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# Industrial Wastewater Treatment by Photochemical Processes Based on Solar Energy

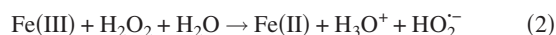
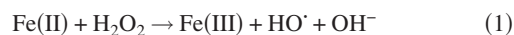
*Background:* The solar photo-Fenton process has enormous potential for becoming a viable alternative to conventional processes for the treatment of industrial wastewater. However, the costs associated with the use of artificial irradiation have hindered many times industrial application of these processes. *Method of Approach:* In this work, the photo-Fenton remediation of various industrial wastewaters (containing silicones, pesticides, phenol and hydrocarbons, model, and real) in aqueous systems has been studied using Fe(II), H<sub>2</sub>O<sub>2</sub>, and UV-visible sunlight. Experiments were carried out using a concentrating parabolic trough reactor (PTR) and a nonconcentrating falling-film reactor. *Results:* In general, at low contaminant concentration, more than 90% of the total organic carbon content could be converted to inorganic carbon within about 2–3 h, using sunlight, in reactors of different geometry. *Conclusions:* Solar light can be used either as an effective complementary or alternative source of photons to the photo-Fenton degradation process of a diversity of chemical pollutants. [DOI: 10.1115/1.2391015]

## Introduction

In this work, we present selected results of the investigations carried out at the Center for Chemical Engineering Systems (CCES—University of São Paulo, Brazil), and at the Federal University of Rio Grande do Norte (Natal, Brazil), concerning the feasibility of the solar driven photo-Fenton process using different model pollutants in aqueous systems. Two solar reactor configurations have been used in these investigations: (1) a concentrating parabolic trough reactor (PTR); and (2) a nonconcentrating falling-film reactor.

Of the Advanced Oxidation Processes (AOPs) that have been proposed thus far, we shall focus our attention on the photo-Fenton reaction, that is considered very promising [1]. According to the classical simplified mechanism of the Fenton reaction,

Fe(II) is oxidized to Fe(III), and H<sub>2</sub>O<sub>2</sub> is reduced to the hydroxide ion and the hydroxyl radical (HO<sup>•</sup>), a very reactive species in an aqueous solution:



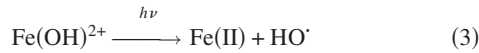
The hydroxyl radical reacts by second order kinetics with the majority of organic substances with low selectivity. The main reactions may involve hydrogen abstraction, the addition to unsaturated bonds or aromatic rings, and electron transfer [2]. Due to the electrophilic nature of the attack, the hydroxyl radical reacts preferably with an aromatic species [3].

The thermal reduction given by reaction (2) is much slower than reaction (1), and ultimately determines the overall process rate. A more detailed description of these reactions, considering hydrated iron-H<sub>2</sub>O<sub>2</sub> complexes is found in the literature [2].

Although chemically very efficient for the removal of organic pollutants, the Fenton reaction notably slows down after the initial conversion of Fe(II) to Fe(III). UV-visible irradiation strongly accelerates the Fenton reaction, improving degradation rates [1–5].

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The optimum  $pH$  range is 2–4, in which the predominant Fe(III) species in aqueous solution is  $Fe(OH)^{2+}$ , which has absorption bands between 200 and 410 nm [6]. This species produces hydroxyl radicals according to:



Fe(III) may form complexes with organic ligands [4,5] that can absorb in the UV-visible range up to *ca.* 600 nm [5] and be photolyzed through a ligand to metal charge transfer reaction, yielding  $Fe^{2+}$  and  $HO^{\cdot}$  with good quantum yields.

An important drawback to industrial applications of photochemical AOPs is the costs associated with the high electrical energy demand for UV lamps. A very interesting alternative is the use of solar light, which looks extremely attractive at sites with an annual global insolation of  $1700 \text{ kWh m}^{-2}$  or higher [7].

The solar radiation incident on the Earth's surface is composed of direct-beam radiation and diffuse radiation [8]. Direct radiation reaches the surface without being scattered or absorbed in the atmosphere. The diffuse component refers to scattered radiation. The sum of the two types is known as global solar radiation. Research efforts attempt to understand the influence of several interrelated factors such as altitude, latitude, local weather patterns, topographical and geographical features, climate, and atmospheric conditions (e.g., haze, clouds, and airborne particulate matter). Several comprehensive articles have been published in the last years concerning R&D directed toward solar photocatalytic reactors [9]. Most simple and developed are parabolic trough reactors (PTR), in which parabolic collectors concentrate direct rays onto fluid-filled transparent receiver tubes positioned along the line of focus in the trough [9]. The application of AOPs to the remediation of industrial effluents is an interesting alternative to reduce pollutant concentration and/or toxicity in order to enable the disposal or further processing in biological treatment plants.

## Equipments and Experimental Procedures

Hydrogen peroxide ( $H_2O_2$  analytical grade, 30% w/w in water, Merck) and ferrous sulfate heptahydrate ( $FeSO_4 \cdot 7H_2O$ , >98%, Sigma Aldrich) were used in the experiments. Reactant solutions were prepared with distilled water.

Experiments in the solar reactors were performed in two different equipments: (1) a concentrating parabolic trough reactor (PTR); and (2) a nonconcentrating falling-film reactor. A view of the PTR reactor used is shown in Fig. 1(a). It consisted of nine flowthrough borosilicate glass tubes (internal diameter of 11 mm and length of 1.2 m) arranged in series, and connected to a reservoir tank. A centrifugal pump provided liquid circulation between the reactor tubes and the tank for operation in the recirculating batch mode. Each glass tube was positioned at the line focus of a parabolic trough collector of a  $0.26 \text{ m}^2$  reflecting surface, made up of polished aluminum as the reflective material. The PTR was mounted on a fixed platform inclined  $23^\circ$  (from the ground) and facing North, according to the geographical localization of São Paulo, Brazil (latitude  $23^\circ 32.0'S$  and longitude  $46^\circ 37.0'W$ ).

The falling-film reactor [Fig. 1(b)] consisted of a stainless-steel plate surface (45.4 cm wide and 83 cm long), with a collecting surface area of approximately  $0.38 \text{ m}^2$ . The collector was fitted with a 4-mm thick borosilicate glass cover, which served to avoid evaporation, convection losses, and atmospheric contamination of the reaction medium during the experiments. The reactor was connected to a 10 L reservoir tank. A centrifugal pump provided liquid circulation between the reactor and the tank for operation in the recirculating batch mode. In Natal, Brazil (latitude  $5^\circ 42.0'S$  and longitude  $35^\circ 12.0'W$ ) the reactor was mounted on a fixed platform inclined  $15^\circ$  (from ground) and facing North. The additional  $10^\circ$  increment of the inclination above the latitude proved to be necessary to obtain an adequate draining of the film. In São Paulo, it was inclined  $23^\circ$  and facing North.

