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# Enhanced Solar-Photocatalytic Degradation of Combined Chlorophenols Using Ferric Ions and Hydrogen Peroxide

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**ABSTRACT:** The influences of ferric ions ( $\text{Fe}^{3+}$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) on the degradation of combined chlorophenols during solar/ $\text{TiO}_2$  process were investigated. 4-Chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) were used as a chlorophenols combined mixture.  $\text{Fe}^{3+}$  ions have shown considerable effect on the solar-photocatalytic degradation rate of the mixture and its intermediates. Different amounts of  $\text{Fe}^{3+}$  ions were used, and the optimum value was 10 mg/L. At these conditions, three major intermediates were detected including hydroquinone (HQ), phenol (Ph), and 4-chlorocatechol (4-cCat). However, the concentrations of these aromatic intermediates were less than that of using  $\text{TiO}_2$  alone as well as the degradation time was reduced to 150 min.  $\text{H}_2\text{O}_2$  was also effectively used as a degradation enhancer at various concentrations together with  $\text{Fe}^{3+}$  ions in order to improve the solar-photocatalytic degradation rate and the optimum value was 3.41 mM. The degradation efficiency of the combined mixture increased sharply in the presence of  $\text{H}_2\text{O}_2$ . Additionally, an extremely high degradation rate of the main pollutants and their intermediates was achieved when using  $\text{Fe}^{3+}$  ions and  $\text{H}_2\text{O}_2$  together with  $\text{TiO}_2$ . Furthermore, only two intermediates HQ and Ph were observed in this case. The complete degradation of the main chlorophenolic compounds and their intermediates was achieved within 130 min of solar irradiation.

## 1. INTRODUCTION

Chlorinated phenolic compounds such as 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) have been categorized as nonbiodegradable toxic pollutants and have been harmful and dangerous to human, animal, and plant life.<sup>1</sup> For instance, people who have long-term exposure to these toxic contaminants especially at high doses may be more susceptible to carcinogenic diseases.<sup>2</sup> These organic contaminants can be generated and released into the environment in polluted water from sources including petroleum refineries, plastic, and pesticide chemical industries.<sup>3</sup>

Chlorophenols present in water have been widely treated through many different biological and chemical methods. One of the most effective chemical methods which has been reported in the literature is advanced oxidation processes (AOPs).<sup>4,5</sup> The AOPs can be categorized into two main types including homogeneous and heterogeneous processes which can be conducted with or without the use of irradiation. The common homogeneous process called photo-Fenton is the reaction between iron ions and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in the presence of light.<sup>6</sup> Among all heterogeneous methods, the photocatalytic degradation process has been stated as an appropriate technique to destroy and mineralize refractory organic pollutants.<sup>7</sup> The efficiency of this method usually comes by using a suitable photocatalyst such as titanium dioxide ( $\text{TiO}_2$ ) and UV/solar source. However, the main drawbacks of photocatalytic processes is the recombination of charges between  $e^-$  and  $h^+$  leading to reduce the degradation efficiency.<sup>8</sup> To overcome this issue, many techniques have been used in order to enhance the photocatalytic degradation efficiency such as the structural modification and doping of photocatalysts with metals or dyes.<sup>9–11</sup> However, these methods might not be economically feasible for large-scale applications due to the expensive chemicals used and the high calcination temperatures applied.<sup>12</sup> Therefore, the use of metals

like iron ions ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) as additives in the photocatalytic process could reduce the operating cost as well as the experimental procedures. For example, Ortiz-Gomez et al.<sup>13</sup> used ferric ions ( $\text{Fe}^{3+}$ ) as an additive in the photocatalytic degradation process of phenol and other hydroxylated compounds. They concluded that the use of a small amount of  $\text{Fe}^{3+}$  can effectively enhance the mineralization of phenol and its intermediates.

