

Article

Mild Fenton Processes for the Removal of Preservatives: Interfering Effect of Methylisothiazolinone (MIT) on Paraben Degradation

Victoria Duarte-Alvarado, Lucas Santos-Juanes, Antonio Arques and Ana María Amat * 

Grupo de Procesos de Oxidación Avanzada, Departamento de Ingeniería Textil y Papelera, Universitat Politècnica de València, Plaza Ferrándiz y Carbonell 1, 03801 Alcoy, Spain

* Correspondence: aamat@txp.upv.es; Tel.: +34-966528471

Abstract: The degradation of various preservatives used in the cosmetics industry, including five parabens and their most employed substitute, methylisothiazolinone (MIT), was investigated. A mild photo-Fenton process was applied using low iron concentrations (5 mg/L) at a pH of five, instead of the traditional acidic value of three. At these conditions, the paraben degradation was very low after one hour of reaction and it was necessary to present humic-like substances (HLS) acting as iron chelators to improve the process. Values obtained when MIT was treated were very low, also in the presence of HLS, indicating that their complexing effect was not acting properly. When MIT was added to the mixture of parabens an inhibitory effect was found in the presence of HLS. A possible complex between iron and MIT was suggested and the studies of hydrogen peroxide consumption and Job's plot technique confirmed this hypothesis. Evidence of the formation of this inactive complex, so far never reported, will be essential in future work when dealing with this compound using Fenton processes. Furthermore, this fact points out the importance of using mixtures of model contaminants instead of a single one or a group of the same family, since their ability to form active or inactive complexes with iron can strongly change the behavior of the whole system.

Keywords: Fenton; parabens; methylisothiazolinone; complexing agents; humic-like substances; preservative mix; cosmetics industry



Citation: Duarte-Alvarado, V.; Santos-Juanes, L.; Arques, A.; Amat, A.M. Mild Fenton Processes for the Removal of Preservatives: Interfering Effect of Methylisothiazolinone (MIT) on Paraben Degradation. *Catalysts* **2022**, *12*, 1390. <https://doi.org/10.3390/catal12111390>

Academic Editors: Paola Calza and Sixto Malato

Received: 30 September 2022

Accepted: 8 November 2022

Published: 9 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

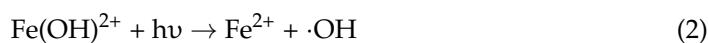
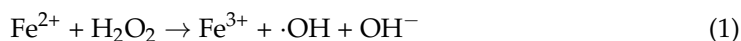
1. Introduction

The agrochemical, medical and cosmetic industries use a variety of techniques to extend the life of their products. One of the most frequently used methods is the use of preservatives; substances that inhibit the growth of microorganisms and prevent oxidation in cosmetics. Parabens, esters of 4-parahydroxybenzoic acid (PHBA), are among the most widely used preservatives due to their great effectiveness, and their presence in ground and surface water has been increasingly detected. They are antimicrobial preservatives found in cosmetics, toiletries, medications, and food, and are among the most commonly found of the emerging pollutants [1]. Parabens have been reported to have potential characteristics similar to those of endocrine-disrupting compounds and their potential detrimental effects on the environment and living beings have become a public concern [2,3]. Several recommendations and legislations from different important societies and administrations (Society on Consumer Safety, the Food and Drug Administration, and the European Union) indicate urgency in controlling the usage and environmental discharge of parabens. [4] Alternatives to parabens include methylisothiazolinone (MIT), an isothiazolinone family chemical, with similar functions that is being used in commercial formulations [5,6]. Within the isothiazolinone family, methylisothiazolinone is one of the most widely used preservatives in cosmetics [7]. Isothiazolinones were found in 18% of cosmetics from local supermarkets, 7.9% of cosmetics from herbal shops, and 2.6% of dermo-cosmetics in a study conducted in Spain [8].

These types of pollutants, usually included on the emerging pollutants group, are resistant to traditional wastewater decontamination systems. Different institutions and research groups have reported its growing presence in water treated by conventional methods [9,10]. Therefore, the use of alternative methods to avoid the presence of these preservatives in aquatic environments seems important. Among these alternative methods, advanced oxidation processes can play an important role due to their capacity to convert contaminants resistant to traditional methods into harmless products [4].

Advanced oxidation processes (AOP), characterized by their ability to generate highly reactive species such as hydroxyl radicals, have been shown to be a good alternative for treating contaminants that cannot be effectively removed by classical processes [11]. Among the known advanced oxidation treatments, the Fenton and related processes have proven to be an effective alternative for removing a wide variety of emerging contaminants [12]. The Fenton process is based on the generation of highly reactive species, in particular hydroxyl radicals, through the decomposition of H₂O₂ in the presence of iron salts in a process that is accelerated upon irradiation [13].

In the absence of other ligands, the species responsible of iron reduction, Fe(OH)²⁺, reaches its maximum concentration at pH = 2.8. However, at higher pH values, the formation of iron oxides and/or hydroxides unable to take part in the Fenton process occurs. In order to prevent this inactivation, addition of compounds capable of acting as iron ligands (L) should be considered. If the Fe-L complex is able to provide an electron transfer process to regenerate Fe(II), then the photo-Fenton process can be kept efficient even at different pH domains according to Equations (1)–(4). In fact, this is a methodology employed to extend the applicability of the photo-Fenton process towards neutral media [14–17].



These process modifications are known as Fenton-like processes. It has been shown that Fe (III) can be strongly complexed with different polydentate ligands [18,19]. Macromolecules have been employed as chelating agents; among them, humic-like substances (HLS) [20] have been used in photo-Fenton processes with satisfactory results. The ability of HLS to expand the pH range up to five in photo-Fenton processes could be due to the interaction of hydroxyl and carbonyl groups present in these substances with Fe (III) that allows the formation of stable complexes [21]. It is important to take into account that sometimes the contaminants themselves can act as iron complexing agents, so the presence of any of these compounds among the contaminants studied can considerably modify the behavior of the system [22,23]. For this reason, it is convenient to work with mixtures of contaminants where the possible complexing effect of some of them is attenuated.

There are some previous studies on paraben and MIT degradation by application of advanced oxidation processes. Paraben degradation was previously studied using titanium dioxide (TiO₂) [24] photocatalysis [25], ozone [26], and photo-Fenton [27,28]. Regarding MIT, degradation of isothiazolinones by ozone [29] and UV light has been also studied [30,31]. However, as far as we know, there are no studies on the treatment of the mixture of paraben–MIT, and given the wide use that both families of compounds have, they are likely to be found together in effluents.

With this background, the aim of this work is to investigate the degradation of mixtures of parabens and MIT by photo-Fenton processes at pH conditions close to neutrality. Among the different possible strategies of applying Fenton-like processes, different humic-like substances derived from coffee and urban biowastes have been used. Their role as iron ligands has been studied, as well as possible cross-effects between target contaminants.

2. Results and Discussion

2.1. Paraben Degradation

Before starting the photo-Fenton experiments, several photolysis tests were carried out at different pH conditions to ensure that the parabens were not degraded by sunlight. For this purpose, UVA-Visible light from the solar simulator was irradiated on the reactor containing the contaminants with no reagents added. None of the compounds were degraded, therefore it can be determined that the parabens studied do not suffer photolysis under the tested conditions.

Different degradation experiments were carried out, both Fenton and photo-Fenton, using 5 mg/L Fe(III) salts as catalyst from FeCl₃·6H₂O, and hydrogen peroxide in stoichiometric quantity to ensure complete oxidation of the organic matter. The Fenton or photo-Fenton processes can be carried out employing ferrous or ferric salts since these processes involve the cyclic oxidation and reduction of iron salts. However, the kinetically limiting step is the reduction of Fe(III) to form Fe(II) that closes the redox cycle. Employing Fe(III) salts ensures that there is a catalytic process and not only a reaction between iron (II) and hydrogen peroxide. This fact is more important when working at pH values different from the optimal.

