

Treatment of 1,10-phenanthroline laboratory wastewater using the solar photo-Fenton process

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Abstract

The red Fe^{2+} -phenanthroline complex is the basis of a classical spectrophotometric method for determination of iron. Due to the toxicity of this complexing agent, direct disposal of the wastewaters generated in analytical laboratories is not environmentally safe. This work evaluates the use of the solar photo-Fenton process for the treatment of laboratory wastewaters containing phenanthroline. Firstly, the degradation of phenanthroline in water was evaluated at two concentration levels (0.1 and 0.01%, w/v) and the efficiencies of degradation using ferrioxalate (FeOx) and ferric nitrate were compared. The 0.01% w/v solution presented much higher mineralization, achieving 82% after 30 min of solar irradiation with both iron sources. The solar photo-Fenton treatment of laboratory wastewater containing, in addition to phenanthroline, other organic compounds such as herbicides and 4-chlorophenol, equivalent to 4500 mg L^{-1} total organic carbon (TOC) resulted in total degradation of phenanthroline and 25% TOC removal after 150 min, in the presence of either FeOx or ferric nitrate. A ratio of 1:10 dilution of the residue increased mineralization in the presence of ferrioxalate, achieving 38% TOC removal after 120 min, while use of ferric nitrate resulted in only 6% mineralization over the same period.

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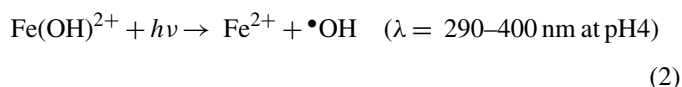
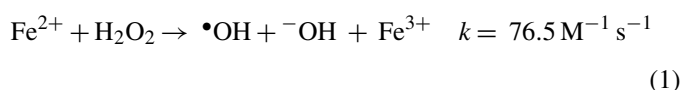
Keywords: Advanced oxidation processes; Ferrioxalate; Iron complexes; Laboratory wastewater

1. Introduction

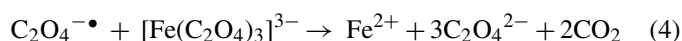
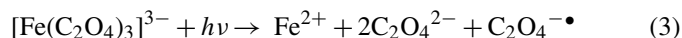
The reaction of ferrous ions with 1,10-phenanthroline (phenanthroline) generates a stable red complex which is the basis for the classical spectrophotometric method of Fe^{2+} determination through complexation with phenanthroline [1]. This method is widely used in teaching and also in water and wastewater analysis laboratories. Due to the high toxicity and mutagenicity of this reagent [2], its destruction is an indispensable step before discharging. Another problem is that laboratory wastewaters may contain other contaminants, making the treatment process more complex.

The photo-Fenton process is considered suitable for the treatment of a variety of wastewaters due to its high efficiency and nonselectivity in the oxidation of organic compounds. The generation of the highly oxidizing hydroxyl radical ($E^\circ = 2.73 \text{ V}$) [3] during the decomposition of H_2O_2 in the presence of ferrous

ions and its regeneration under irradiation are considered to be responsible for the high efficiency of the process (Eqs. (1) and (2)) [4–6].



The use of ferrioxalate (FeOx) as source of iron increases, in general, the efficiency of the process, especially when solar light is applied. The high quantum yield of $\text{Fe}(\text{II})$ generation (Eqs. (3) and (4)) ($\phi_{\text{Fe}(\text{II})} = 1.24$ at 300 nm) and the high absorption in the UV-vis region improves the efficiency of the solar process [7].



Some important advantages of the photo-Fenton process are its simplicity of operation and the possibility of using solar light, which reduces energy costs [8–10]. These features allow for the

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in situ treatment of laboratory wastewaters, which have generally complex composition and are generated in small volumes. The on-site treatment of such wastewaters is environmentally advantageous since it avoids the need for storage, risk during transport or inappropriate discharges.

Although the photo-Fenton process appears to be an alternative for the treatment of wastewaters containing iron ions as part of the mixture, the strong complexation of these ions by phenanthroline may hinder the photodegradation process, as previously observed for nitrogen-containing compounds [10]. Due to this concern, the aim of this work is to investigate the degradation efficiency of laboratory wastewaters containing phenanthroline using the solar photo-Fenton process.

