Research Article

Treatment of Effluent from a Factory of Paints Using Solar Photo-Fenton Process

Alam Gustavo Trovó,[1] Oswaldo Gomes Jr.,[1] and Antonio Eduardo da Hora Machado[1,2]

[1] *Instituto de Química, Universidade Federal de Uberlândia, 38400-902 Uberlândia, MG, Brazil*
[2] *Departamento de Química, Universidade Federal de Goiás, 75704-020 Catalão, GO, Brazil*

Correspondence should be addressed to Alam Gustavo Trovó; alamtrovo@iqufu.ufu.br

We evaluated the use of Fenton reactions induced by solar radiation in the treatment of effluent from a factory of paints for buildings, after prior removal of the suspended solids. The increase of H_2O_2 concentration from 100 to 2500 mg L^{-1} for a $[Fe^{2+}] = 105$ mg L^{-1} contributed to the reduction of DOC, COD, and toxicity. Our best results were achieved using 1600 mg L^{-1} H_2O_2, with 90% of DOC and COD removal and a complete removal of the toxicity with respect to *Artemia salina*. Additionally, through increasing Fe^{2+} concentration from 15 to 45 mg L^{-1}, the DOC removal rate increased 11 times, remaining almost constant in the range above 45 until 105 mg L^{-1}. Under our best experimental conditions, 80% of DOC removal was achieved after an accumulated dose of 130 kJ m^{-2} of UVA radiation (82 ± 17 min of solar irradiation under an average UVA irradiance of 34.1 ± 7.3 W m^{-2}), while 40% of DOC removal was reached after 150 min under only thermal Fenton reactions. The results suggest the effectiveness of implementation of solar photo-Fenton process in the decontamination and detoxification of effluents from factories of paints for buildings.

1. Introduction

Wastewaters containing toxic compounds may originate from household and personal care activities as well as from industrial processes. Most of the compounds present in these wastewaters are not treatable by conventional technologies due to the high stability, toxicity, and/or low biodegradability [1, 2].

Having regard to the above information, many studies aimed at the elimination of toxic and recalcitrant compounds are based on the application of advanced oxidation processes (AOPs) [3–8], since the nonselective attack of the hydroxyl radicals usually converts toxic compounds into carbon dioxide, water, and inorganic ions [9]. However, the main disadvantage of AOPs is high cost of maintenance of the artificial sources of radiation and equipment for ozone production. On the other hand, solar radiation can be used as radiation source in heterogeneous photocatalysis and photo-Fenton process, reducing the energetic costs [10–13]. The photo-Fenton process has the advantage to be a homogeneous process, favouring a better contact between reagent species

and also avoiding an additional step for removal of catalyst, which is usual when dealing with heterogeneous processes.

Although the photo-Fenton process has been applied in the treatment of wastewaters of different compositions (containing pesticides, pharmaceuticals, petroleum, dyes, and colorants, among other compounds), no attempts have been published concerning the use of the photo-Fenton process combined with solar radiation as an alternative to the treatment of effluent from factories of paints for buildings, searching its decontamination and detoxification. Most of the articles published concerning the treatment of wastewaters containing dyes and pigments involve the study of synthetic effluents containing one or more target compounds in ultrapure water and/or using artificial irradiation, a situation far from the reality [14–18]. Few studies have been reported using real effluents [10, 11, 19, 20].

Therefore, the aim of the present work is to evaluate at lab scale the influence of H_2O_2 concentration on the soluble fraction of the organic load (dissolved organic carbon (DOC) and chemical oxygen demand (COD)), as well as on the toxicity removal during the application of the solar

photo-Fenton process in the treatment of a real effluent, seeking to meet discharge standards and/or reuse in the manufacturing process or in other activities inherent to the industrial plant. Under the best concentration defined in this study for H_2O_2, the influence of Fe^{2+} on the kinetics of DOC removal was evaluated, aiming to know the time of treatment and estimate its potential of application. The evaluation of the concentration of Fe^{2+} and H_2O_2 is determinant to establish the process efficiency. This information is necessary for an economic and operational evaluation before scaling up to a large scale. In addition, the knowledge about the behaviour of the effluent toxicity during application of the photocatalytic process allows us to make the necessary adjustments so that the process is feasible in large-scale applications.

2. Materials and Methods

2.1. Reagents. All solutions, except the effluent, were prepared using ultrapure water.

$FeSO_4 \cdot 7H_2O$ (Vetec) was used to prepare aqueous $0.25 \, mol \, L^{-1} \, Fe^{2+}$ stock solution; H_2O_2 (30% w/w), H_2SO_4, NaOH, and Na_2SO_3, all from Vetec, were used as received. A solution of ammonium metavanadate (Vetec) was prepared at a concentration of $0.060 \, mol \, L^{-1}$ in $0.36 \, mol \, L^{-1} \, H_2SO_4$ and used for H_2O_2 quantification.

The effluent was kindly provided by a factory of paints for buildings, whose main activity is the production of acrylic paints. The composition of the effluent was not made available by the company. In general, this kind of effluent must contain acrylic resin, organic and inorganic pigments (titanium dioxide, phthalocyanines, etc.), charges (carbonates, silicates, etc.), additives (dispersants, humectants, surfactants, etc.), and organic and inorganic salts, among others [21].

