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# Effect of Salinity on the Photo-Fenton Process

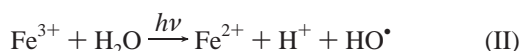
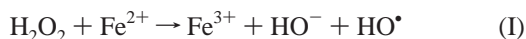
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The existence or presence of diverse hydrocarbons and persistent pollutants in seawater or saline wastewater due to different industrial activities is considerable. The photo-Fenton process is suggested as a possible treatment, but the effect of salinity must be explored. An experimental design is carried out to elucidate the influence of NaCl on the efficiency of the process. According to the results, the global TOC removal is not influenced by the presence of chloride, but the process becomes much slower, even more than 10 times in some of the operating conditions. If solar irradiation is possible, photo-Fenton seems a good option to treat polluted water with high salinity.

## Introduction

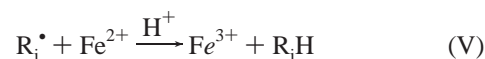
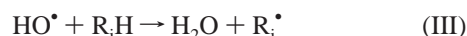
Advanced oxidation processes (AOPs) are promising methods for the remediation of contaminated wastewaters containing non-biodegradable organic pollutants.<sup>1</sup> They are mostly based on the production of hydroxyl radical HO• in water, which is the most powerful oxidizing species after fluorine (2.80 and 3.03 V, respectively).<sup>2</sup> The capability of exploiting the high reactivity of HO• radicals in driving oxidation processes is suitable for achieving the complete abatement and mineralization of the pollutants through even less reactive species.<sup>3</sup> Some of these AOPs, such as photo-Fenton or photocatalysis, are based on the interaction of chemical reagents or catalysts with a light source. The present study deals with a photo-Fenton (or photo-assisted Fenton) process (Ph-F). As it is classically described, hydroxyl radicals are produced in this technique by the decomposition of hydrogen peroxide when reacting with ferrous ions (Fenton reaction;<sup>4</sup> reaction I). Irradiation with sunlight, an artificial light source of wavelength 180–400 nm,<sup>5</sup> or even in the visible spectra<sup>6</sup> increases the rate of contaminant degradation mainly by stimulating the Fe<sup>3+</sup> to Fe<sup>2+</sup> reduction<sup>5</sup> (reaction II).



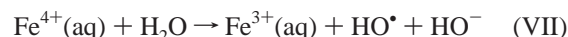
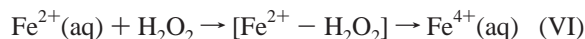
Many photochemical reactions are possible in photo-Fenton systems. Diverse aspects such as the emission spectrum of the light source, concentration, and absorbance of photoactive species and quantum efficiencies affect the contribution of a given reaction of the complex photo-Fenton mechanism.<sup>7</sup> Another effect that has to be considered is the influence of some organic species on the reactivity of iron and consequently on the rate or course of the reaction. As stated by Chen and Pignatello,<sup>8</sup> quinones may act as photocatalysts in the presence of Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> and may cause a reduction even above wavelengths where Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> are not photolyzed, which might enhance the degradation rate. Quinones are frequently found as intermediates of photo-Fenton degradation of aromatic pollutants.

As it is generally accepted, hydroxyl radicals formed by this complex reaction mechanism oxidize organic species (reaction

III), generating organic–radical species, which undergo oxidation up to mineralization, dimerize (reaction IV), or are reduced (reaction V).<sup>4</sup>

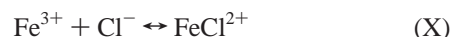


A modern interpretation of Fenton (and photo-Fenton) mechanism assumes that other oxidizing intermediates such as highly valent iron complexes (Fe<sup>4+</sup>) are formed during oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> (reactions VI and VII).<sup>9</sup>



It has been reported that the presence of inorganic ions, such as chloride or sulfate, may decrease the efficiency of the oxidation processes based on the hydroxyl radical HO•.<sup>10</sup> In this sense, De Laat et al.<sup>11</sup> point out that inorganic anions, such as Cl<sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, H<sub>2</sub>PO<sub>4</sub><sup>−</sup>/HPO<sub>4</sub><sup>2−</sup>, and so forth, may produce significant effects on the overall reaction rates in the Fenton process. Anions can capture hydroxyl radicals producing less reactive (than hydroxyl radicals) anion radicals that may react with hydrogen peroxide.

