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Solar photo-Fenton treatment of petroleum extraction wastewater

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ABSTRACT

The purpose of this study is to investigate the treatment of petroleum-extraction wastewater by means of a photo-Fenton like process using sunlight as irradiation source. According to the experimental results, a reduction of the wastewater UV absorption spectral intensity indicates that polycyclic aromatic hydrocarbons and aromaticity removal of approximately 92.7 and 96.2%, respectively, were obtained after 7 h of sunlight exposure using 485.3 mmol L^{-1} of hydrogen peroxide. For the investigated treatment condition, the H_2O_2 optimum concentration was 485.3 mmol L^{-1} since an increment in H_2O_2 concentration did not promote a significant increment in treatment efficiency. H_2O_2 single oxidation was also important during the photo-Fenton treatment. A moderate level of mineralization was also observed. Finally, photo-Fenton process using sunlight was able to reduce sample acute phytotoxicity by about 50%.

Keywords: Advanced oxidation; Hydrocarbons; PAH; Petroleum wastewater; Photo-Fenton

1. Introduction

Petroleum wastewater is the main residue generated during the production process since substantial amounts of saline water are produced along with the oil. As a result, biorecalcitrant hydrocarbons present in this wastewater may disable biological treatments, thus requiring the use of effective technologies to achieve acceptable treatment levels. The treatment of oil field waters is mandatory, because of in addition to petroleum derivatives, large amounts of added chemicals such as corrosion and scale inhibitors, demulsifiers, defoamers, and biocides present in the wastewater at concentrations of mg L^{-1} should not be dumped into marine environments [1,2].

Among the hydrocarbon classes present in petroleum wastewater, aromatics and polycyclic aromatic hydrocarbons (PAH) are the main sources of environmental contamination in this type of effluent [3,4]. In an attempt to minimize environmental contamination by petroleum-extraction wastewater, new pollution control techniques have been employed in several branches of extraction and transformation industries, and the search for new technologies applicable to wastewater treatment has grown substantially [5–8].

Advanced oxidative processes are extremely efficient technologies that can destroy organic

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compounds, often present in low concentrations [9–13]. Fenton's reaction has proven to be a promising technology in wastewater treatment [14]. A number of studies have been conducted, showing that the combination of iron and hydrogen peroxide, called Fenton's reaction [15], is an effective oxidant for a wide variety of organic substrates [16–18]. The degradation of organic compounds in Fenton's reaction is performed by hydroxyl radicals (OH). These are generated through the decomposition of H_2O_2 catalyzed by Fe^{+2} in an acidic medium. There are two Fenton's reaction categories: the standard Fenton reaction between hydrogen peroxide and Fe^{+2} ions in solution, and the Fenton-like reaction where hydrogen peroxide reacts with Fe^{+3} or immobilized oxides [19]. In the presence of light, Fenton's reaction promotes the so-called photo-Fenton process and a higher quantity of ·OH is produced. This is achieved using low-energy photons in the visible light spectrum, such as those generated by sunlight, making this technique economically viable [20].

The present study aims to assess the suitability of the photo-Fenton-like process using solar light for the treatment of petroleum wastewater, mainly with respect to PAH, aromaticity and acute ecotoxicity removal.

2. Experimental

2.1. Wastewater characterization

Wastewater used in this research was produced together with oil at the petroleum extraction unit (Petrobras S.A.) located in the state of Rio Grande do Norte, in the northeast of Brazil. Samples were characterized before the experiments to obtain their chemical and physical properties. Wastewater characterization was determined by the quantification of pH, chemical oxygen demand (COD), and metal content such as Fe_{total}, Mn, Cu, Pb, Zn, Cr, Cd, and Ni according to the Standard Methods for the Examination of Water and Wastewater methodology [21]. Metal analyses were performed with a Varian AA240 FS atomic absorption spectrometer. The pH measurements were taken on a Digimed DM20 pH meter.

Table 1
Wastewater characterization

Parameters	Values
Iron	$0.93\,mg\,L^{-1}$
Copper	$0.04\,mg\,L^{-1}$
Manganese	$0.79\,mg\,L^{-1}$
Cadmium	$0.05\,mg\,L^{-1}$
Lead	$0.76\,mg\,L^{-1}$
Zinc	$0.02\,mg\,L^{-1}$
Chromium	ND*
Nickel	ND*
COD	$220\,mg\,O_2\,L^{-1}$
pH	7.9

*ND = Not detected.