2. Materials and methods

2.1. Chemicals

Potassium ferrioxalate ($K_3Fe(C_2O_4)_3 \cdot 3H_2O$) was prepared and purified as described previously [11]. An aqueous potassium ferrioxalate (FeOx) stock solution was prepared at a concentration of 0.25 M and stored in the dark at room temperature for a maximum period of one week. $FeSO_4$ (Carlo Erba), $Fe(NO_3)_3 \cdot 9H_2O$ (Mallinkrodt) and H_2O_2 30% (w/v) (Merck) were used. Ammonium metavanadate (Vetec) solution was prepared at the concentration of 0.06 M in 0.36 M H_2SO_4 , and 1,10-phenanthroline ($C_{12}H_8N_2$) was purchased from Mallinkrodt. All the solutions were prepared with distilled water.

2.2. Solar photodegradation procedure and energy dose measurements

The photodegradation experiments were carried out during autumn and winter in Brazil ($21^\circ 47'S$; $48^\circ 10'W$), exposing 4.5 cm deep (250 mL) solutions in open dark glass vessels to solar light. The UV dose accumulated during exposure was measured using a radiometer (PMA 2100 Solar Light Co) in

the UVA region (320–400 nm) with the sensor placed horizontally. To evaluate the photodegradation of phenanthroline, 0.01 and 0.1% (w/v) solutions (80 and 800 mg L^{-1} total organic carbon (TOC); 0.55 and 5.5 mM, respectively) were prepared, and the pH was adjusted to 2.5 with 3.0 M H_2SO_4 . Required volumes of FeOx or $Fe(NO_3)_3$ and H_2O_2 stock solutions were added immediately before irradiation. The initial $[H_2O_2/Fe^{3+}]$ ratio was 10. This ratio was selected considering the optimum results reached in previous works [10,12]. Stepwise additions of the same initial amount of H_2O_2 were made every 30 min to replace the consumed H_2O_2 . Experiments were also carried out with laboratory residues containing phenanthroline from Fe^{2+} determinations, in which initial TOC was 4500 mg L^{-1} . Besides phenanthroline, the residues contained other organic compounds such as 4-chlorophenol, formaldehyde and the herbicides diuron and tebuthiuron.

2.3. Chemical analysis

Absorption spectra of phenanthroline solutions in the 200–700 nm region were measured before and after irradiation using a UV–vis spectrophotometer (Shimadzu 1240) after appropriate dilution indicated on figure legends. Mineralization was evaluated by TOC analysis using a TOC analyzer (TOC-5000A SHIMADZU). In the case where FeOx was used as the iron source, the overall TOC concentration also includes the oxalate content of the reagent. Residual H_2O_2 concentration was determined spectrophotometrically after reaction with ammonium metavanadate [13]. All the analyses were carried out immediately after withdrawal of samples to avoid further reaction.

3. Results and discussion

Phenanthroline (in the absence of Fe^{2+}) shows two typical absorption bands, at 227 and 267 nm, as can be seen in Fig. 1A (curve 1). After addition of $Fe(NO_3)_3$ and H_2O_2 the phenanthroline spectrum showed a decrease in the absorption at 267 nm

