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Evaluation of operational parameters involved in solar photo-Fenton degradation of a commercial pesticide mixture

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ABSTRACT

Photo-Fenton degradation of a mixture of commercial pesticides typically used in greenhouse agriculture, Vydate® (10% oxamyl), Metomur® (20% methomyl), Couraze® (20% imidacloprid), Ditimur-40® (40% dimethoate) and Scala® (40% pyrimethanil), has been evaluated. The experiments were performed at an original dissolved organic carbon of 200 mg/L (40 mg/L of each commercial pesticide). A battery of degradation studies was carried out under sunlight at the Plataforma Solar de Almeria in a pilot plant specially developed for photo-Fenton applications. Photo-Fenton efficiency gradually rose with temperature. Nevertheless, at 50 °C there was a decrease in efficiency. The influence of Cl^- and SO_4^{2-} between 100 and 2000 and 50 and 500 mg/L, respectively, was also analyzed. A central composite experimental design and its surface response analysis were employed to study the effect of these anions.

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1. Introduction

In the last few years, exponential growth of intensive agriculture in the Mediterranean Basin has polluted water with pesticides. These compounds are usually toxic, recalcitrant to biological treatment, and tend to accumulate in the environment, causing pollution to be long-term. EU legislation has become increasingly strict, and has designated pesticides as Priority Organic Pollutants (POPs) [1] to protect and improve the quality of European water sources. The European Commission has adopted a proposal for a new Directive to protect surface water from pollution [2]. The proposed Directive, which is required to support the Water Framework Directive (WFD), will set limits on surface-water concentrations of hazardous chemical substances posing particular risk to animal and plant life in the aquatic environment and to human health. This proposal is part of the new chemical pollution of water strategy introduced by the WFD.

In this context, the development of specific detoxification technologies is required for wastewater with these POPs. Advanced oxidation processes (AOPs) have been described as efficient chemical-oxidative technologies for the decontamination of a wide variety of wastewater containing recalcitrant substances [3]. AOPs are characterized by the production of hydroxyl radicals ($^{\bullet}OH$), which are powerful unselective oxidants (2.8 V vs. standard hydrogen electrode) able to oxidize and mineralize almost any organic molecule, yielding CO_2 and inorganic anions. Of the AOPs, Fenton and Fenton-like reactions are among the most widely employed and studied for oxidizing organic pollutants in many applications [4]. The first proposals for wastewater treatment applications were reported in the sixties [5]. Yet it was not until the early nineties when the first articles on application of photo-Fenton (or photoassisted/light-enhanced Fenton process) to wastewater treatment were published [6–10] However, the number of publications on photo-Fenton has risen continuously over the last fifteen years, to-date surpassing 500 peer-reviewed publications (source: http://www.scopus.com). Photo-Fenton seems to be the most apt of all the AOPs for being driven by sunlight, because soluble iron-hydroxyls, and especially iron–organic acid complexes, not only absorb ultraviolet radiation, but even part of the visible light spectrum. The photo-Fenton system is therefore a very efficient reaction system for the generation of radicals for oxidative processes.

This study evaluates the influence of some important parameters involved in the practical application of solar photo-Fenton, such as the presence of certain inorganic species and the temperature inside the photoreactor. Both these parameters affect the system kinetics, and have been studied in depth by several different authors as reviewed recently by Pignatello et al. [4]. But to our knowledge no study has ever evaluated these parameters as a whole, taking into account other treatment operating parameters, such as hydrogen peroxide consumption, iron concentration and treatment time.

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The present study evaluates the influence of temperature and the presence of Cl^- and SO_4^{2-} on other operating parameters during the solar photo-Fenton degradation of a mixture of five commercial pesticides present in wastewaters coming from intensive agriculture activities (washing waters from dosing equipments, fruits and vegetables washing, etc.) in order to scale up the technology to real application. A central composite design was applied for the salt influence study.