As previously described, wastewater was characterized in terms of metals, COD, and pH. Table 1 presents the obtained measurements. Due to the presence of iron in the raw wastewater, sample pH was adjusted to 3.0 with sulfuric acid p.a. to favor the photo-Fenton-like reaction before adding hydrogen peroxide. Therefore, photodegradation experiments were carried out without adding external source of iron. Chromium and nickel were not detected and initial sample pH was approximately 7.9. To ensure reproducibility, the characterization experiments were carried out in triplicate.

Hydrocarbons analysis was also performed, for this, the absorption spectrum of the standard PAH mix solution at a concentration of $1\,mg\,L^{-1}$ is shown in Fig. 1(a) and the wastewater absorption spectrum in Fig. 1(b). The wavelength corresponding to the identified peaks can be seen in Table 2.

From Table 2 it is possible to observe that the highest peak in the wastewater spectrum was at 230.5 nm (peak 5), which was also observed in the absorption spectrum of the standard PAH solution (peak 5). Although the presence of other organic compounds in the wastewater may influence absorbance removal, the peak at 230.5 nm was chosen as an indicator of PAH removal, since it is present in the standard PAH solution. The calibration curve was then constructed using the 230.5 nm absorbance of standard PAH mix dilutions (highest sample peak). Light absorption was also measured at a wavelength of 254 nm.

The initial PAH concentration in the sample was $1.6\,mg\,L^{-1}$. The 254 nm absorbance of the untreated sample was $2.3\,cm^{-1}$.

2.2. Wastewater photodegradation experiments

Photodegradation experiments were carried out by exposing the sample to H_2O_2/solar radiation after adjusting the sample pH to 3 (with H_2SO_4) to favor Fenton reactions. Initially, 30 mL of the sample was transferred to each experimental unit (glass Petri dishes) with a surface area of $63.6\,cm^2$. Pre-established amounts of a standard H_2O_2 solution were added and samples were then exposed to sunlight for 1–7 h.

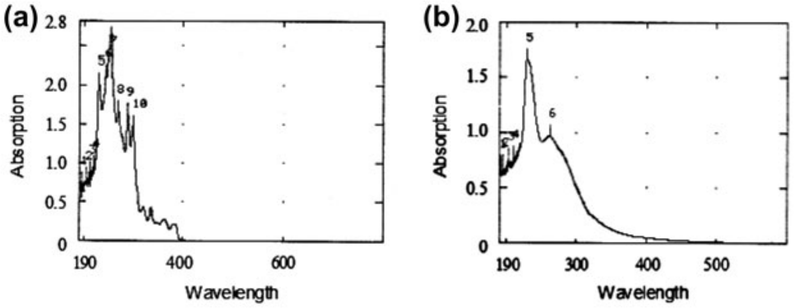

Fig. 1. (a) absorption spectrum of standard PAH mix containing 16 PAH; (b) absorption spectrum of the wastewater sample.

Table 2
Wavelength of peaks identifies in Figs. 1(a) and 1(b)

Peak	Fig. 1(a) (nm)	Fig. 1(b) (nm)
1	197.0	192.0
2	206.5	196.5
3	212.5	203.5
4	219.5	210.5
5	230.5	230.5
6	244.0	262.5
7	254.0	–
8	269.5	–
9	289.0	–
10	299.0	–

Experiments were conducted in October in Recife, Brazil (8° 04′03′′ S; 34° 55′00′′ W) at the same time of day in order to avoid incident radiation variance. The average solar radiation was approximately17 mJ $m^{-2}s^{-1}$ in the wavelength range of 380–780 nm.

Hydrogen peroxide concentrations in the experimental units were 8.8, 50.0, 247.0, 485.3 and 1,132 mmol L^{-1}, equivalent to 0.02, 0.10, 0.50, 1.00, and 2.00 mL of 51% H_2O_2 standard solution. Samples with 0.02, 0.10, and 0.50 mL of H_2O_2 solution were exposed to sunlight for 6 h. The other two samples were irradiated for periods of time between 1 and 7 h since a greater concentration of hydrogen peroxide would need less time to degrade contaminants. The experiment with higher H_2O_2 concentration (485.3 mmol L^{-1}) was repeated in the absence of light to determine the contribution of H_2O_2 alone in the organic compounds oxidation.