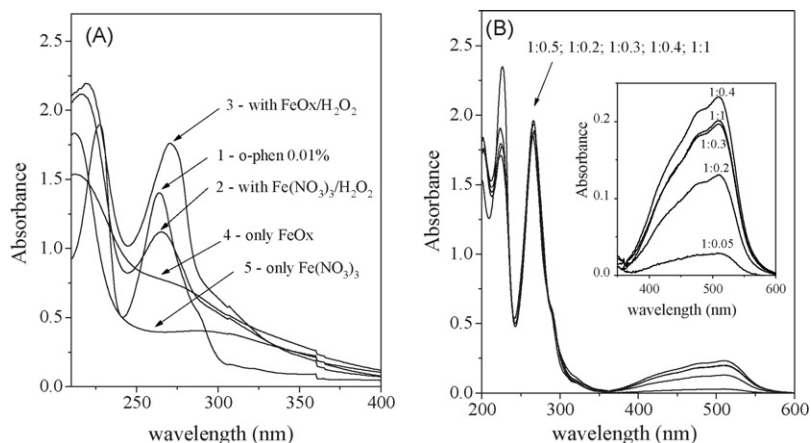


Fig. 1. (A) Absorption spectra of 0.01% (w/v) phenanthroline in the presence and absence of 1.0 mM FeOx or $Fe(NO_3)_3$ and 10 mM H_2O_2 (dilution 1:10) and comparison to absorption spectra of FeOx and $Fe(NO_3)_3$ and (B) absorption spectra of 0.1% (w/v) phenanthroline solution after additions of different molar ratios of Fe^{2+} (pH 2.5) (dilution 1:100).

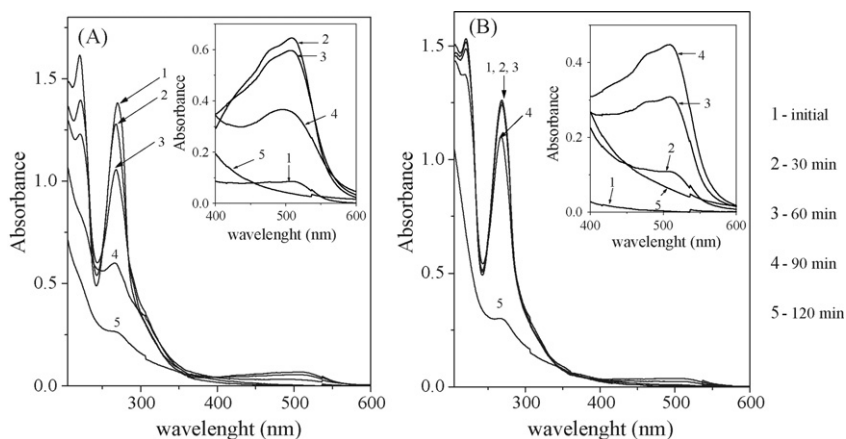


Fig. 2. Absorption spectra of 0.1% (w/v) phenanthroline solution in the presence of (A) FeOx and (B) Fe(NO₃)₃ during solar photo-Fenton degradation (1:100 dilution). Initial concentrations: [FeOx] = [Fe(NO₃)₃] = 1.0 mM; [H₂O₂] = 10 mM. Step additions of H₂O₂ every 30 min. UV dose = 15.0 J cm⁻² (120 min).

(curve 2), which was not observed when only Fe(NO₃)₃ was added without H₂O₂ (data not shown). In contrast, the addition of ferrioxalate and H₂O₂ resulted in a slight shift to 270 nm and higher absorption (curve 3), which can be attributed to the high absorption of ferrioxalate in this region (curve 4). Furthermore, the addition of Fe²⁺ to phenanthroline solution results in the formation of the red complex, with maximum absorption at 510 nm, as can be seen in Fig. 1B, while no change in the absorption band at 267 nm was observed. The complexation with Fe²⁺ does not affect the absorption band at 267 nm, which is attributed to intraligand transitions [14]. Despite the small changes observed in the absorption band at 267 nm by the addition of Fe(III), this band was used as an indication of phenanthroline degradation, comparing the decrease of its absorption during irradiation with the initial absorption in each system.

3.1. Degradation of 1,10-phenanthroline

Before applying the solar photo-Fenton process to a laboratory phenanthroline residue, the procedure was evaluated using a phenanthroline solution prepared at the concentration used in the spectrophotometric method for iron determination (0.1% w/v). The solar irradiation of this solution in the presence of either 1.0 mM Fe(NO₃)₃ or FeOx and 10 mM H₂O₂ resulted in significant changes in the UV–vis spectra with time. It can be observed in Fig. 2A that the absorption band at 267 nm decreases progressively in the presence of FeOx. On the other hand, the absorption at 510 nm starts to increase due to the formation of the Fe²⁺-phenanthroline complex, reaching its maximum after 30 min. This indicates that Fe²⁺ is generated during irradiation, reaching a maximum at the same time as the phenanthroline starts to be degraded. The decrease at 267 nm after 30 min evidences the degradation of phenanthroline.