In order to obtain a reference behavior of the pollutants, experiments were carried out under the optimal pH conditions, 2.8. Figure 1 shows the degradation of the paraben mixture expressed as the sum of all of them. As can be seen, all the parabens present in the solution suffered very fast degradation by means of the photo-Fenton process, since they all were degraded completely in less than 10 min. In the Fenton experiment, the absence of light prevents the photoreduction of iron (III), being the thermal reductive step the responsible of iron reduction, which is slower than the one driven by light. This fact makes the process slower, therefore the oxidation of the compounds became slower, and 30 min were needed to eliminate all the parabens.

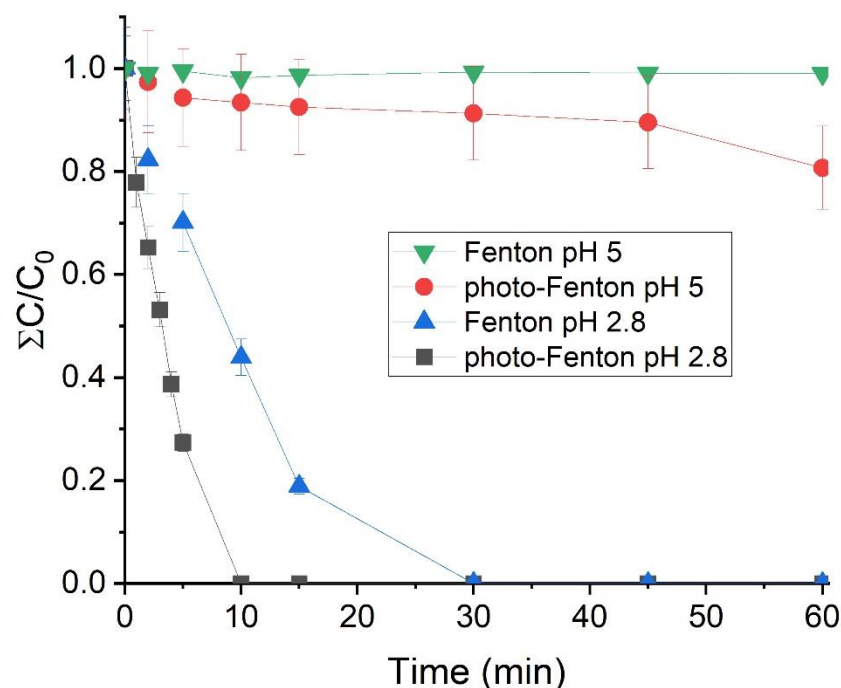


Figure 1. Paraben degradation by Fenton and photo-Fenton processes at optimal pH 2.8 and at pH 5. [methylparaben] = 5 mg·L⁻¹, [ethylparaben] = 5 mg·L⁻¹, [propylparaben] = 5 mg·L⁻¹, [butylparaben] = 5 mg·L⁻¹, [benzylparaben] = 5 mg·L⁻¹, [H₂O₂] = 26.8 mg·L⁻¹ (stoichiometric).

Table 1 shows the values of the pseudo-first-order kinetic constants of the studied parabens, both in the Fenton experiment and in the photo-Fenton experiment. As can be seen, benzylparaben is the compound that is eliminated more rapidly and therefore has a

higher kinetic constant ($k = 0.311 \text{ min}^{-1}$ in the photo-Fenton process and $k = 0.230 \text{ min}^{-1}$ in the dark). On the other hand, methylparaben is the compound that takes the longest to degrade ($k = 0.223 \text{ min}^{-1}$ in the photo-Fenton process and $k = 0.134 \text{ min}^{-1}$ in darkness), appreciating a general trend of higher kinetic to the bigger the paraben. This behavior should be expected since the reactivity of the aromatic ring of the benzyl with the hydroxyl radical is higher compared to the saturated hydrocarbons, all of them present in the substituents of parent compound. However, the presence of the aromatic ring in the parent compound makes the differences between all compounds not too high. If the attention is focused on the differences between Fenton and photo-Fenton kinetic constants, an increase of about 25–30% is observed in reactions carried out in the presence of light. It is verified again that the light speeds up the reducing step and consequently the whole process.

Table 1. Pseudo-first-order kinetic constants of parabens by Fenton and photo-Fenton degradation processes expressed in min^{-1} .

Compound	Fenton at pH 2.8	Photo-Fenton at pH 2.8	Photo-Fenton at pH 5	Photo-Fenton at pH 5 with HLS
Methylparaben	0.134	0.223	0.0025	0.0095
Ethylparaben	0.177	0.236	0.0023	0.0109
Propylparaben	0.181	0.237	0.0026	0.0116
Isobutylparaben	0.165	0.238	0.0024	0.0119
Benzylparaben	0.230	0.311	0.0038	0.0167

After carrying out the previous experiment under the theoretical optimal conditions, other conditions were tested, working at pH closer to neutrality to see how pH influences the degradation of the contaminants present.

To determine the rate of degradation of five parabens, experiments with each paraben separately at pH 5 were performed, midway between 3 (optimal) and 7 (neutral). Under these conditions, the Fenton process had no effect on the parabens. Applying the photo-Fenton process, none of the parabens were removed after 120 min of the treatment carried out in the same conditions than the experiments performed at pH 2.8:5 mg/L of each paraben, stoichiometric amount of hydrogen peroxide. This result was expectable since at this initial pH the formation of non-soluble compounds of iron (III) can be important in reducing the amount of soluble active iron to act as the catalyst of the process. Instead of the high decrease of the efficiency of the process, the reactivity of the different parabens against the reactive species formed during the process remained invariable, the benzylparaben being the easiest paraben to degrade and the most resistant one being the methylparaben.

As shown in Table 1, if the pseudo-first-order kinetic constants are compared between photo-Fenton processes at pH 2.8 and pH 5, a decrease of about two order magnitude is obtained. This fact clearly indicates a drastic change in the amount of iron available to act as a catalyst.

As commented in the introduction section, the presence of organic complexants of iron can extend the working pH range from acidic conditions to values closer to neutrality. In order to improve the efficiency of the process at pH 5, a natural complexing agent was added to the solution: humic-like substances (HLS) isolated from coffee wastes at a concentration of 25 mg/L, maintaining the initial conditions of contaminant and reagent concentrations.

In this case, the positive effect attributed to the presence of HLS acting as complexing agents was observed through the percentage of degradation of the parabens at different times. For instance, during the first 60 min, about 20% were degraded without the addition of HLS, while with the addition of HLS, approximately 50% were degraded, so a clear difference is observed when using HLS or not using them. On the other hand, after 2 h of experimentation applying the photo-Fenton treatment without any type of humic-like substance, a degradation percentage of 50% was achieved, while with the use of HLS, all parabens were eliminated. This shows that the use of HLS at pH 5 improves the process,

which makes sense, since at these pHs, iron salts are not stable in solution and tend to precipitate in the form of oxides and hydroxides. HLS can form stable complexes with iron; thus, they remain stable in solution and therefore active. This resulted in parabens having four times higher degradation kinetic values and after 2 h of treatment all parabens present in the solution were completely degraded, as shown in Figure 2.

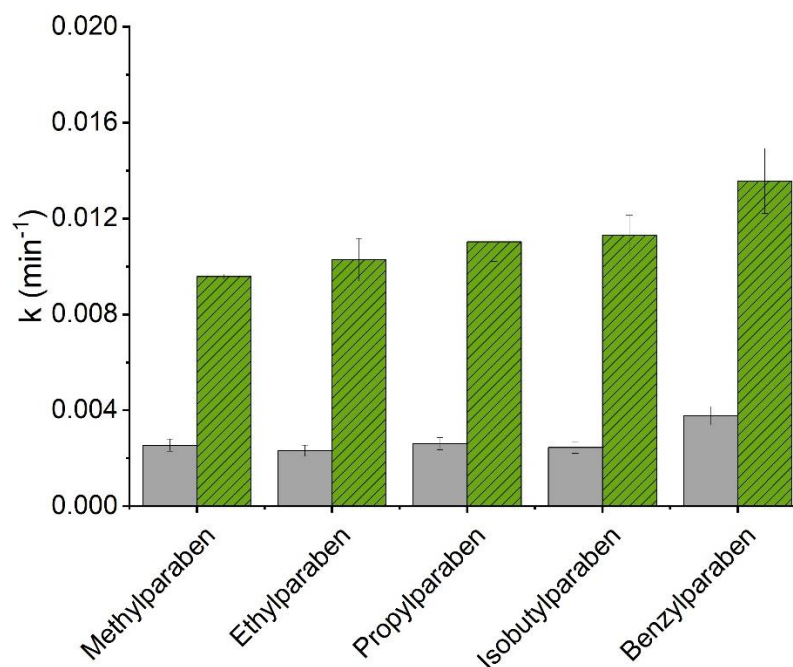


Figure 2. Degradation kinetics of different parabens at pH 5 by the photo-Fenton process (grey) and by the photo-Fenton process in the presence of HLS (green with stripes).