PAH concentration was measured through chromatographic analysis and UV spectrum intensity, as described in the following section. COD test was performed to measure the organic matter oxidation along the reaction time. COD was carried out according to APHA [21]. Sample toxicity was monitored with a toxicity test using *Lactuca sativa* seeds according to Dutka [22]. To avoid interference in analysis, hydrogen peroxide was quenched prior to COD and toxicity tests by adding catalyse (2.950 U/mg bovine liver; 100 mg L^{-1}) acquired from Sigma-Aldrich after adjusting the sample pH to a range between 6 and 8.

2.3. Oil fraction extraction

Prior to chromatographic analysis, oil fraction, specifically PAH content, was extracted from the wastewater using a simple liquid–liquid extraction. Thus, 30 mL of sample was added to three 6 mL aliquots of redistilled dichloromethane (DCM) (Merck, Brazil). For each aliquot, the separation funnel containing the mixture was vigorously agitated for 5 min, and then allowed to rest for 5 min for later collection and concentration. It was concentrated in a rotaevaporator to a final volume of 5 mL for subsequent analysis.

2.4. Hydrocarbon analysis

2.4.1. Spectroscopic analysis

Total sample of PAH concentration was assessed before and after photo-Fenton treatment, using absorption spectroscopy (Aquamate V4.60 UV spectrophotometer, Thermo Scientific, USA). The absorbance of the sample in specific wavelengths was also measured. To obtain the absorption spectrum of the PAH mixture, absorption of 1 mg L^{-1} PAH mix standard solution (AccuStandard, Z-014G) containing 16 PAH (Acenaphthene, Acenaphthylene, Anthracene, Benzo (a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(ghi)perylene, Benzo(k)fluoranthene, Chrysene, Dibenzo(a,h)anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd) pyrene, Naphthalene, Phenanthrene, Pyrene) was recorded. A calibration curve was then built using a wavelength of 230.5 nm, representing the highest PAH peak found in the wastewater sample and standard PAH mix. Reduction of absorption at 254 nm was also investigated since this is considered as a fast and simple indicator of wastewater aromaticity [23].

2.4.2. Chromatographic analysis

The PAH mix standard used in chromatographic analyses was the same used in absorption spectroscopy. The EPA 8270 method was applied for PAH quantification using gas chromatography (GC). Before GC analysis, 30 mL of sample was concentrated to 5 mL using DCM. The method was reproduced in a gas chromatography column coupled to a mass spectrometer (Shimadsu models GC-17A and QP5050A, respectively). A DB-5 MS capillary column (length = 30 m, inner diameter = 0.25 and film thickness = 0.25 μm) was used with an injector temperature of 280 ℃ (splitless). Chromatographic conditions also included an initial oven temperature of 80–120 ℃ with a ramp of 20 ℃ min^{-1}, and 120–285 ℃ with 2.8° C min^{-1}. To increase the sensitivity of the method, the compounds detection by chromatographic analysis was performed using the selective ion monitoring method which detects only compounds that present predetermined molecular ion in their mass spectrum and ions selected for each compounds. The quantification of HPA was performed using an analytical curve of eight points beginning at a concentration of 0.5 mg L^{-1} and ending at 4.0 mg L^{-1}, prepared diluting the mix containing the 16 HPA (AccuStandard, code-Z 014G).

2.5. Toxicity test

Acute ecotoxicity of the raw and treated samples was determined through toxicity testing using *L. Sativa* seeds to assess variations in phytotoxicity samples. Measurements were taken before and after the treatment. Samples were combined with seeds in the first day of growth, corresponding to the germination period [22].

In order to perform the test, a paper disc was placed on a petri dish (9 cm in diameter) and soaked with 4 mL of the samples at concentrations (v/v) of 3, 10, 30, 70 and 100%. Seeds were then uniformly distributed onto the paper. Toxicity was estimated by calculating inhibition concentration (IC_{50}). A concentration of IC_{50} causes an inhibitory response in 50% of the exposed organisms. After exposure, the length of each root was measured and inhibition percentage was calculated according to the following equation:

$$\%\ \text{Inhibition} = 100 - [(x\ \text{sample}/x\ \text{control})^{*}100] \qquad (1)$$

where x is the root length.