Similar behavior is observed in the case of Fe(NO₃)₃ (Fig. 2B), however the reaction is slower, as can be seen by the decrease in the absorption band at 267 nm, which only starts after around 90 min (curve 4). This time also corresponds to the maximum absorption at 510 nm, as for FeOx in 30 min. The total disappearance of the band at 510 nm is also observed in

both cases after 120 min irradiation. The slower degradation of phenanthroline in the presence of Fe(NO₃)₃ can be attributed to the strong ligand effect of phenanthroline, a bidentate N,N-ligand, which hinders the catalytic decomposition of H₂O₂ as previously reported [15].

Considering mineralization, the TOC concentration starts to decline only after around 60 min in the presence of FeOx and H₂O₂, and after around 90 min with Fe(NO₃)₃ and H₂O₂, indicating the higher efficiency of FeOx (Fig. 3). After 120 min, solar irradiation of the solution containing FeOx resulted in 43% TOC removal, while only 12% was removed in the presence of Fe(NO₃)₃ (Fig. 3). It is important to observe that the decrease of TOC concentration in the presence of ferrioxalate cannot be attributed only to its photolysis since its contribution to the initial carbon content is less than 10% (72 mg L⁻¹ in 800 mg L⁻¹). Precipitation of iron was observed after 90 min irradiation in the solution containing FeOx, and after 120 min in the solution con-

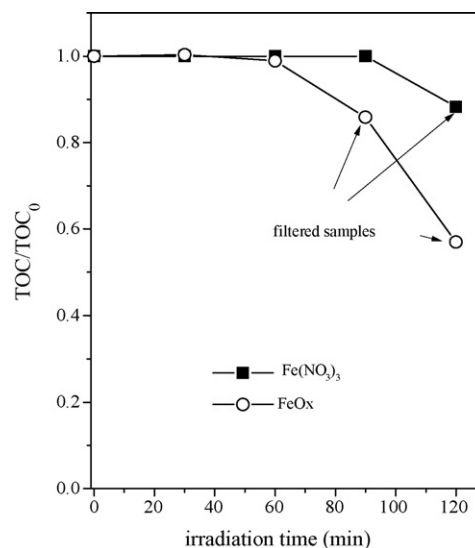


Fig. 3. Influence of the iron source on the TOC removal of 0.1% (w/v) phenanthroline solution during solar irradiation. Initial concentrations: [Fe(NO₃)₃] = [FeOx] = 1.0 mM; [H₂O₂] = 10 mM. Step additions of H₂O₂ every 30 min. UV dose = 15.0 J cm⁻² (120 min).

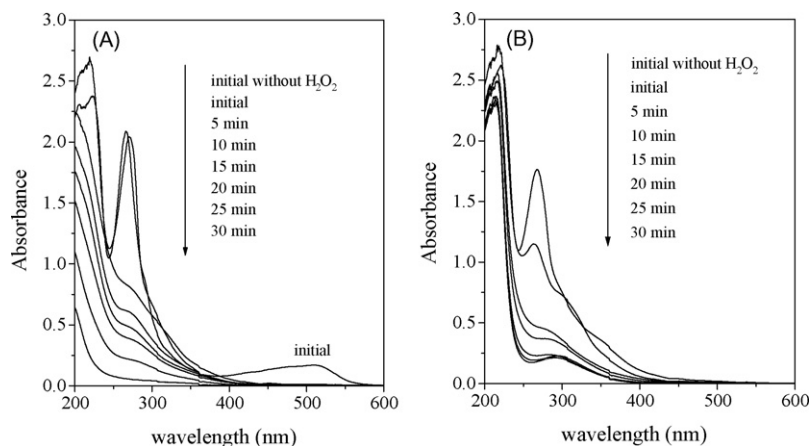


Fig. 4. Absorption spectra of 0.01% (w/v) phenanthroline solution in the presence of (A) FeOx and (B) Fe(NO₃)₃ during solar photo-Fenton degradation (1:3 dilution). Initial conditions: [FeOx]=[Fe(NO₃)₃]=1.0 mM; [H₂O₂]=10 mM. Step additions of H₂O₂ every 30 min. UV dose FeOx=3.31 J cm⁻²; UV dose Fe(NO₃)₃=3.75 J cm⁻² (30 min).

taining Fe(NO₃)₃. Analyses of these samples were carried out after filtration through 0.45 μm polyvinylidene fluoride membranes and consequently, the results correspond to the dissolved fraction of organic carbon.

