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Degradation of the herbicide tebuthiuron using solar photo-Fenton process and ferric citrate complex at circumneutral pH

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Abstract

The influence of pH on the degradation of the herbicide tebuthiuron (TBH) was investigated using *in situ* generated Fe(III)–citrate complexes (Fe:cit) submitted to the photo-Fenton process under solar irradiation. Using Fe:cit in a wide pH range (2.5–7.5), 100–78% TBH oxidation was achieved respectively from a UV dose of $2.0\,\mathrm{J\,cm^{-2}}$ (15 min). Moreover, the oxidation of TBH obtained in the presence of Fe:cit at pH 6.0 was higher than that obtained using $Fe(NO_3)_3$ at pH 2.5. A similar behavior is observed for the removal of total organic carbon (TOC) in TBH solutions. In the presence of Fe:cit, 20% and 85% of TOC was removed at pH 7.5 and 2.5, respectively, after $7.5\,\mathrm{J\,cm^{-2}}$ irradiation, while no mineralization was observed employing $Fe(NO_3)_3$ for the same UV dose. Using $Fe(NO_3)_3$, mineralization was observed only after $11\,\mathrm{J\,cm^{-2}}$ (8%). A higher mineralization rate was obtained with $Fe(NO_3)_3$ only when a concentration three times higher was employed at pH 2.5. Besides the high efficiency of TBH degradation observed using the ferric citrate complex in the solar photo-Fenton process, it also offers the advantage of application at a pH of up to 7.5.

Keywords: Advanced oxidation processes; Complexes; Herbicides; Photolysis

1. Introduction

Sugar cane cultivation is the largest single agricultural activity in the state of São Paulo (Brazil) and the herbicide tebuthiuron (TBH) is the most commonly used for weed control. TBH and some of its metabolites were detected in surface water in the city of Ribeirão Preto, São Paulo [1], evidencing contamination and the need for an efficient process to remove pesticide residues. Over the last two decades advanced oxidation processes (AOP) have been intensively investigated for application in water and wastewater treatment. They are considered to be good alternatives when conventional treatment of wastewater cannot be applied, due to their efficiency in oxidizing a great variety of organic contaminants by generating a highly oxidative hydroxyl radical ($^{\bullet}OH$) [2].

The photo-Fenton process has received great attention in particular for its solar-irradiation-induced mineralization of contaminants. This process is based on the photoreduction of Fe(III) to Fe(II), which reacts with hydrogen peroxide in acid medium to generate additional $^{\bullet}OH$ (equations (1) and (2)) [3]

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH \qquad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad k = 63\,\mathrm{M^{-1}\,s^{-1}} \qquad (2)$$

The high absorption of iron salts in the UV–vis region, especially when complexed to polycarboxylates, makes a considerable portion of the solar spectrum available for this process, reducing its operating costs [4,5]. The ferrioxalate complex is the one that is most employed for this goal resulting, in general, in a higher efficiency under solar irradiation than that obtained for iron salts (equations (3) and (4)) [6–8]

$$[Fe(C_2O_4)_3]^{3-} + h\nu \rightarrow [Fe(C_2O_4)_2]^{2-} + C_2O_4^{\bullet -} \qquad (3)$$

$$C_2O_4^{\bullet -} + [Fe(C_2O_4)_3]^{3-} \rightarrow [Fe(C_2O_4)_2]^{2-} + C_2O_4^{2-} + 2CO_2 \qquad (4)$$

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The high quantum yield of Fe(II) generation has been pointed out as one of the main reasons for the high efficiency of iron(III) complexes with citric acid, oxalic acid and other carboxylic acids [4,6,9].

In a previous work, the efficiency of the solar photo-Fenton degradation of TBH using ferrioxalate and iron nitrate was compared. The use of ferrioxalate resulted in a much higher degradation efficiency for TBH, diuron and dichloroacetic acid [8]. The same effect was observed for the treatment of wastewater from washing bottles of pesticides containing a mixture of TBH and diuron [10].

Iron complexes have also been used with the aim of extending the optimum pH range (between pH 2.5 and 3.0) of the Fenton process [11]. Thus Fe(III) may be solubilized by complexation at higher pH values [12]. Low pH values limit the application of the Fenton process for effluents, water and soil treatment, as well as its combination with biological processes, since acidification and neutralization steps add costs to the overall process.

