 2.4. Analytical Measurements

The concentration of pollutants was monitored using liquid chromatography. A Perkin Elmer model Flexar UHPLC FX-10, equipped with a Brownlee Analytical column (DB-C18) from Merck, Germany, was used as the stationary phase. The eluents consisted of UHPLC grade acetonitrile (supplied by Panreac (Barcelona, Spain) with a richness greater than 99.9%) and formic acid 10mM (supplied by PROLABO, Tokyo, Japan).

An eluent gradient was applied, starting with a mixture of 20% acetonitrile and 80% formic acid, and gradually increasing to 90% acetonitrile and 10% formic acid. The column temperature was set to 35 °C, and a flow rate of 0.3 mL/min was used. The wavelengths used in the detector were 274 nm for MIT and 254 nm for all the parabens.

The data were analyzed using time–response curves. To track the evolution of the concentration of each contaminant, normalized concentrations ( $C/C_0$ ) were obtained and plotted as a function of time. To simplify the understanding of some results, in certain cases, the sum of all the parabens was plotted instead.

Samples were also analyzed with UV-vis spectroscopy, using a UH5300 spectrometer (Hitachi, Madrid, Spain). Spectra were recorded in the 220–750 nm range.

### 3. Results

#### 3.1. UV Treatment of Parabens at Different pH Values

In this study, the aim was to find a treatment that could be applied to industrial waters containing preservatives such as parabens or methylisothiazolinone (MIT) since conventional treatments do not yield satisfactory degradation results for these compounds. It seemed interesting to investigate the effect of each treatment on parabens and MIT individually in a first stage and then evaluate the effect of treatments on more complex mixtures containing both types of compounds.

In a previous study [16], in which the authors investigated the degradation of parabens using solar driven processes and the photolysis controls were performed under simulated solar conditions with UVA-Visible light, none of the parabens were found to undergo any transformation by photolysis at any pH. Based on these findings, subjecting the same mixture of parabens (methylparaben, ethylparaben, propylparaben, isobutylparaben, and benzylparaben) to different pH conditions (acidic pH, pH = 3; natural pH of the mixture, pH = 5; and basic pH, pH = 9) under exposure to 254 nm UV light to examine their effect

on these compounds was considered to be interesting. The degradation evolution of each paraben with photolysis time is provided in the Supplementary Material (Figure S1).

All parabens showed some degree of degradation, with benzylparaben degrading the fastest (reaching complete degradation within 1 h of treatment at any pH). Isobutylparaben followed closely in degradation rate, while the degradation rate decreased as the chain length decreased, with methylparaben exhibiting the slowest degradation. No significant differences in degradation rate were observed among the pH conditions investigated.

Figure 1a shows the degradation of the paraben mixture expressed as the sum of all of them at different pH values under UVC irradiation.