2. Experimental

2.1. Chemicals

Commercial formulations of Vydate® (10%, w/v, oxamyl, $C_7H_{13}N_3O_3S$), Metomur® (20%, w/v, methomyl, $C_5H_{10}N_2O_2S$), Couraze® (20%, w/v, imidacloprid, $C_{16}H_{22}ClN_3O$), Ditimur-40® (40%, w/v, dimethoate, $C_5H_{12}NO_3PS_2$) and Scala® (40%, w/v, pyrimethanil, $C_{12}H_{13}N_3$) were used as received. Diagram 1 shows the pesticide chemical structures. Analytical standards (>98%) for chromatographic analyses were purchased from Sigma–Aldrich.

Distilled water used in the pilot plant was supplied by the Plataforma Solar de Almería (PSA) distillation plant (conductivity < 10 μS/cm, Cl^- = 0.2–0.3 mg/L, $NO_3^- < 0.2$ mg/L, organic carbon < 0.5 mg/L). The photo-Fenton experiments were performed using $Fe(NO_3)_3{\cdot}9H_2O$, reagent-grade hydrogen peroxide (30%, w/v) and nitric acid (65%) for pH adjustment (around 2.7–2.9) to avoid sulfate interference from reagents, all purchased from Panreac.

2.2. Analytical determinations

High-performance liquid chromatography (HPLC) (Agilent Technologies, series 1100) was used to monitor the pesticide concentrations during degradation with a UV-DAD detector and a C-18 column (LUNA 5 μm, 3 mm × 150 mm from Phenomenex) as the stationary phase. The mobile phase consisted of a mixture of 15% HPLC-grade acetonitrile, and 85% ultrapure water (Millipore Co.). Detection was done at three different wavelengths depending on the pesticide: 210 nm (dimethoate and pyrimethanil), 234 nm (methomyl and oxamyl) and 270 nm (imidacloprid). Mineralization was followed by measuring the dissolved organic carbon (DOC) by direct injection of filtered samples into a Shimadzu-5050A TOC analyzer with an NDIR detector and calibrated with standard solutions of potassium phthalate. Total iron concentration was monitored by colorimetric determination with 1,10-phenanthroline, according to ISO 6332, using a Unicam-2 spectrophotometer. Hydrogen peroxide was analyzed by a fast, simple spectrophotometric method using ammonium metavanadate, which allows the H_2O_2 concentration to be determined immediately based on a red orange peroxovanadium cation formed during the reaction of H_2O_2 with metavanadate, maximum absorption of which is at 450 nm. The peroxide concentrations are calculated from absorption measurements by a relation found by Nogueira et al. [11]. Anion concentrations (Cl^-, NO_3^- and SO_4^{2-}) were determined with a Dionex DX-600 ion chromatograph using a Dionex Ionpac AS11-HC 4 mm × 250 mm column. The gradient program for anion determination was pre-run for 5 min with 20 mM NaOH, an 8-min injection of 20 mM of NaOH, and 7 min with 35 mM of NaOH, at a flow rate of 1.5 mL/min.

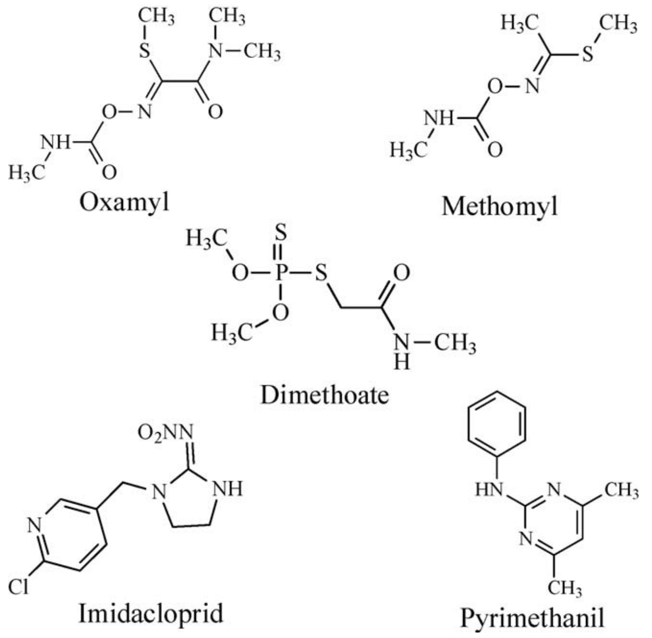

Diagram 1. Pesticide chemical structures.

