

Application of the photo-Fenton process to the treatment of wastewaters contaminated with diesel

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Abstract

The application of the photo-Fenton process for the treatment of wastewaters contaminated with diesel oil was investigated. This particular process has been widely studied for the photochemical degradation of highly toxic organic pollutants. Experiments were performed according to a factorial experimental design at two levels and two variables: H₂O₂ concentration (5–200 mM) and Fe²⁺ concentration (0.01–1 mM). Experimental results demonstrated that the photo-Fenton process is technically feasible for the treatment of wastewaters containing diesel oil constituents, with total mineralization. A combination of factorial experimental design and gradient descent techniques was employed to optimize the amount of the Fenton reagents, resulting in Fe²⁺ (0.1 mM) and H₂O₂ (50 mM). These optimized levels did not exceed the limit for disposal of ferrous ions (0.27 mM) proposed at the local environmental legislation.

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1. Introduction

The increasing number of vehicles has provoked the appearance of a corresponding number of gas stations for the distribution of fuels such as gasoline and diesel oil. In Brazil, there is a significant occurrence of fuel spills from storage tanks as a result of corrosion or structural failure, resulting in a contamination of soil and

underground waters (Manzochi, 2001; Corseuil and Marins, 1994; Corseuil, 1994). The development of adequate techniques for the remediation of these contaminated waters by fuels is thus very important. The utilization of photo-oxidative methods for the treatment of wastewaters offers several advantages, particularly the feasibility of total elimination of the organic pollutants (Krutzler and Bauer, 1999; Legrini et al., 1993; Andreozzi et al., 1999; Espulgas et al., 1994; Mansilla et al., 1997; Ince, 1999; Salah et al., 2004). In spite of the proven efficiency of biological processes for the treatment of many types of wastewaters, they do exhibit limitations with respect to the range of

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concentration and toxicity of the pollutants (Piras, 1993; Braun and Oliveros, 1997; Sýkora et al., 1997). In the case of waters contaminated by derivative hydrocarbons of petroleum, for example, significant amounts of benzene, toluene, ethyl-benzene and xylenes (BTEX) can be observed. Among the photo-oxidative processes, the photo-Fenton system, which consists in the combination of hydrogen peroxide (H_2O_2), ferrous ions (Fe^{2+}) and UV irradiation (Will et al., 2004), has been largely studied for the oxidation of wastewaters containing highly toxic organic compounds (Moraes et al., 2004a,b; Legrini et al., 1993; Mansilla et al., 1997).

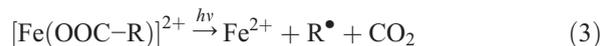
The photo-Fenton process can be divided into the following stages (Pignatello, 1992; Bossmann et al., 1998): the first step is the so-called Fenton reaction, in which ferrous ions (Fe^{2+}) are oxidized to ferric ions (Fe^{3+}) in acidic aqueous solution, as shown in Eq. (1), giving rise to hydroxyl radicals (HO^\bullet).



The ferric ions, represented by the complex $[\text{Fe}(\text{OH})]^{2+}$, is reduced back to Fe^{2+} by UV irradiation, according to Eq. (2).



The ferric species can also form complexes with the initial organic compounds and/or degradation products, leading to photo-reduction back to Fe^{2+} according to Eq. (3).



The generated hydroxyl radicals oxidize the target organic compounds (RH), shown in Eq. (4).



Hydrogen peroxide concentration plays a more crucial role in deciding the overall efficacy of the degradation process. Usually, it has been observed that the percentage degradation of the pollutant increases with the amount of hydrogen peroxide (Lin and Lo, 1997; Rivas et al., 2001). The hydrogen peroxide is a well-known radical scavenger and, in concentrations above to 3%, is a biocidal agent (Costa et al., 1990), therefore, should be careful with high concentrations in the cases where Fenton oxidation is used as a pre-treatment to biological processes (Ito et al., 1998).