2.2. Photodegradation Procedure and Solar Irradiance Measurements. All experiments were carried out between 10 am and 14 pm, in a range of temperatures varying between 27 and 33°C, during autumn using a batch reactor located in our lab, in Uberlândia, Brazil (18°55′08″S; 48°16′37″W). The solutions containing reagents and effluent, after adjustment of pH and filtering, were exposed to sunlight under clear sky conditions, in open vessels of dark glass (same deep, but with different surface area), and maintained under constant magnetic stirring. Three types of glass containers were used: the first one with $0.21 \times 0.21 \, m$ (volume of 3.3 L and surface area of $0.044 \, m^2$), the second with 13 cm of diameter (volume of 0.98 L and surface area of $0.013 \, m^2$), and the third with diameter of 6 cm (volume of 0.21 L and surface area of $0.0028 \, m^2$), all with 7.2 cm of depth. Each glass container was filled with the effluent, resulting in a depth of 7 cm.

Two sets of experiments involving the photo-Fenton treatment were performed. One is controlled dosing of H_2O_2 (ranging from 100 up to $2500 \, mg \, L^{-1}$), monitoring Fe^{2+} and Fe^{3+} concentrations, the removal of DOC and COD as well as the toxicity. The second set is evaluating the effect of different iron concentrations (15, 45, 75, and $105 \, mg \, L^{-1}$) on the kinetics of DOC removal and consumption of H_2O_2.

The first one was done using containers of $0.21 \times 0.21 \, m$ and $105 \, mg \, L^{-1} \, Fe^{2+}$. For these experiments, H_2O_2 was added to the containers in small portions, in the order of a few $mg \, L^{-1}$. The consumption of H_2O_2 was monitored during solar exposure without control of the dose of the incident UVA radiation. After consuming all H_2O_2, an aliquot was taken for analyses. A new portion of H_2O_2 was added, and another sample was taken after consumption of all the H_2O_2. This cycle was repeated until a cumulative concentration of $2500 \, mg \, L^{-1}$ of H_2O_2 has been added. The procedure described as "addition, total consumption, sample collection, and new addition" is important as it prevents the occurrence of reactions in the dark during storage after collection of the sample and possible interference in toxicity tests and the analysis of COD. In these experiments, aliquots (70 mL) of the photolysed solution were collected immediately after the confirmation of the total consumption of the added H_2O_2. Considering this procedure, it is recommended that the experimental data must be expressed in terms of H_2O_2 consumption and not on the basis of the accumulated radiation dose or even the reaction time.

In the second set of experiments (kinetic experiments), containers of 13 cm diameter were used. Two sets of experiments were performed: the first one involves the correlation between reaction time and accumulated dose of UVA, and the other relates the reaction directly to the dose of UVA radiation. In the first set of experiments, aliquots of 30 mL were collected at intervals of 20 min up to 60 min of reaction and at very 30 min above 60 min of reaction up to 150 min. For the second, aliquots were collected after exposure to the same dose of UVA radiation. This procedure was done to facilitate the comparison of results, since for the same dose of UVA, the same amount of photons is obtained, providing the same level of degradation for a similar exposition [10, 11, 22]. The measurements of UVA irradiance and dose were done using a solar light PMA2100 photometer/radiometer, equipped with a UVA detector (320–400 nm).

We used an initial concentration of H_2O_2 equal to 1600 $mg \, L^{-1}$, determined in previous experiments, which is able to induce an almost complete reduction in DOC and COD. Due to the fast consumption of H_2O_2, new additions were done at each $78.3 \, kJ \, m^{-2}$ accumulated, in the experiments when $45 \, mg \, L^{-1} \, Fe^{2+}$ were used, and at each $47.1 \, kJ \, m^{-2}$ of UVA, when 75 or $105 \, mg \, L^{-1} \, Fe^{2+}$ were used.

Before photo-Fenton experiments, the initial pH of the effluent was adjusted between 2.5 and 2.8, the optimum pH range for Fenton reactions [23, 24], using a solution of H_2SO_4, which caused the precipitation of the suspended solids. The suspended solids in the effluent were, then, removed by filtration, using membranes with mean pore size of $0.45 \, \mu m$, after a previous decantation. An aqueous solution containing Fe^{2+}, acidified with sulfuric acid, was added to the filtered effluent. Acidification of this solution was to prevent the oxidation of Fe^{2+} to Fe^{3+}. Shortly after the addition of Fe^{2+}, a new adjustment of pH to the range between 2.5 and 2.8 was done. So, before exposing the solution to sunlight, the H_2O_2 was added.

After sampling and before analysis, for the experiments involving the controlled dosage of H_2O_2, the pH of the aliquots was adjusted to the range between 6 and 8 before filtration through membranes with mean pore size

TABLE 1: Composition of the studied effluent.