The ferric citrate complex is a good alternative for iron solubilization in the Fenton and photo-Fenton processes. Although its photolysis shows a lower quantum yield for Fe(II) generation than that observed for ferrioxalate, citrate is less toxic, is readily available and can be used at higher pH values than oxalate (up to pH 9.0) [9,13,14]. In the presence of the ferric citrate complex, total oxidation of 2,4-dichlorophenoxyacetic acid (2,4-D) was obtained after 7 min of irradiation at pH 6.0 [15]. Ferric citrate complexes were also employed in the As(III) oxidation at high pH values [16].

In this work, the effect of *in situ* generated Fe(III)-citrate complexes (Fe:cit) on photo-Fenton degradation efficiency of TBH at circumneutral pH in a homogeneous system was studied.

2. Materials and methods

2.1. Chemicals

All solutions were prepared using distilled water. $Fe(NO_3)_3\cdot 9H_2O$ was purchased from Mallinckrodt and citric acid (Synth) was used as ligand. H_2O_2 30% (w/w) was purchased from Synth. Ammonium metavanadate (Vetec) 0.06 M was prepared in 0.36 M H_2SO_4 (Merck) and used for hydrogen peroxide determination. Commercial tebuthiuron herbicide was used in the degradation experiment after appropriate dilution to obtain a 0.5 mM solution. Analytical grade tebuthiuron was purchased from "Dr. Ehrenstorfer GmbH" and used as standard for the HPLC analysis. HPLC-grade Methanol (Mallinkrodt) and acetic acid (Merck) were used in the HPLC analysis.

2.2. Photodegradation procedure and solar irradiance measurements

The photodegradation experiments were performed exposing 250 mL of 0.5 mM TBH solution ($TOC = 54\,mg\,L^{-1}$) to solar light in an open dark-glass vessels 4.5 cm deep [17], containing 1.0 mM iron complex and 10 mM H_2O_2 without magnetic stirring. The H_2O_2 was replaced after its total consumption, which occurred after solar irradiations of 1.9, 7.9 and 16.2 $J\,cm^{-2}$ for the solutions at pH 2.5, an irradiation of 7.9 $J\,cm^{-2}$ for solutions at pH 4, 14.3 $J\,cm^{-2}$ for solutions at pH 5 and 6 and 22.1 $J\,cm^{-2}$ for the $Fe(NO_3)_3$ solution at pH 2.5. Iron-complex solutions were prepared by directly mixing aqueous solutions of $Fe(NO_3)_3$ and citric acid at the same molar iron-to-ligand ratio (1:1). After preparing the iron complex, the pH of each solution was adjusted to the desired value to fall within the range of 2.5–7.5 by adding H_2SO_4 or NaOH. For comparison, an experiment in the presence of $Fe(NO_3)_3$ and H_2O_2 without citric acid at pH 2.5 was also performed. The photodegradation experiments were carried out in Araraquara, Brazil (21°47′S; 48°10′W) in winter and spring. Irradiation energy accumulated during solar exposure was measured using a radiometer (PMA 2100, Solar Light Co.) in the UVA region (320–400 nm) with the sensor placed horizontally. For a good comparison of the results, the samples were withdrawn for analysis after exposure to the same UV dose with irradiation times up to 4 h [18].

2.3. Chemical analysis

The concentration of TBH during irradiation was determined by reversed-phase HPLC analysis using a Shimadzu LC10 AVP with diode array detector (SPD-M10A) and a C-18 column (Luna, 5 μm, 250 mm × 4.6 mm from Phenomenex). Methanol/acetic acid 1% (60:40) was used as eluent at a flow rate of 1 $mL\,min^{-1}$. TBH and degradation products were firstly extracted from aqueous samples using solid phase C-18 cartridges to avoid further reaction. The samples were then eluted with methanol before determination. The mineralization of TBH was evaluated by TOC analysis using a TOC analyzer (TOC-5000A SHIMADZU). In the case where Fe:cit was used, the TOC concentration includes the citrate content as well as the target compound and intermediates generated. TOC concentration is expressed as a relative concentration (TOC/TOC_0). Residual H_2O_2 concentration was determined spectrophotometrically from the absorption at 450 nm after reaction with ammonium metavanadate [19]. Absorption spectra during TBH degradation were also recorded using a UV Mini 1240 spectrophotometer (SHIMADZU) after appropriate dilution.

3. Results and discussion

The photodegradation of TBH in the presence of 1.0 mM Fe:cit was evaluated in the pH range of 2.5–7.5 after the addition of H_2O_2. Experiments using $Fe(NO_3)_3$ and H_2O_2 without the addition of citric acid were carried out only at pH 2.5 since above this value iron precipitation occurs hindering the photo-Fenton process.