Another effective solution for reducing the  $e^-/h^+$  recombination and enhancing the photocatalytic degradation efficiency is the use of strong inorganic oxidants such as  $\text{S}_2\text{O}_8^{2-}$  and  $\text{H}_2\text{O}_2$ . The addition of  $\text{H}_2\text{O}_2$  to the photocatalytic process helps to accelerate the rate of phenol decomposition by effectively generating hydroxyl radicals that can mineralize organic pollutants.<sup>14</sup> For instance, Aceituno et al.<sup>15</sup> degraded metol using  $\text{TiO}_2/\text{H}_2\text{O}_2/\text{UV}$  and concluded that the  $\text{H}_2\text{O}_2$  oxidant can increase the activity of  $\text{TiO}_2$  leading to enhance the photocatalytic degradation efficiency. Also Nogueira et al.<sup>16</sup> showed by applying the factorial analysis that the roles of both iron and  $\text{H}_2\text{O}_2$  in the solar photodegradation of 4-CP are much more important than that of  $\text{TiO}_2$ . Pouloupoulos and Philippopoulos<sup>17</sup> proved that addition of  $\text{Fe(III)}$  could enhance the photocatalytic oxidation of 4-CP markedly only in the presence of  $\text{H}_2\text{O}_2$ .

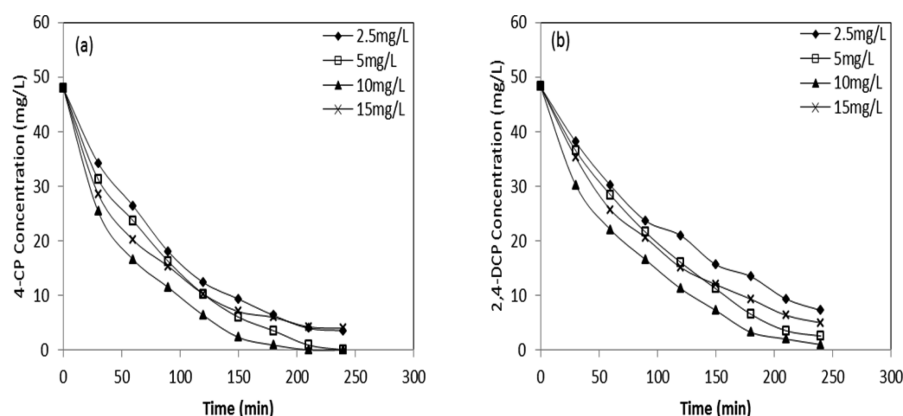
Most of the research studies have used either iron metals or inorganic oxidants in the photocatalytic process. Additionally, all of them have been implemented to degrade one compound.<sup>18–20</sup> However, in real wastewater many toxic organic contaminants can exist, and there is a need to develop

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**Figure 1.** Effect of ferric ions ( $\text{Fe}^{3+}$ ) on the photocatalytic degradation of (a) 4-CP and (b) 2,4-DCP (0.5 g/L  $\text{TiO}_2$ , 1000 mW/cm<sup>2</sup> light intensity).

efficient and economic treatment methods. Therefore, the aim of this study is to investigate the solar-photocatalytic degradation of combined chlorophenols mixture containing 4-CP and 2,4-DCP using a new method which is a hybrid photo-Fenton/photocatalytic (photocatalytic-Fenton) degradation process. The role of hydroxyl radicals in the degradation and a comparison with other existing methods are discussed in detail. Also, the degradation pathways and the reaction mechanism of the chlorophenols mixture are studied.

## 2. EXPERIMENTAL METHODS

**2.1. Materials.** 4-Chlorophenol (4-CP, 99%), 2,4-dichlorophenol (2,4-DCP 98%), hydroquinone (HQ, 98%), 4-chlorocatechol (4-cCat, 99%), phenol (Ph, 99%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30w/w%), and iron(III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) were purchased from Sigma-Aldrich. Titanium(IV) oxide Aeroxide P25 was purchased from Acros Organics (99.5%, New Jersey, USA); this powder is 80% anatase and 20% rutile, with a primary particle size of 21 nm. All chemicals were used as received without further purification. Hydrochloric acid (HCl, 32%) was used to adjust the pH of the reacting mixture. All solutions were prepared with deionized and ultrapure water.