2.3. Experimental set-up

2.3.1. Solar reactors

Photo-Fenton experiments were carried out under sunlight in a pilot plant specially developed for photo-Fenton applications, installed at the Plataforma Solar de Almeria (PSA). It is equipped with on-line measurement sensors for T, pH and dissolved oxygen, and connected to a PC for data acquisition and process control decisions. The plant also incorporates heating and cooling devices to control reaction solution temperatures during an experiment. A diagram of this system has been published elsewhere [12]. It consists of four compound parabolic collectors (CPCs), a reservoir tank, a recirculation pump and connecting tubing. Solar ultraviolet radiation (UV) was measured by a global UV radiometer (KIPP&ZONEN, model CUV 3) mounted on a platform tilted 37° (the same as the CPCs). With Eq. (1), combination of the data from several days' experiments and their comparison with other photocatalytic experiments is possible [13].

$$t_{30W,n} = t_{30W,n-1} + \Delta t_n \frac{UV}{30}\frac{V_i}{V_T}; \quad \Delta t_n = t_n - t_{n-1} \tag{1}$$

where t_n is the experimental time for each sample, UV is the average solar ultraviolet radiation measured during Δt_n, and t_{30W} is a "normalized illumination time". In this case, time refers to a constant solar UV power of 30 W/m^2 (typical solar UV power on a perfectly sunny day around noon). V_T is the total volume of the water loaded in the pilot plant (75 L), V_i is the total irradiated volume (44.6 L).

All photo-Fenton experiments were carried out at an initial DOC of 200 mg/L (40 mg/L of each commercial pesticide), at a pH adjusted to 2.7–2.9 and hydrogen peroxide concentration kept between 100 and 300 mg/L throughout the process. The mixture of pesticides was added directly into the pilot plant and homogenized by turbulent recirculation for half an hour. In experiments with water containing chloride and sulfate, the salts were added at the same time as the pesticide mixture. With the collectors covered, the pH was adjusted and iron salt was added. Then 200 mg/L of hydrogen peroxide were added and the collectors were uncovered, which is when photo-Fenton began. Hydrogen peroxide was measured frequently and consumed reagent was continuously replaced so as to maintain an excess of H_2O_2 (100 and 300 mg/L).

2.4. Experimental design

A central composite design was employed to evaluate the influence of chloride and sulfate concentration on photo-Fenton degradation of a mixture of commercial pesticides. This design includes low (−) and high (+) levels, and center points for Cl^- and SO_4^{2-} concentrations. It is based on a star design with two variables (Cl^- and SO_4^{2-}) at two levels, consisting of three types of experiments: 2^k coded values (in our case $k = 2$ and consists of four experiments), four modified axial or star points (±1.01 and 0 instead of normalized ±1.41 in order to avoid negative concentration values) and three replicates of the central point (0,0). Eleven experiments were performed according to this experimental design; varying both salt concentrations within a range usually found in natural water. The limits for the Cl^- and SO_4^{2-} concentrations were 100–2000 and 50–500 mg/L, respectively, simulating the typical wastewater range. The Minitab15® software statistical tool was employed to analyze the central composite design and to plot the response surfaces. The response factors considered in this study were H_2O_2 consumption and the illumination time (t_{30W}) needed to achieve pesticide active ingredient degradation below 1 mg/L and 50% mineralization of the initial DOC. Both parameters are considered critical points in the optimization and economic evaluation of a photo-Fenton degradation process. Of the operating costs, the cost of hydrogen peroxide is the most important, and illumination time governs the solar plant size, i.e., total surface of solar collectors, which make up the most important investment cost [14]. Moreover, they are considered the most important elements in the overall environmental impact of solar photo-Fenton [15].