The quite long period of irradiation before some mineralization starts to be observed is probably related to the complexation of freshly generated Fe²⁺ in the system, indicated by the increase in the absorption at 510 nm, which can hinder the peroxide decomposition via the Fenton reaction. It has been verified that the oxidation of the Fe(phen)₃²⁺ complex is dependent on its first dissociation step, which is slow [16]. This can explain the observation that the phenanthroline degradation begins only when the Fe²⁺-phenanthroline complex starts to be decomposed, as indicated by decrease in the absorption at 510 nm.

It is also important to mention that no absorption band appeared at 600 nm, which would be visible as a blue color. This absorption band has been attributed to Fe(phen)₃³⁺ [14] and was probably not observed in our case due to the instability of such complex in this oxidizing medium.

The appearance of an absorption band at 510 nm was also observed during irradiation of phenanthroline in the presence of FeOx without H₂O₂, which indicates the formation of the Fe²⁺-phenanthroline complex. However, no decrease in the absorption at 267 nm or removal of TOC was observed. This complex was formed in the absence of H₂O₂ as a result of FeOx photolysis generating Fe²⁺, which is then complexed by phenanthroline. The irradiation of phenanthroline in the presence of Fe(NO₃)₃ without H₂O₂ did not result in the appearance of the 510 nm band, for up to 120 min, probably due to the much lower quantum yield of Fe²⁺ generation in the absence of oxalate.

The irradiation of phenanthroline (0.1% w/v) in the presence of H₂O₂, but absence of iron, resulted in no change in the absorption band at 267 nm up to 120 min. The same behavior was observed for the dark reaction in the presence of Fe(NO₃)₃ and H₂O₂.

In order to increase the efficiency of phenanthroline degradation, especially concerning TOC removal, the original

phenanthroline solution was diluted to 0.01% (w/v). At this concentration, a significant decrease of the 267 nm absorption band of phenanthroline was already observed in the first 5 min of irradiation in the presence of ferrioxalate or Fe(NO₃)₃, as shown by the spectra in Fig. 4.

A significant removal of TOC is observed after 30 min of solar irradiation in the presence of either FeOx or Fe(NO₃)₃, achieving 82% in both cases, although the mineralization was slightly faster with iron nitrate due to the lower initial carbon content when compared to FeOx (Fig. 5). The same mineralization rate is then observed subsequently, with both iron sources achieving 90% after 60 min. After this time further mineralization is very slow even with new additions of H₂O₂. The lower efficiency is related to the precipitation of iron after 45 min due to the increase in pH from 2.5 to 3.5.

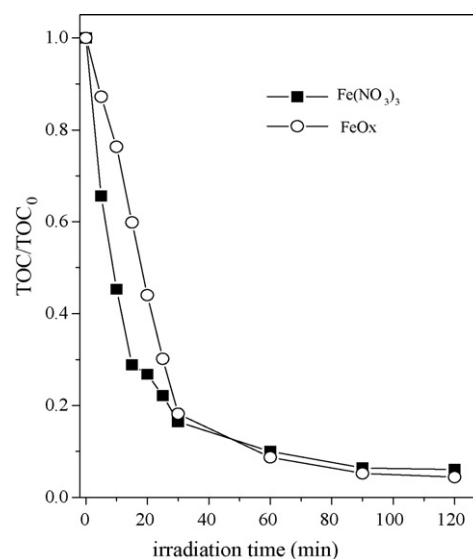


Fig. 5. Influence of the iron source on the TOC removal of 0.01% (w/v) phenanthroline solution during solar irradiation. Initial concentrations: [Fe(NO₃)₃]=[FeOx]=1.0 mM; [H₂O₂]=10 mM. Step additions of H₂O₂ every 30 min. UV dose = 13.1 J cm⁻² (120 min).