**2.2. Solar-Photocatalytic Degradation Experiments.** A combined chlorophenols mixture (50 mg/L of both 4-CP and 2,4-DCP) was degraded under solar light using  $\text{TiO}_2$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , and  $\text{H}_2\text{O}_2$ . A Pyrex glass beaker of 15.5 cm height and 11 cm diameter was employed as a reactor, equipped with a magnetic stirrer, and the volume of suspension used was 1 L. The experiments were conducted using Solar Simulator (Sun 2000 210 × 210 mm, Abet Technologies Model 11044) to irradiate the reactor. The light intensity of the Solar Simulator was 1000 mW/cm<sup>2</sup>. The pH values of the solutions were monitored using a pH meter (SP-701LI 120). The combined mixture was dissolved in distilled water and transferred to the photoreactor before adding  $\text{TiO}_2$ . After that, the photocatalyst 0.5 g/L  $\text{TiO}_2$  and the desired amounts of ferric ions ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and/or  $\text{H}_2\text{O}_2$  were suspended in 200 mL and then added to the mixture. All suspensions, which contain  $\text{TiO}_2$ , were magnetically stirred in the dark for 30 min to attain adsorption-desorption equilibrium between chemical components and  $\text{TiO}_2$ . Then, the lamp was turned on, and the timer was set to zero to start measuring the reaction time. All experiments were carried out at room temperature ( $26 \pm 1$  °C). At specific time intervals of 30 min, 5 mL was withdrawn and filtered by PTFE 0.45  $\mu\text{m}$  membrane filters to separate the

catalyst particles from the liquid phase, and then the composition of the liquid phase was analyzed by HPLC. The photocatalytic degradation efficiency of each compound at different irradiation times was calculated using eq 1

$$\eta = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

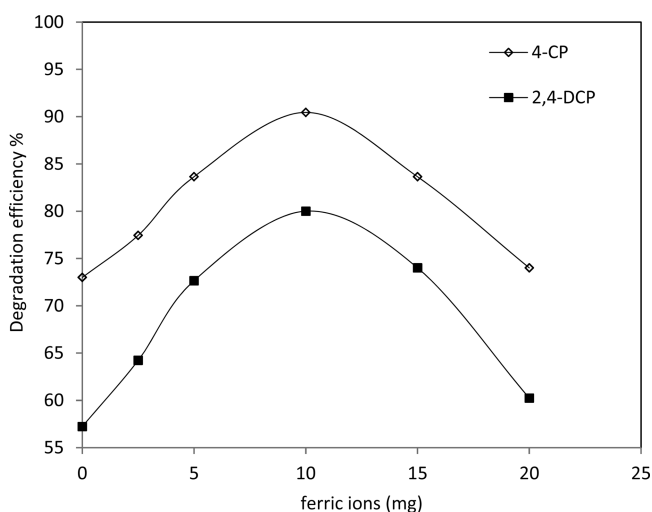
where  $\eta$  is the degradation efficiency,  $C_0$  is the initial concentration, and  $C_t$  is the concentration of the compound at any irradiation time.

**2.3. HPLC Analysis.** 4-CP, 2,4-DCP, and their intermediates were identified and quantified by HPLC analysis. Detection of 4-CP and 2,4-DCP was done at 265 nm and 275 nm, respectively, using a Varian Prostar 210 chromatograph with UV-vis detector and a C18 reverse phase column (25 cm × 4.6 mm × 5  $\mu\text{m}$ ). The mobile phase was a mixture of acetonitrile, acetic acid, and water delivered in the ratio of 0.1 (v/v) with a flow rate of 1 mL/min. The temperature of the column was kept at 25 °C throughout all the analysis. Injection volume for all samples was 5  $\mu\text{L}$ . The identification of the intermediates by HPLC was performed by the comparison of the retention time of the peak in the discharged sample with that in the standard sample. The concentrations of compounds were calculated using the equations derived from the calibration measurements for authentic samples.