The interaction of chloride on the Fenton mechanism may be due to complexation of Fe<sup>2+</sup>/Fe<sup>3+</sup> with Cl<sup>−</sup> (reactions VIII–XI) or scavenging of hydroxyl radicals (reaction XII)<sup>11,12</sup> which may further generate chloride radicals Cl•, which are less reactive than the hydroxyl radical.



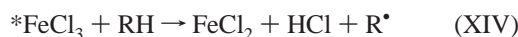
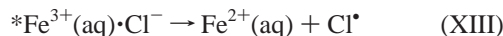
As indicated by Sima and Makánová,<sup>13</sup> Fe<sup>3+</sup> forms complexes



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which undergo thermal or photochemical reduction to  $\text{Fe}^{2+}$ . In the presence of chloride,  $\text{Fe}^{3+}$  forms complexes with unidentate ligands which by absorption of photons drive to complexed or noncomplexed  $\text{Fe}^{2+}$  species, furthermore generating chloride radicals or organic radicals, if organic compounds are present (reactions XIII and XIV)



where the species indicated as  $^*\text{Fe}$  are photoexcited species.

Most of the studies of saline wastewater treatment have been carried out with the Fenton process, that is, without light irradiation. Few works have studied the effects on photo-Fenton treatment. For example, Maciel et al.<sup>14</sup> showed that the abatement of phenol and total organic carbon (TOC) removal in the Fenton process in moderately saline media was improved when using the photo-Fenton process. However, in the highest NaCl concentration tested, the TOC removal achieved was moderate.

A high content of inorganic salts, especially sodium chloride, has been shown in different kinds of wastewaters, such as waters generated during the manufacture of pesticides, herbicides, pharmaceuticals, and dyes.<sup>15</sup> Processes like oil and gas recovery or crystallization also generate wastewater containing a high concentration of salts.<sup>14</sup> Saline wastewater or soil contaminated with hydrocarbons can be found as well in petroleum-based industry sites,<sup>16</sup> as a result of petroleum spills in the sea or over coastal areas or as a result of accidents during transportation.<sup>17,18</sup>

The aim of the present work is to study the effect of NaCl on the photo-Fenton process. Chemical or photochemical oxidation processes, such as AOPs, seem to be appropriate to reduce organic pollution in saline effluents. An experimental design is performed to elucidate the interactive influences of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  (Fenton's reagents) initial concentrations ( $[\text{H}_2\text{O}_2]_0$  and  $[\text{Fe}^{2+}]_0$ , respectively) with NaCl concentration ( $[\text{NaCl}]$ ).

## Materials and Methods

**Photo-Fenton Device and Procedures.** The device consists of a 2.2 L cylindrical reservoir, with three UV 8 W fluorescent tubes placed inside (Philips F8T5/BLB; 340–400 nm with a maximum at 370 nm). The vessel is covered with aluminum foil to avoid losses of light and to avoid the influence of external sources. The device is also equipped with a magnetic stirrer. Photon flow arriving in the system is estimated to be 9.15  $\mu\text{einstein/s}$  by means of actinometry (see analytical methods). A scheme of the installation is shown in Figure 1.

The target solution consists of 2 L of a 200  $\text{mg} \cdot \text{L}^{-1}$  (1.56 mM) 4-chlorophenol (4-CP) aqueous solution. A volume of a concentrated 4-CP solution is acidified with sulfuric acid at a pH of approximately 3 to avoid iron precipitation. Then the necessary amounts of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (as a source of  $\text{Fe}^{2+}$ ) and NaCl are added, and the volume is brought to 2 L. The solution is fed into the reactor and mixed thoroughly. Then the pH is fixed at 2.8. Temperature is maintained at 27 °C. UV fluorescent lamps are switched on to reach stable irradiation. After 5 min, the necessary amount of  $\text{H}_2\text{O}_2$  is added into the reactor under magnetic stirring. The system is allowed to react until all the  $\text{H}_2\text{O}_2$  is consumed. Through the process, samples are withdrawn in timed intervals and immediately quenched with some drops