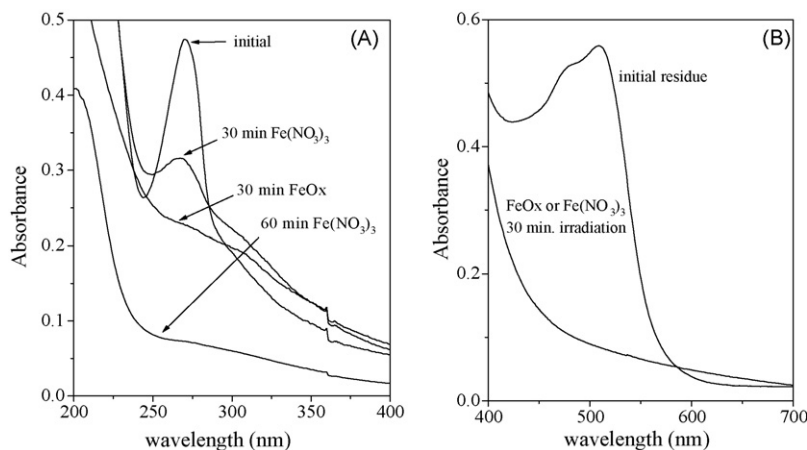


Fig. 6. Absorption spectra of phenanthroline laboratory residue during solar photo-Fenton degradation. (A) Absorption spectra between 200–400 nm obtained after 1:50 dilution and (B) absorption spectra between 400–700 nm without dilution. Initial concentrations: $[\text{FeOx}] = [\text{Fe}(\text{NO}_3)_3] = 1.0 \text{ mM}$; $[\text{H}_2\text{O}_2] = 10 \text{ mM}$. Step additions of H_2O_2 every 30 min. UV dose = 2.70 J cm^{-2} (30 min).

3.2. Treatment of laboratory residues containing phenanthroline

The laboratory phenanthroline residue from Fe^{2+} determinations was generated in our research laboratory and contained, besides phenanthroline, other organic compounds as described previously (Section 2). The UV–vis spectrum before irradiation shows a high absorption band at 270 nm (Fig. 6A), which is attributed not only to phenanthroline, but also to other organic compounds present in the residue such as 4-chlorophenol and the herbicides diuron and tebuthiuron. The spectrum also shows a band at 510 nm, characteristic of the $\text{Fe}(\text{II})$ -phenanthroline complex (Fig. 6B). As the residue is irradiated with solar light, a sharp decrease of the 270 nm band is observed in only 30 min, which is more pronounced in the presence of ferrioxalate than with iron nitrate, and the signal disappears after 60 min in both cases, indicating the total degradation of phenanthroline. The band at 510 nm also disappears completely indicating the decomposition of the phenanthroline complex.

The irradiation of the laboratory residue in the presence of 1.0 mM FeOx or $\text{Fe}(\text{NO}_3)_3$ and 10 mM H_2O_2 resulted in slow mineralization, achieving 25% in 150 min with both iron sources (Fig. 7—solid symbols). In order to increase the mineralization efficiency, sodium oxalate was added to the sample containing FeOx , however TOC removal after 240 min irradiation (around 35%) was similar to that obtained using $\text{Fe}(\text{NO}_3)_3$ without added oxalate. Despite the low percentage of TOC removed, the amount of organic carbon totally oxidized was 1350 mg L^{-1} .

Considering the good mineralization results obtained previously using the diluted solution of phenanthroline (0.01%, w/v), treatment of the residue after 1:10 dilution was also undertaken in order to evaluate any improvement in the mineralization efficiency. A 1:10 dilution of the residue resulted in a TOC content of 436 mg L^{-1} . Irradiation of the diluted residue after addition of FeOx resulted in a TOC removal of 38% in 120 min (Fig. 7—open symbols). It is important to point out that this result was obtained under 9.4 J cm^{-2} UV dose which is much lower than that observed for 120 min in the experiment without

dilution (12.4 J cm^{-2}). In the case of FeOx , the high quantum yield of Fe^{2+} photogeneration contributed to the fast consumption of H_2O_2 via dark Fenton reaction and, consequently, to the efficiency of degradation. Furthermore, the higher formation constant of the Fe^{3+} -oxalate complex ($\log \beta_3 = 20$) relative to Fe^{3+} -phenanthroline ($\log \beta_3 = 14$) permits the generation of Fe^{2+} via the photolysis of ferrioxalate. On the other hand, in the presence of $\text{Fe}(\text{NO}_3)_3$ only 6% mineralization and low consumption of H_2O_2 was observed. The low consumption of H_2O_2 is a consequence of the low quantum yield of Fe^{2+} generation and can lead to the accumulation of H_2O_2 in the solution. This can also contribute to the lower efficiency of degradation due to the scavenging of $\bullet\text{OH}$ radicals by H_2O_2 , generating the less