Generally, the degradation rate increases with an increase of the iron ions concentration (Lin and Lo, 1997), though the extent of increase is sometimes

observed to be marginal above a certain concentration as reported by Rivas et al. (2001). In fact, an excess of ferrous ions can provoke an inhibition of the photochemical degradation process, because, at these levels, the Fe^{2+} can compete with the organic compounds by the oxidant agents (hydroxyl radicals), as indicated in Eq. (5) (Torrades et al., 2003; Pérez et al., 2002).



Other factor that can be detrimental for the performance of the degradation process, in high iron ions concentration, it is the reduction of the penetration of the UV radiation in the system, caused by the significant opacity of the solution in these conditions. Furthermore, the local environmental legislation (CONAMA 20) establishes a maximum limit of ferrous ions content for disposal (0.27 mM). These ions are classified as secondary or aesthetic pollutants because they can affect the color and the flavor of the water. Furthermore, in excess, iron poses a threat to cells and tissues, because iron can catalyze the generation of radicals, which attack and damage cellular macromolecules and promote cell death and tissue injury (Papanikolaou and Pantopoulos, 2005; Gurzau et al., 2003), causing problems for the health of the aquatic life. Because of these all cited reasons, it is very important to establish the optimum loading of iron ions under similar conditions unless data are available in the literature.

In this work, the application of the photo-Fenton process was studied for the treatment of waters contaminated by diesel oil. The amounts of the Fenton reagents were optimized by a combination of experimental design methodology and the gradient descent techniques.

2. Experimental

2.1. Materials and methods

Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and hydrogen peroxide (H_2O_2 ; 30%) were used as the source of hydroxyl radicals. A quenching solution containing potassium iodide (KI; 0.1 M), sodium sulfite (Na_2SO_3 ; 0.1 M) and sodium hydroxide (NaOH; 0.1 M) was used to interrupt the oxidation reactions in the samples. The pH was adjusted by addition of concentrated sulfuric acid (H_2SO_4). All chemical compounds were analytical grade. Commercial diesel oil was employed as the model pollutant.

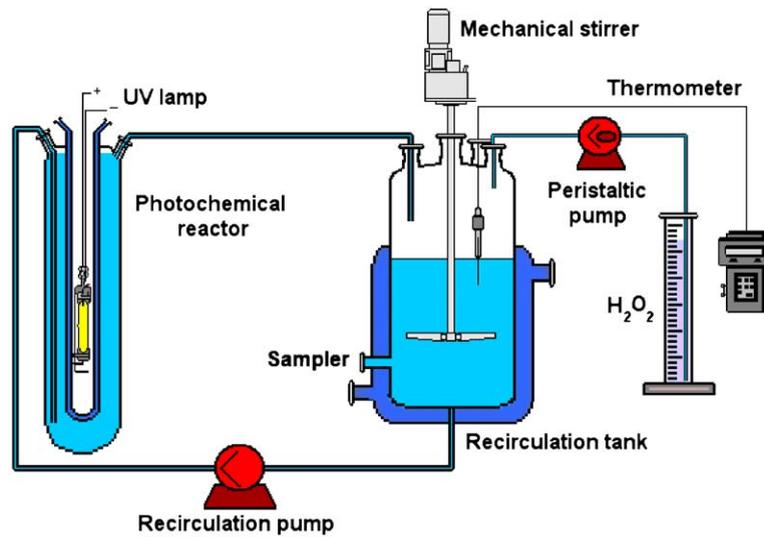


Fig. 1. Photochemical reactor experimental set-up.

2.2. Preparation of the synthetic wastewater

The synthetic wastewater was obtained by equilibrating 200 mL of diesel oil with 2 L of distilled water during 1 h with magnetic stirring. The mixture was then left standing for 1 h to ensure complete separation of the liquid phases. The aqueous phase

was collected and filtered twice through quantitative filter paper (2.0 μm).