In Table 1, the values of each one of the kinetic constants can be observed for both the photo-Fenton experiment at pH 5 with and without HLS. As shown, benzylparaben is the compound that is eliminated more quickly and therefore has a higher kinetic constant ($k = 0.0167 \text{ min}^{-1}$ in the presence of HLS and 0.0038 min^{-1} without them). This table shows the trend of lower kinetics when the aliphatic chain is smaller, and benzylparaben always has a faster degradation regardless of the experimental conditions. At pH 5 in the absence of HLS, the kinetic constants are very small, and this trend is not seen as clearly; however, benzylparaben is significantly more reactive.

Once the reactivity of the different parabens studied was verified, it was considered appropriate to analyze whether their reactivities are related with their toxicities. It must be considered that the biggest problem these compounds have is their toxicity. For this purpose, the free program of the Environmental Protection Agency test (EPA) was consulted. It can be observed that the parabens with the shortest chain are the least toxic in all cases, methylparaben being the least toxic, and benzylparaben being the most toxic, based on LC50 studies on fathead minnows and *Daphnia magna*, bioconcentration factor, and developmental toxicity tests. It should be noted that LC50 stands for “lethal concentration”, which refers to the concentration that causes the death of 50% of the group of animals tested. With respect to these typical toxicity tests, this is the trend with few exceptions. These toxicity data are related to our degradation results, since the reactivity is greater for benzylparaben and, therefore, the most dangerous is the one that degrades the fastest. For more information on absolute values and test types see Table S1.

2.2. Methylisothiazolinone Degradation

As discussed in the introduction, many of these parabens are being replaced by methylisothiazolinone in commercial products. Before starting with degradation studies of methylisothiazolinone, its toxicity must also be considered, since it is the main substitute

for parabens. It was noted for the same tests that MIT is about 10 times less toxic than methylparaben and about 100 times less toxic than benzylparaben according to LC50 studies on fathead minnows and *Daphnia magna* extracted from EPA toxicity tests. So, it seems that this substitution on the market has a certain logic from an environmental point of view. Its toxicity data is provided as Supplementary Material (Table S2). However, it remains to be seen how this product degrades in the presence of hydroxyl radicals when a similar treatment is applied. The same experimental conditions that were seen before with parabens were repeated with MIT. It was found that photolysis has no effect at both pH 2.8 and pH 5, just as it occurred with parabens. The photo-Fenton and Fenton process in the dark at optimal pH were studied to see exactly what the degradation of MIT in the photo-Fenton process is attributed to. At pH 2.8, MIT is degraded in approximately 15 min using a stoichiometric amount of oxidant by the photo-Fenton. Both the photolytic and Fenton processes gave negligible degradations; therefore, the presence of irradiation and Fenton reagents separately are necessary but not sufficient conditions for the effective degradation of MIT at pH 2.8. The synergistic effect of both factors is necessary to decontaminate the water from methylisothiazolinone (Figure 3).

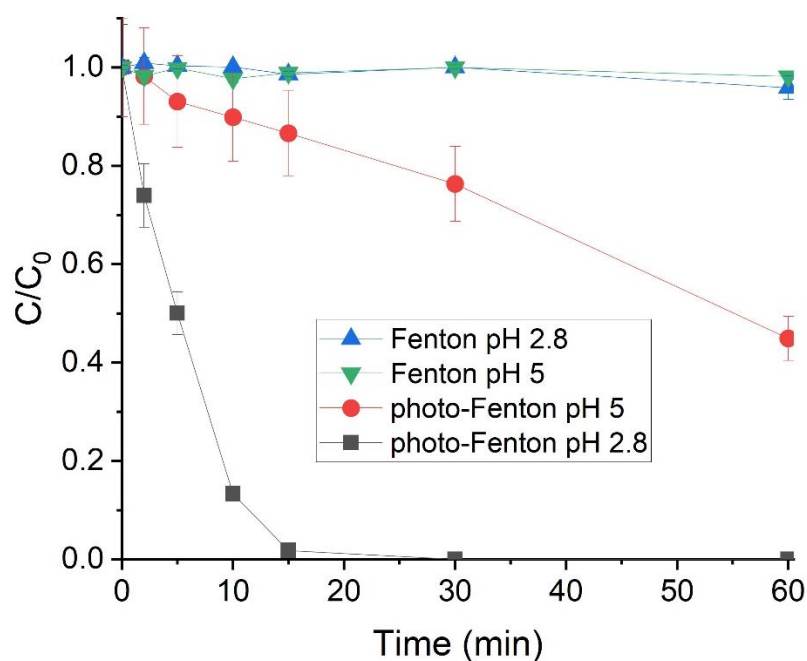


Figure 3. MIT degradation by Fenton and photo-Fenton processes at pH 2.8. and at pH 5. $[\text{Fe (III)}] = 5 \text{ mg}\cdot\text{L}^{-1}$, $[\text{H}_2\text{O}_2] = 5 \text{ mg}\cdot\text{L}^{-1}$ (stoichiometric), $[\text{MIT}] = 5 \text{ mg}\cdot\text{L}^{-1}$.

When the experiments were repeated at pH 5, the percentages of MIT degradation in the photo-Fenton treatment decreased significantly as previously seen for parabens. This effect was observed when comparing the pseudo-first-order kinetic constants for MIT degradation: photo-Fenton at pH 2.8 ($k = 0.201 \text{ min}^{-1}$) and at pH 5 ($k = 0.009 \text{ min}^{-1}$), while the Fenton process constants are practically zero.

Following the same procedure as the one used for the degradation of parabens, HLS extracted from coffee waste were added to the solution (25 mg/L) in order to improve the efficiency of the process by complexing the iron in solution to form active photocatalytic species. In this case, no enhancement of the process was observed.

As with coffee-derived HLS, no improvement was observed, the experiment was repeated under the same conditions (25 mg/L) using a different HLS obtained from urban biowastes supplied by ACEA Pinerolese waste treatment plant (Pinerolo, Italy): HLS CVT230 [32], but the effect was also negative. As shown in Figure 4, the degradation of MIT was negligible in the presence of HLS of both types, so its use was completely discarded. In none of the cases was hydrogen peroxide completely consumed. This indicates that the

iron is not being effectively complexed by the HLS, since in the absence of dissolved iron at pH 5, the redox cycle by which the reaction continues, and hydrogen peroxide is consumed, does not develop correctly.

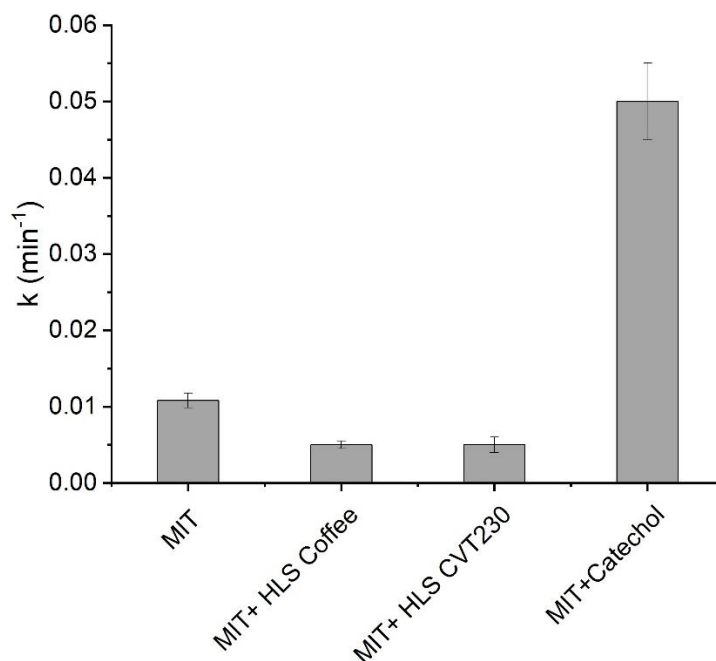


Figure 4. Effect of different complexing agents on the kinetics of MIT degradation at pH 5. [MIT] = 5 mg·L⁻¹, [H₂O₂] = 5 mg·L⁻¹ (stoichiometric), [Fe (III)] = 5 mg·L⁻¹, [HLS Coffee] = 25 mg·L⁻¹, [HLS CVT230] = 25 mg·L⁻¹, [Catechol] = 25 mg·L⁻¹.