3. Results and discussion

3.1. Wastewater photodegradation experiments

Results of photodegradation experiments are shown in Fig. 2. According to the obtained data, the treatment was able, even at low hydrogen peroxide concentrations, to achieve removals higher than 70% for 230.5 and 254 nm absorptions. This significant removal may be attributed to the combination of hydrogen peroxide oxidation and photo-Fenton reaction, which was favored by the natural presence of iron in the sample. Samples exposed to 6 h of sunlight irradiation and different H_2O_2 concentrations (8.8, 50.0, 247.0, and 485.3 mmol L^{-1}) improved absorbance removal at 230.5 and 254 nm according to the H_2O_2 concentration increase. The highest removal rate was achieved using the highest hydrogen peroxide concentration (485.3 mmol L^{-1}). PAH removals, represented by absorbance at 230.5 nm, ranged from 68% to 85% and aromatic removal between 78 and 90%. Fig. 3 shows the absorption spectrum following 6 h of solar/H_2O_2 treatment using 485.3 mmol L^{-1} of hydrogen peroxide. The reduction of the absorption spectrum intensity indicates that the photochemical process acted on the degradation of organic components in the water.

In Fig. 3, peak six of the UV–vis absorption spectrum refers to the wavelength of 230.5 nm, that represented the PAH presence in the wastewater. In order to verify, if the method was able to reach higher absorbance removals, a new set of experiments was performed. In this new set of experiments, the

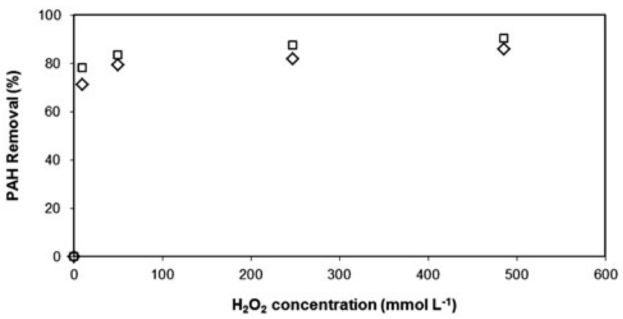

Fig. 2. 230.5 (◇) and 254 (□) nm removal obtained with different H_2O_2 concentrations during 6 h of treatment.

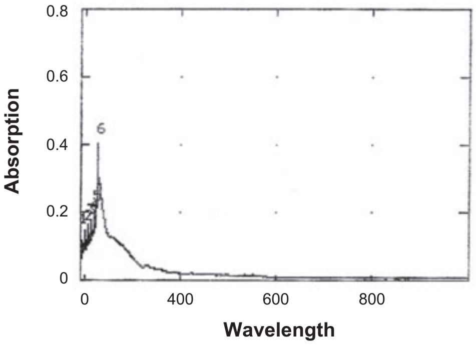

Fig. 3. Absorption spectrum of wastewater after 6 h of SOLAR/H_2O_2 treatment.

hydrogen peroxide concentrations used for treatment with H_2O_2/solar were 485.3 and 1,132 mmol L^{-1}. A blank experiment only with the use of H_2O_2 was also carried out using 485.3 mmol L^{-1} of H_2O_2. The concentration of 1,132 mmol L^{-1} was employed to determine whether increased concentration would improve the absorbance removal. Figs. 4 and 5 illustrate the 230.5 and 254 nm absorbance removed for the aforementioned hydrogen peroxide concentrations.

After 7 h of reaction, the treatment using hydrogen peroxide alone, showed a residual hydrogen peroxide of 479.4 mmol L^{-1}. Thus, only 0.3 mmol L^{-1} of H_2O_2 was needed to degrade 34% of the aromatics and approximately 20% of the PAH in the wastewater. Thus, an important contribution of H_2O_2 was observed, however irradiation was needed to increase process efficiency.