2.3. Experimental set-up

The scheme of the photochemical reactor is shown in Fig. 1. It consisted of an annular photochemical reactor

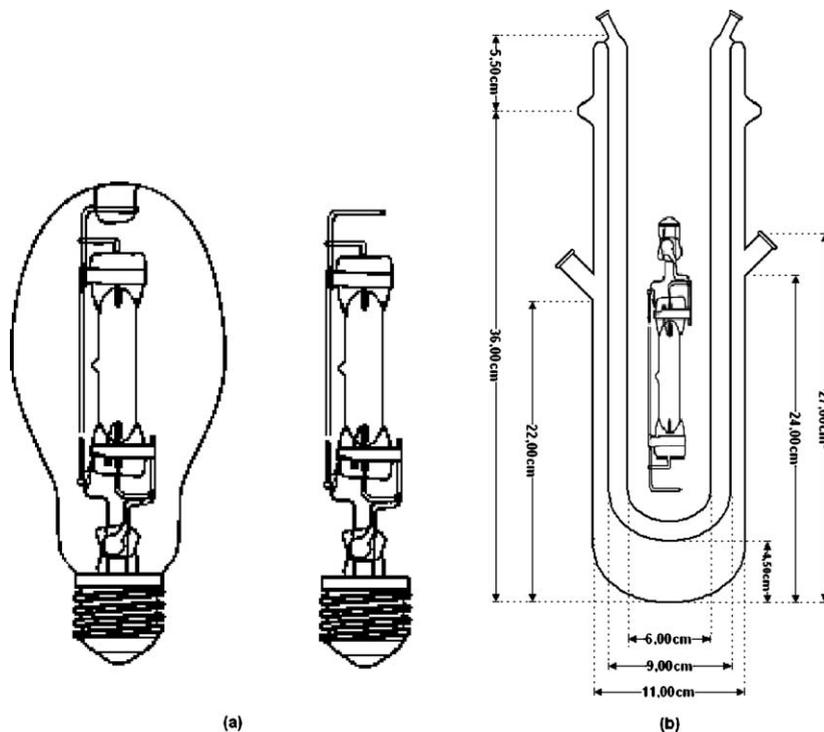


Fig. 2. Schemes of the (a) Philips HLP-N lamp and (b) the corresponding photochemical immersion well and reactor.

(net volume of 1 L) connected to a jacketed glass circulation tank (volume of 2 L) fitted with a mechanical stirrer. The temperature of the solution was controlled by means of a thermostatic bath at 33 °C. The solution (2.2 L) was circulated through the reactor at a flow rate of about 1.5 L/min by means of a centrifugal pump. Aqueous hydrogen peroxide solution (100 mL) was added to the system at the flow rate of 0.83 mL/min by a peristaltic pump in order to reach the desired amount of this reagent.

A medium pressure mercury vapor UV lamp (Hanovia, 450 W) Philips HPL-N (see Fig. 2a) was used as the radiation source. It was placed in a water-cooled immersion well made of borosilicate (ACE GLASS® photochemical reactor) (see Fig. 2b).

2.4. Experimental procedure

The mixture tank was charged with the synthetic wastewater, the circulation pump was turned on and the initial pH of the solution was adjusted to 3. The UV lamp was turned on, the solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (100 mL) was totally added and the timing of the reaction was started along with the onset of slow addition H_2O_2 (100 mL total), during the first 2 h of reaction.

Duplicate aliquots (5 mL each) of the reaction mixture were collected for analysis at appropriate time intervals during the reaction. Quenching solution (2 mL) was added to one of the samples to interrupt the reaction, which was then filtered (0.22 μm Millipore Durapore membrane) to remove the precipitated iron-containing species and analyzed for remaining total organic carbon (Shimadzu TOC-5000A TOC analyzer). The other sample was used to record the absorption spectrum on a Varian Cary 50 UV–Visible spectrophotometer. Analogous experimental procedures have been described in our previous works (Moraes et al., 2001, 2004a,b).