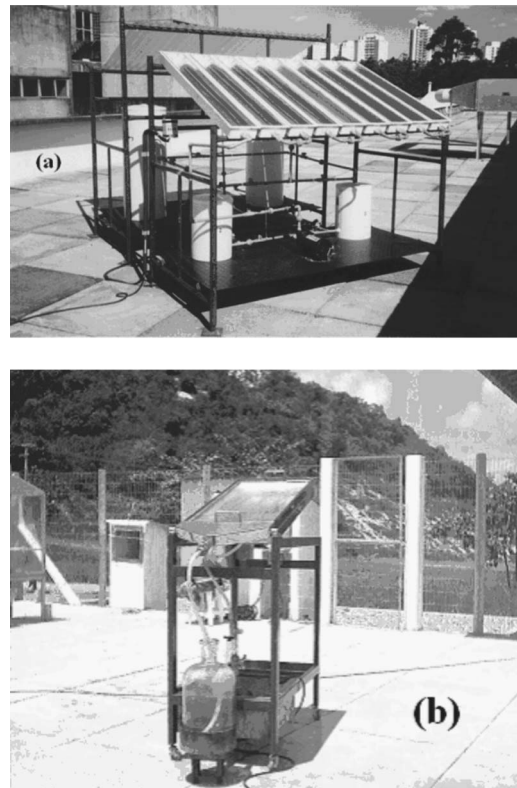
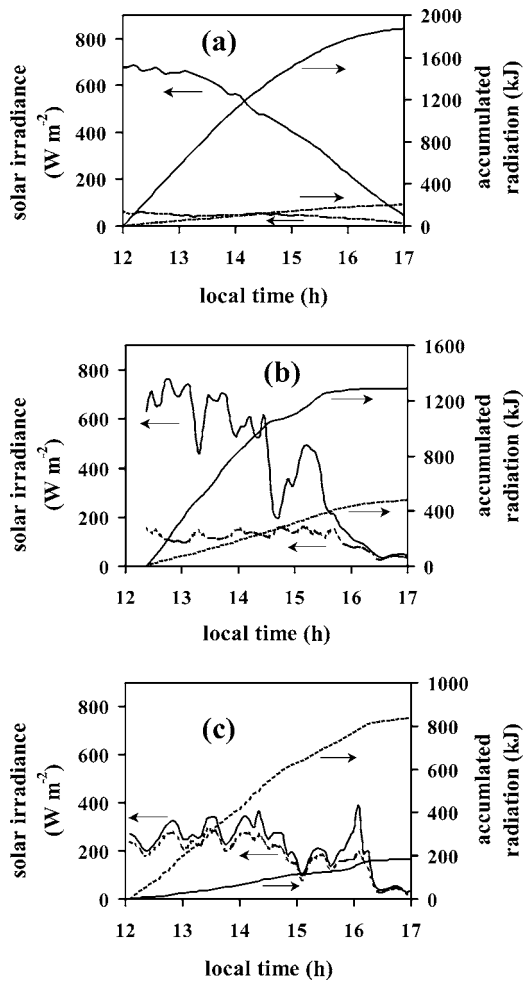


Fig. 1 (a) View of the solar parabolic-through reactor (PTR). (b) View of the solar falling-film reactor

The experimental procedure was nearly the same in all runs. A given volume of the pollutant aqueous solution at an initial given concentration was firstly introduced into the reservoir tank and then circulated in the reactor system at a fixed flow rate.  $pH$  was initially adjusted at 3.0 by the addition of  $H_2SO_4$ , and then continuously monitored. An aqueous solution of  $FeSO_4 \cdot 7H_2O$  was added, and the system was exposed to light. The  $H_2O_2$  aqueous solution at a specified concentration was then continuously added at a controlled flow rate, by means of a peristaltic pump, or in fixed amounts at chosen time intervals. In this paper,  $[Fe(II)]$  is the concentration at time  $t=0$ , and  $[H_2O_2]$  is referred to the total volume of the aqueous solution in the system or is the concentration of the hydrogen peroxide aqueous solution pumped to the reactor at a constant feed rate. The liquid bulk temperature was monitored during each experiment. The experiments were typically initiated at about 12:00 p.m. with a total period of reaction (solar exposure) of 3–5 h.

Samples of 10 mL were withdrawn from the reservoir tank at specified times for the characterization of pollutant degradation. A quenching solution containing KI ( $100 \text{ mmol L}^{-1}$ ),  $Na_2SO_3$  ( $100 \text{ mmol L}^{-1}$ ), and NaOH ( $100 \text{ mmol L}^{-1}$ ) was added to the samples in the proportion 5:2 v/v (sample:solution) in order to decompose residual  $H_2O_2$  and precipitate iron species; all samples were filtered through a  $0.22 \mu\text{m}$  Durapore membrane (Millipore) before analyses, which were performed immediately after taking the samples. The concentration of dissolved organic carbon (DOC) was measured using the Shimadzu 5000A equipment. The chemical oxygen demand (COD) was measured by the closed-reflux colorimetric method [10], using dichromate as the oxidant in strong acidic media. The biochemical oxygen demand ( $BOD_5$ ) of the final treated solution was measured by the respirometric method [10] using the Oxitop IS 12 manometric respirometer (WTW).

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**Fig. 2 Typical radiation measurements.** Incident solar radiation (irradiance, in  $\text{W m}^{-2}$ ) and the corresponding accumulated radiant energy (in kJ) for groups A (clear, sunny days with the sky free or almost free from moving clouds) (a); B (sky moderately covered with clouds) (b); and C (heavily clouded days) (c). Left ordinate axis: measured global radiation (—) and measured diffuse radiation (---). Right ordinate axis: accumulated direct radiant energy (—) and accumulated diffuse radiant energy (---)

physical Institute, University of São Paulo) provided radiation data. Global solar radiation was measured by means of a pyranometer (Eppley, model PBW) in the range 285 to 2800 nm. The diffuse component of the global solar radiation was measured by means of a pyranometer (Eppley, model PSP) with a shading ring to eliminate direct radiation. A correction for this shading is estimated and applied to the diffuse radiation [8]. Data were recorded every five minutes and stored prior to the data analysis. In Fig. 2, irradiation conditions are classified in groups A, B, and C according to typical solar irradiance profiles, and the corresponding accumulated radiant energy. All solar experiments were carried out within a few weeks, so that seasonal effects were not important. Ferrioxalate actinometry [2] indicated an average polychromatic photon flux equal to  $1.9 \times 10^{21}$  photons  $\text{s}^{-1}$ .

## Results and Discussion

**Silicone Degradation.** Silicones are applied in the textile industry as softeners. Common aqueous formulations contain the aminosilicone poly[dimethyl, methyl (amino-ethyl amino-isobutyl) siloxane] with hydroxyl end groups (approx. 20% w/w in water), and nonionic surfactants (C9/C11-oxo alcohol polygly-

**Table 1 Experimental conditions and main results of the experiments carried out with silicone emulsions**

Experiment <sup>a,b</sup>	$[\text{H}_2\text{O}_2]^c$ (mmol $\text{L}^{-1}$ )	$[\text{Fe(II)}]^d$ (mmol $\text{L}^{-1}$ )	$\text{COD}_0^e$ (mg $\text{L}^{-1}$ )	$t_{50}^f$ (minutes)	COD% removal after 300 min
1A	500	2.8	629	29	88
2A	387.5	0.5	671	43	89
3A	50	2.8	694	49	89
4A	162.5	0.5	692	89	79
5A	387.5	5.0	636	20 <sup>g</sup>	88
6A	275	2.8	680	66	85
7A	162.5	5.0	662	88	89
1B	500	2.8	653	91	63
1C	500	2.8	585	81	72
2C	387.5	0.5	630	163 <sup>g</sup>	84
3B	50	2.8	621	114	87
4B	162.5	0.5	692	99	66
5B	387.5	5.0	600	42	82
6B	275	2.8	669	77	86
7B	162.5	5.0	699	88	88

<sup>a</sup> $T=40^\circ\text{C}$  and  $\text{pH}_0=2.8-3.0$  in all experiments; total volume of aqueous emulsion: 2 L; circulation flow rate:  $1.5 \text{ L min}^{-1}$ ; total experiment time: 300 min.