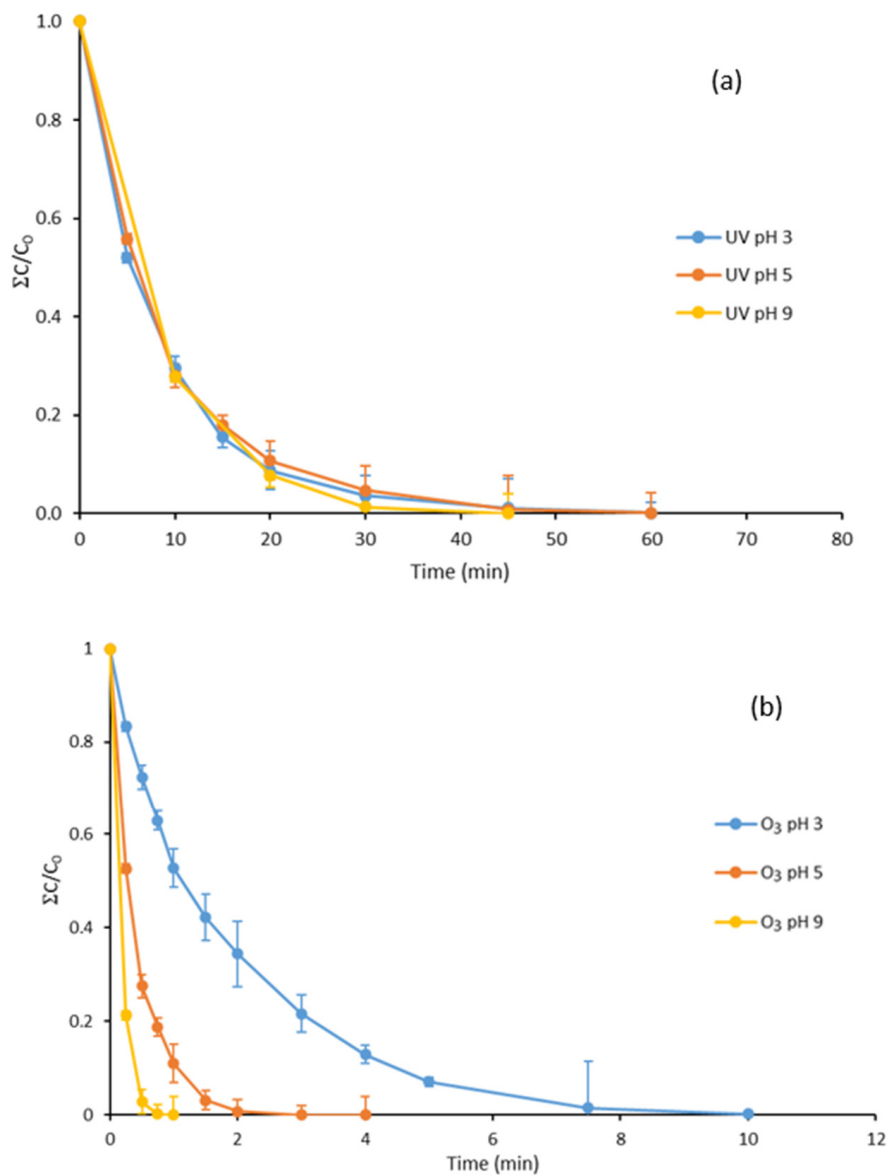
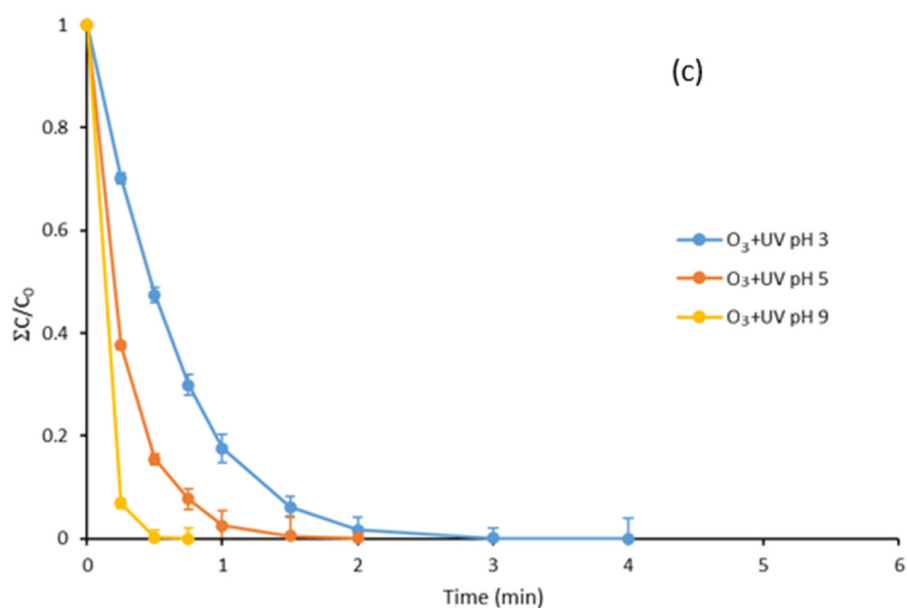


Figure 1. Cont.



**Figure 1.** Paraben degradation at different pH values. (a) with UVC (254 nm) treatment; (b) with ozone treatment; (c) with ozone and UVC light treatment. [methylparaben] = 5 mg·L<sup>-1</sup>, [ethylparaben] = 5 mg·L<sup>-1</sup>, [propylparaben] = 5 mg·L<sup>-1</sup>, [butylparaben] = 5 mg·L<sup>-1</sup>, [benzylparaben] = 5 mg·L<sup>-1</sup>. O<sub>3</sub> dose = 0.2 g/h.