Since humic-like substances, which are medium-strength complexing agents, were not able to complex the iron as in the case of parabens, a very strong complexing agent used in previous works [33] was employed. This agent is called catechol, a phenolic compound that is able to form iron (III) complexes that are active and stable at the working pH of five. The catechol organic functional compound presents high binding capacity with Fe (III) (Log K₁ = 20.01) [34]. The presence of catechol (25 mg/L) produced an increase in the degradation process with pseudo-first-order kinetic constants three times higher than in the absence while the hydrogen peroxide was nearly consumed. This consumption of hydrogen peroxide is an example of how the formation of the active complex between iron and catechol allows the redox cycle to end and the reaction to continue.

2.3. Degradation of Parabens with MIT

Since the degradation of MIT at the same conditions as the parabens was negligible, the possible inhibitory effect of the MIT was studied by adding this compound to the paraben mixture. All the experiments were carried out at pH 5 by photo-Fenton, and the HLS used were those extracted from coffee waste since these are the ones used previously with parabens.

As shown in Figure 5, the use of HLS benefits the process, increasing its kinetics significantly due to the formation of complexes with iron. On the other hand, the presence of methylisothiazolinone on the degradation of parabens causes an inhibitory effect of the photo-Fenton process, decreasing the kinetics with respect to the process in the absence of MIT. This negative effect can be attributed to the formation of a non-active complex of Fe-MIT that stops the process.

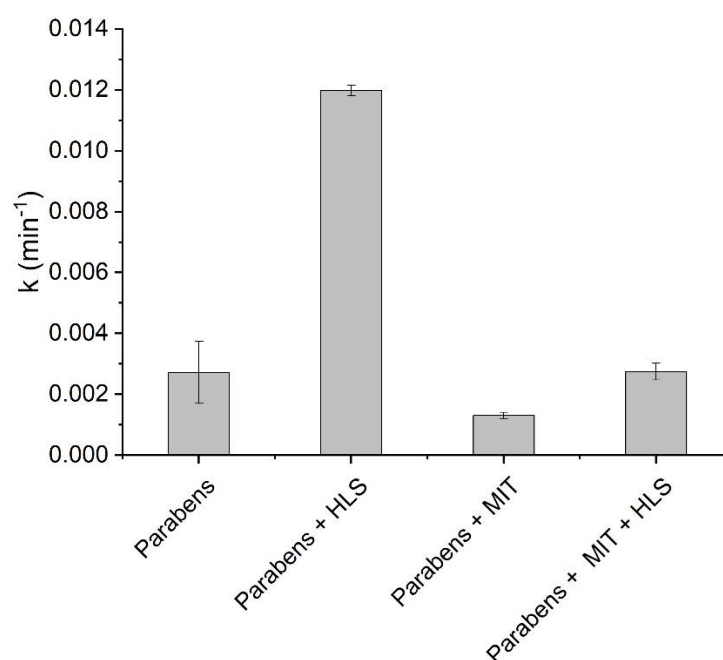


Figure 5. Effect of MIT on the degradation kinetics of parabens, in the presence and absence of HLS. [MIT] = 5 mg·L⁻¹, [parabens] = 5 mg·L⁻¹ each, [H₂O₂] = 31.8 mg·L⁻¹ (stoichiometric), [Fe (III)] = 5 mg·L⁻¹, [HLS Coffee] = 25 mg·L⁻¹.

To check these results, the competitive effect of the use of HLS (that favors the process) and MIT (that inhibits the process) was evaluated. As seen in the last bar in Figure 5, the effect of HLS is not sufficient to degrade parabens since MIT continues to inhibit such degradation. It seems that the role of the MIT as an iron complexing agent is crucial at this pH value. While at pH 2.8 this possible interaction is not important and the formation of the active aquacomplex Fe (OH)²⁺ is not very affected, at pH 5 the speciation of iron in active or inactive catalysts could explain the behavior observed. Only the presence of a strong complexing agent such as catechol can compete with MIT in the formation of active complexes and the process can degrade the pollutants efficiently. However, the use of HLS cannot compete with MIT to form complexes, and the process is completely ineffective.

2.4. Evidence of the Fe-MIT Complex Formation

Since the speciation of iron in solution becomes more relevant at these pH values higher than the optimum, a possible non-active complex between MIT and iron could explain the inhibitory effect observed when MIT is present. To deal with the mechanistic aspects involved in these different behaviors with different complexing agents, further experiments were carried out and are explained in depth in the following section.

The negative effect of MIT was not only seen in the degradation of parabens but also in the consumption of peroxide, translating into a low consumption of peroxide, as a sign that the redox cycle was not closed, and the reaction was not able to continue. So, the experiments were repeated to see how much peroxide was consumed at each time by the spectrophotometric method and whether there was a relationship. Another possibility would be to prove the formation of the complex using a Job's plot-type technique.

After studying the effect of MIT on hydrogen peroxide consumption, a correlation was observed between the percentage of pollutants removal and the consumption of hydrogen peroxide (Figure 6). The reaction indicated that iron (II) is able to decompose peroxide, resulting in iron (III) and radicals. Iron (III) must return to iron (II) by the photo-reductive process involving the complex. If the complex is not active, iron (III) does not revert to iron (II) and does not decompose peroxide. If the peroxide decomposition rate is low, the redox cycle is not fully completed.