Parameter	Value
Dissolved organic carbon (mg C L^{-1})[b]	307
Dissolved organic carbon (mg C L^{-1})[c]	237
Dissolved inorganic carbon (mg C L^{-1})[b]	83.5
Dissolved inorganic carbon (mg C L^{-1})[c]	6.2
Chemical oxygen demand (mg O$_2$ L^{-1})[b]	1232
Chemical oxygen demand (mg O$_2$ L^{-1})[c]	672
Toxicity (*A. salina*) (%)[c]	100
pH[a]	7.6
Solids in suspension (mg L^{-1})[a]	2040
Total dissolved iron (mg L^{-1})[b]	0.05
Total chloride (mg L^{-1})[b]	8.2
Total chloride (mg L^{-1})[c]	4.1
Total phosphorus (mg L^{-1})[c]	3.2
Total N (mg L^{-1})[b]	34.9
Total N (mg L^{-1})[c]	28.1
N-NH$_4^+$ (mg L^{-1})[b]	28.5
N-NH$_4^+$ (mg L^{-1})[c]	26.9
Color[a]	Lilac
Color[b]	Lilac
Color[c]	Colorless
Odor[a]	Fetid
Odor[b]	Fetid
Odor[c]	Similar but less intense

[a]Raw effluent.
[b]Raw effluent, after filtration using 0.45 μm mean pore size membranes.
[c]After pH adjustment between 2.5 and 2.8, precipitation, and filtration using 0.45 μm mean pore size membranes.

of 0.45 μm, while for the kinetics experiments, an excess of a 2.0 mol L^{-1} solution of Na$_2$SO$_3$ was added to the samples before pH adjustment and filtration, ensuring the removal of the remaining H$_2$O$_2$ and stopping the Fenton reactions. For the kinetics experiments, only DOC and H$_2$O$_2$ analyses were done, since the presence of sulfite does not cause interference in these analyses.

Control experiments (direct photolysis, H$_2$O$_2$/solar, H$_2$O$_2$ dark, Fe^{2+}/solar, and Fenton) were also performed in containers with 6 cm diameter using 1600 mg L^{-1} H$_2$O$_2$ and 105 mg L^{-1} Fe^{2+}.

2.3. Analytical Determinations and Toxicity Bioassays. The efficiency of the photo-Fenton process was evaluated by monitoring the following experimental parameters: electronic absorption, consumption of H$_2$O$_2$, amount of Fe^{2+} and Fe^{3+}, COD, DOC, and toxicity, evaluated using *Artemia salina*.

The DOC decay was followed using a TOC analyser (Shimadzu TOC-VCPH/CPN) equipped with an ASI-V autosampler. COD determinations were carried out according to the 5220D Standard Methods [25]. The H$_2$O$_2$ concentration was estimated using a photometric method proposed by Nogueira et al. [26]. The absorbance values were obtained from UV-Vis spectra in the range between 190 and 800 nm, using a Shimadzu UV-1650 PC spectrophotometer. The Fe^{2+}

content was determined directly, using a methodology based on the reaction between Fe^{2+} and 1,10-phenantroline [25]. The concentration of Fe^{3+} was estimated by the difference between the total iron, determined after reduction with hydroxylamine, and the content of Fe^{2+}. The toxicity tests were done evaluating the immobilization of *A. salina* [27].

3. Results and Discussion

3.1. Characterization of the Effluent. Paints for buildings can be considered as a stable mixture, in basic medium, of solids in a volatile component (water or organic solvent, in this case, water). A third group of components is the additives. Although they represent a small fraction of the composition, they are responsible for important features for the paints, as wetting and dispersing action for pigments and charges and corrosion protection, among others.

A brief characterization of the effluent used in this study is presented in Table 1. The raw effluent, a mixture of different dyes, is opaque with a milky appearance and a slightly lilac color, possessing an expressive amount of suspended solids (2040 mg L^{-1}) and a pH close to neutrality. The soluble fraction has a moderate organic load (DOC = 307.0 mg C L^{-1} and COD = 1232 mg O$_2$ L^{-1}).

Considering that the optimum pH range for Fenton reactions occurs between 2.5 and 2.8 [23, 24], the pH of the effluent was adjusted to this range before performing the photo-Fenton experiments. However, after acidification, the equilibrium that kept the solids suspended due to the dispersant action of the additives, was compromised, leading to a rapid precipitation. Simultaneous to precipitation, a complete color removal was observed, most likely due to the adsorption of the pigments on the surface of the solids. With the removal of the suspended solids, a partial but expressive DOC and COD reduction, respectively, from 307 to 237 mg L^{-1} and from 1232 to 672 mg L^{-1} (Table 1), was quantified. Similar behavior was also observed for the inorganic fraction (total chloride and nitrogen and nitrogen as ammonium). In addition, the pH adjustment contributed to the elimination of carbonates and bicarbonates, reducing the dissolved inorganic carbon from 83.5 to 6.2 mg C L^{-1} (Table 1), which is extremely advantageous since these species act as scavengers of hydroxyl radicals [28]. On the other hand, although a complete color removal was reached after pH adjustment and filtration of solids, much of the organic load remained in solution, which presented 100% of toxicity to *A. salina* (Table 1).

From this point, the authors decided to apply the photo-Fenton process as an alternative to degrade only the soluble fraction of the organic load to discharge standards and/or its reuseain, and not the solid phase. So, before all photodegradation experiments and after pH adjustment, the effluent was submitted to decantation and filtration using 0.45 μm mean pore size membranes.