### 3.2. Ozone Degradation of Parabens at Different pH Values

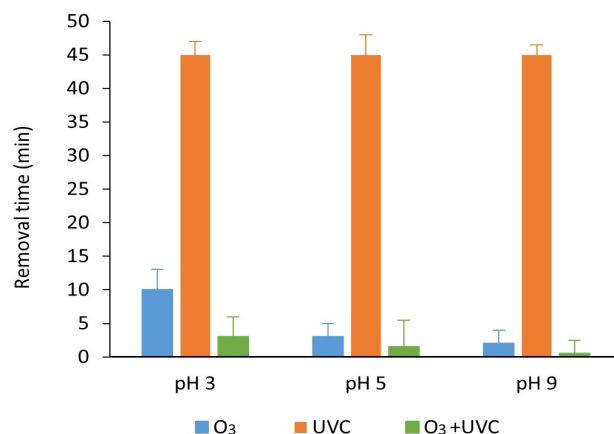
Once the effects of UVC treatment on these compounds were analyzed, we considered interesting to examine the effect of a highly oxidative process such as ozone on these molecules. Similar to the UVC treatment, it is observed that when an ozone flow rate of 0.2 g/h is applied to the reactor containing the paraben mixture, benzylparaben degrades more rapidly at any pH value, being completely eliminated in less than 5 min under the least favorable conditions (pH = 3), while methylparaben takes slightly over 10 min to be completely eliminated. This effect is to be expected, since it has been demonstrated that one of the initial reactions occurring in the treatment of parabens with ozone is the hydroxylation of the aromatic ring. Benzylparaben, in addition to the benzoic ring, has an additional non-deactivated benzene ring, so it will be hydroxylated before the benzoic ring, facilitating the subsequent oxidation of the compound. Among the parabens with aliphatic chains, the longer the chain, the faster the reaction rate, with isobutylparaben degrading the fastest with no detectable presence after 7 min of treatment. Figure 1b shows the ozone degradation of the sum of the parabens, and the kinetic constants of degradation for each paraben with ozone are provided in the Supplementary Material in Table S1.

### 3.3. Degradation with Ozone and UV Light of Paraben Mixture at Different pH Values: Synergistic Effect

Normally, ozone exhibits a synergistic effect when combined with other agents capable of generating hydroxyl radicals, such as UVC radiation or the addition of oxidants like hydrogen peroxide or peroxydisulfate [32]. For this reason, the degradation of this mixture of compounds at different pH values when subjected to simultaneous treatment with O<sub>3</sub> and UV radiation at 254 nm was studied. The results obtained are shown in Figure 1c.

It can be observed that the synergistic effect of both treatments is evident under the most unfavorable pH conditions (acidic pH) where the degradation time was reduced from 10 min for the O<sub>3</sub> treatment to just over 2 min in the combined O<sub>3</sub>/UV treatment. These results are considered logical since at acidic pH, the degradation of the contaminants occurs as the ozone directly attacks the paraben molecules since the production of hydroxyl radicals under these conditions is negligible. On the other hand, at basic pH, the indirect

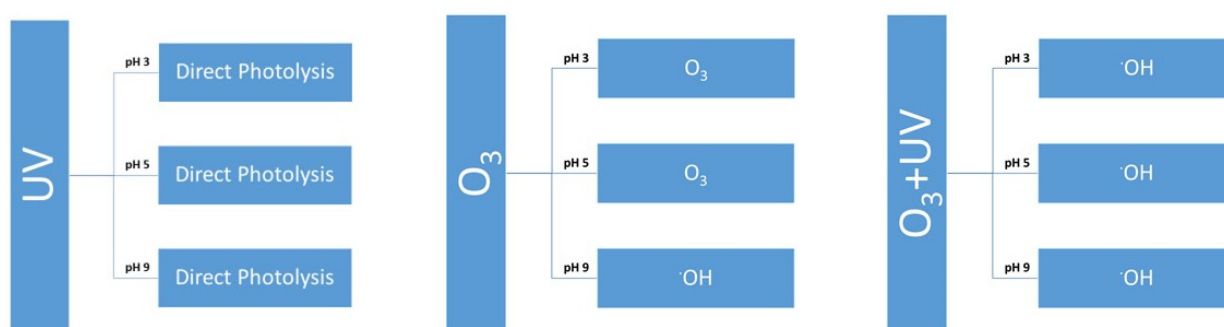
mechanism predominates due to the considerable amount of hydroxyl radicals present, so the addition of UVC radiation to the degradation process only slightly reduces the reaction time. This effect is best illustrated in Figure 2.



**Figure 2.** Comparison of paraben degradation by ozone, UVC light (254 nm) and O<sub>3</sub>/UV (254 nm) treatment at different pH values. Time necessary for the disappearance of the initial molecule. Initial concentration of each pollutant: [methylparaben] = 5 mg·L<sup>-1</sup>, [ethylparaben] = 5 mg·L<sup>-1</sup>, [propylparaben] = 5 mg·L<sup>-1</sup>, [butylparaben] = 5 mg·L<sup>-1</sup>, [benzylparaben] = 5 mg·L<sup>-1</sup>. O<sub>3</sub> dose = 0.2 g/h.

This effect is more clearly observed when comparing the kinetic constants of the process at different pH values (Table 1). Ozone treatment with UV light at pH 3 produces a kinetic constant of 2.26, which is slightly higher when performed at the natural pH of the solution (pH 5). However, this value is multiplied by almost six (12.94) when the treatment is carried out at pH 9.

In order to clarify the main mechanisms or reactive species involved in each case, a figure that summarizes the techniques was applied, and the conditions and the main pathway of degradation were created (Figure 3).



**Figure 3.** Schematic description of the main mechanisms or reactive species involved in the three processes applied (UV, O<sub>3</sub> and O<sub>3</sub> + UV) at the different pHs tested (3, 5 and 9).