<sup>b</sup>Irradiation conditions: A: clear, sunny days with the sky free or almost free from moving clouds; B: sky moderately covered with clouds; C: heavily clouded days.

<sup>c</sup> $\text{H}_2\text{O}_2$  concentration of the solution fed to the reactor, at a rate of  $4 \times 10^{-4} \text{ L min}^{-1}$ .

<sup>d</sup> $\text{Fe(II)}$  concentration at time  $t=0$ .

<sup>e</sup>Initial COD of the aqueous emulsion.

<sup>f</sup>Time required to achieve a COD removal of 50%.

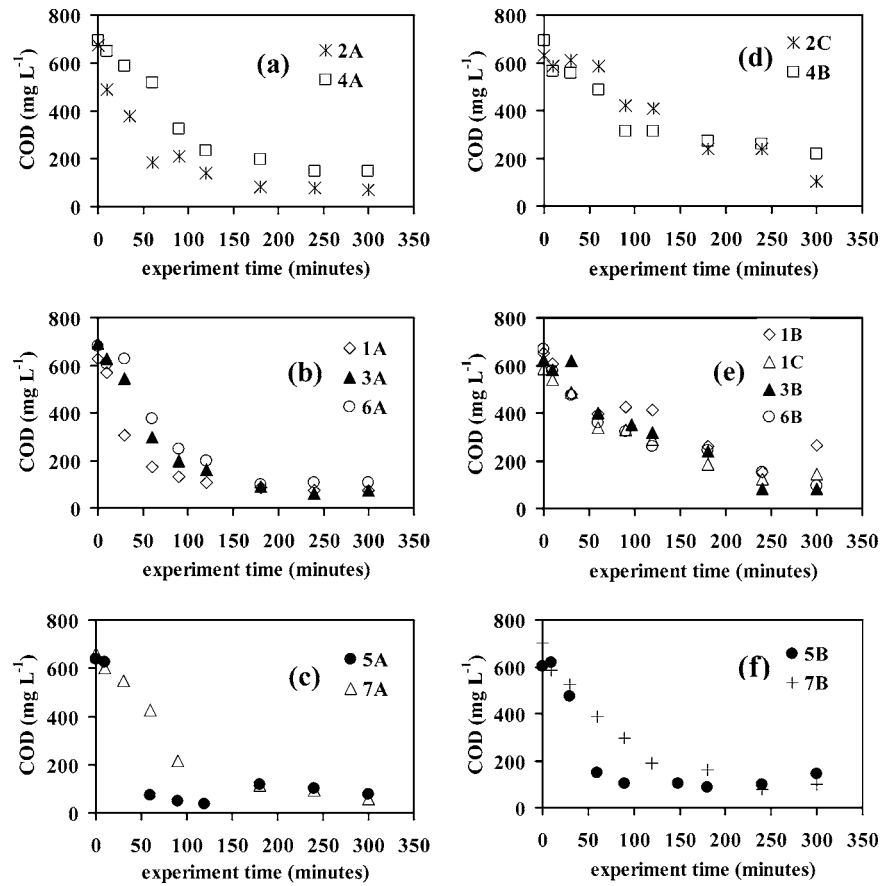
<sup>g</sup>Values estimated from the COD-time curves.

col ethers, with 5 to 11 ethoxy groups (approx. 10% w/w in water). Silicones and silicone derivatives are found to be exceptionally resistant to hydrolytic, oxidative, and biological breakdown under conventional wastewater treatment.

The photo-Fenton degradation of aminosilicone compounds in water emulsions has been investigated by the authors using the PTR reactor in São Paulo, Brazil, under variable weather conditions [7]. The conditions of the experiments and the main results are described in Table 1. The temperature of the silicone-in-water emulsion was kept at  $40^\circ\text{C}$  in all experiments by means of a thermostatic bath. All experiments have been carried out with the PTR reactor connected to a 1 L jacketed reservoir tank, using the commercial aqueous silicone formulation, diluted with distilled water (initial concentration,  $1290 \text{ mg L}^{-1}$ ; average  $\text{COD}_0 \cong 653 \text{ mg L}^{-1}$ ). Neither photolysis under solar light, nor thermal degradation in the range  $30^\circ\text{C}-50^\circ\text{C}$  took place [11]. Also, no change in the COD of the aminosilicone polymer emulsion was observed when only  $\text{Fe(II)}$  and solar light, or only  $\text{H}_2\text{O}_2$  and solar light, were used.

The COD-time curves for the photo-Fenton experiments carried out at variable  $\text{H}_2\text{O}_2$  and  $\text{Fe(II)}$  concentrations are presented in Figs. 3(a)–3(c). The accumulated direct energy input was comparable in experiments 1A–7A (irradiation conditions of group A, Fig. 2), with radiation measurements indicating an average energy input rate of about  $10 \text{ kJ min}^{-1}$  in the first 120 min. Also, a comparison of experiments carried out at different irradiation conditions is presented in Figs. 3(d)–3(f) (irradiation conditions of groups B and C, Fig. 2).

For example, in both experiments 1A and 5A [Figs. 3(b) and 3(c), respectively], in which  $[\text{H}_2\text{O}_2]$  and  $[\text{Fe(II)}]$  are high, a rapid decrease of COD was observed. In experiment 5A, carried out at a higher  $[\text{Fe(II)}]$  level, about 70 min of irradiation were required to achieve the ultimate COD percent removal. For experiments 2A and 4A [Fig. 3(a)], carried out at  $[\text{Fe(II)}]=0.5 \text{ mmol L}^{-1}$ , the differences in the time necessary to achieve a given COD removal, and in the total percent removal after about 180 min, were probably due to the effect of  $[\text{H}_2\text{O}_2]$ , since direct radiation inputs, and the ratio of diffuse to direct radiation, matched in this time interval. The effect of  $[\text{H}_2\text{O}_2]$  was more significant at a higher  $[\text{Fe(II)}]$  level ( $5.0 \text{ mmol L}^{-1}$ ), as was the case of experiments 5A and 7A