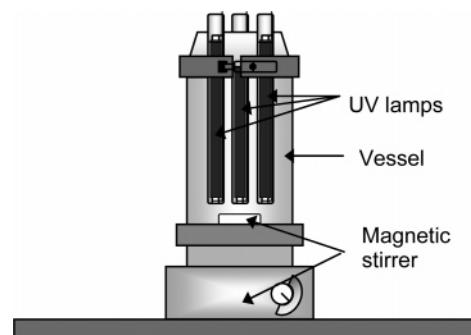


Figure 1. Scheme of the photo-Fenton reactor.

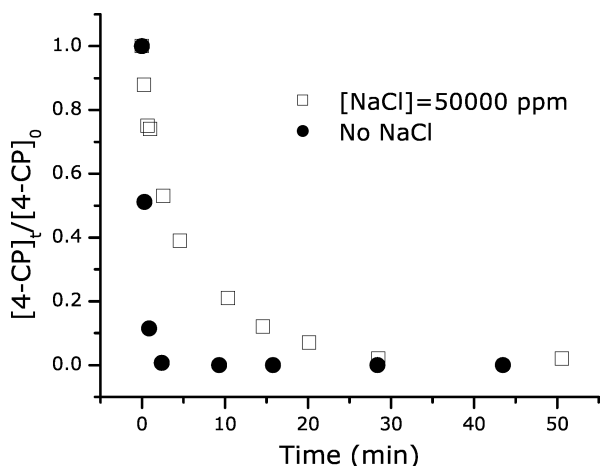
Table 1. Central Composite Design: List of Operating Conditions and TOC Removal Results

experiment number	$[\text{H}_2\text{O}_2]_0$ (ppm)	$[\text{Fe}^{2+}]_0$ (ppm)	$[\text{NaCl}]$ (ppm)	TOC removal ( $\pm 0.021$ )
1	524.5	18.5	26500	0.61
2	524.5	18.5	26500	0.65
3	524.5	35.0	26500	0.75
4	242.0	28.3	12527	0.21
5	807.0	28.3	12527	0.67
6	242.0	8.7	12527	0.11
7	524.5	18.5	26500	0.61
8	50.0	18.5	26500	0.06
9	524.5	18.5	26500	0.61
10	1000	18.5	26500	0.80
11	524.5	18.5	26500	0.65
12	242.0	8.7	40473	0.23
13	807.0	28.3	40473	0.82
14	524.5	2.0	26500	0.75
15	807.0	8.7	40473	0.78
16	524.5	18.5	3000	0.62
17	807.0	8.7	12527	0.74
18	242.0	28.3	40473	0.13
19	524.5	18.5	50000	0.61

of a  $\text{NaHSO}_3$  40% (w/v) solution for measuring the TOC or in the same volume of methanol for measuring the concentration of 4-CP by means of the HPLC. Samples are filtered with Millipore Millex-GV PVDF 0.22  $\mu\text{m}$  filters.

**Experimental Design.** A solution of 200 ppm of 4-CP as a model compound and with different concentrations of NaCl is treated with different initial concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ . The concentrations of salt and Fenton's reagents range from mild conditions ( $[\text{H}_2\text{O}_2]_0 = 50$  ppm;  $[\text{Fe}^{2+}]_0 = 2$  ppm;  $[\text{NaCl}] = 3000$  ppm) to highly concentrated ( $[\text{H}_2\text{O}_2]_0 = 1000$  ppm;  $[\text{Fe}^{2+}]_0 = 35$  ppm;  $[\text{NaCl}] = 50\,000$  ppm). The central composite design (CCD) generates an experimental design of 19 experiments, with 5 replicates of the center point, which are randomly placed (Table 1). Statistical treatment of the data is performed by Statgraphics Plus 4.1 software.