When evaluating degradation results from experiments performed at pH 2.5, the strong beneficial effect of the iron citrate complex on the oxidation of TBH is observed (Fig. 1A). The herbicide was completely oxidized after a 0.86 $J\,cm^{-2}$ UV dose (7 min), while only 40% oxidation was achieved after 2.8 $J\,cm^{-2}$ using $Fe(NO_3)_3$. Although the degradation efficiency of the iron citrate complex decreases as the pH increases, TBH oxidation is still higher than that observed in the presence of $Fe(NO_3)_3$. For a

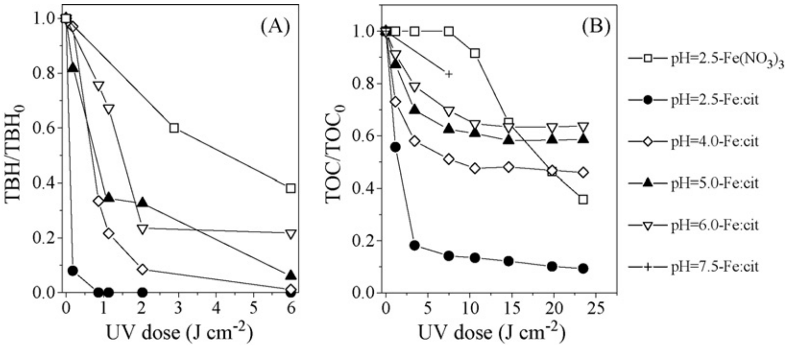

Fig. 1. Influence of iron source and pH on (A) TBH oxidation (B) TOC decay during solar irradiation. Initial conditions: [TBH] = 0.5 mM; [Fe(NO$_3$)$_3$ = citric acid] = 1.0 mM; [H$_2$O$_2$] = 10 mM.

solution at pH 6.0, 76% of the initial concentration of TBH was removed after an irradiation of 2.0 J cm^{-2} for 15 min. At higher pH (7.5), similar results are obtained only after a much higher UV dose (7.5 J cm^{-2}). The increase of pH results in a lower initial consumption of H$_2$O$_2$ (1.1 J cm^{-2}) as can be seen from Table 1, which contributes to a lower hydroxyl radical generation and consequently to a lower TBH degradation efficiency.

Similar behavior is observed for the UV dose dependence of TOC removal (Fig. 1B). Despite the higher initial TOC content in the presence of Fe:cit, the mineralization increases from 20% to 85% when decreasing the pH from 7.5 to 2.5 after an irradiation of 7.5 J cm^{-2}, while no TOC removal was observed employing ferric nitrate after the same UV dose. On the other hand, mineralization starts to occur after an irradiation of 11 J cm^{-2} with ferric nitrate reaching 64% at a UV dose of 23.5 J cm^{-2} (almost 3 h) (Fig. 1B). The higher TOC removal obtained in the beginning of the irradiation with Fe:cit can be partially attributed to citrate degradation (equation (5) [9,14]), since citrate contributes 72 mg L^{-1} of carbon to the solution at the concentration used (1.0 mM)

$$\mathrm{C(OH)(COOH)(CH_2COOH)_2} + 2\mathrm{Fe(III)} + h\nu \rightarrow \mathrm{CH_3COCH_3} + 2\mathrm{Fe(II)} + 3\mathrm{CO_2} + 2\mathrm{H^+} \quad (5)$$

However, the advantage of citrate is demonstrated by a higher TBH oxidation, evaluated from HPLC analysis.

The improvement in photo-Fenton degradation of TBH in the presence of the iron–citrate complex can be attributed to the photoactivity of the Fe:cit species, which generates Fe(II) with a relatively high quantum yield. When the pH value increases, the predominant species is Fe(OH)(Cit)$^-$ which exhibits lower photoactivity with a quantum yield of Fe(II) generation of 0.28-0.21 for pH 4–6 at 436 nm [9,14,16,20]. This explains the decrease in TBH degradation at higher pH values. Nevertheless for all pH values, the quantum yields of iron–citrate complexes are higher than that observed for the Fe(OH)$^{2+}$, which is the main Fe(III) species in solution when Fe(NO$_3$)$_3$ is present in the absence of citrate, which is 0.017 ± 0.003 at 360 nm [4], thus favoring the degradation of TBH.

Table 1
Initial consumption rate of H$_2$O$_2$ at different initial pH for the Fe:cit complex and Fe(NO$_3$)$_3$ at pH 2.5 (marked with an asterisk)

pH	Rate (mmol L^{-1} s^{-1})
2.5	19×10^{-3}
4.0	14×10^{-3}
5.0	3.1×10^{-3}
6.0	0.20×10^{-3}
6.0 (3 mM)	2.7×10^{-3}
2.5*	0.75×10^{-3}
2.5 (3 mM)*	5.1×10^{-3}

* Fe(NO$_3$)$_3$.