**Fig. 3** Degradation of silicone in water emulsions by the photo-Fenton reaction carried out in the solar PTR reactor under insolation conditions of groups A, B, and C (see Fig. 2 for the meaning of groups). Total volume of aqueous emulsion: 2 L; circulation flow rate:  $1.5 \text{ L min}^{-1}$ ; temperature:  $40^\circ\text{C}$ . (a)  $[\text{Fe(II)}]=0.5 \text{ mmol L}^{-1}$ : 2A ( $[\text{H}_2\text{O}_2]=387.5 \text{ mmol L}^{-1}$ ); 4A ( $[\text{H}_2\text{O}_2]=162.5 \text{ mmol L}^{-1}$ ). (b)  $[\text{Fe(II)}]=2.8 \text{ mmol L}^{-1}$ : 1A ( $[\text{H}_2\text{O}_2]=500 \text{ mmol L}^{-1}$ ); 3A ( $[\text{H}_2\text{O}_2]=50 \text{ mmol L}^{-1}$ ); 6A ( $[\text{H}_2\text{O}_2]=275 \text{ mmol L}^{-1}$ ). (c)  $[\text{Fe(II)}]=5.0 \text{ mmol L}^{-1}$ : 5A ( $[\text{H}_2\text{O}_2]=387.5 \text{ mmol L}^{-1}$ ); 7A ( $[\text{H}_2\text{O}_2]=162.5 \text{ mmol L}^{-1}$ ). (d)  $[\text{Fe(II)}]=0.5 \text{ mmol L}^{-1}$ : 2C ( $[\text{H}_2\text{O}_2]=387.5 \text{ mmol L}^{-1}$ ); 4B ( $[\text{H}_2\text{O}_2]=162.5 \text{ mmol L}^{-1}$ ). (e)  $[\text{Fe(II)}]=2.8 \text{ mmol L}^{-1}$ : 1B ( $[\text{H}_2\text{O}_2]=387.5 \text{ mmol L}^{-1}$ ); 1C ( $[\text{H}_2\text{O}_2]=500 \text{ mmol L}^{-1}$ ); 3B ( $[\text{H}_2\text{O}_2]=50 \text{ mmol L}^{-1}$ ); 6B ( $[\text{H}_2\text{O}_2]=275 \text{ mmol L}^{-1}$ ). (f)  $[\text{Fe(II)}]=5.0 \text{ mmol L}^{-1}$ : 5B ( $[\text{H}_2\text{O}_2]=387.5 \text{ mmol L}^{-1}$ ); 7B ( $[\text{H}_2\text{O}_2]=162.5 \text{ mmol L}^{-1}$ ).  $[\text{Fe(II)}]$  refers to the iron concentration at time  $t=0$ .  $[\text{H}_2\text{O}_2]$  refers to the concentration of the  $\text{H}_2\text{O}_2$  aqueous solution pumped to the reactor at a constant feed rate ( $4 \times 10^{-4} \text{ L min}^{-1}$ ).

[Fig. 3(c)]. On the other hand, the comparison of experiments 2C and 5B [Figs. 3(d) and 3(f), respectively], carried out at  $[\text{H}_2\text{O}_2]=387.5 \text{ mmol L}^{-1}$ , reveals a four-fold decrease in the time needed to remove 50% of the initial COD ( $t_{50}$ ) when  $[\text{Fe(II)}]$  increased from 0.5 to 5.0  $\text{mmol L}^{-1}$ . The behavior of 5B, carried out with the sky moderately covered with clouds, could be associated with a combined effect of higher  $\text{Fe(II)}$  content and higher direct radiation input than in experiment 2C.

On cloudy days, the variation of the accumulated direct energy input from one run to another was significant, and consequently the levels of  $\text{H}_2\text{O}_2$  and  $\text{Fe(II)}$  concentrations should be higher to achieve a desired aminosilicone removal. The strong abatement in the direct radiation input on a heavily clouded day [experiment 2C, Fig. 3(d)] considerably affected silicone degradation in comparison with the same run carried out on a sunny day [experiment 2A, Fig. 3(a)]. In this case, an almost four-fold increase in the time required to achieve a COD removal of 50% was observed. Concerning experiments 3A and 3B [Figs. 3(b) and 3(e), respectively] the accumulated direct radiant energy was virtually the same in both cases. However, as a consequence of moving clouds, the COD-time profiles were quite different. Also, the results ob-

tained in experiments 1A, 3A and 6A [Fig. 3(b)] suggest that on clear days diffuse radiation could be in part used as a photon source, albeit less efficiently than direct solar radiation.

**Pesticide Degradation.** Pesticides can be present in wastewater from industry and farm work operations (rinse water from spray equipment and empty pesticide containers, post-harvest washing of fruits and vegetables, etc.). An example of the first case is the wastewater generated in the production of 2,4-dichlorophenoxyacetic acid (2,4-D), which contains 2,4-D, phenol, and high  $\text{NaCl}$  concentration (about  $60 \text{ g L}^{-1}$ ) [12]. The second case may be exemplified by the contamination of water with the herbicide clomazone [2-(2-chlorobenzyl)-4,4-dimethyl-1,2-oxazolidin-3-one].

In the present work, the photo-Fenton degradation of the herbicide clomazone in aqueous solutions ( $\text{COD}_0=271 \pm 35 \text{ mg L}^{-1}$  and  $\text{DOC}_0=97 \pm 10 \text{ mg L}^{-1}$ ) is discussed. The authors used the PTR reactor located in São Paulo, Brazil [13]. The conditions of the experiments and the main results are described in Table 2. Solar irradiation conditions were in average similar to those illustrated in Fig. 2(a), and the temperature varied freely in all experi-

**Table 2 Experimental conditions and main results of the experiments carried out with clomazone solutions**

Experiment <sup>a</sup>	H <sub>2</sub> O <sub>2</sub> :C <sup>b</sup>	[Fe(II)] <sup>c</sup> (mmol L <sup>-1</sup> )	DOC <sub>0</sub> <sup>d</sup> (mg L <sup>-1</sup> )	t <sub>50</sub> <sup>e</sup> (minutes)	DOC% removal after 180 min
CLZ-S2	1.625	1.0	114.7	23	100
CLZ-S3	0.5	0.55	99.3	67	85.4
CLZ-S4	1.625	0.1	118.2	31	98.4
CLZ-S5	3.875	0.1	94.9	54	78.8
CLZ-S6	5.0	0.55	124.3	12	88.3
CLZ-S7	3.875	1.0	103.7	16	91.8

<sup>a</sup>Temperature varied freely in all experiments in the range 29–45°C; pH<sub>0</sub>=3.0 and clear, sunny days with the sky free or almost free from moving clouds in all experiments; total volume of aqueous solution: 5 L; circulation flow rate: 30 L min<sup>-1</sup>; total experiment time: 180 min.

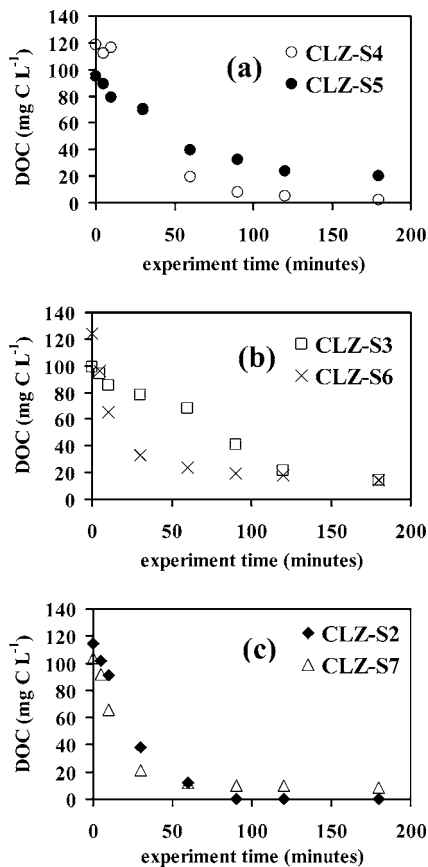
<sup>b</sup>H<sub>2</sub>O<sub>2</sub>:C molar ratio calculated from the nominal DOC<sub>0</sub> (100 mg L<sup>-1</sup>); H<sub>2</sub>O<sub>2</sub> solution feed rate: 8.3 × 10<sup>-4</sup> L min<sup>-1</sup>.