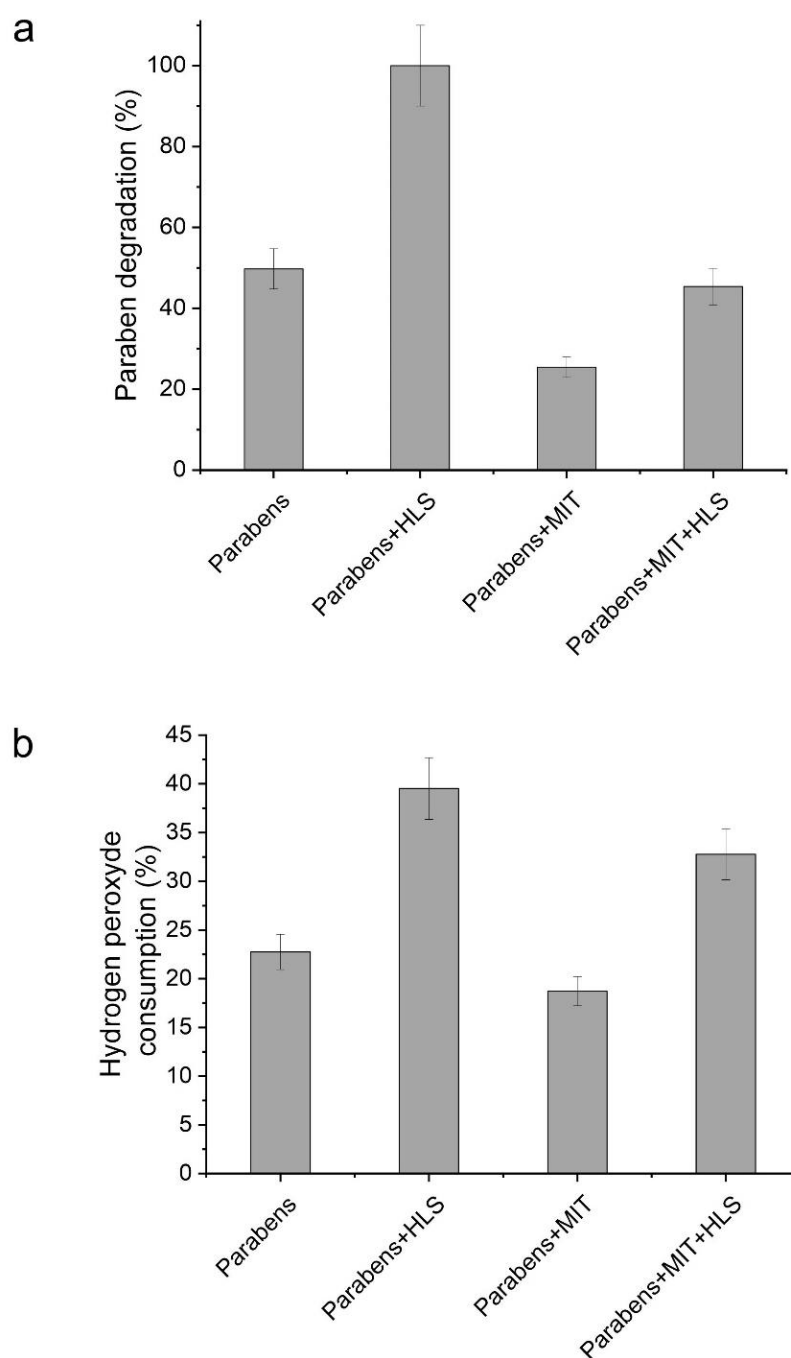


Figure 6. (a) Percentage degradation of parabens after two hours in the presence and absence of MIT and HLS; (b) hydrogen peroxide consumption after two hours of the degradation of parabens in the presence and absence of MIT and HLS.

For example, the presence of HLS as iron complexants strongly enhanced the degradation of the parabens from 50% to 100% degradation after two hours of reaction. In a similar way, the consumption of hydrogen peroxide increased from the 23% to the 40% of the stoichiometric amount. When MIT was present, its inhibitory effect was observed in both parameters, degradation and hydrogen peroxide consumption. In the case of parabens + MIT, the degradation only achieved about 20% and hydrogen peroxide consumption was close to 20%.

As seen in Figure 6b, the consumption of hydrogen peroxide was in all cases lower than the 50% of the stoichiometric amount. For this reason, it was considered interesting to perform the same experiments employing half the stoichiometric amount of hydrogen peroxide. The results comparing the degradation employing the stoichiometric and half the stoichiometric amount of hydrogen peroxide are presented in Figure 7. In all cases, the use of half the concentration of hydrogen peroxide produced lower degradation percentages. In the case of the parabens, parabens + MIT and parabens + MIT + HLS, the differences range from negligible to low. This fact confirms that the low degradation achieved is not related to the amount of available hydrogen peroxide but to the fact that active iron is not present in adequate concentration, due to its precipitation or due to the formation of the inactive complex with MIT. However, in the sample with parabens + HLS, the presence of the complexant of iron ensures its activity and the absence of MIT avoids its inactivation. For these reasons the amount of hydrogen peroxide becomes limiting, and therefore the degradation achieved using half the stoichiometric amount of hydrogen peroxide is clearly lower than achieved using twice the amount of hydrogen peroxide.

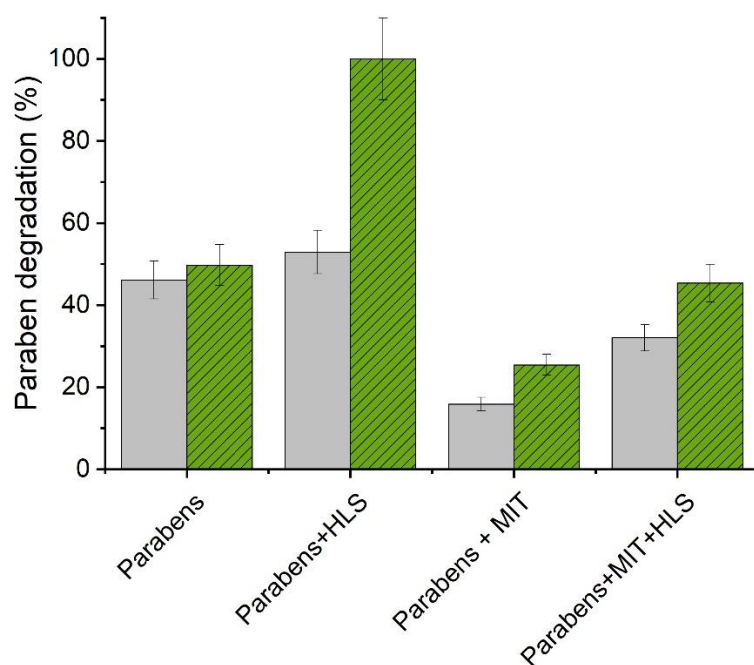


Figure 7. Percentage degradation of parabens after two hours in the presence and absence of MIT and HLS using half the concentration of hydrogen peroxide (grey) vs. using the total concentration of hydrogen peroxide (green with stripes).

Next, a Job's plot analysis was carried out in order to find the molar ratio of the Fe-MIT complex. First, the spectra of the equimolar solutions of iron and MIT in different ratios were obtained. The point of minimum absorbance of the spectra was taken as the notable place since a shift of this point was observed when the amount of MIT was increasing. Starting from this remarkable point, the Job's plot was plotted against the mole fraction of iron (III) (Figure 8). An increase in the corrected absorbance value is observed, indicating an increase in the amount of complex. This increase reaches its maximum at molar fraction of 0.8 and decreases for higher molar fraction values. This maximum corresponds to a complex 1:4 being the ferric anions surrounded by four MIT molecules. This complex should be the main responsible of the photo-Fenton inhibition at pH 5.

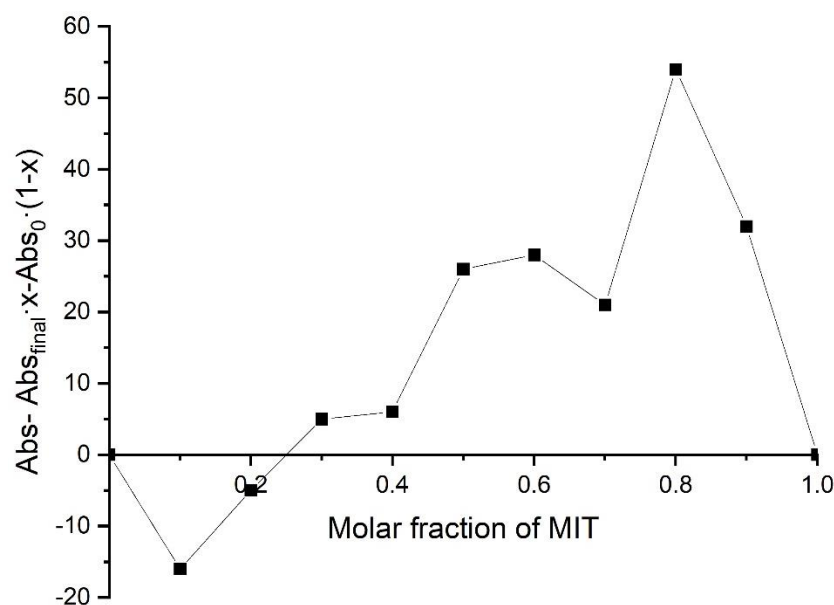


Figure 8. MIT + Fe³⁺ JobPlot at pH 5.

At pH 5, the formation of insoluble and inactive iron species, reduces the amount of iron available to act as a catalyst in the Fenton processes. The addition of complexing agents can improve the solubility of iron but will only be useful if the complex is able to produce the reduction of iron (III) to iron (II). For this reason, the evolution of iron in solution, can shed some light about the amount of iron that could act as a catalyst. This evolution is represented in Figure 8a where the normalized concentration of iron is plot vs the time of reaction in different conditions. Iron concentration was determined by the o-phenanthroline method described in the experimental section. If the process is carried out at pH 2.8 the amount of iron remains maximum during 1 h without suffering any decrease in its concentration. When the same process is carried out at pH 5, the amount of iron in solution decreases drastically to achieve the 15% of the maximum. If HLS are added to the solution at pH 5 the iron in solution rises to a value about 20%. Finally, the addition of MIT to the solution produces the low amount of iron in solution of approximately 10%. It has to be highlighted that some initial values represent only a percentage of the total iron (III) added, since the formation of insoluble/complex species is very fast.