Fig. 4 shows PAH removal of around 92.7% for the peroxide treatment at a concentration of 485.3 mmol L^{-1} and 85% for 1,132 mmol L^{-1} after 7 h of treatment. Fig. 5 indicates that aromatic hydrocarbon removal was 96% for peroxide treatment at a concentration of 485.3 mmol L^{-1} and 98% for 1,132 mmol L^{-1} after 7 h of treatment. Treatments with H_2O_2/solar using hydrogen peroxide concentrations of 1,132 and 485.3 mmol L^{-1} showed a similar degradation rate, assuming that an increment of H_2O_2 concentration greater than 485 mmol L^{-1} would not increase the organic degradation rate. This inhibition could be associated to the ·OH scavenger promoted by the excess of H_2O_2, which would also affect aromatic removal. Concerning the organic matter oxidation, the COD analysis revealed that after 6 h of treatment the sample had COD near 113 mg $O_2\,L^{-1}$, corresponding to a decrease of approximately 53% of the initial value.

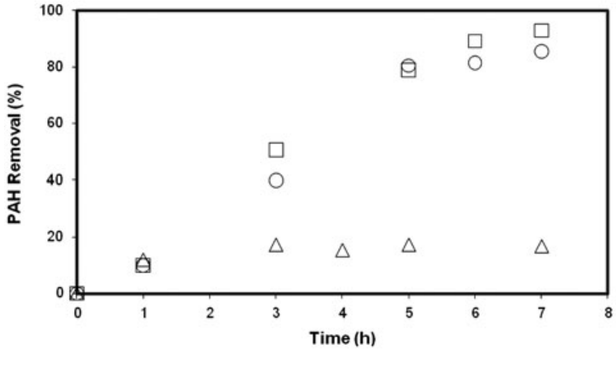

Fig. 4. $ABS_{230.5}$ removal. Δ = H_2O_2 485 mmol L^{-1}; □ = Solar/H_2O_2 485 mmol L^{-1}; ○ = Solar/H_2O_2 1,132 mmol L^{-1}.

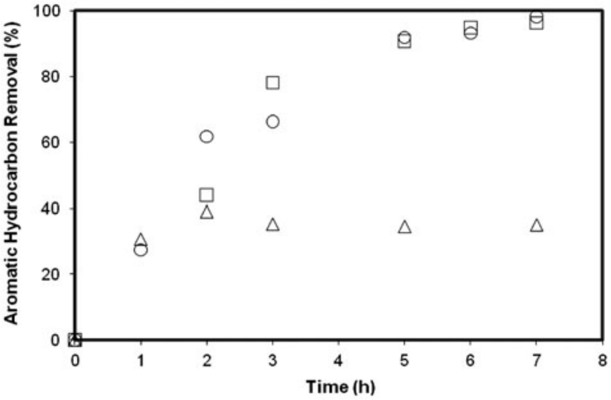

Fig. 5. ABS_{254} removal. Δ = H_2O_2 485 mmol L^{-1}; □ = Solar/H_2O_2 485 mmol L^{-1}; ○ = Solar/H_2O_2 1,132 mmol L^{-1}.

It is important to remark that the used system was not provided with a refrigerated system, thus allowing the temperature to achieve values around 40°C. However, at this condition the ·OH generation is favored in Fenton processes with low iron concentration [24].

3.2. Chromatographic analysis

In this section of the study, a GC-MS method to detect 16 PAHs was applied: (Acenaphthene, Acenaphthylene, Anthracene, Benzo(a)anthracene, Benzo (a)pyrene, Benzo(b)fluoranthene, Benzo(ghi)perylene, Benzo(k)fluoranthene, Chrysene, Dibenzo(a,h)anthracene, Fluoranthene, Fluorene, Indeno(1,2,3-cd) pyrene, Naphthalene, Phenanthrene, and Pyrene). Among them, only Naphthalene was detected in the sample. The quantification limit was 0.3 mg L^{-1}. The naphthalene concentration in the wastewater, measured in triplicate, before the treatment was 2.09 ± 0.05 mg L^{-1}. Since, by chromatographic analysis only the naphthalene was detected in the sample, the absorption peak with wavelength 230.5 nm was used as an evidence of Naphthalene removal, however due to the complexity of the sample one cannot affirm that this specific peak corresponds only to Naphthalene.