**Analytical Methods.** TOC is analyzed by means of a Shimadzu TOC-VCSN TOC analyzer. The concentration of 4-CP is quantified by means of a high performance liquid chromatograph (HPLC) supplied by Waters Corporation (Milford, MA). The column used was a TR-016059 Tracer Extrasil ODS2 supplied by Tecknokra S. Coop. C. Ltd. (Barcelona, Spain) with a length of 250 mm, an inner diameter of 4.6 mm, and a pore diameter of 5  $\mu\text{m}$ . The mobile phase used was a mixture of acetonitrile (Panreac Quimica, S.A., Spain) and Milli-Q quality water of 40:60 (% by vol), acidified to pH 3 by the addition of phosphoric acid (Panreac Quimica, S.A., Spain). To measure the photon flow arriving at the system, actinometry is carried out. Actinometry is based on the photochemical decomposition of oxalic acid in the presence of uranyl nitrate.<sup>19</sup> The decomposition rate is directly proportional to the photon flow arriving at the system.



**Figure 2.** Normalized 4-CP evolution through two experiments.  $[\text{H}_2\text{O}_2]_0 = 524.5$  ppm;  $[\text{Fe}^{2+}]_0 = 18.5$  ppm.

**Table 2.** Observed Pseudo-First-Order Kinetic Constants for 4-CP Removal

experiment	[NaCl] (ppm)	$k_{\text{obs}}$ ( $\text{min}^{-1}$ )
1	26500	$1.07 \pm 0.18$
16	3000	$2.98 \pm 0.08$
19	50000	$0.45 \pm 0.02$
no NaCl	0	$2.60 \pm 0.19$

## Results and Discussion

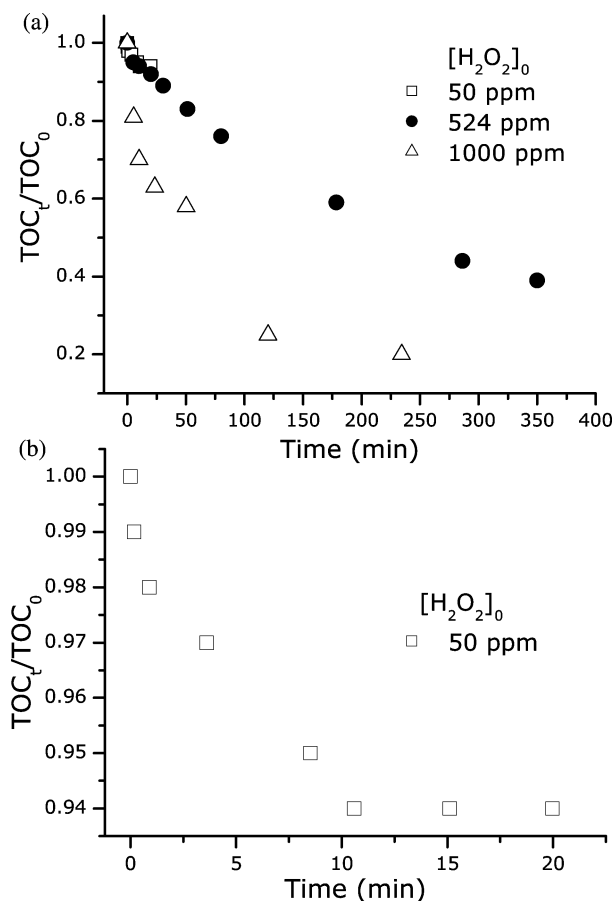
**Effect on 4-CP and TOC Abatements.** The effect of salinity on the 4-CP removal rate is shown in Figure 2. The presence of chloride slows down the removal rate, but the final removal obtained is the same. This fact is observed in all experiments with the same amount of reagents but different concentrations of NaCl. In a more detailed approach, the pseudo-first-order kinetic constants can be taken into account. The 4-CP degradation rate in the early minutes of the experiment can be simplified as shown in eq 1.