The UV-Vis absorption spectrum of the effluent after pretreatment reveals a high absorbance only in the UV region (190–400 nm), probably due to the presence of aromatic compounds (Figure 1(b)).
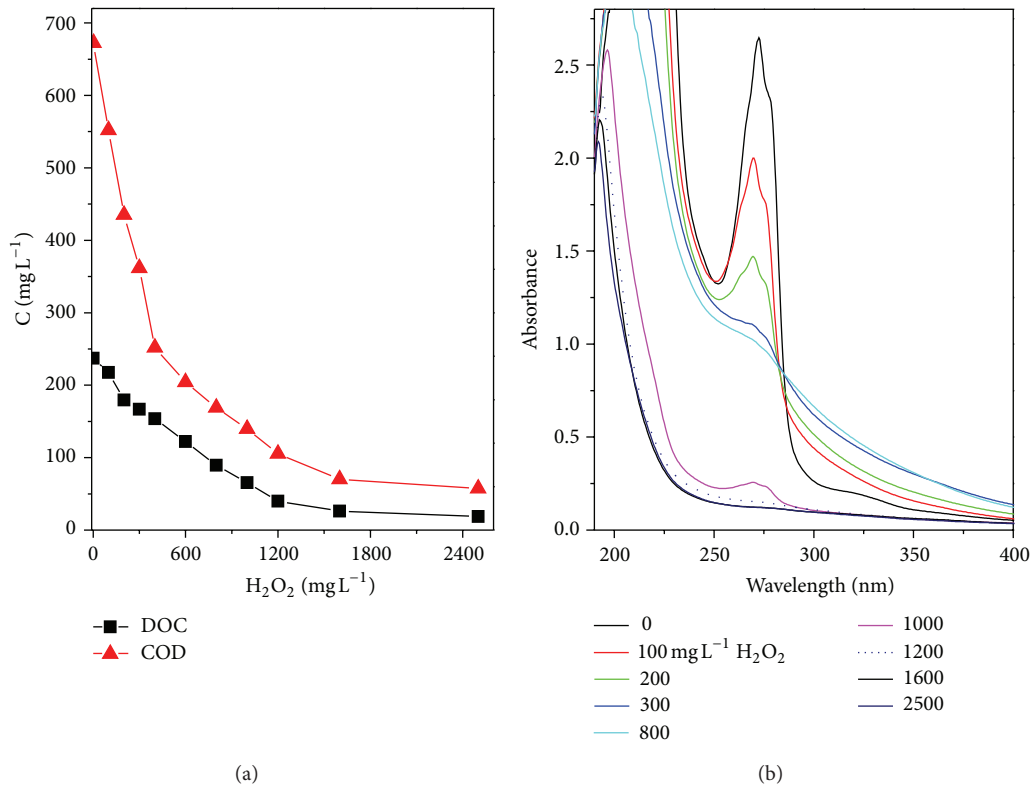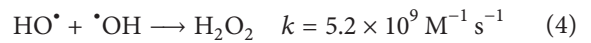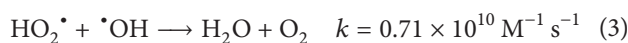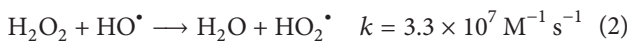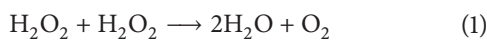
(a)

(b)

FIGURE 1: Influence of the H_2O_2 concentration on the soluble fraction of the (a) organic load DOC and COD, (b) UV absorbance removal of the effluent, obtained during solar photo-Fenton reaction, using different H_2O_2 concentrations. Experimental conditions: initial DOC = 237 mg CL^{-1}; initial COD = 672 mg O_2 L^{-1}; Fe^{2+} = 105 mg L^{-1}; and pH = 2.5–2.8.

3.2. Application of Photo-Fenton Process Mediated by Solar Radiation

3.2.1. Influence of the H_2O_2 Concentration. The H_2O_2 concentration is an important operational parameter for Fenton reactions, since an excess of this reagent, or its absence, tends to reduce drastically the efficiency of the process. The excess of H_2O_2 favors self-decomposition reactions (1) and reactions that consume hydroxyl radicals without however promoting the degradation of organic matter (2)–(4), committing the efficiency of the process [27, 29–32]. In view of this, in the first part of this study, a set of experiments was carried out aiming to find the best H_2O_2 concentration in the range from 100 to 2500 mg L^{-1}, in the presence of 105 mg L^{-1} Fe^{2+}, capable to maximize DOC and COD removal (Figure 1). In addition, the toxicity of the effluent was monitored throughout the process in order to assess the viability and the potential use of photo-Fenton reactions in the treatment of this kind of effluent. In these experiments, the dose of UVA radiation was not controlled the solutions were exposed to the sunlight until the total consumption of the H_2O_2 was added:

$$H_2O_2 + H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (1)$$

$$H_2O_2 + HO^\bullet \longrightarrow H_2O + HO_2^\bullet \quad k = 3.3 \times 10^7 \, M^{-1} \, s^{-1} \quad (2)$$

$$HO_2^\bullet + {}^\bullet OH \longrightarrow H_2O + O_2 \quad k = 0.71 \times 10^{10} \, M^{-1} \, s^{-1} \quad (3)$$

$$HO^\bullet + {}^\bullet OH \longrightarrow H_2O_2 \quad k = 5.2 \times 10^9 \, M^{-1} \, s^{-1} \qquad (4)$$

For the experiments with controlled H_2O_2 dosage, after addition of the first dose of 100 mg L^{-1} of this reagent, the color of the effluent changed from light orange to dark gray, suggesting the formation of dark colored intermediates. New additions of H_2O_2 up to 2500 mg L^{-1} were done. Although there has not been a complete removal of color of the solution, there was a significant reduction in its intensity. This suggests the persistence of the colored intermediates. Despite that the color of the effluent can limit the action of the incident radiation, a fast COD decay from 672 to 250 mg O_2 L^{-1} was achieved using 400 mg L^{-1} H_2O_2, and 105 mg L^{-1} Fe^{2+}, under solar irradiation. Using 1600 mg L^{-1} H_2O_2 a COD of 70 mg O_2 L^{-1} was reached (Figure 1(a)).