3. Results and discussion

The study presented in this paper is part of a larger study evaluating the main parameters governing pilot-scale solar photo-Fenton wastewater treatment. A first part recently accepted [16] dealt with the comparison of Fe^{2+} and Fe^{3+} at different concentrations in Fenton and photo-Fenton, along with evaluation of process toxicity and biodegradability. Toxicity and biodegradability thresholds were reached at 50% mineralization of the original DOC, and when active ingredients in the pesticide formulations were below 1 mg/L, respectively. One of the main conclusions arrived at was that the use of ferrous or ferric ions as the catalyst source in photo-Fenton reactions was not critical, as results were comparable for both in terms of degradation of active ingredients and mineralization. Iron concentration tests performed showed that process efficiency was higher and hydrogen peroxide consumption lower as the Fe concentration rose until its stabilization between 20 and 55 mg/L. However, due to the photoreactor design (5-cm light pathlength), 20 mg/L iron concentration is enough to absorb all the solar irradiation [17], and also more advisable, as the effluent is more compatible with follow-up biotreatment [18].

In view of these results, Fe^{3+} at 20 mg/L was used to study the influence of temperature and chloride and sulfate concentrations on photo-Fenton degradation of the commercial pesticide mixture.

3.1. Influence of temperature

It is well known that temperature is an important parameter of the photo-Fenton process [4,19,20]. Therefore, its influence on photo-Fenton degradation of the commercial pesticide mixture has been studied. A battery of experiments was carried out at four different temperatures (25, 35, 42 and 50 °C) in order to find the most favorable process condition. Fig. 1 shows the mineralization of the pesticide mixture at the four temperatures tested. Temperatures over 50 °C were not tested, as solar CPC photocatalytic plants cannot be operated at higher temperatures in real applications.

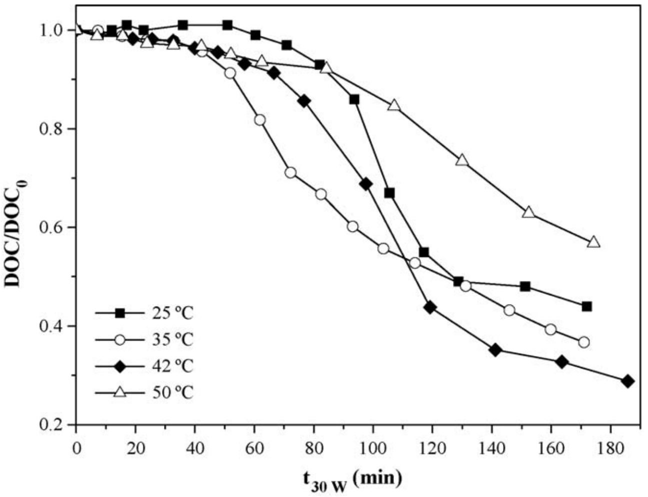

Fig. 1. Mineralization of the pesticide mixture (DOC_0 = 200 mg/L and 20 mg/L Fe^{3+}) at different temperatures (25, 35, 42 and 50 °C).