3. Results and discussion

3.1. Comparison of different degradation systems

In order to study and compare the performances of the photo-Fenton system and others degradation processes, four experiments were specially carried out in the treatment of water containing diesel oil constituents: UV-photolysis (exclusive use of UV irradiation), the thermal Fenton reaction ($[\text{Fe}^{2+}] = 0.1 \text{ mM}$ and $[\text{H}_2\text{O}_2] = 50 \text{ mM}$; without UV irradiation), UV/ H_2O_2 ($[\text{H}_2\text{O}_2] = 50 \text{ mM}$; with UV irradiation) and the photo-Fenton process ($[\text{Fe}^{2+}] = 0.1 \text{ mM}$ and $[\text{H}_2\text{O}_2] = 50 \text{ mM}$; with UV irradiation). The results of these experiments are showed in Fig. 3. As observed in previous works (Moraes et al.,

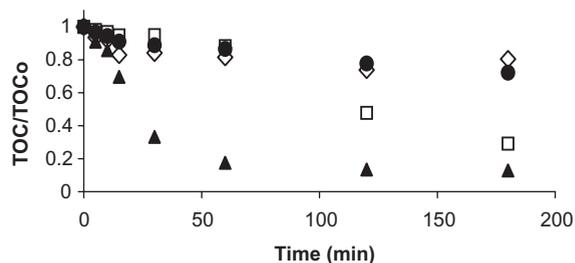


Fig. 3. Normalized TOC (Total of Organic Carbon) measurements during the degradation of diesel oil in aqueous medium at pH 3 and 33 °C via: ● UV-photolysis; ◇ thermal Fenton reaction ($[\text{Fe}^{2+}] = 0.1 \text{ mM}$ and $[\text{H}_2\text{O}_2] = 50 \text{ mmol/L}$ reaction); □ $\text{H}_2\text{O}_2/\text{UV}$ ($[\text{H}_2\text{O}_2] = 50 \text{ mmol/L}$ reaction) and ▲ photo-Fenton reaction ($[\text{Fe}^{2+}] = 0.1 \text{ mM}$ and $[\text{H}_2\text{O}_2] = 50 \text{ mmol/L}$ reaction).

2004a,b; Kochany-Lipczynska, 1992), the UV-photolysis and the thermal Fenton processes were not able to promote the complete mineralization. The percentage of removal, after the total reaction time (3 h), in the UV-photolysis case, corresponded to 28% of the total initial organic charge. In the second case, the obtained percentage of removal was 26%, which was possible because of the reaction between ferrous ions and the hydrogen peroxide, generating the hydroxyl radicals, as showed in Eq. (1). The limiting reagent for this process corresponds to the ferrous ions, present in much lower concentration than hydrogen peroxide. However, the processes that use UV radiation combined with chemical reagents presented better results. The UV/ H_2O_2 , for example, was able to mineralize 71%, but the initial degradation rates were much lower than the ones obtained in the photo-Fenton process, in this last case, in just 30 min, 67% of the total initial organic charge was removed. In spite of this process requiring the use of ferrous ions, the drastic reduction of the irradiation time is a very positive point, because the main barrier for the industrial application of the photochemical processes is the costs associated to the power consumption and irradiation exposure. Furthermore, the superior profit, presented by the photo-Fenton process, it was obtained with the use of a reduced initial ferrous ions concentration (0.1 mM). Another important factor is that this concentration is much lower than the limit for disposal established in the local environmental legislation (0.27 mM); in other words, in this special condition, an application of an additional process, for iron removal, cannot be necessary.