While irradiation with UV-C always produces degradation by direct photolysis, its combination with ozone always generates hydroxyl radicals (mainly). The variations of pH only affect ozone treatments that can act directly at high and mild acidic pH values, while at basic pH values the indirect mechanism that undergoes the generation of hydroxyl radicals is predominant.

To compare the treatments, the synergy factor was calculated using Equation (1), where the synergy factor is defined as the ratio of the combined constant of the two processes (O<sub>3</sub> + UV light) to the sum of the constants of the two individual processes (ozone process constant + UV process constant). A synergy effect is considered when this factor is greater than one, while a factor less than one indicates an antagonistic effect, i.e., a negative effect

on the overall process. In this case, it can be observed that at any pH a synergy effect occurs, but it is more pronounced at an acidic pH (synergy factor greater than 3) where the ozonation process is less favorable.

$$\text{Synergy } O_3 + UV = \frac{KO_3 + UV}{KO_3 + KUV} \quad (1)$$

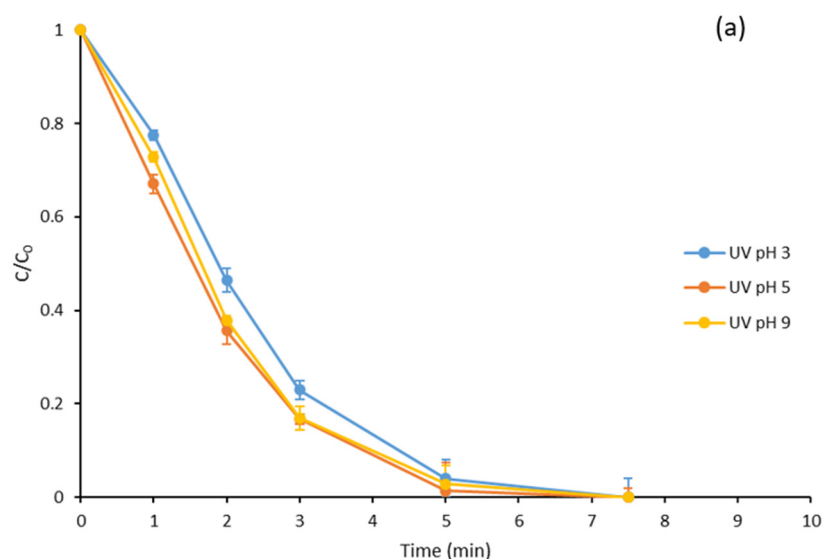
**Table 1.** Kinetic constants of the degradation of the paraben mixture by different treatments, ozone, UV light (254 nm), and O<sub>3</sub>/UV (254 nm) treatment at different pH values. Initial concentration of each pollutant: [methylparaben] = 5 mg·L<sup>-1</sup>, [ethylparaben] = 5 mg·L<sup>-1</sup>, [propylparaben] = 5 mg·L<sup>-1</sup>, [butylparaben] = 5 mg·L<sup>-1</sup>, [benzylparaben] = 5 mg·L<sup>-1</sup>. O<sub>3</sub> dose = 0.2 g/h. Synergy factor of both treatments.

Treatment	pH 3	pH 5	pH 9
O <sub>3</sub>	0.589	2.642	8.254
UVC	0.107	0.110	0.153
O <sub>3</sub> + UVC	2.260	3.709	12.937
Synergy	3.247	1.348	1.539