<sup>c</sup>Fe(II) concentration at time t=0.

<sup>d</sup>Initial DOC of the aqueous solution.

<sup>e</sup>Time required to achieve a DOC removal of 50%.

ments in the range 29°C–45°C. The comparison of DOC-time curves for experiments carried out at constant Fe(II) concentration and variable H<sub>2</sub>O<sub>2</sub>:C molar ratio (Fig. 4, Table 2) shows that at



**Fig. 4 Degradation of the pesticide clomazone in water solutions by the photo-Fenton reaction carried out in the solar PTR reactor. Total volume of aqueous solution: 5 L; circulation flow rate: 30 L min<sup>-1</sup>; temperature: 29°C–45°C. H<sub>2</sub>O<sub>2</sub> solution feed rate: 8.3 × 10<sup>-4</sup> L min<sup>-1</sup>. (a) [Fe(II)]=0.1 mmol L<sup>-1</sup>: CLZ-S4 (H<sub>2</sub>O<sub>2</sub>:C=1.625); CLZ-S5 (H<sub>2</sub>O<sub>2</sub>:C=3.875). (b) [Fe(II)]=0.55 mmol L<sup>-1</sup>: CLZ-S3 (H<sub>2</sub>O<sub>2</sub>:C=0.5); CLZ-S6 (H<sub>2</sub>O<sub>2</sub>:C=5). (c) [Fe(II)]=1.0 mmol L<sup>-1</sup>: CLZ-S2 (H<sub>2</sub>O<sub>2</sub>:C=1.625); CLZ-S7 (H<sub>2</sub>O<sub>2</sub>:C=3.875). [Fe(II)] refers to the iron concentration at time t=0. H<sub>2</sub>O<sub>2</sub>:C refers to the molar ratio calculated from the nominal DOC<sub>0</sub> (100 mg L<sup>-1</sup>).**

[Fe(II)]=0.55 mmol L<sup>-1</sup>, the time necessary to remove 50% of the initial DOC (t<sub>50</sub>) varied from 12 to 67 min when H<sub>2</sub>O<sub>2</sub>:C varied from 5 to 0.5 [experiments CLZ-S6 and CLZ-S3, respectively, Fig. 4(b)]; the corresponding DOC removals were similar after 120 min of solar irradiation, about 86%. At the maximum Fe(II) concentration, t<sub>50</sub> varied from 16 to 23 min when H<sub>2</sub>O<sub>2</sub>:C varied from 3.875 to 1.625 [experiments CLZ-S7 and CLZ-S2, respectively, Fig. 4(c)]. The total mineralization of clomazone was achieved in 90 min (experiment CLZ-S2).

The comparison of the experiments in which H<sub>2</sub>O<sub>2</sub>:C was held at 1.625 and [Fe(II)] was varied (Fig. 4, Table 2) shows that the value of t<sub>50</sub> in experiment CLZ-S2 was higher than in CLZ-S4 [Figs. 4(c) and 4(a), respectively]. This behavior could be associated with the significant temperature increase observed in experiment CLZ-S4 (from 28°C to 46°C) in comparison with CLZ-S2 (31°C to 41°C), increasing the thermal oxidation reactions. The comparison of experiment CLZ-S5 with experiments CLZ-S4 (at constant [Fe(II)]), and with CLZ-S7 (at constant H<sub>2</sub>O<sub>2</sub>:C) deserves careful analysis. At H<sub>2</sub>O<sub>2</sub>:C=3.875, the increase of Fe(II) concentration from 0.1 to 1.0 mmol L<sup>-1</sup> led to a decrease in t<sub>50</sub> from 54 to 16 min (experiments CLZ-S5 and CLZ-S7, respectively), while at 180 min, DOC percent removals were 79% and 92% in experiments CLZ-S5 and CLZ-S7, respectively. Even considering the differences in initial DOC, Fig. 4 shows that the performance of experiment CLZ-S5 was poor in comparison with CLZ-S4, carried out at a lower H<sub>2</sub>O<sub>2</sub>:C ratio [Fig. 4(a)]. This was due to the changes of sky conditions during the experiment CLZ-S5.

**Phenol Degradation.** Phenol is a common pollutant in a wide variety of industrial wastewaters. The remediation of industrial effluents containing very low levels of phenol by adsorption may not be economically viable and often merely transfers pollutants from one phase to another. Also, phenol concentrations higher than ca. 200 mg C L<sup>-1</sup> restrict the use of conventional biological activated-sludge systems. Therefore, photochemical processes seem to be attractive as a pretreatment of phenolic wastewaters.

The photo-Fenton degradation of phenol was simultaneously performed in the PTR (only one tube used) and the falling-film reactors in São Paulo, Brazil [14] (Fig. 5). The temperature was kept at 50°C in all experiments by means of a thermostatic bath connected to the reservoir tank. At the H<sub>2</sub>O<sub>2</sub> and Fe(II) used, the COD-time curves obtained for the reactors operated at DOC<sub>0</sub> = 100 mg C L<sup>-1</sup> were very similar [Fig. 5(a)]. However, at DOC<sub>0</sub> = 1000 mg C L<sup>-1</sup> the incident sunlight photon flux was apparently the rate-limiting factor [Fig. 5(b)], and the PTR reactor was apparently more efficient than the falling-film reactor. Figures 6 and 7 show the results of the experiments carried out in the PTR at initial phenol concentrations equal to 100 and 550 mg C L<sup>-1</sup>, respectively, along with the corresponding irradiance-time profiles. A fast decrease in DOC was observed in the experiments carried out at DOC<sub>0</sub> = 100 mg C L<sup>-1</sup>, while a gradual decrease in DOC was observed at DOC<sub>0</sub> = 550 mg C L<sup>-1</sup>. The experimental curves would be significantly different, however, if more peroxide were present in the reaction solution. At 50°C, the higher converted fraction observed in Fig. 6, about 90% removal of the initial DOC, in comparison with the percent removal of about 45% (Fig. 7), is a consequence of the higher ratio of the reactants to phenol in this experiment. However, the amount of reacted organic compounds was larger in the experiments at higher initial phenol concentration, indicating the high dependence of the degradation rate on its initial concentration.

The effect of the solar irradiance was evaluated by means of a series of 13 additional runs carried out in the PTR in the same operating mode as the previous ones, at initial phenol concentrations corresponding to DOC<sub>0</sub> values of 632 ± 4% mg C L<sup>-1</sup>. The experiments were carried out on randomly selected days, under different insolation conditions. The volume of phenol solution used in these experiments was varied in the range from 6 to 20 L.