## 3. RESULTS AND DISCUSSION

**3.1. Solar/ $\text{TiO}_2$ / $\text{Fe}^{3+}$  Photocatalytic Degradation.** According to the literature the degradation efficiency of the solar/ $\text{TiO}_2$ /oxidant process is higher in an acidic medium than in a basic medium, and thus all experiments were carried out under acidic conditions at pH 3.<sup>11,21</sup> The solar photocatalytic degradation of the combined mixture (50 mg/L of both 4-CP and 2,4-DCP) using 0.5 g/L  $\text{TiO}_2$  and different concentrations of ferric ions  $\text{Fe}^{3+}$  was investigated at pH 3. Figure 1 shows the influence of  $\text{Fe}^{3+}$  on the photocatalytic degradation of both 4-CP and 2,4-DCP in the combined mixture. It can be seen that the degradation increases with the increase of  $\text{Fe}^{3+}$  concentration up to 10 mg/L, and then the degradation starts decreasing. The inhibition of the degradation at high  $\text{Fe}^{3+}$  concentration due to it acts as recombination centers for the  $e^-/h^+$  pairs (eqs 12 and 13).<sup>22</sup> Considering the irradiation time of 150 min (where most of the formed intermediates fully degraded) the maximum achieved photocatalytic degradation efficiencies (eq 1) of 4-CP and 2,4-DCP were 91% and 81% respectively, at 10 mg/L ferric ion, as shown

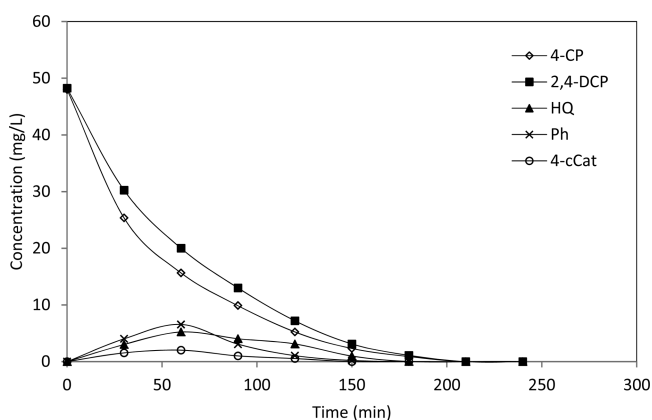
in Figure 2. Ortiz-Gomez et al.<sup>13</sup> studied the influence of ferric ions on the photocatalytic degradation of phenol and found



**Figure 2.** Effect of ferric ions ( $\text{Fe}^{3+}$ ) on the degradation efficiency of 4-CP and 2,4-DCP (0.5 g/L  $\text{TiO}_2$ , 1000  $\text{mW}/\text{cm}^2$  light intensity).

that the optimum value of ferric ions loading was 5 mg/L. They also stated that there is no significant difference between using ferric or ferrous ions in terms of photocatalytic efficiency.

During the solar irradiation time, three organic intermediates namely HQ, Ph, and 4-cCat were detected as shown in Figure 3. The maximum amounts of all these intermediates were at 60

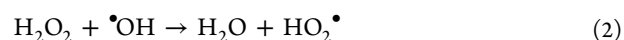


**Figure 3.** Concentration profiles of the combined mixture 50 mg/L of both 4-CP and 2,4-DCP with the optimum value of ferric ions  $\text{Fe}^{3+}$  (10 mg/L) (0.5 g/L  $\text{TiO}_2$ , 1000  $\text{mW}/\text{cm}^2$ ).

min, but most of them were degraded at 150 min solar irradiation time. Compared to our previous work,<sup>23</sup> where no ferric ions were used, the solar photocatalytic degradation time has been significantly reduced from 240 min to about 150 min. This could be attributed to  $\text{Fe}^{3+}$  used as an electron acceptor that will effectively reduce the  $\text{e}^-/\text{h}^+$  recombination by trapping the photogenerated electron ( $\text{e}^-$ ) as well as generating more  $\bullet\text{OH}$  radicals.<sup>24</sup>