3.2. Determination of the optimum experimental conditions

The optimal concentrations of the Fenton reagents (Fe^{2+} and H_2O_2) were determined by a series of

Table 1
Experimental conditions for diesel oil degradation in aqueous medium

Factorial experimental designs	Experimental conditions		Exp.
	H ₂ O ₂ (mmol/L reaction) ^a	Fe ²⁺ (mM)	
1	100	0.3	1A
	200	1.0	1B
	100	0.3	1C
	200	1.0	1D
	150	0.65	1E
2	50.0	0.1	2A
	100.0	0.1	2B
	50.0	0.3	2C
	100.0	0.3	2D
	75	0.2	2E
3	25	0.2	3A
	75	0.2	3B
	25	0.4	3C
	75	0.4	3D
	50	0.3	3E
4	25	0.05	4A
	75	0.05	4B
	25	0.2	4C
	75	0.2	4D
	50	0.1	4E
5	5	0.01	5A
	50	0.01	5B
	5	0.1	5C
	50	0.1	5D
	25	0.05	5E

^a Total number of millimoles of H₂O₂ added to the reservoir per liter of reaction mixture.

experiments. Based on the gradient descent technique, it was possible to establish a logical sequence of experiments for the minimization of the Fenton

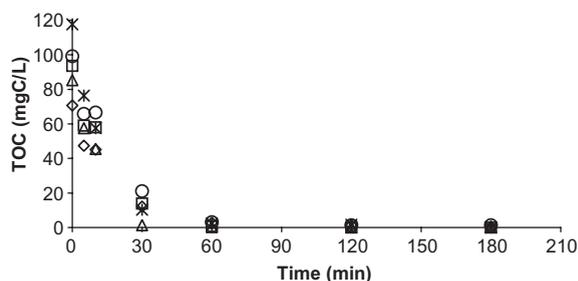


Fig. 5. Degradation profiles of diesel oil in aqueous medium (set 1) at pH 3 and 33 °C: (*) [H₂O₂]=200 mmol/L reaction and [Fe²⁺]=1 mM; (◇) [H₂O₂]=200 mmol/L reaction and [Fe²⁺]=0.3 mM; (□) [H₂O₂]=100 mmol/L reaction and [Fe²⁺]=1 mM; (△) [H₂O₂]=100 mmol/L reaction and [Fe²⁺]=0.3 mM and (○) [H₂O₂]=150 mmol/L reaction and [Fe²⁺]=0.65 mM.

reagents concentrations. The set of experiments was carried out according to five factorial experimental designs at two levels and two variables, as indicated in Table 1. The employed technique has, as the main objective, to change (or move) the experimental domain studied. The sequence of experiments (or the new factorial experimental design) changes the domain of the variables out of the previous factorial experimental design. Other alternative for the optimization of the variables it would be the application of the surface response methodology (Fernández et al., 2004). Fig. 4 shows the displacements of the experimental domains studied, focusing on the use of the smallest amount of reagents, principally the iron salt because of local environmental constraints, while maximizing the extent of mineralization (99%).

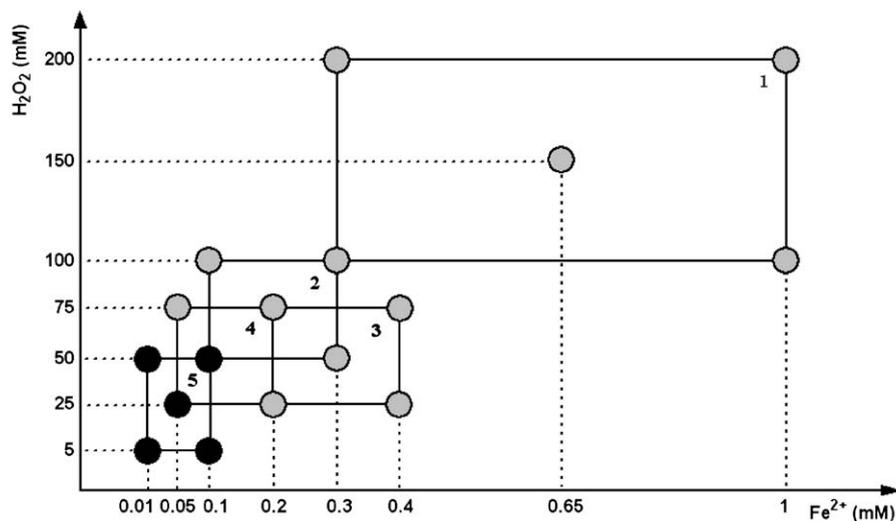


Fig. 4. The sets of factorial experimental designs, as function of Fe²⁺ and H₂O₂ concentrations in the photo-Fenton process.