Only a slight improvement in COD removal was observed when increasing the H_2O_2 concentration from 1600 up to 2500 mg L^{-1}, respectively, 70 to 57 mg O_2 L^{-1}, probably due to the formation of acids of low molecular weight, refractory to oxidation [33, 34]. Similar behavior was observed for DOC removal (Figure 1(a)) and for the absorption maxima at 224 and 272 nm (Figure 1(b)). Using 1600 mg L^{-1} H_2O_2, 90% of DOC removal and 100% of removal of the absorbance peaks at 224 and 272 nm were obtained (Figure 1), suggesting a high efficiency of the photo-Fenton process in removing the organic load and decontamination of this class of effluent. Therefore, the use of H_2O_2 concentrations higher than
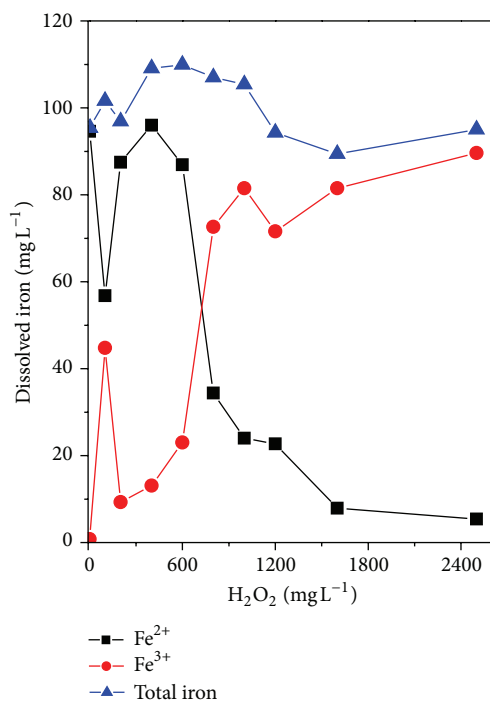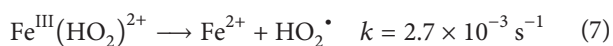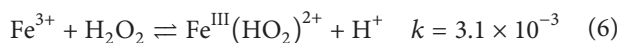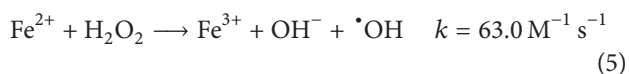
FIGURE 2: Dependence on Fe^{2+}, Fe^{3+}, and total dissolved iron concentrations and different concentrations of hydrogen peroxide, during photo-Fenton treatment of the soluble fraction of the effluent. Experimental conditions: DOC = 237 mg C L^{-1}; COD = 672 mg O_2 L^{-1}; Fe^{2+} = 105 mg L^{-1}; and pH = 2.5–2.8.

1600 mg L^{-1} is not justifiable (Figure 1). The H_2O_2 concentration defined as the best in this study (1600 mg L^{-1}), is very near to the stoichiometric ratio of H_2O_2 (1428 mg L^{-1}), considering that 1 g COD ≡ 0.03125 mol O_2 ≡ 0.0625 mol H_2O_2 = 2.125 g H_2O_2 [35].

Parallel to DOC, COD, and absorbance analysis, the concentrations of Fe^{2+}, Fe^{3+} and the total dissolved iron (Fe^{2+} + Fe^{3+}) were also evaluated for different concentrations of H_2O_2 (Figure 2). These are also important parameters to determine the efficiency of the photo-Fenton process in the degradation of the organic load, since in most cases part of the iron added tends to be complexed by degradation of by-products [19]. In view of this, new additions of iron ions could be required to reach adequate degradation efficiency. In addition, it is important to know the changes in the concentration of Fe^{2+} and Fe^{3+}, since the amount of hydroxyl radicals generated by reactions mediated by Fe^{2+} (5) is higher than that generated by Fe^{3+}, once the regeneration of ferrous ions from ferric ions ((6) and (7)) is the limiting step in the catalytic cycle of iron:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad k = 63.0 \, M^{-1} \, s^{-1} \tag{5}$$

$$Fe^{3+} + H_2O_2 \rightleftharpoons Fe^{III}(HO_2)^{2+} + H^+ \quad k = 3.1 \times 10^{-3} \tag{6}$$

$$Fe^{III}(HO_2)^{2+} \longrightarrow Fe^{2+} + HO_2^{\bullet} \quad k = 2.7 \times 10^{-3} \, s^{-1} \tag{7}$$

As before mentioned, the presence of colored intermediates was observed for concentrations of H_2O_2 up to 2500 mg L^{-1}. This tends to affect the photochemical regeneration of ferrous ions since the absorption of photons by Fe^{3+} complexes is more difficult in strongly colored solutions, even under stirring (Figure 2) [36]. Considering this, we can consider that at the beginning of the experiments, the thermal Fenton process probably prevails over the photo-Fenton. Therefore, the regeneration of ferrous ions probably should occur, in this case, by the action of H_2O_2 ((6)-(7)).