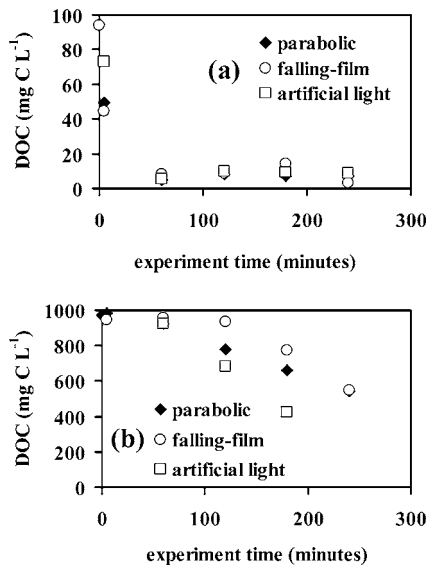


Fig. 5 Degradation of phenol in water solutions by the photo-Fenton reaction carried out in the solar PTR (one tube used), the falling-film reactor, and in an artificially irradiated photo-chemical reactor (450 W medium pressure mercury lamp).  $[H_2O_2]=100 \text{ mmol L}^{-1}$ ,  $[Fe(II)]=1.0 \text{ mmol L}^{-1}$ . Total volume of aqueous solution: 6 L (PTR and falling-film reactors) and 3 L (artificially irradiated reactor); circulation flow rate:  $1.2 \text{ L min}^{-1}$ ; temperature:  $50^\circ \text{C}$ . (a)  $DOC_0=100 \text{ mg C L}^{-1}$ . (b)  $DOC_0=1000 \text{ mg C L}^{-1}$ .  $[Fe(II)]$  refers to the iron concentration at time  $t=0$ .  $[H_2O_2]$  refers to the total volume of the aqueous solution in the system;  $H_2O_2$  solution feed rate:  $8.3 \times 10^{-4} \text{ L min}^{-1}$ .

The irradiated volume was varied from about 0.1 to 1.0 L by using the appropriate number of tubes of the PTR reactor, each tube accounting for approx. 0.11 L. The results summarized in Fig. 8

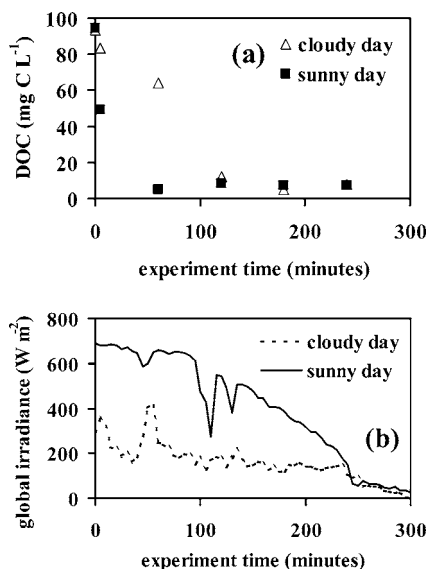


Fig. 6 (a) Degradation of phenol in water solutions by the photo-Fenton reaction carried out in the solar PTR reactor (one tube used) and (b) corresponding global irradiance-time profiles.  $DOC_0=100 \text{ mg C L}^{-1}$ ;  $[H_2O_2]=100 \text{ mmol L}^{-1}$ ,  $[Fe(II)]=1.0 \text{ mmol L}^{-1}$ . Total volume of aqueous solution: 6 L; circulation flow rate:  $1.2 \text{ L min}^{-1}$ ; temperature:  $50^\circ \text{C}$ .  $[Fe(II)]$  refers to the iron concentration at time  $t=0$ .  $[H_2O_2]$  refers to the total volume of the aqueous solution in the system;  $H_2O_2$  solution feed rate:  $8.3 \times 10^{-4} \text{ L min}^{-1}$ .

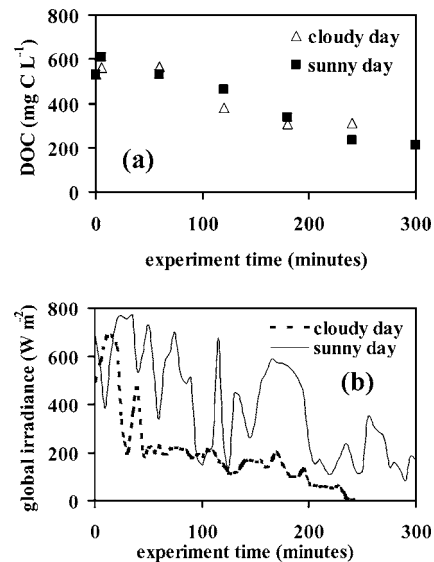


Fig. 7 (a) Degradation of phenol in water solutions by the photo-Fenton reaction carried out in the solar PTR reactor (one tube used) and (b) corresponding global irradiance-time profiles.  $DOC_0=550 \text{ mg C L}^{-1}$ ;  $[H_2O_2]=100 \text{ mmol L}^{-1}$ ,  $[Fe(II)]=1.0 \text{ mmol L}^{-1}$ . Total volume of aqueous solution: 6 L; circulation flow rate:  $1.2 \text{ L min}^{-1}$ ; temperature:  $50^\circ \text{C}$ .  $[Fe(II)]$  refers to the iron concentration at time  $t=0$ .  $[H_2O_2]$  refers to the total volume of the aqueous solution in the system;  $H_2O_2$  solution feed rate:  $8.3 \times 10^{-4} \text{ L min}^{-1}$ .

are restricted to values of the remaining fraction of the initial DOC higher than about 0.5. Under such conditions the concentration of the organic compounds during the reaction apparently did not affect the reaction rate significantly. Also, in the experiments carried out in this work, the observed changes in irradiance intensity, associated with moving or stationary clouds, were not large enough to affect significantly the performance of the solar reactors. The experimental results (a total of 94 measurements) correlated to  $E$  according to a linear expression, suggesting a first-order dependence of the converted fraction of organic compounds on the accumulated sunlight energy. Based on the experimental results with the artificially irradiated reactors, a nonlinear dependence is expected for a higher percent removal of the contaminant, since in these cases  $DOC/DOC_0$  tends asymptotically to a constant, low value.

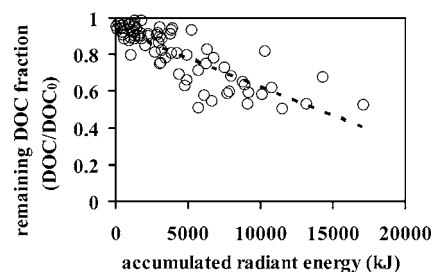
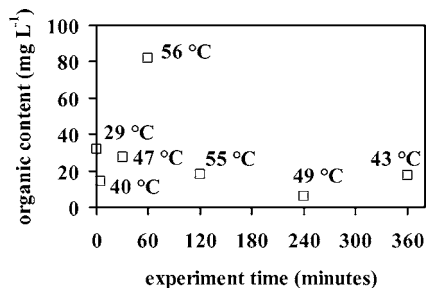


Fig. 8 Remaining fraction of the initial DOC as a function of the accumulated radiant energy per unit collector area, for the photo-Fenton experiments carried out with phenol solutions in the PTR under different insolation conditions (the number of tubes varied from one to nine).  $[H_2O_2]=70 \text{ mmol L}^{-1}$ ;  $[Fe(II)]=0.5 \text{ mmol L}^{-1}$ . Total volume of aqueous solution: 6 L; circulation flow rate:  $1.2 \text{ L min}^{-1}$ ; temperature:  $50^\circ \text{C}$ .  $[Fe(II)]$  refers to the iron concentration at time  $t=0$ .  $[H_2O_2]$  refers to the total volume of the aqueous solution in the system;  $H_2O_2$  solution feed rate:  $8.3 \times 10^{-4} \text{ L min}^{-1}$ .