$$-\frac{d[4\text{-CP}]}{dt} = k_{\text{obs}}[4\text{-CP}] \quad (1)$$

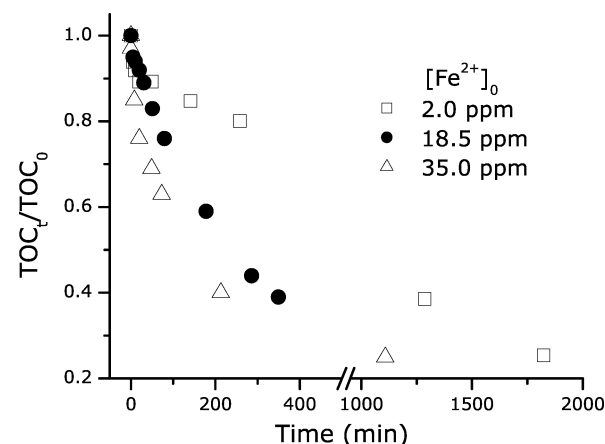
The constant  $k_{\text{obs}}$  is the previously mentioned pseudo-kinetic constant and is calculated by linear regression with a confidence coefficient of 95%. This constant gathers the effects of Fenton's reagent and light radiation. Experiments with the same initial concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  (524.5 and 18.5 ppm, respectively) and different concentrations of NaCl are examined. Results and confidence intervals are shown in Table 2. The experiments with lower concentration of NaCl are proven to have faster kinetics, which means that the production rate of hydroxyl radicals is faster. It can be pointed out that  $k_{\text{obs}}$  with 3000 ppm of NaCl in the solution has the same order of magnitude as that in the experiment without NaCl, which means that at this NaCl concentration the process is not significantly affected. On the other hand,  $k_{\text{obs}}$  is drastically lower for the experiment with 26 500 ppm of NaCl and even less with 50 000 ppm, which means that with this NaCl concentrations, the process kinetics are strongly affected.

In Figures 3 and 4 the evolution of TOC under different conditions is shown. It is remarkable that with higher  $[\text{H}_2\text{O}_2]_0$ , the TOC removal achieved is higher. On the other hand, with different  $[\text{Fe}^{2+}]_0$  the same TOC conversion is achieved, but the removal rate is higher with higher  $[\text{Fe}^{2+}]_0$ .

In Figure 5, the progress of the TOC in the course of two experiments is shown. One is carried out with the highest

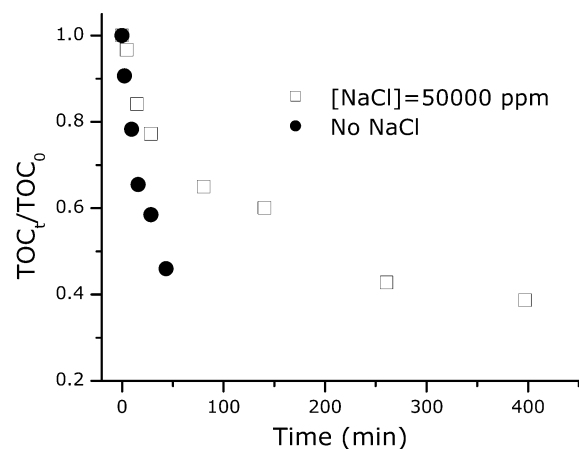


**Figure 3.** TOC evolution in the presence of NaCl. Effect of  $[\text{H}_2\text{O}_2]_0$ .  $[\text{Fe}^{2+}]_0 = 18.5$  ppm;  $[\text{NaCl}] = 26500$  ppm. (a) Three experiments. (b) Enlargement of experiment at  $[\text{H}_2\text{O}_2]_0 = 50$  ppm.

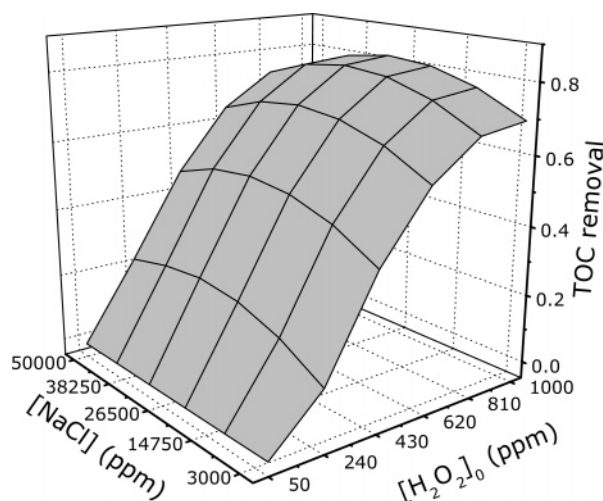


**Figure 4.** TOC evolution in the presence of NaCl. Effect of  $[\text{Fe}^{2+}]_0$ .  $[\text{H}_2\text{O}_2]_0 = 524.5$  ppm;  $[\text{NaCl}] = 26500$  ppm.