As presented in Figure 2, between 75 and 90% of the initial concentration of Fe^{2+} was converted to Fe^{3+}, when the H_2O_2 added resulted in an initial concentration between 1000 and 1600 mg L^{-1}. As discussed before, the increase in the initial concentration of H_2O_2 from 1600 to 2500 mg L^{-1} contributed only to a minimal improvement in COD and DOC removal. Besides the formation of carboxylic acids of low molecular weight, the low COD and DOC removal may also be associated with the low concentration of Fe^{2+} and high concentration of Fe^{3+} in the reaction medium after adding H_2O_2, giving an initial concentration between 1000 and 1600 mg L^{-1} (Figure 2), which helps to reduce the efficiency of generation of hydroxyl radicals ((5)–(7)). In other words, once the regeneration of ferrous ions is very slow ((6)-(7)), the degradation of the organic load will depend on the rate of regeneration of Fe^{2+} from Fe^{3+}, mediated by H_2O_2 ((6)-(7)).

A probable consumption of H_2O_2 (Figure 1(a)) without apparent contribution in the removal of COD and DOC could have occurred due to the regeneration of Fe^{2+} ((6)-(7)) [31, 32] as well as self-decomposition reactions and scavenging of hydroxyl radicals ((1)–(4)).

The role of H_2O_2 concentration in the toxicity during the photo-Fenton process was also evaluated, once the soluble fraction of the effluent presented 100% toxicity to *A. salina* (Figure 3). After the photo-Fenton process using H_2O_2 in the range of 100 up to 1600 mg L^{-1}, the toxicity was reduced to 0%. On the other hand, for an H_2O_2 concentration of 2500 mg L^{-1}, the reduction of toxicity was from 100 to 23% (Figure 3). It is probable that this effect is related to the formation of carboxylic acids, that tend to be toxic to *A. salina* [33], as also reported in studies involving *Daphnia magna* in the degradation of sulfamethoxazole and amoxicillin [37, 38].

As presented and discussed above, the results demonstrate the feasibility and potential of photo-Fenton process both in decontamination (Figure 1) and detoxification (Figure 3) of effluent from factories of acrylic paints for buildings. Considering using concentrations of H_2O_2 of 1600 mg L^{-1}, COD, DOC, and toxicity removal between 90 and 100% were obtained, an initial concentration of 1600 mg L^{-1} H_2O_2 was used for the kinetics experiments, evaluating the iron ions concentration.

3.2.2. Influence of the Fe^{2+} Concentration. The initial Fe^{2+} concentration is important in two aspects, one is related to the penetration of light through the solution, and the other is related to the efficiency of the photo-Fenton process in generating hydroxyl radicals since Fe^{2+} catalyzes the decomposition of H_2O_2, generating hydroxyl radicals (5). However,
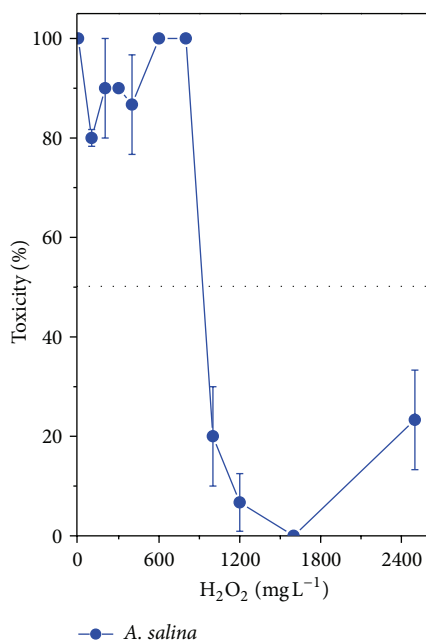
FIGURE 3: Evaluation of the toxicity to *A. salina* during photo-Fenton treatment of the soluble fraction of the effluent, using different concentrations of H_2O_2. Experimental conditions: DOC = 237 mg C L^{-1}; COD = 672 mg O_2 L^{-1}; Fe^{2+} = 105 mg L^{-1}; and pH = 2.5–2.8.

it is known that an excess of Fe^{2+} can act as scavenger of hydroxyl radicals (8), compromising the efficiency of the process [31]:

$$Fe^{2+} + HO^{\bullet} \longrightarrow Fe^{3+} + HO^{-} \quad k = 3.2 \times 10^8 \, M^{-1} \, s^{-1} \quad (8)$$

The effect of the iron concentration on Fenton and photo-Fenton processes was evaluated in previous studies. It was observed that the rate of degradation increases with a given concentration of iron ions, regarded as the concentration that results in the best experimental conditions, which, on the other hand, is dependent on the composition of the effluent and type of reactor [10, 11, 19, 27, 39, 40].

In this study, four sets of experiments using different iron concentrations (15, 45, 75, and 105 mg L^{-1}) were done using an initial H_2O_2 concentration of 1600 mg L^{-1}. As the initial dose of H_2O_2 was rapidly consumed, new additions were done at each 78.3 kJ m^{-2} of accumulated dose of UVA radiation in the assays done with 45 mg L^{-1} Fe^{2+} and at each 47.1 kJ m^{-2} of accumulated dose of UVA radiation in the assays done with 75 and 105 mg L^{-1} Fe^{2+}. Using the lower iron concentration (15 mg L^{-1}), a low rate for DOC removal was verified when compared to the other iron concentrations (45, 75, and 105 mg L^{-1}) (Figure 4(a)).

It can be observed in Figure 4(a), the occurrence of an induction period in the reactions is induced by the lowest iron concentration. For the largest concentrations of iron, induction periods were not observed, suggesting that the limiting step of the reaction for the lower iron concentrations must be the regeneration of Fe^{2+} [39, 40], once these experiments also showed an initial darkening of the effluent, in

general attributed to the formation of reaction intermediates [8, 34, 37]. However, after a period between 5 and 50 minutes, there was a complete removal of the dark color, which occurs faster (5–10 min) when the larger concentrations of Fe^{2+} were employed.