As commented before, a complex can be active or inactive to produce the iron photoreduction but in all cases has to keep iron in solution and stop the precipitation processes. This fact contradicts the results presented in Figure 9a, since the values of dissolved iron in the presence of HLS and MIT are almost as low as in their absence. However, the determination method used is also based on the formation of complexes that have to compete due to the different complexation constants and the concentration of each of them. To evaluate this effect, the initial samples in the presence of MIT and HLS were allowed to react with o-phenanthroline and their absorbances were measured to see the evolution of the concentration. As can be seen in Figure 9b, although the initial concentration values are very low, the colored complex with o-phenanthroline continues forming and the concentration value rises with time until it reaches a value very close to the maximum.

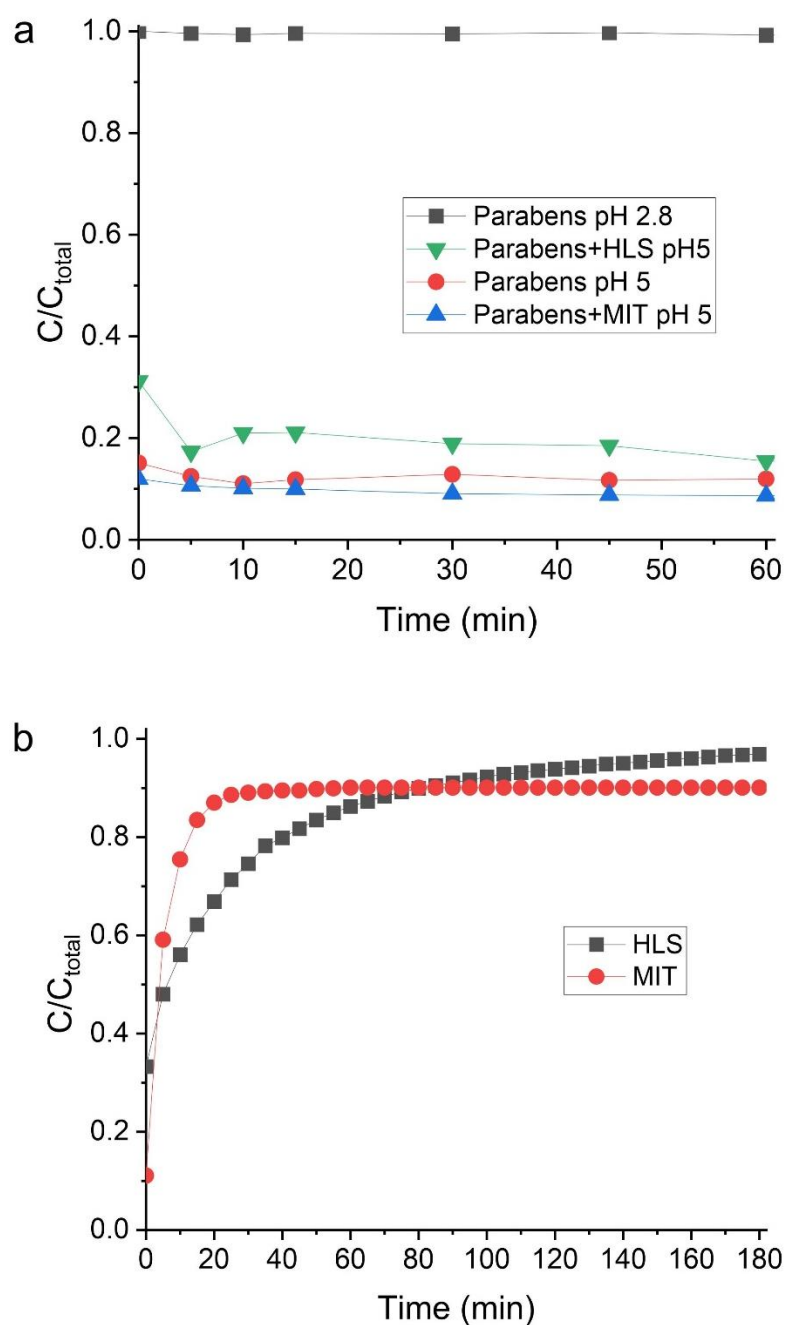


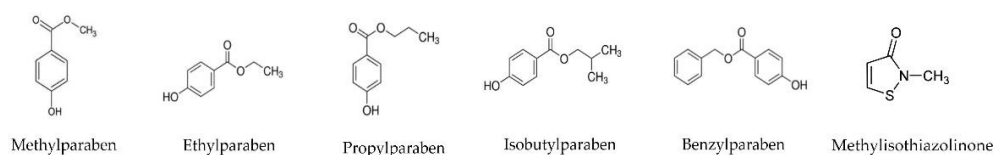
Figure 9. (a) Iron in solution measured by the colorimetric method; (b) stability of iron with different complexing agents through to time at pH 5. $[MIT] = 5 \text{ mg}\cdot\text{L}^{-1}$, $[\text{Fe (III)}] = 5 \text{ mg}\cdot\text{L}^{-1}$, $[\text{HLS Coffee}] = 25 \text{ mg}\cdot\text{L}^{-1}$.

It can be concluded that both complexants have the ability to keep iron in solution but only HLS are able to close the iron redox cycle and maintain the Fenton process running while the inactivity of the MIT complex with iron causes the loss of efficiency in the process.

3. Materials and Methods

3.1. Materials

High purity pollutants (>98%) used as target pollutants 2-methyl-4-isothiazolin-3-one (MIT), methylparaben (MP), ethylparaben (EP), propylparaben (PP), isobutylparaben (IP) and benzylparaben (BP) (shown in Scheme 1) were obtained from Sigma-Aldrich (Madrid, Spain).



Scheme 1. Structures of pollutants used.

Hydrogen peroxide (33% *w/v*) supplied by PanReac was used as the oxidant, and iron (III) chloride hexahydrate (>98%) from Scharlau was used as the iron source, both necessary to perform the Fenton process. In order to stop the reactions before their analysis, the samples were diluted with methanol (99.9%), supplied by PanReac (Barcelona, Spain). Sodium hydroxide solutions prepared from the pure product (>98%) supplied by PanReac and dilute sulfuric acid solutions prepared from the concentrated product (96%), also from PanReac, were used to control the solutions pH. Humic-like substances extracted from coffee waste following the procedure previously described [19] were used as the complexing agent. All aqueous solutions were prepared with ultra-pure water, obtained from a Millipore Milli-Q™ system supplied by Merck Ibérica, Spain.

The eluents for liquid chromatography were aqueous solutions of formic acid (99%) supplied by PROLABO (Barcelona, Spain) and acetonitrile (>99.9%) supplied by PanReac.

3.2. Reactions

The initial concentration of pollutants was 5 mg/L each, accounting for 5 mg/L of MIT and 5 mg/L of each paraben studied (25 mg/L of parabens). All experiments were carried out in 250 mL cylindrical Pyrex reactors with continuous stirring under irradiance of a solar simulator (described below). The corresponding dark Fenton experiments and direct photolysis ones were also carried out in the same conditions. Once the contaminant solution was prepared, the pH was adjusted to 3 and the iron was added at a concentration of 5 mg/L. When the iron complexant was used (humic-like substances), it was added before the iron at a concentration of 25 mg/L. This iron/HLS ratio was previously described to be adequate to optimize the iron complexation and minimize the effects produced by the addition of extra organic matter [20]. After adding the iron, the pH was carefully adjusted to 5 for the experiment. This pH value, right in the middle of the optimal value (3) and neutrality (7), has been determined as optimal for the use of HLS as iron complexing agents in Fenton-like processes [21]. Finally, the corresponding amount of hydrogen peroxide calculated to produce the complete oxidation of the pollutants was introduced into the solution and the reaction started. Other experiments were done by adding half the stoichiometric amount of hydrogen peroxide.