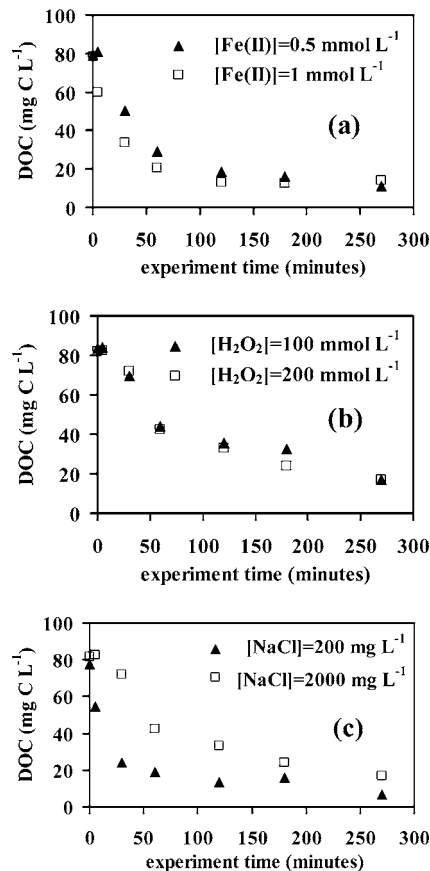


**Fig. 9 Remediation of the oil-field produced water by the photo-Fenton reaction carried out in the solar falling-film reactor.**  $[\text{H}_2\text{O}_2]=200 \text{ mmol L}^{-1}$ ;  $[\text{Fe}(\text{II})]=1.0 \text{ mmol L}^{-1}$ . Total volume of aqueous solution: 7.7 L; circulation flow rate:  $17 \text{ L min}^{-1}$ ; temperature:  $25^\circ\text{C}$ – $60^\circ\text{C}$ .  $[\text{Fe}(\text{II})]$  refers to the iron concentration at time  $t=0$ .  $[\text{H}_2\text{O}_2]$  refers to the total volume of the aqueous solution in the system;  $\text{H}_2\text{O}_2$  solution feed rate:  $1.7 \times 10^{-3} \text{ L min}^{-1}$ . The number close to each data point refers to the temperature of the reaction system at each sampling time.

**Remediation of Oil-Field-Produced Wastewater and Degradation of Gasoline in Water.** There is a growing interest in applying low-cost processes for the remediation of oil-field produced water, characterized by high NaCl concentrations (*ca.*  $2000 \text{ mg L}^{-1}$ ), in view of the large volumes produced daily and the need of a satisfactory destination. In what follows, some results concerning the use of the photo-Fenton process for the remediation of a real oil-field produced wastewater are discussed. The authors have also studied the solar degradation of raw gasoline in model aqueous systems (initial organic carbon concentration of about  $70\text{--}80 \text{ mg C L}^{-1}$ ,  $[\text{NaCl}]=200\text{--}2000 \text{ mmol L}^{-1}$ ) [15]. The falling-film reactor was used in Natal, Brazil, and all experiments were carried out under similar conditions of solar irradiation. The temperature of the system was not controlled and varied between  $25\text{--}60^\circ\text{C}$ .

In the experiments carried out with oil-field-produced wastewater, the initially slightly cloudy yellow mixture became transparent as the reaction proceeded. In the absence of the Fenton reagents, solar irradiation resulted in an *increase* in the concentration of hydrocarbons in the aqueous phase, which accompanied the gradual increase in the temperature of the aqueous phase due to insolation. The temperature increase of the aqueous phase caused by solar irradiation (thermal effect) favors the solubilization of organic compounds in the microemulsion that exists in the oil-field produced wastewater, thus increasing the concentration of hydrocarbons in the aqueous phase. At the same time, the photo-Fenton degradation reduced the organic content. Figure 9 shows this interesting phenomenon in the case where the  $\text{H}_2\text{O}_2$  addition was interrupted between 30 and 60 min of reaction, resulting in a considerable increase in the dissolved organic content of the solution in this period. Subsequently, the remaining hydrogen peroxide solution was added in two equal parts, at 60 and 120 min, respectively, with a consequent rapid fall in the organic content in this time interval. Therefore, in the beginning the rate of reaction was higher, probably due to the rapid decomposition of the aromatic constituents, and photodegradation predominated over the thermal effect. With the increase in temperature, more hydrocarbons solubilized in the aqueous phase, increasing the content of organic compounds in this phase after all the added  $\text{H}_2\text{O}_2$  had been consumed.

In the case of the model gasoline-in-water system, Fig. 10 shows that at fixed  $\text{H}_2\text{O}_2$  and NaCl concentrations, the experiments performed at the maximum  $[\text{Fe}(\text{II})]$  showed the highest initial degradation rates. Also, the increase in  $\text{H}_2\text{O}_2$  concentration did not result in a directly proportional increase in the average degradation rate. Nevertheless, the highest pollutant removals were observed at the maximum  $[\text{H}_2\text{O}_2]$ . On the other hand, the



**Fig. 10 Degradation of raw gasoline in water systems by the photo-Fenton reaction carried out in the solar falling-film reactor.** (a)  $[\text{H}_2\text{O}_2]=100 \text{ mmol L}^{-1}$ ;  $[\text{NaCl}]=200 \text{ mg L}^{-1}$ . (b)  $[\text{Fe}(\text{II})]=0.5 \text{ mmol L}^{-1}$ ;  $[\text{NaCl}]=2000 \text{ mg L}^{-1}$ . (c)  $[\text{Fe}(\text{II})]=1.0 \text{ mmol L}^{-1}$ ;  $[\text{H}_2\text{O}_2]=200 \text{ mmol L}^{-1}$ . Total volume of aqueous solution: 7.6 L; circulation flow rate:  $17 \text{ L min}^{-1}$ ; temperature:  $25^\circ\text{C}$ – $60^\circ\text{C}$ .  $[\text{Fe}(\text{II})]$  refers to the iron concentration at time  $t=0$ .  $[\text{H}_2\text{O}_2]$  refers to the total volume of the aqueous solution in the system;  $\text{H}_2\text{O}_2$  solution feed rate:  $1.7 \times 10^{-3} \text{ L min}^{-1}$ .

effect of NaCl was more pronounced than that of any of the other variables examined. The strong inhibitory effect of chloride anions ( $\text{Cl}^-$ ), which impedes the complete mineralization of the pollutants, has been suggested to involve the formation of complexes between  $\text{Fe}^{3+}$  and  $\text{Cl}^-$  [15], which affect the photochemical reduction of  $\text{Fe}^{3+}$  and/or the net yield of hydroxyl radicals. In the range of experimental conditions considered, on average, 60% of the initial organic content was mineralized in the first 180 min, this amount ranged between 66%–91% after 270 min of solar exposure.

## Conclusions

Solar radiation can successfully replace artificial irradiation in the photo-Fenton oxidative degradation of pollutants of different chemical structures contained in diluted aqueous systems, including aminosilicone polymers, pesticides, phenols, and hydrocarbons. Solar chemical facilities for special applications may therefore become economically feasible, especially for the batch remediation of small wastewater volumes (*ca.*  $10 \text{ m}^3$  per day). According to the case studies discussed in this work, the remediation was shown to be possible, even on cloudy days, provided  $[\text{H}_2\text{O}_2]$  and  $[\text{Fe}(\text{II})]$  are conveniently selected. In the case of the parabolic trough reactor, the experimental results revealed an important interaction of  $\text{Fe}(\text{II})$  and  $\text{H}_2\text{O}_2$  concentrations (manipulated, controllable variables), and the ratio of the direct to diffuse

components of solar radiation (nonmanipulated, uncontrollable variables) in the photo-Fenton degradation. This was a direct consequence of the role played by absorbed photons upon Fe(II) recovery from Fe(III) and hydroxyl radical generation, which enhances thermal Fenton reactions and ultimately determined the rate at which oxidation proceeded. Therefore, in the design of solar reactors special attention must be paid to the efficiency of the system relative to the light field distribution, since the removed fraction of the pollutants usually seems to be linearly dependent on the amount of incident light energy.