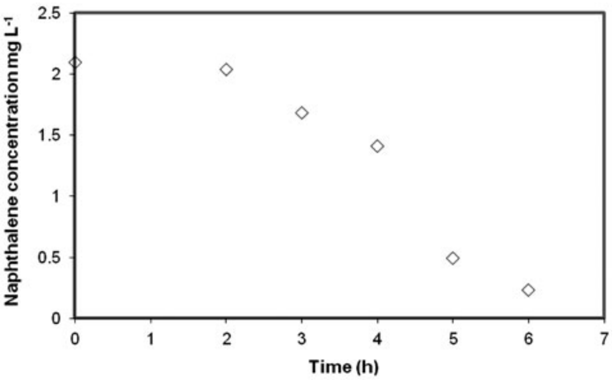

Fig. 6. Naphthalene concentration during H_2O_2/Solar treatment. $[H_2O_2] = 485.3\,mmol\,L^{-1}$.

Fig. 6 presents the naphthalene concentration recorded during 7 h of solar irradiation using solar/H_2O_2 treatment with an H_2O_2 concentration of $485.3\,mmol\,L^{-1}$. The naphthalene concentration did not decrease significantly in the first 2 h of treatment. This fact could be explained by the presence of more reactive compound, which competes for the available ·OH in the first hour of reaction. A naphthalene removal around 76% was observed. After 6 h of treatment, the naphthalene concentration was below the quantification limit.

The results presented in this work are in agreement with similar works dealing with hydrocarbons, TOC, and COD removal from waters containing petroleum -related contaminants [25,26].

3.3. Toxicity assessment

The last section of this work assesses the toxicity of the treated samples. For testing purposes, the inhibition percentage of *L. sativa* seed germination cultivated in solutions of different sample concentrations (3, 10, 30, 70, and 100%) was measured. Analysis was carried out over the course of treatment and samples were combined with seeds for a period of 120 h. Results are shown in Fig. 7, where the graph represents inhibition as a function of sample concentration.

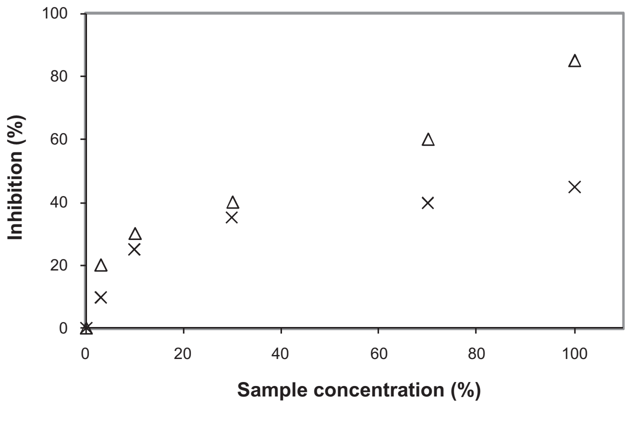

Fig. 7. Inhibition percentage of the seeds germination in diverse sample concentrations. Δ = raw wastewater and X = treated wastewater.

Fig. 7 indicates no significant change in sample toxicity up to 30% of sample concentration. However, at 100% sample concentration, there is an apparent reduction in the inhibition percentage of the cultivated seed in treated water compared to untreated water. Therefore, it was possible to calculate IC_{50} for the raw and treated sample, thus 6 hours of treatment in presence of $485.3\,mmol\,L^{-1}$ of H_2O_2 increased IC_{50} from 50.7 to 99.9%. Since the increase of IC_{50} implies toxicity reduction, it can be stated that the resulting by-products had lower acute phytotoxicity than the untreated sample.

4. Conclusions

The present study demonstrated that the solar photo-Fenton-process is an alternative for the treatment of waters contaminated with PAH, especially those resulting from petroleum extraction. The method showed its capacity for absorbance removal. These absorbances represented PAH content and aromatic content in the medium. PAH and aromaticity removal of around 92% and 96%, respectively, were achieved through the treatment with hydrogen peroxide at a concentration of $485.3\,mmol\,L^{-1}$, after 7 h of sunlight exposure. Treatments with H_2O_2/solar at hydrogen peroxide concentrations of 1,132 and $485.3\,mmol\,L^{-1}$ had a similar degradation rate. This indicates an excess oxidant in the experiment, which did not promote any increase in the removal rate. Among the hydrogen peroxide concentrations used in the H_2O_2/solar treatment, $485.3\,mmol\,L^{-1}$ proved to be the most efficient. Under the applied experimental conditions, a COD reduction of about 53% was observed. In addition, the toxicity study shows that the proposed method reduces sample phytotoxicity by about 50%.

Acknowledgments

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