An Oriel Instruments (Newport, United States) model 81160-1000 sunlight simulator was used as the irradiation source. This equipment has a power of 450 W. It consists of a Xenon lamp that produces a spectrum similar to sunlight. A filter system was used to prevent irradiation below 300 nm from producing effects on the sample that would not occur under the actual solar radiation.

Samples were extracted at predetermined time intervals and inactivated with methanol as a radical scavenger when introduced into their corresponding vials to prevent the reaction from continuing in the future analysis in the UHPLC (Ultra-High-Performance Liquid Chromatography). Samples were taken at time intervals between 2 min and 30 min depending on the experiment. The vials have a capacity of 2 mL, containing 0.3 mL of methanol and 1.7 mL of sample. All experiments were done in duplicate, and the error bars were added in the figures.

3.3. Analysis

The concentration of pollutants was monitored by liquid chromatography. A Perkin Elmer (Madrid, Spain) model Flexar UHPLC FX-10, equipped with a reverse phase column C18 was employed. The eluents consisted in formic acid 10 mM and pure acetonitrile grade UHPLC. A gradient of the eluents was applied starting from 20% acetonitrile and 80%

formic acid and reaching 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 employed. The wavelengths employed in the detector were 274 nm for the MIT and 254 nm for all the parabens.

The determination of iron and hydrogen peroxide was performed using colorimetric methods. In the case of iron analysis, a sample of 4 mL was taken and 1 mL of 1,10-phenanthroline and 1 mL of a buffer solution (250 g L⁻¹ of ammonium acetate and 700 mL L⁻¹ of acetic acid) were added. After the addition of a few crystals of ascorbic acid the absorbance of iron was measured at 510 nm.

For the determination of hydrogen peroxide, a sample volume between 1 and 8 mL (depending on the expected concentration) was used, 1030 microliters of ammonium metavanadate solution (0.06 M ammonium metavanadate in 0.36 M sulfuric acid) were added and the flask was filled to a volume of 10 mL with distilled water. The absorbance was measured at 450 nm.

To make the absorbance measurements, a Hitachi UH 5300 spectrophotometer equipped with double beam was employed. Quartz cuvettes were used in all analysis.

To determine the formation of MIT-iron complexes, Job's plot methodology was employed. In this method, equimolar solutions of the two compounds that form the complex are performed. The total molar concentration of the compounds forming the complex remains constant, but their mole fractions are varied. Absorbance, a measurable parameter that is proportional to complex formation, is plotted against the mole fractions of these two components. A special point is determined from the plot and the binding stoichiometry is calculated from the ratio of mole fractions at that special point. A scan of each solution for wavelengths between 220 and 500 nm was performed. Once the data is obtained, $Abs - Abs_{final} \cdot x - Abs_0 \cdot (1-x)$ is plotted against the molar fraction.

4. Conclusions

The degradation of a mixture of five parabens and their most employed substitute, MIT, was studied by the photo-Fenton process at mild conditions (pH 5 and $[Fe^{3+}] = 5 \text{ mg/L}$) and the results were compared with those obtained at the optimal pH of 2.8. In both cases, faster degradation was observed for benzylparaben than for those with aliphatic chains, because of the higher reactivity of $\cdot OH$ towards the aromatic ring. At pH 5 the photo-Fenton process was very inefficient, needing the addition of humic-like substances to act as complexing agents to enhance the efficiency of the process.

In the case of MIT, its removal was very slow at pH 5, even in the presence of HLS from different sources. Only in the presence of catechol, a compound that shows high affinity for iron, MIT degradation was reached at pH = 5. This was attributed to the formation of an inactive Fe-MIT complex that inhibits the photo-Fenton process.

When MIT was introduced in the paraben mix sample, it was observed that the photo-Fenton process was inhibited and the degradation of the parabens was not effective, even in the presence of HLS. This fact, together with a decrease observed in peroxide consumption, is again attributable to the formation of an inactive Fe-MIT complex at pH 5. A Job's plot methodology was also employed to determine the molar ratio of the complex and it was found to be 1:4, a very stable complex form.

Based on these results, further research is needed in order to gain further insight into cross-effects among MIT and other isothiazolinones in photo-Fenton processes, since the presence of these compounds in effluent is growing. Finally, the study of these samples at neutral pH and the complexing ability of new natural HLS is important for ensuring the applicability of the Fenton processes with real wastewaters.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal12111390/s1>, Table S1: Paraben's toxicity data extracted from Environmental Protection Agency (EPA) Test and Table S2: MIT's toxicity data extracted from Environmental Protection Agency (EPA) Test.

Author Contributions: Conceptualization, formal analysis, methodology, investigation, writing—original draft, V.D.-A.; conceptualization, supervision, validation, writing—review and editing, L.S.-J.; supervision, writing—review and editing, funding acquisition, project administration, A.M.A.; writing—review and editing, A.A. All authors have read and agreed to the published version of the manuscript.