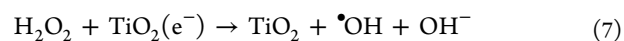
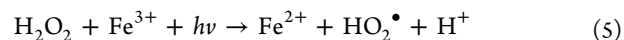
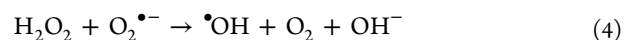
**3.2. Solar/ $\text{TiO}_2$ / $\text{Fe}^{3+}$ / $\text{H}_2\text{O}_2$  Hybrid Process.** In order to enhance the efficiency of the Solar/ $\text{TiO}_2$ / $\text{Fe}^{3+}$  process, different concentrations of  $\text{H}_2\text{O}_2$  were used. To determine the optimum value of  $\text{H}_2\text{O}_2$ , all operating conditions (light intensity,  $\text{TiO}_2$ ,  $\text{Fe}^{3+}$ , and pH) were kept constant. It is evident from Figure 4 that the maximum degradation of 4-CP and 2,4-DCP in the

combined mixture was achieved at 3.41 mM  $\text{H}_2\text{O}_2$  leading to the maximum efficiencies (using eq 1 at  $C_t = 150$  min) of 97% and 91% for 4-CP and 2,4-DCP, respectively (see Figure 5). Aceituno et al.<sup>15</sup> investigated the effect of  $\text{H}_2\text{O}_2$  on the photocatalytic degradation of metol under UV irradiation, and the complete degradation was achieved at 0.4 M of  $\text{H}_2\text{O}_2$  within about 2 h UV irradiation. This low concentration (3.41 mM) of  $\text{H}_2\text{O}_2$  played a significant role in this photocatalytic process by generating more  $\bullet\text{OH}$  radicals which are powerful oxidants for aromatic compounds and enhancing the degradation efficiency. In addition,  $\text{H}_2\text{O}_2$  can be effectively converted to  $\bullet\text{OH}$  radicals by the photocatalytic reaction.<sup>25</sup> However, increasing the amount of  $\text{H}_2\text{O}_2$  further highly reduced the degradation efficiency due to the consumption of  $\bullet\text{OH}$  radicals by  $\text{H}_2\text{O}_2$  eq 2<sup>26</sup>

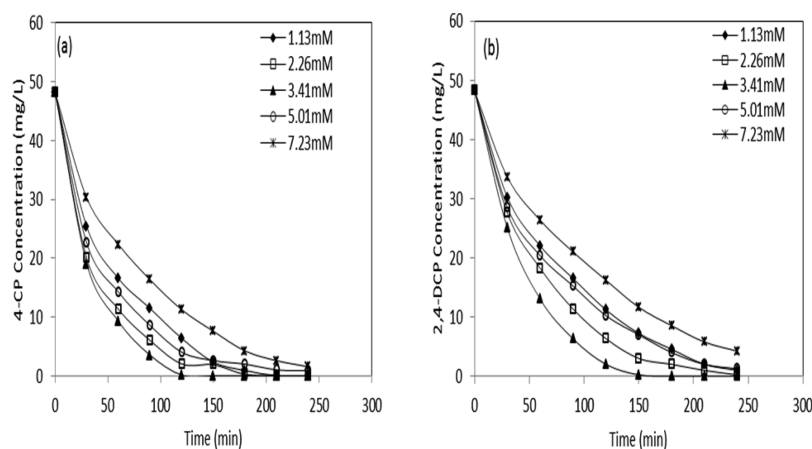


where  $\text{HO}_2\bullet$  is a free radical but it is less reactive than  $\text{OH}\bullet$  radicals.

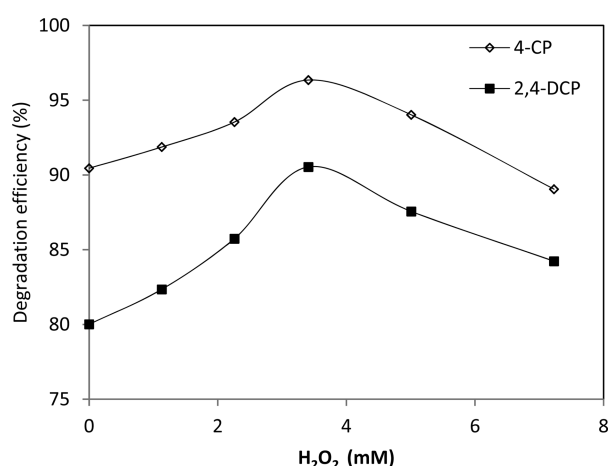
The mechanism of generating the  $\bullet\text{OH}$  radicals with added  $\text{H}_2\text{O}_2$  in the photocatalytic reaction system have been suggested in several studies.<sup>25,27,28</sup>