As expected, photo-Fenton efficiency (faster pesticide degradation, shorter illumination time required for substantial mineralization and less hydrogen peroxide consumption) rose gradually with temperature in experiments at 25, 35 and 42 °C. This could be explained by a faster rate of ferrous regeneration from ferric ion, which is even faster as the temperature increases, allowing Fe^{2+} available to generate hydroxyl radicals. This effect has been observed before [19,21]. Nevertheless, at 50 °C the degradation process was significantly slower, reducing only 44% of the original DOC in 175 min of illumination time, while at 42 °C, 70% was mineralized in this time. This is because in the 50 °C experiment, a significant loss of iron by precipitation was detected at the beginning of the process. In the first 10 min of illumination time, 50% of the iron was precipitated, with a consequent decrease in photo-Fenton process efficiency. Precipitation, which is temperature dependent, is faster and heavier at higher temperatures [22]. Therefore, decrease in catalyst concentration has a negative effect on the process, neutralizing the advantage of higher temperature. This decrease in photo-Fenton degradation rate at around 45 °C was also observed by Pérez-Moya et al. [23] in the degradation of 2-chlorophenol. The authors related this decrease to the rise in hydrogen peroxide decomposition rate with temperature. Otherwise, there were no important differences in H_2O_2 consumption in the experiments shown in Fig. 1 at the four temperatures tested, which means that the temperature only affected illumination time, but did not modify H_2O_2 consumption. In this case, hydrogen peroxide was still being used efficiently in all the experiments, as iron precipitation was the reason for lower efficiency. As the best operating temperature range for practical applications was found to be 35–45 °C, 35 °C was selected for further study.

3.2. Influence of Cl^- and SO_4^{2-}

Inorganic ions (Cl^-, SO_4^{2-}, PO_4^{3-}, etc.) present in natural wastewater may have a significant effect on the photo-Fenton degradation rate of organic compounds due to complexation of these ions with Fe^{2+} or Fe^{3+}, or to the scavenging of hydroxyl radicals and formation of less reactive inorganic ions [24]. Therefore, the second goal of this study was to evaluate the influence of Cl^- and SO_4^{2-} anions on the rate at which photo-Fenton degrades the commercial pesticide mixture, as these ions are commonly present in tap waters and rural and municipal wastewaters from the Mediterranean Basin zone in the selected concentration ranges (100–2000 and 50–500 mg/L, respectively). Eleven photo-Fenton degradation experiments were carried out with varied amounts of Cl^- and SO_4^{2-}, according to the central composite design described above. In view of the results of the previous iron and temperature studies, the general operating conditions were set at 200 mg/L of initial DOC, 20 mg/L of Fe^{3+} and 35 °C. In this case, HNO_3 (65%) was used for pH adjustment and $Fe(NO_3)_3 \cdot 9H_2O$ was added as ferric iron salt so as not to add more sulfate to the solution. Consequently, there was a fixed amount of NO_3^- anions in the solution (approximately 150 mg/L) in all the experiments, in addition to Cl^- and SO_4^{2-} anions. Previously published articles have reported the negligible influence of NO_3^- on photo-Fenton [24,25]. Degradation of the active ingredients contained in the commercial pesticide mixture (oxamyl, methomyl, imidacloprid, dimethoate and pyrimethanil) was also monitored during the experiments by HPLC analysis, and the concentration of the anions Cl^-, SO_4^{2-} and NO_3^- was measured in samples from each experiment in order to assure the correct ion content (results not shown). The distribution of the Cl^- and SO_4^{2-} concentration throughout the experiments and the results are summarized in Table 1. As explained above, the critical parameters to be evaluated for comparison are H_2O_2 consumption and illumination time. For interpretation of results, these variables were evaluated at two different points in the photo-Fenton process: 50% mineralization and degradation of the active ingredients (to below 1 mg/L). These limits were selected based on the toxicity and biodegradability results found in the study mentioned above.

The response surfaces built up with the experimental data in Table 1 (95% confidence level) represent the effect of chloride and sulfate at different concentrations on H_2O_2 consumption and illumination time required for the elimination of the active ingredients (to below 1 mg/L) and for 50% mineralization. The results are shown in Figs. 2 and 3.