amount of NaCl tested, and the other is carried out with the same reagent concentration but without salt. As shown in the figure, TOC removal is around 60% in both experiments and even higher in the presence of NaCl. This fact is due to the low participation of Fenton's scavenging reactions, which are mainly induced by iron. The difference of time for the complete depletion of  $\text{H}_2\text{O}_2$  is significant. Interestingly, TOC conversion achieved with 18.5 ppm of  $\text{Fe}^{2+}$  seems to be lower than with 2 and 35 ppm of  $\text{Fe}^{2+}$  (compare Figures 4 and 5). In the experiment with less iron, we suggest that quinones might enhance the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  which used to occur at low iron concentrations. Also, a considerable number of scavenging reactions, mostly participated by iron, are not



**Figure 5.** Normalized TOC evolution through two experiments.  $[\text{H}_2\text{O}_2]_0 = 524.5$  ppm;  $[\text{Fe}^{2+}]_0 = 18.5$  ppm.



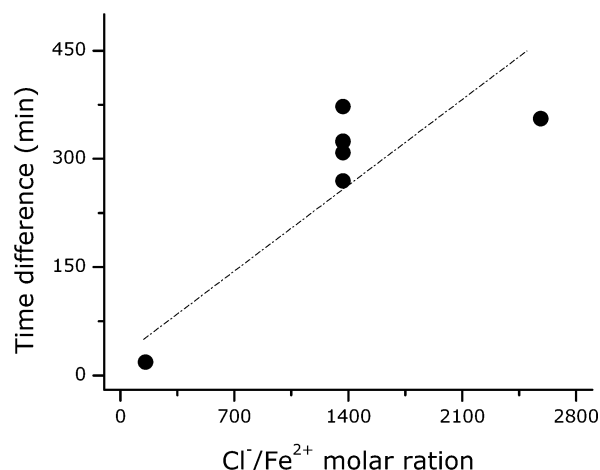
**Figure 6.** Response surface representing TOC removal by photo-Fenton in the presence of NaCl.  $[\text{Fe}^{2+}]_0 = 18.5$  ppm.

promoted. We have not found any convincing explanation for the high conversion with 35 ppm of  $\text{Fe}^{2+}$ . However, the difference is not assessed to be statistically significant, because in the rest of the experiments carried out with 524.5 ppm of  $[\text{H}_2\text{O}_2]_0$  conversion ranges from 61 to 65% (refer to Table 1).

In Figure 6, a response surface representing TOC removal in the presence of NaCl is shown. According to the results and as shown in Figure 6, TOC removal is only affected by  $\text{H}_2\text{O}_2$  loading. It can be emphasized that neither the presence of NaCl nor  $\text{Fe}^{2+}$  concentration produces a significant influence on TOC removal. It should be pointed out that in most of the works concerning the (non-photo-enhanced) Fenton process, TOC removal was significantly affected by the presence of chloride in concentrations of NaCl higher than 2500 mg/L.<sup>14</sup> The response surface can be mathematically described as a quadratic function with the effect of each variable and their interactions. If only the statistically significant variables are taken into account, the function is simplified as described by eq 2. In this case, only  $[\text{H}_2\text{O}_2]_0$  is affecting TOC removal response, as stated above.

$$\begin{aligned} \text{TOC removal} = & -0.20 (\pm 0.08) + 2.21 \times \\ & 10^{-3} (\pm 3.1 \times 10^{-4}) [\text{H}_2\text{O}_2]_0 - \\ & 1.23 \times 10^{-6} (\pm 2.8 \times 10^{-7}) [\text{H}_2\text{O}_2]_0^2 \quad (2) \end{aligned}$$