The hydroxyl radical reacts by second order kinetics with the majority of organic substances, and at rates often approaching the diffusion-controlled limit (unit reaction efficiency per encounter). The reactor design must therefore take into account the strong interdependence between light absorption, mass transport, and reaction kinetics in heterogeneous AOP or more strongly absorbing homogeneous AOPs. In heterogeneous systems, like the photocatalytic process based on TiO<sub>2</sub> (or in cases where two phases coexist, like the oil-field produced wastewater), mass-transfer limitations to chemical reactions can occur. In a simple batch photochemical reactor, in which the TiO<sub>2</sub> particles are maintained in suspension in the aqueous phase by stirring or recirculation, a major problem is the limited depth of penetration of the incident radiation into the suspension due to the strong scattering of light by the catalyst particles. Photochemical reactors also require the additional operations of physical separation of the catalyst from the solution at the end of the irradiation for recycling. Alternative reactor design strategies that address this last problem include the use of fixed catalyst beds. The homogeneous photo-Fenton process has several operational and environmental advantages over other photochemical systems. Mass-transfer limitations are much less important, and the degradation process is kinetically limited by the rate of incidence of photons, and by the rate of photon absorption in the useful wavelength. In solar reactors, the ratio between irradiated and nonirradiated reaction volumes is important, as both Fenton and photo-Fenton reactions take place. Also, the process produces no new pollutants and requires only small quantities of iron salt. At the end of the reaction, if necessary, the residual Fe(III) can be precipitated as iron hydroxide by increasing the pH. Any residual hydrogen peroxide that is not consumed in the process will spontaneously decompose into water and molecular oxygen. The sensitivity of the ferrioxalate-based photo-Fenton process to both UV and visible light makes it particularly attractive for applications in which the sun is employed as the radiation source.

Despite significant advances in the last years, the widespread, successful application of the photo-Fenton technology in the treatment and decontamination of industrial residues and wastewaters is still not a reality. In parallel with the development of solar reactors or hybrid lamp/solar reactors, the selection of the best solar setup will ultimately depend not only on the efficiency of the photo-Fenton process, but also on considerations such as whether peak periods match available insolation, and on its variation along daylight operation. Long-term trends and seasonal variations in direct and diffuse radiation levels in a particular region are therefore the basis for the design of efficient solar systems. Complete decontamination of complex industrial wastes may require the sequential application of several different decontamination technologies such as pretreatment with a photochemical AOP fol-

lowed by a biological treatment. Hence, the reactor design for photochemical AOPs should permit facile integration with other effluent decontamination technologies.

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## References

- [1] Oliveros, E., Legrini, O., Hohl, M., Müller, T., and Braun, A. M., 1997, "Industrial Waste Water Treatment: Large Scale Development of a Light-Enhanced Fenton Reaction," *Chem. Eng. Process.*, **36**, pp. 397–405.
- [2] Bossmann, S. H., Oliveros, E., Göb, S., Siegwart, S., Dahlen, E. P., Payawan, L., Straub, M., Wörner, M., and Braun, A. M., 1998, "New Evidence against Hydroxyl Radicals as Reactive Intermediates in the Thermal and Photochemically Enhanced Fenton Reactions," *J. Phys. Chem. A*, **102**(28), pp. 5542–5550.
- [3] Krutzler, T., and Bauer, R., 1999, "Optimization of a Photo-Fenton Prototype Reactor," *Chemosphere*, **38**, pp. 2517–2532.
- [4] Emilio, C. A., Jardim, W. F., Litter, M. I., and Mansilla, H. D., 2002, "EDTA Destruction Using the Solar Ferrioxalate Advanced Oxidation Technology (AOT). Comparison with Solar Photo-Fenton Treatment," *J. Photochem. Photobiol. A*, **151**, pp. 121–127.
- [5] Fallmann, H., Krutzler, T., Bauer, R., Malato, S., and Blanco, J., 1999, "Applicability of the Photo-Fenton Method For Treating Water Containing Pesticides," *Catal. Today*, **54**, pp. 309–319.
- [6] Pozdnyakov I. P., Glebov, E. M., Plyusnin, V. F., Grivin, V. P., Ivanov, Y. V., Vorobyev, D. Y., and Bazhin, N. M., 2000, "Mechanism of Fe(OH)<sup>2+</sup> (aq) Photolysis in Aqueous Solution," *Pure Appl. Chem.*, **72**, pp. 2187–2197.
- [7] Teixeira, A. C. S. C., Guardani, R., and Nascimento, C. A. O., 2003, "Solar Photochemical Degradation of Aminosilicones Contained in Liquid Effluents. Process Studies and Neural Network Modeling," *Ind. Eng. Chem. Res.*, **42**, pp. 5751–5761.
- [8] Duffie, J. A., and Beckman, W. A., 1991, *Solar Engineering of Thermal Processes*, 2nd ed., Wiley, New York.
- [9] Malato, S., Blanco, J., Vidal, A., and Richter, C., 2002, "Photocatalysis with Solar Energy at a Pilot-Plant Scale: an Overview," *Appl. Catal., B*, **37**, pp. 1–15.
- [10] Clesceri, L. S., Greenberg, A. E., Eaton, A. D., and Franson, M. A. H., 1998, in *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, American Water Works Association and Water Environment Federation, Washington, DC.
- [11] Teixeira, A. C. S. C., Guardani, R., Braun, A. M., Oliveros, E., and Nascimento, C. A. O., 2005, "Degradation of an Aminosilicone Polymer in a Water Emulsion by the Fenton and the Photochemically Enhanced Fenton Reactions," *Chem. Eng. Process.*, **44**, pp. 923–931.
- [12] Luna, A. J., 2005, "Degradação Fotoquímica do fenol, 2, 4-Diclorofenol e Ácido, 2, 4-Diclorofenoxiacético em Meio de Alta Salinidade," Ph.D. Thesis, Universidade de São Paulo, São Paulo, Brazil.
- [13] Teixeira, A. C. S. C., Stollar, G., Guardani, R., and Nascimento, C. A. O., 2005, "Degradation of Agrochemicals in Wastewaters by The Photo-Fenton Process: Experimental Study Using UV Mercury Vapor Lamps and Solar Irradiation," *Proc. XXI Congresso Interamericano de Ingeniería Química (CHIQ)*, Lima, Peru.
- [14] Will, I. B. S., Moraes, J. E. F., Teixeira, A. C. S. C., Guardani, R., and Nascimento, C. A. O., 2004, "Photodegradation of Wastewater Containing Organic Compounds in Solar Reactors," *Sep. Purif. Technol.*, **34**, pp. 51–57.
- [15] Moraes, J. E. F., Silva, D. N., Quina, F. H., Chiavone-Filho, O., and Nascimento, C. A. O., 2004, "Utilization of Solar Energy in the Photodegradation of Gasoline in Water and of Oil-Field-Produced," *Environ. Sci. Technol.*, **38**, pp. 3746–3751.