It has been reported that photo-Fenton process efficiency is noticeably lowered in presence of chloride and sulfate ions [26]. There are two different reasons for this:

(1) Decreased generation of hydroxyl radicals because of the formation of chloro- and sulfato-Fe(III) complexes that affect the distribution and reactivity of the iron species ($FeCl^+$, $FeCl^{2+}$, $FeCl_2^+$, $FeSO_4^+$, $Fe(SO_4)_2^-$).
(2) Scavenging of hydroxyl radicals and formation of inorganic radicals ($Cl_2^{\bullet-}$ and $SO_4^{\bullet-}$), which are less reactive than $^{\bullet}OH$.

As observed in Fig. 2a and b, the presence of sulfate did not significantly affect the H_2O_2 consumption needed for the degradation of the pesticides below 1 mg/L and the 50% of mineralization (only between 12 and 15% of variation). Nevertheless, there was a slight increase in consumption between approximately 0 and 300 mg/L of SO_4^{2-}. This can be justified because in the presence of small quantities of SO_4^{2-}, part of the H_2O_2 is inefficiently consumed by $SO_4^{\bullet-}$ (Reactions (2)–(4)), which raises overall H_2O_2 consumption. However, at higher sulfate concentrations, the H_2O_2 consumed decreased gradually. Furthermore, it has also been reported [27] that sulfate radicals are predominant oxidizing species under high concentrations of sulfate, and in this case, as they are also powerful oxidizing species, they may also contribute to the degradation of organic solutes.

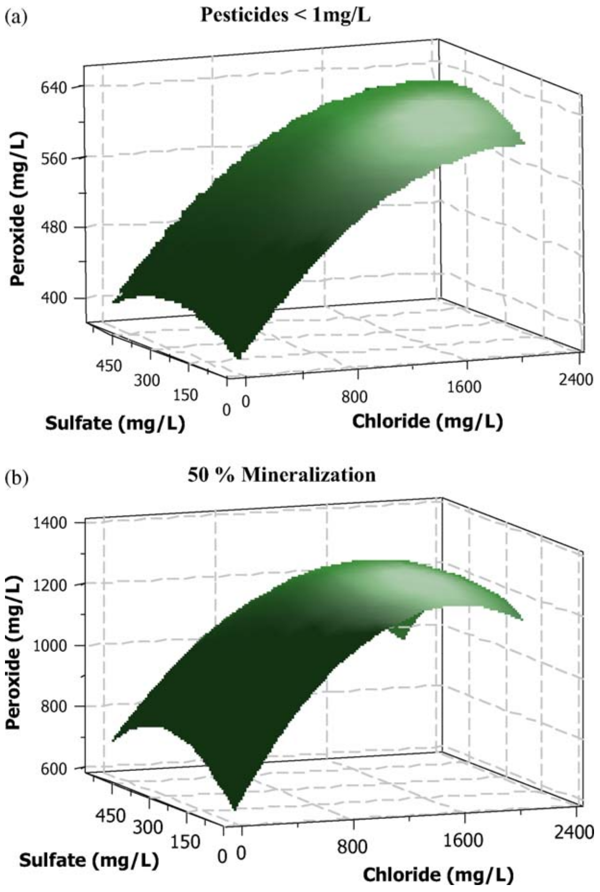

Fig. 2. Response surfaces for hydrogen peroxide consumption in the presence of Cl^- and SO_4^{2-}: (a) for degradation of pesticides (<1 mg/L) and (b) for 50% mineralization.

Table 1
Central composite design matrix (two variables at two levels). Response factor results (t_{30W} and H_2O_2 consumption).