#### 3.4. UV Treatment of Methylisothiazolinone at Different pH Values

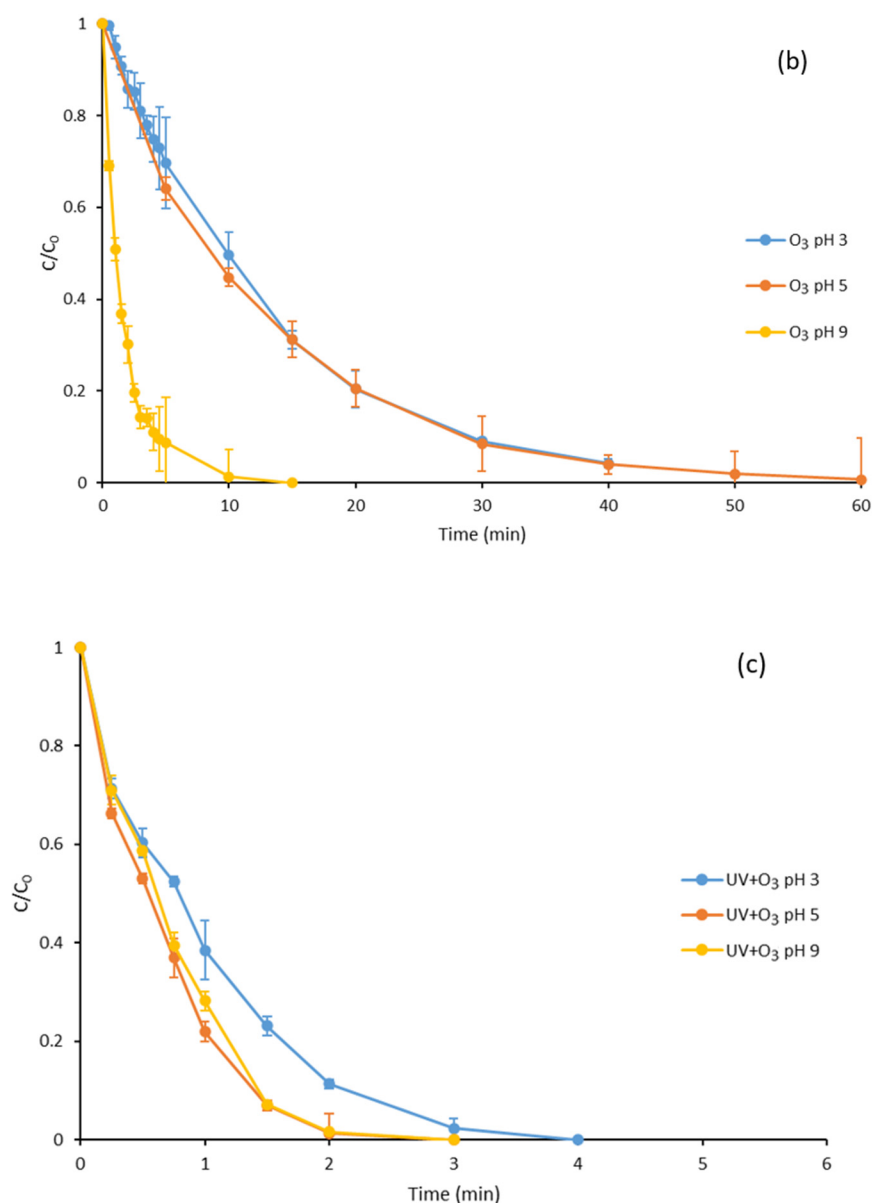
As mentioned in the introduction, there is a current trend of seeking substitutes for parabens as major preservatives. In this regard, methylisothiazolinone is one of the most widely used compounds. In previous studies [16], we found that the toxicity of methylisothiazolinone is about 100 times lower than that of benzylparaben and about 10 times lower than that of methylparaben in LC50 studies conducted on *Daphnia magna* and other fish species. Therefore, from an environmental perspective, the current trend to replace parabens with methylisothiazolinone seems logical.

Degradation experiments on MIT (5 mg/L) with 254 nm UVC radiation showed much faster degradation compared to parabens. Complete removal of the molecule was achieved in less than 7 min, with no significant differences observed when the reaction was repeated at different pH values. This behavior is logical because when absorption spectra of MIT were recorded at different pH values, it was observed that their extinction coefficients at 254 nm were similar [29] (Figure 4a).



**Figure 4.** Cont.





**Figure 4.** MIT degradation at different pH value. (a) by UV treatment; (b) by ozone treatment; and (c) by ozone and UVC light (254 nm) treatment. [MIT] = 5 mg·L<sup>-1</sup>, O<sub>3</sub> dose = 0.2 g/h.

### 3.5. Ozone Degradation of Methylisothiazolinone at Different pH Values

The behavior of MIT (methylisothiazolinone) with ozone is indeed different from that observed in the paraben mixture. The degradation of MIT is slower compared to the degradation of parabens. At pH 9, the parabens had disappeared in less than 1 min, while MIT requires 15 min for complete elimination. Furthermore, when exposed to UV light, parabens required almost 1 h to completely degrade, whereas MIT disappears within 7 min at any pH when irradiated with UV light (See Figure 4b).

These differences in degradation rate suggest that the chemical structure and properties of MIT may influence its reactivity and susceptibility to different treatment methods. The structure of MIT does not have a strong affinity for direct ozone attack, which is why its reaction with ozone at acidic or neutral pH is very slow. It requires the formation of hydroxyl radicals to undergo oxidation through an indirect pathway.

The observed low reactivity of the MIT ring towards ozone has recently been observed in reverse osmosis concentrates [40], confirming the limited contribution of direct

ozone reaction and highlighting the role of hydroxyl radicals ( $\bullet\text{OH}$ ) in the degradation process [32].