Funding: Authors want to acknowledge the financial support of Spanish Ministerio de Ciencia, Innovación y Universidad (RTI 2018-097997-B-C31, Calypsol Project) and Generalitat Valenciana AICO/2021/014.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Daughton, C.G.; Ternes, T.A. Pharmaceuticals and personal care products in the environment: Agents of subtle change? *Environ. Health Perspect.* **1999**, *107*, 907–938. [[CrossRef](#)] [[PubMed](#)]
2. Nowak, K.; Jablonska, E.; Ratajczak-Wrona, W. Controversy around parabens: Alternative strategies for preservative use in cosmetics and personal care products. *Environ. Res.* **2021**, *198*, 110488. [[CrossRef](#)] [[PubMed](#)]
3. Chen, M.-H.; Yu, B.; Zhang, Z.-F.; Ma, W.-L. Occurrence of parabens in outdoor environments: Implications for human exposure assessment. *Environ. Pollut.* **2021**, *282*, 117058. [[CrossRef](#)] [[PubMed](#)]
4. Vale, F.; Sousa, C.A.; Sousa, H.; Santos, L.; Simoes, M. Parabens as emerging contaminants: Environmental persistence, current practices and treatment processes. *J. Clean. Prod.* **2022**, *347*, 131244. [[CrossRef](#)]
5. Amat, A.M.; Arques, A.; Lopez-Perez, M.F.; Nacher, M.; Palacios, S. Effect of Methylisothiazolinone on Biological Treatment: Efficiency of SBRs and Bioindicative Studies. *Environ. Eng. Sci.* **2015**, *32*, 479–485. [[CrossRef](#)]
6. Silva, V.; Silva, C.; Soares, P.; Garrido, E.M.; Borges, F.; Garrido, J. Isothiazolinone Biocides: Chemistry, Biological and Toxicity Profiles. *Molecules* **2020**, *25*, 991. [[CrossRef](#)]
7. Abad-Gil, L.; Lucas-Sanchez, S.; Jesus Gismera, M.; Teresa Sevilla, M.; Procopio, J.R. Determination of paraben-, isothiazolinone- and alcohol-type preservatives in personal care products by HPLC with dual (diode-array and fluorescence) detection. *Microchem. J.* **2021**, *160*, 105613. [[CrossRef](#)]
8. Pastor-Nieto, M.A.; Alcantara-Nicolas, F.; Melgar-Molero, V.; Perez-Mesonero, R.; Vergara-Sanchez, A.; Martin-Fuentes, A.; Gonzalez-Munoz, P.; de Eusebio-Murillo, E. Preservatives in Personal Hygiene and Cosmetic Products, Topical Medications and Household cleaners Spain. *Actas Dermo-Sifiliogr.* **2017**, *108*, 758–770. [[CrossRef](#)]
9. Vasilachi, I.C.; Asiminicesei, D.M.; Fertu, D.I.; Gavrilescu, M. Occurrence and Fate of Emerging Pollutants in Water Environment and Options for Their Removal. *Water* **2021**, *13*, 181. [[CrossRef](#)]
10. Yu, X.; Sui, Q.; Lyu, S.; Zhao, W.; Liu, J.; Cai, Z.; Yu, G.; Barcelo, D. Municipal Solid Waste Landfills: An Underestimated Source of Pharmaceutical and Personal Care Products in the Water Environment. *Environ. Sci. Technol.* **2020**, *54*, 9757–9768. [[CrossRef](#)]
11. Marin, M.L.; Lhiaubet-Vallet, V.; Santos-Juanes, L.; Soler, J.; Gomis, J.; Argues, A.; Amat, A.M.; Miranda, M.A. A photophysical approach to investigate the photooxidation mechanism of pesticides: Hydroxyl radical versus electron transfer. *Appl. Catal. B-Environ.* **2011**, *103*, 48–53. [[CrossRef](#)]
12. Jain, B.; Singh, A.K.; Kim, H.; Lichtfouse, E.; Sharma, V.K. Treatment of organic pollutants by homogeneous and heterogeneous Fenton reaction processes. *Environ. Chem. Lett.* **2018**, *16*, 947–967. [[CrossRef](#)]
13. Pignatello, J.J.; Oliveros, E.; MacKay, A. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Crit. Rev. Environ. Sci. Technol.* **2006**, *36*, 1–84. [[CrossRef](#)]
14. Ahile, U.J.; Wuana, R.A.; Itodo, A.U.; Sha’Ato, R.; Dantas, R.F. A review on the use of chelating agents as an alternative to promote photo-Fenton at neutral pH: Current trends, knowledge gap and future studies. *Sci. Total Environ.* **2020**, *710*, 134872. [[CrossRef](#)]
15. Clarizia, L.; Russo, D.; Di Somma, I.; Marotta, R.; Andreozzi, R. Homogeneous photo-Fenton processes at near neutral pH: A review. *Appl. Catal. B-Environ.* **2017**, *209*, 358–371. [[CrossRef](#)]
16. Santos-Juanes, L.; Amat, A.M.; Arques, A. Strategies to Drive Photo-Fenton Process at Mild Conditions for the Removal of Xenobiotics from Aqueous Systems. *Curr. Org. Chem.* **2017**, *21*, 1074–1083. [[CrossRef](#)]
17. Soriano-Molina, P.; Miralles-Cuevas, S.; Oller, I.; Garcia Sanchez, J.L.; Sanchez Perez, J.A. Contribution of temperature and photon absorption on solar photo-Fenton mediated by Fe³⁺-NTA for CEC removal in municipal wastewater. *Appl. Catal. B-Environ.* **2021**, *294*, 120251. [[CrossRef](#)]
18. Klammerth, N.; Malato, S.; Agueera, A.; Fernandez-Alba, A. Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: A comparison. *Water Res.* **2013**, *47*, 833–840. [[CrossRef](#)]
19. Tolardo, V.; Garcia-Ballesteros, S.; Santos-Juanes, L.; Vercher, R.; Amat, A.M.; Arques, A.; Laurenti, E. Pentachlorophenol Removal from Water by Soybean Peroxidase and Iron(II) Salts Concerted Action. *Water Air Soil Pollut.* **2019**, *230*, 140. [[CrossRef](#)]
20. Caram, B.; Garcia-Ballesteros, S.; Santos-Juanes, L.; Argues, A.; Garcia-Einschlag, F.S. Humic like substances for the treatment of scarcely soluble pollutants by mild photo-Fenton process. *Chemosphere* **2018**, *198*, 139–146. [[CrossRef](#)]

21. Garcia Ballesteros, S.; Costante, M.; Vicente, R.; Mora, M.; Amat, A.M.; Arques, A.; Carlos, L.; Garcia Einschlag, F.S. Humic-like substances from urban waste as auxiliaries for photo-Fenton treatment: A fluorescence EEM-PARAFAC study. *Photochem. Photobiol. Sci.* **2017**, *16*, 38–45. [[CrossRef](#)] [[PubMed](#)]
22. Yin, R.; Chen, Y.; Hu, J.; Lu, G.; Zeng, L.; Choi, W.; Zhu, M. Complexes of Fe(III)-organic pollutants that directly activate Fenton-like processes under visible light. *Appl. Catal. B-Environ.* **2021**, *283*, 119663. [[CrossRef](#)]
23. Sciscenko, I.; Mora, M.; Mico, P.; Escudero-Onate, C.; Oller, I.; Arques, A. EEM-PARAFAC as a convenient methodology to study fluorescent emerging pollutants degradation: (fluoro)quinolones oxidation in different water matrices. *Sci. Total Environ.* **2022**, *852*, 158338. [[CrossRef](#)]
24. Zuniga-Benitez, H.; Penuela, G.A. Methylparaben removal using heterogeneous photocatalysis: Effect of operational parameters and mineralization/biodegradability studies. *Environ. Sci. Pollut. Res.* **2017**, *24*, 6022–6030. [[CrossRef](#)] [[PubMed](#)]
25. Ajiboye, T.O.; Oyewo, O.A.; Onwudiwe, D.C. Photocatalytic removal of parabens and halogenated products in wastewater: A review. *Environ. Chem. Lett.* **2021**, *19*, 3789–3819. [[CrossRef](#)]
26. Tay, K.S.; Rahman, N.A.; Bin Abas, M.R. Ozonation of parabens in aqueous solution: Kinetics and mechanism of degradation. *Chemosphere* **2010**, *81*, 1446–1453. [[CrossRef](#)]
27. Lucas, M.S.; Peres, J.A. Removal of Emerging Contaminants by Fenton and UV-Driven Advanced Oxidation Processes. *Water Air Soil Pollut.* **2015**, *226*, 273. [[CrossRef](#)]
28. Zuniga-Benitez, H.; Munoz-Calderon, A.; Penuela, G.A. Removal of a mix of benzophenones and parabens using solar photo-Fenton and a cylinder parabolic collector in aqueous solutions. *J. Environ. Chem. Eng.* **2018**, *6*, 7347–7357. [[CrossRef](#)]
29. Yang, Z.-W.; Wang, W.-L.; Lee, M.-Y.; Wu, Q.-Y.; Guan, Y.-T. Synergistic effects of ozone/peroxymonosulfate for isothiazolinone biocides degradation: Kinetics, synergistic performance and influencing factors. *Environ. Pollut.* **2022**, *294*, 118626. [[CrossRef](#)]
30. Russo, D.; Cochran, K.H.; Westerman, D.; Puma, G.L.; Marotta, R.; Andreozzi, R.; Richardson, S.D. Ultrafast photodegradation of isoxazole and isothiazolinones by UV₂₅₄ and UV₂₅₄/H₂O₂ photolysis in a microcapillary reactor. *Water Res.* **2020**, *169*, 115203. [[CrossRef](#)]
31. Huang, N.; Shao, W.-T.; Wang, W.-L.; Wang, Q.; Chen, Z.-Q.; Wu, Q.-Y.; Hu, H.-Y. Removal of methylisothiazolinone biocide from wastewater by VUV/UV advanced oxidation process: Kinetics, mechanisms and toxicity. *J. Environ. Manag.* **2022**, *315*, 115107. [[CrossRef](#)] [[PubMed](#)]
32. Gomis, J.; Carlos, L.; Prevot, A.B.; Teixeira, A.C.S.C.; Mora, M.; Amat, A.M.; Vicente, R.; Argues, A. Bio-based substances from urban waste as auxiliaries for solar photo-Fenton treatment under mild conditions: Optimization of operational variables. *Catal. Today* **2015**, *240*, 39–45. [[CrossRef](#)]
33. Moreno-Andres, J.; Valles, I.; Garcia-Negueroles, P.; Santos-Juanes, L.; Arques, A. Enhancement of Iron-Based Photo-Driven Processes by the Presence of Catechol Moieties. *Catalysts* **2021**, *11*, 372. [[CrossRef](#)]
34. Perron, N.R.; Wang, H.C.; DeGuire, S.N.; Jenkins, M.; Lawson, M.; Brumaghim, J.L. Kinetics of iron oxidation upon polyphenol binding. *Dalton Trans.* **2010**, *39*, 9982–9987. [[CrossRef](#)]