It should be noted that no TOC decrease was observed for TBH when exposed to irradiation in the absence of iron and H$_2$O$_2$ indicating that no photolysis occurred nor losses due to evaporation. Furthermore, no degradation of tebuthiuron was observed in the presence of Fe:cit and H$_2$O$_2$ at pH 2.5 and 6.0 but without any irradiation. Moreover, no degradation of tebuthiuron was observed in the presence of H$_2$O$_2$ and absence of iron under solar irradiation. In contrast, 7% TBH oxidation was observed in the presence of Fe(NO$_3$)$_3$ and H$_2$O$_2$ in the dark (pH 2.5) after 30 min due to the thermal Fenton reaction (equations (6), (7) and (2))

$$\mathrm{Fe^{3+}} + \mathrm{H_2O_2} \rightleftarrows \mathrm{FeOOH^{2+}} + \mathrm{H^+} \qquad k = 0.001 - 0.01\,\mathrm{M^{-1}\,s^{-1}} \quad (6)$$

$$\mathrm{FeOOH^{2+}} \rightarrow \mathrm{Fe^{2+}} + \mathrm{HO_2}^{\bullet} \quad (7)$$

$$\mathrm{Fe^{2+}} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe^{3+}} + {}^{\bullet}\mathrm{OH} + \mathrm{OH^-} \quad (2)$$

In the absence of H$_2$O$_2$, 11%, 13% and 15% TBH degradation was detected under solar irradiation in the presence of Fe(NO$_3$)$_3$ at pH 2.5 and Fe:cit at pH 2.5 and 6.0, respectively after 30 min. This TBH removal in the absence of H$_2$O$_2$ can be explained by the generation of the hydroxyl radical according to equation (1) or even by the *in situ* H$_2$O$_2$ generation in the system containing iron complexes as proposed previously for the degradation of the herbicide 2,4-D in the absence of H$_2$O$_2$ in the system containing ferrioxalate [21]. Similar reactions (equations (8)–(14)) can occur in the present system in the absence of H$_2$O$_2$

$$\mathrm{Fe^{III}(C_2O_4)_n}^{3-2n} + h\nu \rightarrow \mathrm{Fe^{2+}} + (n-1)\mathrm{C_2O_4}^{2-} + \mathrm{C_2O_4}^{\bullet -} \quad (8)$$

$$\mathrm{C_2O_4}^{\bullet -} \rightarrow \mathrm{CO_2} + \mathrm{CO_2}^{\bullet -} \qquad k = 2 \times 10^6\,\mathrm{M^{-1}\,s^{-1}} \quad (9)$$

$$CO_2^{\bullet -} + O_2 \rightarrow CO_2 + O_2^{\bullet -} \quad k = 2.4 \times 10^6\,M^{-1}\,s^{-1} \tag{10}$$

$$Fe^{3+} + O_2^{\bullet -} \rightarrow Fe^{2+} + O_2 \quad k = 1.5 \times 10^8\,M^{-1}\,s^{-1} \tag{11}$$

$$Fe^{III}(C_2O_4)_n{}^{3-2n} + O_2^{\bullet -} \rightarrow O_2 + Fe^{II}(C_2O_4)_n{}^{2-2n} \quad k = 1.0 \times 10^6\,M^{-1}\,s^{-1} \tag{12}$$

$$Fe^{2+} + O_2^{\bullet -} \rightarrow Fe^{3+} + H_2O_2 + OH^- \quad k = 7.2 \times 10^8\,M^{-1}\,s^{-1} \tag{13}$$

$$Fe^{II}(C_2O_4)_n{}^{2-2n} + H_2O_2 \rightarrow Fe^{III}(C_2O_4)^+ + {}^{\bullet}OH + OH^- \quad k = 3.1 \times 10^6\,M^{-1}\,s^{-1} \tag{14}$$

At higher pH, the dominant species is $O_2^{\bullet -}$, which favors the formation of H_2O_2 and consequently ${}^{\bullet}OH$.