The MIT ring's lack of reactivity towards ozone can be attributed to the electronic and chemical structure of the isothiazolinone ring. Ozone is a strong oxidant that tends to react with compounds containing double or triple bonds, such as aromatic rings. In the case of MIT, the isothiazolinone ring does not have readily accessible double or triple bonds for ozone to react with. The only possible point of attack for ozone on the MIT molecule would be the double bond in the ring. However, due to the strong deactivation of the neighboring carbonyl group and the influence of the heteroatoms in the ring, this reaction is not favored. Consequently, ozone exhibits limited reactivity towards the MIT ring, resulting in a slower degradation compared to parabens, which contain more reactive aromatic rings.

One study proposed a reaction mechanism for the reaction of MIT with ozone, which starts with the oxidation of the sulfur atom to sulfate ions, leading to the destruction of the cyclic structure of the molecule [41]. The removal of sulfate ions is responsible for the observed decrease in pH, which was also detected in our study. After ten minutes of reaction, the acidic solution (pH 3) does not show a significant change in pH, whereas the solution at natural pH (pH 5) decreases to pH 3.9, and the pH 9 solution decreases to pH 6.6. This behavior in pH could confirm the suggested mechanism.

### 3.6. Degradation with Ozone and UV Light of Methylisothiazolinone at Different pH Values

Based on the different behavior of MIT compared to the paraben mixture in the different degradation processes studied (UVC photolysis at 254 nm and ozonation), it is interesting to examine how this compound behaves in a combined ozone and UV light treatment. Figure 4c shows the results of the process, where the higher degradation rate of MIT at the three studied pH values is evident. This higher rate is also reflected in the kinetic constants of the reaction, although it can be observed that the synergistic effect is lower compared to the one observed for the paraben mixture. For comparison, the synergy factor was calculated following Equation (1).

The kinetic constants for all processes and the calculation of the synergy factor are shown in Table 2. It can be observed that there is synergy in the processes at any pH. However, in this case, unlike the typical behavior of ozonation processes and the treatment of parabens as seen in the previous section, there are no appreciable differences in the synergy factors.

**Table 2.** Kinetic constants of the degradation of the MIT by different treatments, ozone, UVC light (254 nm) and  $\text{O}_3$ /UVC treatment at different pH values. Initial concentration of each pollutant [methylisothiazolinone] =  $5 \text{ mg}\cdot\text{L}^{-1}$ .  $\text{O}_3$  dose =  $0.2 \text{ g/h}$ . Synergy factor of both treatments.

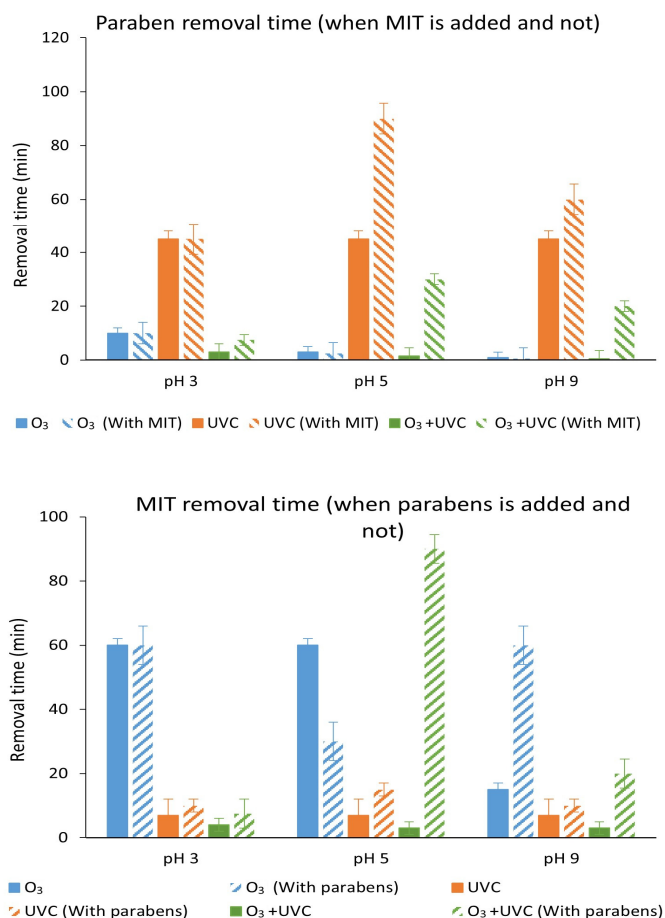
Treatment	pH 3	pH 5	pH 9
$\text{O}_3$	0.084	0.082	0.419
UVC	0.732	0.863	0.657
$\text{O}_3 + \text{UVC}$	1.229	2.120	2.055
Synergy	1.506	2.243	1.909

### 3.7. Degradation with UV Light, Ozone and Ozone Treatment Combined with UV Light of the Mixture of Parabens and Methylisothiazolinone at Different pH Values

The main interest of this paper is to observe the behavior of both types of preservatives (parabens and MIT) in the treatment of water containing both contaminants. In previous studies, [16] the influence of MIT on the degradation of parabens when treated with a photo-Fenton process was observed. When MIT was present in the same water as parabens, there was inhibition of the photo-Fenton process, and effective degradation of parabens could not be achieved due to the formation of an inactive Fe-MIT complex.