The curve of DOC removal can be divided into two parts (up to 78.3 kJ m^{-2} and above 78.3 kJ m^{-2}), Figure 4(a), with exception of the experiment in the presence of 15 mg L^{-1} Fe^{2+}. In the first part, the curve of DOC removal presents apparent pseudo first-order kinetics (k = 0.014, 0.16, 0.18, and 0.20 kJ^{-1} m^2, resp., for the initial dose of Fe^{2+} of 15, 45, 75, and 105 mg L^{-1}). The second part of the curve is characterized by a slow DOC removal rate, due to formation of carboxylic acids of low molecular weight, refractory to oxidation, and because they are able to form complexes with dissolved iron ions [39], reducing the efficiency of the Fenton reactions.

An increase in the rate of DOC removal by a factor of 11 was achieved when the Fe^{2+} concentration increased from 15 to 45 mg L^{-1}, considering an accumulated dose of 78.3 kJ m^{-2} of UVA radiation (Figure 4(a)). On the other hand, in increasing the Fe^{2+} concentration from 45 to 75 and 105 mg L^{-1} no significant improvement was obtained in DOC removal (Figure 4(a)). These results suggest that an iron concentration of 45 mg L^{-1} is enough to trigger the photocatalytic process induced by solar irradiation. So, using 45 mg L^{-1} Fe^{2+}, the photocatalytic regeneration of ferrous ions from ferric was fast enough (Figure 4(b)), ensuring the availability of ferrous ions to consume H_2O_2 and produce more hydroxyl radicals.

After an accumulated dose of 130 kJ m^{-2} of UVA (82 ± 17 min of solar irradiation, equivalent to an average intensity of UVA radiation of 34.1 ± 7.3 W m^{-2}), in the presence of 45 mg L^{-1} of Fe^{2+}, 80% of DOC removal was reached for a consumption of 1650 mg L^{-1} H_2O_2 (Figure 4(a)). This result reinforces the results obtained in experiments using controlled dosing of H_2O_2, in which 90% of DOC removal was achieved using 1600 mg L^{-1} H_2O_2 (Figure 1(a)). In addition, an increase in the time of exposure to solar radiation did not result in significant improvement in DOC removal (Figure 4(a)), probably due to at least three factors: the formation of carboxylic acids of low molecular weight, recombination reactions ((2)–(4)), and scavenging of hydroxyl radicals by Fe^{2+} (8).

Control experiments using the soluble fraction of the effluent were also carried out under the following conditions: (a) absence of Fe^{2+} and H_2O_2 (direct photolysis at pH 2.5–2.8); (b) photolysis without adding Fe^{2+}, in presence of 1600 mg L^{-1} H_2O_2 at pH 2.5; (c) photolysis involving a hydrated complex of iron, using 45 mg L^{-1} Fe^{2+} at pH 2.5–2.8, without H_2O_2; and (d) Fenton process in the dark using 105 mg L^{-1} Fe^{2+} and 1600 mg L^{-1} H_2O_2. These experiments were important to assure that the results found during the photocatalytic assays were consistent and not due to direct photolysis and/or thermal Fenton reactions (Fenton reactions in the dark). No degradation was observed in the conditions from (a) to (c), while 40% of DOC removal was reached in the thermal Fenton reaction in the presence of 105 mg L^{-1}
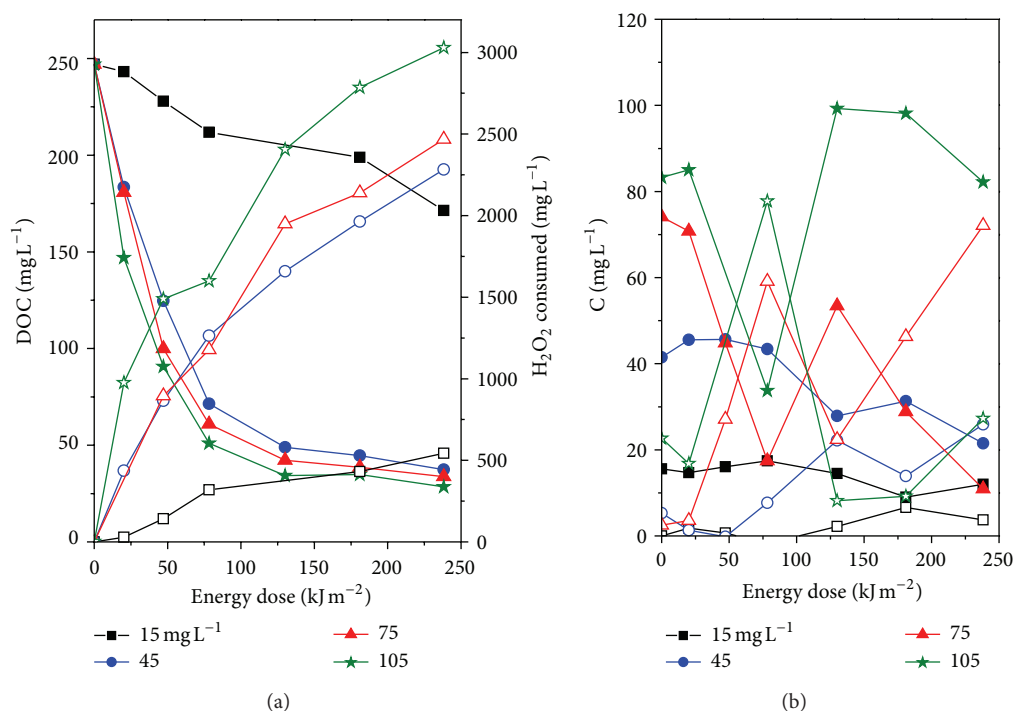
FIGURE 4: Influence of Fe^{2+} concentration on (a) kinetics of DOC removal of the effluent (solid symbols) and consumption of H_2O_2 (open symbols); (b) dissolved iron species (solid symbols: Fe^{2+} concentration, open symbols: Fe^{3+} concentration) during the solar photo-Fenton treatment of the soluble fraction of the effluent under study. Experimental conditions: DOC = 247 mg C L^{-1}; H_2O_2 = 1600 mg L^{-1} replaced in 78.3 kJ m^{-2} to 45 mg L^{-1} Fe^{2+} and 47.1 kJ m^{-2} to 75 and 105 mg L^{-1} Fe^{2+}; and pH = 2.5–2.8. Irradiation time: 128 ± 23 min (238 kJ m^{-2}) and solar light average intensity: 39.6 ± 5.6 W m^{-2}.