Exp.		Anion concentrations		Degradation of active ingredients (<1 mg/L)		50 % mineralization	
		Cl^- (mg/L)	SO_4^{2-} (mg/L)	t_{30W} (min)	H_2O_2 (mg/L)	t_{30W} (min)	H_2O_2 (mg/L)
1	(1,1)	2000	500	160	618.8	260.9	1304.3
2	(1.1,0)	2100	275	100	706.1	252.0	1261.1
3	(1,−1)	2000	50.0	155	621.0	303.8	1248.6
4	(0,−1.1)	1050	26.0	164	615.2	289.9	1403.4
5	(−1,−1)	100	50.0	67.0	569.0	209.0	1292.7
6	(−1.1,0)	0	275	90.0	425.3	202.0	991.6
7	(−1,1)	100	500	85.0	469.3	183.6	908.0
8	(0,1.1)	1050	524	120	389.3	280.7	817.6
9	(0,0)	1050	275	113	625.8	244.1	939.2
10	(0,0)	1050	275	116	594.2	259.4	1164.5
11	(0,0)	1050	275	115	407.7	184.7	608.8

$$HSO_2^- + HO^{\bullet} \rightarrow SO_4^{\bullet-} + H_2O \tag{2}$$

$$SO_4^{\bullet-} + H_2O_2 \rightarrow SO_4^{2-} + H^+ + HO_2^{\bullet} \tag{3}$$

$$SO_4^{\bullet-} + HO_2^{\bullet} \rightarrow SO_4^{2-} + H^+ + O_2 \tag{4}$$

Otherwise, hydrogen peroxide consumption rose noticeably with Cl^- concentration. This can be explained by the presence of some inorganic species, like Cl^-, which act as a hydroxyl radical scavenger. De Laat and Le Truong [28] explained this by less reactive species, such as chlorine atoms ($Cl^{\bullet}$) and dichloride anion radicals ($Cl_2^{\bullet-}$), being generated by Reactions (5)–(7):

$$Cl^- + HO^{\bullet} \rightarrow ClOH^{\bullet-} \tag{5}$$

$$ClOH^{\bullet-} + H^+ \rightarrow Cl^{\bullet} + H_2O \tag{6}$$

$$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet-} \tag{7}$$

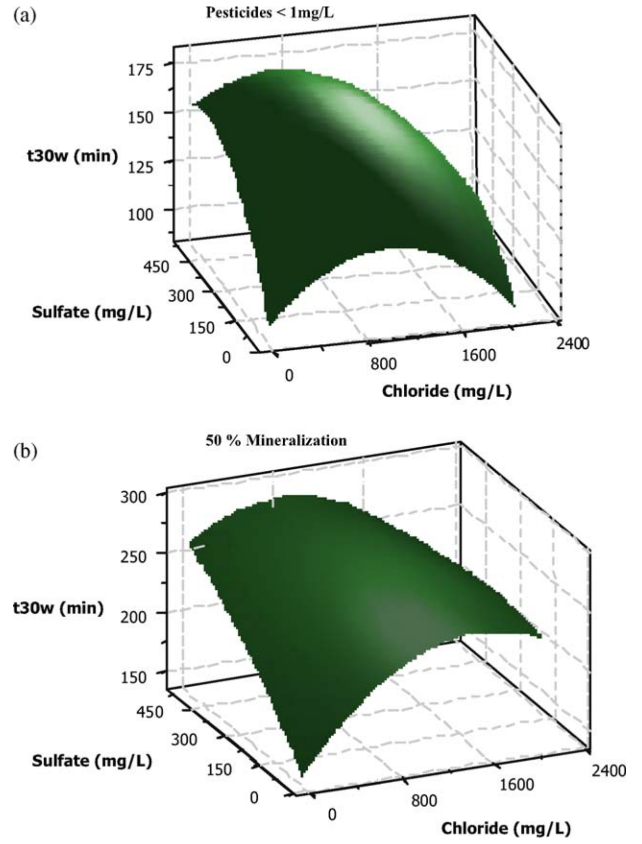

Fig. 3. Response surfaces for illumination time in the presence of Cl^- and SO_4^{2-}: (a) for degradation of pesticides (<1 mg/L) and (b) for 50% of mineralization.