To study whether there is any influence of one type of contaminant on the degradation of the others, photolysis at 254 nm, ozonation, and combined ozone and UVC treatments

were performed on the preservative mixture at the three pH values investigated in this study: pH 3, pH 5, and pH 9. The results are shown in Figure 5.



**Figure 5.** Comparison of paraben and MIT degradation by ozone, UVC light (254 nm), and O<sub>3</sub>/UV (254 nm) treatment at different pH values. Time necessary for the disappearance of the initial molecule. Initial concentration of each pollutant: [methylparaben] = 5 mg·L<sup>-1</sup>, [ethylparaben] = 5 mg·L<sup>-1</sup>, [propylparaben] = 5 mg·L<sup>-1</sup>, [butylparaben] = 5 mg·L<sup>-1</sup>, [benzylparaben] = 5 mg·L<sup>-1</sup>. O<sub>3</sub> dose = 0.2 g/h. The graph above shows the degradation of parabens in the absence and presence of MIT. The lower graph shows the degradation of MIT in the absence and presence of parabens.

In Figure 5 above, a comparison of the behavior of parabens when subjected to different degradation processes at the 3 pH values studied can be observed, either when alone in the solution or when the same processes (UV, ozonation, and ozone with UV light) are performed with the presence of MIT in the solution.

Figure 5 lower shows the comparison of the degradation results of MIT as the only contaminant in solution with those obtained when the process is performed in the presence of both contaminants.

At acidic pH, when the mixture of parabens and MIT is treated with the three studied processes (UV light, ozone, and combined UV light with ozone), no remarkable influences in the degradation of any of these contaminants are observed. However, at the natural pH of the mixture, when treated with ozone, parabens do not modify their behavior, but MIT shows a considerable increase in its degradation rate. On the other hand, in ozonation of the mixture at basic pH, parabens still do not modify their behavior, but MIT shows a decrease in its reaction rate.

In the UV light treatments of the mixture of parabens and MIT, all contaminants show a reduction in their reaction rates, requiring more time to complete their elimination. This

behavior is logical because there is competition among them for the photons that arrive to the solution. Table 3 shows the molar extinction coefficient of each of the pollutants at a 254 nm wavelength. Complete spectra can be found in Figure S2.

**Table 3.** Molar extinction coefficients expressed in  $M^{-1}cm^{-1}$  of each pollutant for a wavelength of 254 nm.

Compound	$\epsilon$ ( $M^{-1}cm^{-1}$ )
Methylparaben	15,123
Ethylparaben	14,562
Propylparaben	20,572
Butylparaben	14,218
Propylparaben	17,119
MIT	4213

Although the molar extinction coefficient of the parabens at 254 nm is higher than for the MIT, MIT showed higher efficiency on being degraded by direct photolysis due to its high quantum yield [29]. Furthermore, a possible deactivation of the excited states of parabens by its interaction with MIT cannot be disregarded.

The same effect of increased degradation time for all contaminants is observed when a combined treatment of ozone and UV light is applied. In this case, the presence of both parabens and MIT in the mixture results in competition for reactive species, including hydroxyl radicals ( $\bullet OH$ ) generated by the combined action of ozone and UV light. The reaction of ozone with water generates hydroxyl radicals, which play a crucial role in the degradation of organic pollutants. However, when both parabens and MIT are present in the mixture, they will compete for these hydroxyl radicals, resulting in a slower degradation rate for each compound compared to when they are treated separately.

Mutual interference of parabens and MIT in the presence of ozone and UV light can lead to longer degradation times for all contaminants in the mixture. This competition for reactive species and the complex interactions among the different compounds in the mixture can influence the overall degradation kinetics and efficiency of the treatment process.

Ozone applied at pH 3 acts mainly by direct reaction, which was efficient with parabens (presence of aromatic ring) and very inefficient with MIT (due to the inactivating groups close to the ring and inserted in it). For these reasons, the interference of MIT in paraben degradation was negligible and vice versa. At this pH, the direct photolysis of the parabens was very inefficient, and the inclusion of MIT did not cause changes in this behavior. However, the amount of radiation available for MIT photolysis was lower due to the absorption of the five parabens and led to a small increase in the time required for MIT removal. Finally, the combination of ozone and UVC radiation showed a slight increase in the time required to degrade the MIT and parabens in the mixture compared to the results obtained for MIT alone. Since this combination of treatments generates the presence of oxidizing radicals, the competition of the extra organic matter present accounts for the extra time required to the complete removal. Although the amount of extra organic matter was very high when parabens were added (mixture of five), the effect was similar since the degradation of MIT via direct reaction was very low, and therefore its interfering effect consuming radicals was higher.