Fe^{2+}, after 150 min of reaction (data not shown), equivalent to the period required to accumulate a dose of UVA radiation of 238 kJ m^{-2} in the experiments under solar irradiation. The lower DOC removal obtained in the thermal Fenton reaction, (d), when compared to the photo-Fenton process induced by solar radiation (90% of DOC removal), suggests a synergetic effect caused by both Fenton processes.

For thermal Fenton reactions, the concentrations of Fe^{2+} and Fe^{3+} and total dissolved iron (Fe^{2+} + Fe^{3+}) were also monitored. During the reaction interval (150 min), the concentration of Fe^{2+} decreased from 102 to 20 mg L^{-1} after a consumption of 1260 mg L^{-1} H_2O_2. At the same time, no increase in the concentration of Fe^{2+} has been observed (data not shown). This agrees with the results obtained using controlled dosing of H_2O_2 (Figure 2).

4. Conclusions

Although, respectively, 62 and 75% of DOC and COD removal were reached using 800 mg L^{-1} H_2O_2 and [Fe^{2+}] = 105 mg L^{-1}, no reduction in the toxicity was observed. This suggests that the earliest intermediates of oxidized pretreated effluent obtained using a low dose of H_2O_2 (up to 800 mg L^{-1}) still present acute toxicity to *A. salina*. A photo-Fenton process involving a H_2O_2 concentration over 1000 mg L^{-1} tends to produce oxidized intermediates with low toxicity (below 20%). Our best results were obtained using a concentration

of H_2O_2 of 1600 mg L^{-1} and [Fe^{2+}] = 105 mg L^{-1}. Under these conditions, a removal of 90% of DOC and COD and of 100% of toxicity was obtained. Only a slight improvement in DOC and COD removal could be observed when increasing the H_2O_2 concentration above 1600 up to 2500 mg L^{-1} (decay from 26 to 19 mg C L^{-1} and from 70 to 57 mg O_2 L^{-1}, resp.) probably due to the formation of carboxylic acids, refractory to oxidation.

The curve of DOC removal is consistent with apparent pseudo first-order kinetics (k = 0.014, 0.16, 0.18, and 0.20 kJ^{-1} m^2, resp., for the initial doses of iron of 15, 45, 75, and 105 mg L^{-1} Fe^{2+}), and an improvement of 11 times on the DOC removal rate was reached when the iron concentration increased from 15 to 45 mg L^{-1}, keeping almost constant from 45 up to 105 mg L^{-1}. Under our best experimental conditions ([Fe^{2+}] = 45 mg L^{-1} and [H_2O_2] = 1600 mg L^{-1}), 80% of DOC removal was achieved after exposure to 130 kJ m^{-2} (82 ± 17 min of solar irradiation and average UVA irradiance of 34.1 ± 7.3 W m^{-2}), while 40% of DOC removal was reached under only thermal Fenton reaction ([Fe^{2+}] = 105 mg L^{-1} and [H_2O_2] = 1600 mg L^{-1}), after 150 min, suggesting a synergetic effect for the combination among the reactions of Fenton and irradiation in the ultraviolet.

These results demonstrate the viability of application of Fenton reactions to the decontamination and detoxification of effluent from factories of paints for buildings, using solar radiation.
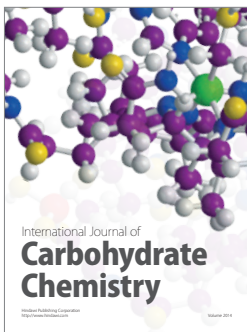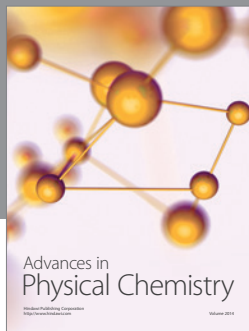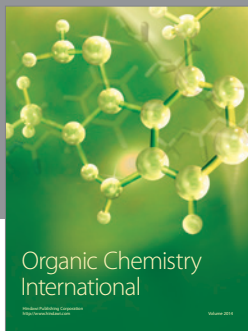
Acknowledgments

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