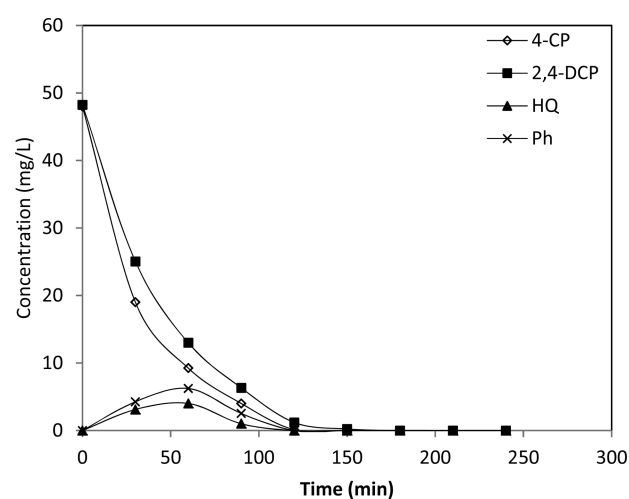
Equations 3-7 obviously explain that  $\text{H}_2\text{O}_2$  reacts by four different ways in the suspension solution all of which lead to generation of  $\bullet\text{OH}$  radicals. First, direct photolysis of  $\text{H}_2\text{O}_2$  by UV light could be the first possibility in this mechanism (eq 3); however, the UV absorption of  $\text{H}_2\text{O}_2$  at 365 nm is extremely low consequently the generation of the hydroxyl radical by photolysis of  $\text{H}_2\text{O}_2$  is highly insignificant.<sup>29</sup> Second, the  $\text{H}_2\text{O}_2$  oxidant might react with superoxide radicals ( $\text{O}_2^{\bullet-}$ ) formed by dissolved oxygen during the solar irradiation time and produced  $\bullet\text{OH}$  radicals (eq 4). However, the amount of  $\text{O}_2$  in the mixture is very low because the experiments were carried out in natural air. Therefore, the amount of  $\bullet\text{OH}$  radicals generated via  $\text{O}_2^{\bullet-}$  has to be very low and inconsiderable. Another chemical reaction route, which can occur in this kind of heterogeneous photo-Fenton degradation process, is the reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{3+}$ . This reaction can be considered as one of the main steps to produce  $\bullet\text{OH}$  radicals due to the influence of solar and UV light (290–400 nm) on  $\text{Fe}^{3+}$  leading to form ferrous ions ( $\text{Fe}^{2+}$ ) and hydroxyl radicals (eqs 5-6).<sup>30</sup> Finally, the most effective degradation reaction in this hybrid degradation process is the reaction of hydrogen peroxide and ferric ions in the presence of  $\text{TiO}_2$  photocatalyst.<sup>17</sup> The presence of  $\text{H}_2\text{O}_2$  together with  $\text{TiO}_2$  can effectively enhance the photocatalytic degradation due to its ability to accept photogenerated electrons from the conduction band leading to enhance the charge separation (eq 7).<sup>31</sup> In addition, it can generate  $\bullet\text{OH}$  radicals according to eqs 3-4. To give this kind of photocatalytic degradation process more enhancements,  $\text{Fe}^{3+}$  ions were added. These ions had a beneficial effect on the photocatalytic activity particularly at low levels due to their acts as  $\text{h}^+/\text{e}^-$  traps and reduce the recombination rate (eqs 8-11).<sup>22</sup>



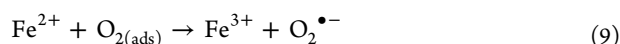
**Figure 4.** Effect of hydrogen peroxide on the photocatalytic degradation of (a) 4-CP and (b) 2,4-DCP (10 mg/L  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.5 g/L  $\text{TiO}_2$ , 1000  $\text{mW}/\text{cm}^2$  light intensity).



**Figure 5.** Effect of hydrogen peroxide on the degradation efficiency of 4-CP and 2,4-DCP (10 mg/L  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.5 g/L  $\text{TiO}_2$ , 1000  $\text{mW}/\text{cm}^2$ ).