At pH 5, the coexistence of direct and indirect mechanisms significantly enhanced MIT degradation with ozone. Since the degradation of parabens by direct mechanism was very efficient and very inefficient for MIT, the presence of the final paraben in the mixture did not change since the competition for radicals was low. However, the presence of the five parabens substantially improved the degradation of MIT because their reaction by direct mechanism favored the reaction of MIT through the formed radicals. When direct photolysis was applied, the efficient absorption of MIT acted as an internal filter preventing the photolysis of parabens. On the contrary, the interfering effect of parabens was lower since their direct photolysis was lower at 254 nm. Finally, the combination of ozone and

UVC produced a moderate increase in the degradation time of the parabens when MIT was added, and a huge increase in the degradation time of MIT. Since this combination favors radical generation at the pH at which radical generation was present, radical oxidation became dominant and the competition between pollutants and radicals produced these increases in degradation time: lower when only MIT was added and very high when the mixture of five parabens was added.

At pH 9, the formation of hydroxyl radicals was the main pathway of pollutant degradation (indirect mechanism) when ozone was applied. The presence of MIT, which involves only small amounts of additional molecules, did not cause variations in the degradation of parabens. On the contrary, the presence of the five parabens produced a strong competition with the radicals and increased the time required for MIT removal. As discussed above, MIT was directly photolyzed with high efficiency and the same occurred at pH 9. The inclusion of some absorbing pollutants resulted in a low increase in the treatment time required. Due to the efficient absorption of MIT, its presence caused an increase in the paraben removal treatment time. Finally, the combination of ozone and UVC radiation at pH 9 produced a degradation based on radical intervention. Since MIT was very efficient in absorbing radiation, its presence increased the paraben degradation treatment time. However, as the main degradation pathway was radical oxidation, the presence of extra organic matter also increased the MIT treatment time.

To summarize, MIT absorbs UVC (254 nm) very efficiently and direct photolysis was always faster than ozone treatment, even at a basic pH where the formation of radicals was predominant. The presence of MIT in the paraben mixture always produced a decrease in efficiency (higher treatment times) when UVC radiation was present. For this reason, ozone is the best treatment for parabens even in the presence of MIT.

#### 4. Conclusions

This study has focused on simultaneous treatment using 254 nm UV light, ozone, and ozone combined with UV light for the most frequently used contaminants in the cosmetic, pharmaceutical, and food industries: parabens and methylisothiazolinone (MIT). The results reveal clear distinctions between these two types of contaminants when subjected to different treatments.

For parabens, ozone treatment requires shorter times for degradation, whereas this process degrades MIT more slowly, as it is unable to react through a direct mechanism. On the other hand, MIT can effectively absorb 254 nm radiation and be efficiently photolyzed, degrading rapidly under UV light alone, while UV treatment is ineffective for parabens, requiring prolonged exposure to light for degradation. When combined treatments of ozone and UV light are applied, both parabens and MIT experience accelerated degradation processes, making this combined process the most efficient for degrading either contaminant.

However, when parabens and MIT are treated together in the same solution, the outcomes differ. In general, treatment times increase by varying degrees due to competition for reactive species and the filtering effect exerted by MIT, which absorbs UV radiation. On the other hand, in ozone treatments at pH 5, where both direct and indirect mechanisms coexist, the effects are opposite. Parabens, which predominantly react through a direct mechanism, see minimal changes in their treatment times due to the presence of MIT. However, MIT, which only reacts through an indirect mechanism, benefits from the hydroxyl radicals formed in the presence of parabens, significantly enhancing its degradation and reducing the time needed for complete elimination.

Therefore, in combined treatments involving all contaminants at a pH close to neutrality, ozone treatment would be the optimal choice for eliminating parabens, while UV radiation would be preferable for eliminating MIT. Based on these findings, further studies on the treatment of mixed contaminants are necessary to select the most suitable effluent treatment for cases involving both types of contaminants. Interactions between reactive species and some contaminants are capable of modifying the degradation of other com-

pounds. The degradation of pollutants using different degradation techniques in isolation and in mixtures with other pollutants should be further investigated.

**Supplementary Materials:** The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15213837/s1>, Figure S1: Degradation of each paraben by different treatments, UV (254 nm), ozone, and O<sub>3</sub>/UV (254 nm) treatment at different pH values; Table S1: Kinetic constants of the degradation of each paraben by different treatments, ozone, and O<sub>3</sub>/UV (254 nm) treatment at different pH values. Figure S2: Full UV spectra of each pollutant and of the mixture of all of them. The concentration of each pollutant was 5 mg·L<sup>-1</sup> when analyzed individually and 0.8 mg·L<sup>-1</sup> in the mixture sample.

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