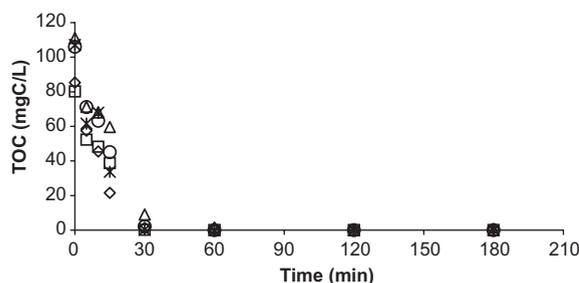


Fig. 6. Degradation profiles of diesel oil in aqueous medium (set 2) at pH 3 and 33 °C: (O) $[H_2O_2]=100$ mmol/L reaction and $[Fe^{2+}]=0.1$ mM; (◇) $[H_2O_2]=100$ mmol/L reaction and $[Fe^{2+}]=0.3$ mM; (□) $[H_2O_2]=50$ mmol/L reaction and $[Fe^{2+}]=0.1$ mM; (Δ) $[H_2O_2]=50$ mmol/L reaction and $[Fe^{2+}]=0.3$ mM and (*) $[H_2O_2]=75$ mmol/L reaction and $[Fe^{2+}]=0.2$ mM.

In order to make the process match environmental restrictions (the limit of disposal of ferrous ions is 0.27 mM, in the Brazilian Environmental Legislation — CONAMA 20) and at the same time be economically more feasible, the experimental domain was progressively shifted to lower levels of the variables $[Fe^{2+}]$ and $[H_2O_2]$ in order to determine the minimum amounts of these reagents that keep a conversion of 99%. For the first two experimental data sets (1–2, Table 1) the degradation profiles were similar and, under all conditions, 99% mineralization were achieved within about 30 min (Figs. 5 and 6), indicating that the Fenton reagents were present in large excess.

In the third sequence of experiments (set 3, Table 1), with $[H_2O_2]$ reduced and $[Fe^{2+}]$ increased, the maximum level of H_2O_2 , 75 mM, gave complete mineralization in 30 min of reaction, while this happened only after 1 h of reaction in the other experimental conditions of the set (Fig. 7).

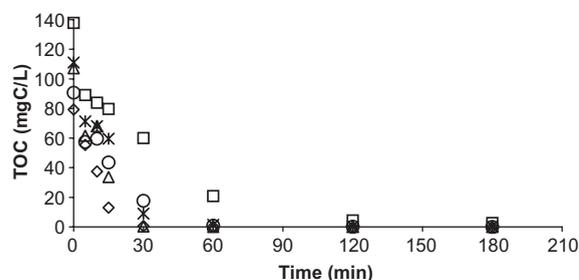


Fig. 7. Degradation profiles of diesel oil in aqueous medium (set 3) at pH 3 and 33 °C: (O) $[H_2O_2]=25$ mmol/L reaction and $[Fe^{2+}]=0.4$ mM; (◇) $[H_2O_2]=75$ mmol/L reaction and $[Fe^{2+}]=0.4$ mM; (□) $[H_2O_2]=25$ mmol/L reaction and $[Fe^{2+}]=0.2$ mM; (Δ) $[H_2O_2]=75$ mmol/L reaction and $[Fe^{2+}]=0.2$ mM and (*) $[H_2O_2]=50$ mmol/L reaction and $[Fe^{2+}]=0.3$ mM.