According to the results, the presence of chloride does not affect the mineralization of organic compounds. Therefore, it



**Figure 7.** Time difference depending on the  $\text{Cl}^-/\text{Fe}^{2+}$  molar ratio in experiments with  $[\text{H}_2\text{O}_2]_0 = 524.5$  ppm. Time difference between an experiment with NaCl and an experiment with the same operating conditions but without NaCl.

seems that the presence of chloride does not affect the amount of oxidizing agents produced but the rate in which they are produced. This fact agrees with the formation of photoactive iron complexes stated in the introduction. The generation of  $\text{Fe}^{3+}$ –Cl complexes (reactions VIII–XI) slows down the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  (reactions XIII and XIV) which is necessary for the continuity of the photo-Fenton mechanism. Consequently, the oxidation of organic matter is slower. Another event that might contribute to the reduction of  $\text{Fe}^{3+}$  and, hence, to the continuity of the process is the generation of quinones, as intermediates of aromatics degradation. However, their presence over the process might be short, because quinones are the earliest byproducts. In most of the experiments a high dose of  $\text{H}_2\text{O}_2$  is used, and high levels of mineralization are achieved.

If the effect on process duration is taken into account it should be emphasized that the influence of NaCl might severely affect the economy of the process. In a previous work,<sup>20</sup> a strong influence of the duration of the process on the operating costs is described. Figure 7 shows the time difference for total depletion of  $\text{H}_2\text{O}_2$  between experiments at  $[\text{H}_2\text{O}_2]_0 = 524.5$  ppm of the current experimental design and experiments with the same operating conditions but without NaCl. The dependence is represented in front of the molar ratio  $\text{Cl}^-/\text{Fe}^{2+}$ . As shown in the figure, when the ratio is higher, that is, when the concentration of salt is high and/or the concentration of  $\text{Fe}^{2+}$  is low, the difference increases significantly. The dashed line indicates a qualitative tendency. This fact reaffirms the importance of the influence of chloride on the iron mechanism and minimizes the possible scavenging of hydroxyl radicals by chloride.

In recent experiments (not shown) we have seen that the presence of anion phosphate ( $\text{PO}_4^{3-}$ ) stops the process almost completely and affects severely TOC removal, like in the Fenton process. Also other authors<sup>21</sup> have dealt with this problem. The formation of iron–phosphate complexes is described as a method in wastewater treatment to precipitate and separate phosphate. Up to now, this problem has been solved by the addition of more iron sulfate to carry out photo-Fenton. This effect should be investigated in more detail to find another solution.

## Conclusions

The presence of chloride slows down the process but, according to our results, does not affect the overall TOC



removal. Thus, the anion seems to affect strongly the iron mechanism, as a result of the generation of iron–chloride complexes, but does not produce scavenging of hydroxyl radicals. In the photochemically enhanced Fenton process, unlike the Fenton process, the generated iron–chloride complexes, which are photoactive,<sup>11</sup> take part in the process but at a slower rate. As during photo-Fenton degradation of 4-CP quinones are generated as intermediates, these conclusions must be a priori restricted to wastewaters containing aromatic compounds, because of the influence of quinones on Fe<sup>3+</sup> reduction. More research with nonaromatic species should be done to know if these conclusions may be extrapolated as a feature of the photo-Fenton process.

Mineralization of organic matter (TOC removal) can be described as a function of H<sub>2</sub>O<sub>2</sub> loading as a sole parameter, which means that Fe<sup>2+</sup> and NaCl do not affect the overall degradation.

The experimental design has been shown to be a suitable tool to study the overall effect of chloride on the TOC removal. To model the behavior of the system it is necessary to perform detailed analysis on the H<sub>2</sub>O<sub>2</sub> degradation kinetics and the Fe<sup>2+</sup>/Fe<sup>3+</sup> remaining in the solution. Although mineralization is not affected by salinity, the process is very slow, and it would be economically unacceptable if an artificial radiation source is used. Solar photo-Fenton is strongly advised.

## Acknowledgment

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