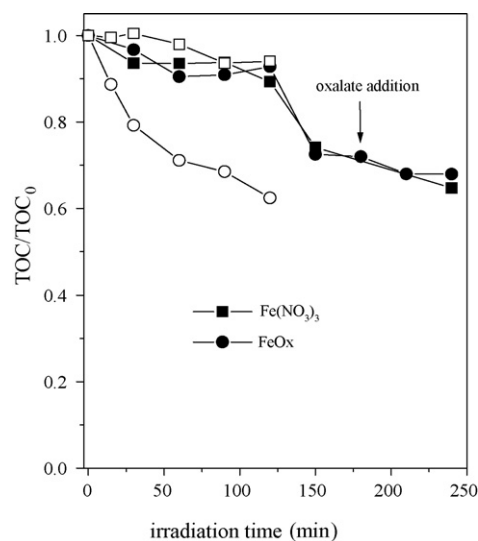
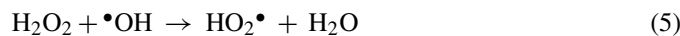


Fig. 7. Influence of the iron source and dilution on the TOC removal of laboratory residues from Fe^{2+} determinations during solar irradiation. Solid symbols: initial TOC = 4500 mg L^{-1} ; open symbols: initial TOC = 436 mg L^{-1} with $\text{Fe}(\text{NO}_3)_3$ and 495 mg L^{-1} with FeOx . Initial concentrations: $[\text{Fe}(\text{NO}_3)_3] = [\text{FeOx}] = 1.0 \text{ mM}$; $[\text{H}_2\text{O}_2] = 10 \text{ mM}$. Step additions of H_2O_2 every 30 min in both solutions. UV dose = 9.4 J cm^{-2} (120 min) and 24.5 J cm^{-2} (240 min).

oxidizing HO_2^\bullet ($E^\circ = 1.42 \text{ V}$ [3]) radical and hence, affecting the efficiency of the process (Eq. (5)) [17].



Considering that the laboratory wastewater already contained iron, the diluted sample was also irradiated in the presence of H_2O_2 without addition of FeOx or $\text{Fe}(\text{NO}_3)_3$. However, the iron present in the wastewater was not sufficient to promote significant mineralization after 120 min (data not shown).

Considering the high TOC removal obtained in a short time (using FeOx), the dilution of phenanthroline residues can be a useful procedure for their treatment, since they are usually generated in small volumes and contain high organic loadings.

4. Conclusions

The results of this work show that phenanthroline can be completely oxidized by the solar photo-Fenton process. Higher mineralization is obtained by the addition of FeOx to laboratory residues from Fe^{2+} determinations than in the presence of $\text{Fe}(\text{NO}_3)_3$, indicating the importance of this iron source to promote the degradation of an iron complexing agent such as 1,10-phenanthroline by the solar photo-Fenton process. The results suggest that, in the presence of 1.0 mM ferrioxalate and step additions of H_2O_2 , 150 min exposure to sunlight is sufficient to remove about 25% of the carbon content and completely oxidize the phenanthroline present in the raw residue and 38% after 120 min from diluted residue (1:10 dilution). Considering that the experiments were carried out in autumn and winter, it is expected that even better results could be achieved in summer when the solar irradiance is higher. The incomplete mineralization of the residue requires further studies such as determination of the wastewater toxicity after application of photo-Fenton process to guarantee the safe disposal especially in cases of high organic load. The suggested procedure is simple and can be carried out *in situ* in laboratories in cases of low organic load, alleviating problems of storage or inappropriate discharge.

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