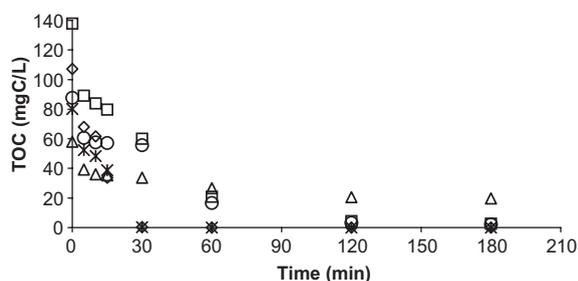


Fig. 8. Degradation profiles of diesel oil in aqueous medium (set 4) at pH 3 and 33 °C: (O) $[H_2O_2]=75$ mmol/L reaction and $[Fe^{2+}]=0.05$ mM; (◇) $[H_2O_2]=75$ mmol/L reaction and $[Fe^{2+}]=0.2$ mM; (□) $[H_2O_2]=25$ mmol/L reaction and $[Fe^{2+}]=0.2$ mM; (Δ) $[H_2O_2]=25$ mmol/L reaction and $[Fe^{2+}]=0.05$ mM and (*) $[H_2O_2]=50$ mmol/L reaction and $[Fe^{2+}]=0.1$ mM.

In the fourth sequence of experiments (set 4, Table 1), incomplete mineralization is observed at the lowest reagent concentrations (Fig. 8). This prompted the last set of experiments (set 5, Table 1; Fig. 9), which leads to the identification of the optimal reagent concentrations as those of experiment 5D ($[H_2O_2]=50$ mmol/L and $[Fe^{2+}]=0.1$ mM), in which the Fe^{2+} concentration is well below the local environmental constraint (0.27 mM).

4. Conclusions

The application of the photo-Fenton process for the treatment of wastewaters contaminated with diesel oil resulted in conversions of up to 99%, in terms of removal of the total organic carbon content. By comparison, UV photolysis alone and the thermal Fenton reaction resulted in degradation of only 28% and 26%, respectively. Furthermore, the UV/ H_2O_2 process was able to mineralize 71%, but requesting a

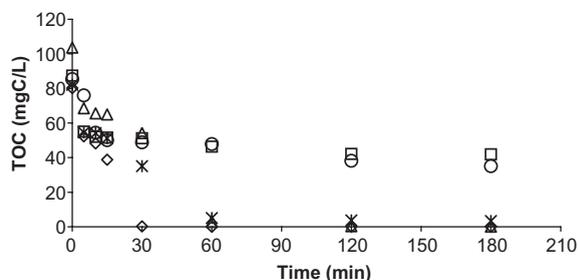


Fig. 9. Degradation profiles of diesel oil in aqueous medium (set 5) at pH 3 and 33 °C: (O) $[H_2O_2]=5$ mmol/L reaction and $[Fe^{2+}]=0.1$ mM; (◇) $[H_2O_2]=50$ mmol/L reaction and $[Fe^{2+}]=0.1$ mM; (□) $[H_2O_2]=5$ mmol/L reaction and $[Fe^{2+}]=0.01$ mM; (Δ) $[H_2O_2]=50$ mmol/L reaction and $[Fe^{2+}]=0.01$ mM and (*) $[H_2O_2]=25$ mmol/L reaction and $[Fe^{2+}]=0.05$ mM.

significant irradiation time; in other words, a high cost related to the power consumption. These facts show the importance of the combined action of H_2O_2 , ferrous ions and UV radiation in the photo-Fenton process for the degradation of the diesel oil in water.

The optimum concentrations of the photo-Fenton reagents for 99% mineralization, determined in this work for the photodegradation of diesel oil in aqueous medium, were: $[\text{H}_2\text{O}_2] = 50 \text{ mmol/L}$ and $[\text{Fe}^{2+}] = 0.1 \text{ mM}$. The iron content is within the local environmental legislation limit for disposal of iron ions (0.27 mM). From an economical point of view, in this condition, it is not necessary to apply another process to remove the iron residual, fact that is very attractive. Furthermore, the electrical energy is the main cost associated with this process, and these conditions result in 99% mineralization in the shortest irradiation time. Moreover, solar energy may also be applied for the treatment of wastewaters contaminated with diesel components like, as shown recently by the authors (Moraes et al., 2004a,b).

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