**Figure 6.** Concentration profiles of the combined mixture 50 mg/L of both 4-CP and 2,4-DCP with 10 mg/L  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 3.41 mM  $\text{H}_2\text{O}_2$  optimum values (0.5 g/L  $\text{TiO}_2$ , 1000  $\text{mW}/\text{cm}^2$ ).



However, recombination centers of  $\text{h}^+/\text{e}^-$  pairs might be formed by iron ions at high  $\text{Fe}^{3+}$  concentrations leading to decrease of the photocatalytic activity (eqs 12–13).<sup>32</sup>



Figure 6 presents the typical concentration profiles of the combined mixture and their intermediates at optimal conditions of  $\text{TiO}_2$ ,  $\text{Fe}^{3+}$ , and  $\text{H}_2\text{O}_2$ . An extremely important finding from this figure is that one of the main intermediates (4-cCat) has disappeared. In addition, the degradation time was considerably reduced from 150 min for Solar/ $\text{TiO}_2/\text{Fe}^{3+}$  system to less than 120 min for the system with  $\text{H}_2\text{O}_2$ .

**3.3. Solar/ $\text{H}_2\text{O}_2/\text{Fe}^{3+}$  Photo-Fenton.** In order to compare the degradation profile of the photo-Fenton process and Solar/ $\text{TiO}_2/\text{Fe}^{3+}/\text{H}_2\text{O}_2$  photocatalysis, a set of photo-Fenton experi-

ments using 3.41 mM and 10 mg/L of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{3+}$  respectively was carried out. The aim of these experiments is to see the effect of  $\text{TiO}_2$  in the Solar/ $\text{TiO}_2/\text{Fe}^{3+}/\text{H}_2\text{O}_2$  hybrid degradation process. Figure 7 shows the concentration profiles of the combined mixture and their intermediates. It is clear that the photo-Fenton degradation efficiencies of the main pollutants and their intermediates are still less than that of Solar/ $\text{TiO}_2/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ . The combined mixture and the intermediates formed were fully degraded at about 200 min (Figure 7) using the photo-Fenton process, while the full degradation needs about 150 min when the Solar/ $\text{TiO}_2/\text{Fe}^{3+}$  process was applied (Figure 6). Additionally, the organic intermediates found here were HQ, Ph, and 4-cCat, whereas only HQ and Ph were observed in Solar/ $\text{TiO}_2/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ . In order to quantify the enhancement of the combined mixture degradation, the half-life times ( $t_{1/2}$ ) were calculated and summarized in Table 1.

**3.4. Intermediates and Mechanism.** Based on the present results, two reactions pathways for (Solar/ $\text{TiO}_2/\text{Fe}^{3+}$ , Solar/ $\text{H}_2\text{O}_2/\text{Fe}^{3+}$ ) and Solar/ $\text{TiO}_2/\text{Fe}^{3+}/\text{H}_2\text{O}_2$  Hybrid Process were proposed (see Figures 8 and 9). Regardless of the difference in the concentrations of the intermediates Figure 8 shows that in the presence of  $\text{Fe}^{3+}$  or  $\text{H}_2\text{O}_2$  together with  $\text{TiO}_2$





#### 4. CONCLUSION

The results obtained in this study show that the solar-photocatalytic degradation of the chlorophenols combined mixture (4-CP and 2,4-DCP) can be effectively enhanced by adding ferric ions and/or hydrogen peroxide. Three different advanced oxidation processes were conducted including Solar/ $\text{TiO}_2/\text{Fe}^{3+}$ , Solar/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ , and Solar/ $\text{TiO}_2/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ . Among these degradation methods Solar/ $\text{TiO}_2/\text{Fe}^{3+}/\text{H}_2\text{O}_2$  has shown the highest degradation efficiency for the main pollutants and their intermediates. In addition, two main intermediates HQ and Ph were observed instead of three (HQ, Ph, and 4-cCat) in the other methods. The relative efficiencies of these processes are in the following order: Solar/ $\text{TiO}_2/\text{Fe}^{3+}$  < Solar/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  < Solar/ $\text{TiO}_2/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ . According to the presented results, two kinetic reaction pathways for this combined mixture were proposed. This reaction mechanism involved all possible intermediates detected during the degradation.

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##### Notes

The authors declare no competing financial interest.

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