Furthermore, less active chloride radicals formed could also react with H_2O_2 (Reactions (8) and (9)) increasing the reagent consumption

$$Cl^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + Cl^- + H^+ \tag{8}$$

$$Cl_2^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + 2Cl^- + H^+ \tag{9}$$

As expected, the illumination time required for both targets is observed to increase between 30 and 40% as the SO_4^{2-} concentration rises (Fig. 3). This gradual decrease in the degradation rate in the presence of growing amounts of SO_4^{2-} anions can be explained by the complexation of Fe(III) by sulfate ions through Reactions (10)–(12) [27]. These sulfato-complexes do not react with hydroxyl radicals, and consequently, the degradation rate is lower, because of the decrease in active iron concentration in solution.

$$Fe^{2+} + SO_4^{2-} \rightarrow FeSO_4 \tag{10}$$

$$Fe^{3+} + SO_4^{2-} \rightarrow FeSO_4^{+} \tag{11}$$

$$Fe^{3+} + 2SO_4^{2-} \rightarrow Fe(SO_4)_2^{-} \tag{12}$$

On the other hand, as Cl^- increased, the illumination time required to degrade the pesticides increased gradually up to ($[Cl^-]$: 1200 mg/L), from which point it started to decrease rapidly ($[Cl^-]$ = 1200–2000 mg/L). This effect can be justified by the action of $Cl^{\bullet}$ and $Cl_2^{\bullet-}$, which are strong oxidants (E_{oSHE}, $Cl^{\bullet}/Cl^-$ = 2.41 V; E_{oSHE}, $Cl_2^{\bullet-}/2Cl^-$ = 2.09 V), and if they are present in high concentrations, they could also oxidize organic solutes easily, oxidizing active ingredients in the formulation, and thereby contributing substantially to the oxidation process. Furthermore, the possible generation of organic radicals from Fe^{3+} complexes could also intervene in pesticide degradation, as explained by other researchers, as in the presence of Cl^-, Fe^{3+} could form complexes with unidentate ligands which by absorption of photons drive complexed or noncomplexed Fe^{2+} species, also generating organic radicals, if organic compounds are present (Reaction (13), *Fe is iron photoexcited) [29]

$$^{*}FeCl_3 + RH \rightarrow FeCl_2 + HCl + R^{\bullet} \tag{13}$$

Furthermore, for mineralization of 50% of the initial DOC, the degradation rate stabilized from $[Cl^-]$ 900 to 2000 mg/L, as in this case a high concentration of chloride radicals and radicals formed from the reaction between chloride radicals and hydrogen peroxide (Reactions (5)–(7)) could compensate the scavenging of $^{\bullet}OH$ by Cl^- permitting a similar reaction but with a higher consumption of H_2O_2 (see Fig. 2). Thus, an excess of chloride provoked high concentration of chlorine radicals reacting with hydrogen peroxide and forming large amounts of $HO_2^{\bullet}$, and therefore reaching reaction times similar to medium chloride concentrations.

It is also important to highlight that for both response factors studied, a high concentrations of chloride in solution moderates the negative effect of the presence of sulfate.

4. Conclusions

(1) Photo-Fenton efficiency rose gradually with temperature until 42 °C, but at higher temperatures, a significant loss of iron by precipitation quickly occurred. Therefore, the optimal operating temperature inside the photoreactor should be between 35 and 45 °C, and no heating and/or thermal isolation are necessary for photo-Fenton wastewater treatment in CPC solar plants, which could operate properly at ambient temperature.

(2) The presence of SO_4^{2-} did not significantly influence H_2O_2 consumption in the concentration range analyzed (0–500 mg/L). The Cl^- ions increased H_2O_2 consumed because less of the chlorine oxidant is generated. However, high concentrations (>1000 mg/L) could contribute to degradation during the first stages of the treatment, easily degrading oxidizable compounds due to the generation of $Cl^{\bullet}$ and $Cl_2^{\bullet-}$.

(3) The presence of both SO_4^{2-} and Cl^- anions did not noticeably reduce the photo-Fenton treatment time in the concentration range usually found in wastewater, otherwise increasing hydrogen peroxide consumption.

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