In the Fe:cit solutions, precipitation occurred in all experiments but only after extended irradiation periods close to a UV dose of 10.6 J cm^{-2}. This is probably due to citrate degradation and the formation of a hydroxo-iron species, hindering further photo-Fenton reaction [22]. The solar degradation of the iron citrate complex was evaluated by irradiating a solution containing 1.0 mM $Fe(NO_3)_3$ and 1.0 mM citric acid at pH 6. It was observed that 15% of the initial carbon content of the citrate was mineralized in the first 41 min of irradiation (6 J cm^{-2}), achieving a plateau with no further mineralization (Fig. 2). This plateau suggests that more recalcitrant compounds are formed such as acetone (equation (5)), which had been suggested as a product of citrate photolysis [9]. The slight decrease of pH from 6.0 to 5.7 suggests that short-chain carboxilic acids are also generated leading to residual carbon content, which is only further removed when in the presence of H_2O_2, achieving another plateau at 54% after a 7.5 J cm^{-2} UV dose.

At least five degradation products were detected in the Fe:cit solution at pH 6 (Fig. 3), when 87% of TBH had been oxidized after 78 min of solar irradiation (7.5 J cm^{-2}). These intermediates were further degraded as can be seen in the final chromatogram (23.5 J cm^{-2}).

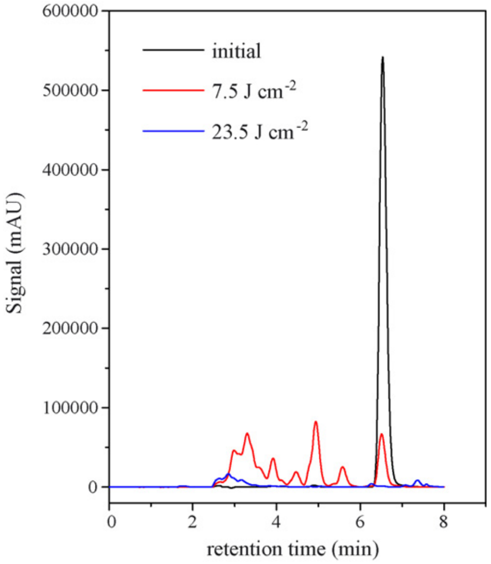

Fig. 3. HPLC chromatograms of TBH degradation in the presence of Fe:cit complex at pH 6. Conditions: [TBH] = 0.5 mM; [Fe:cit] = 1.0 mM; [H_2O_2] = 10 mM; pH = 6.0. Additions of citric acid: 7.490 and 19.782 J cm^{-2}. Addition of H_2O_2: 10.604 J cm^{-2}.

When observing the absorption spectra of TBH solutions during irradiation at pH 6, the decrease of the absorption band at 254 nm can be noted which is attributed both to TBH and to degradation products (Fig. 4). The spectrum after 23.5 J cm^{-2} (3 h) shows a broad absorption band between 250 and 300 nm which corresponds to Fe:cit complex absorption [4], since according to the chromatograms, most of the intermediates generated were already degraded. This broad absorption of the Fe:cit complex also decreases considerably due to the degradation of the complex after long irradiation periods (6 h), as can be seen by the spectrum of the sample after 26.4 J cm^{-2}.

When the initial concentration of the Fe:cit (pH 6.0) was increased to 3.0 mM, a slight improvement in the TBH oxidation

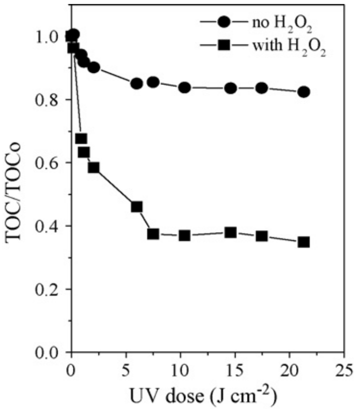

Fig. 2. Mineralization of citrate in the presence and absence of H_2O_2 (photolysis) during the solar irradiation of the iron–citrate complex. Initial conditions: [$Fe(NO_3)_3$] = [citric acid] = 1.0 mM; pH 6.0; [H_2O_2] = 10 mM.

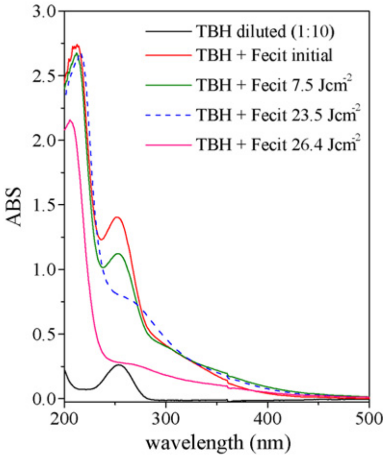

Fig. 4. Absorption spectra during tebuthiuron (TBH) degradation with Fe:cit at pH 6. Additions of citric acid: 7.490 and 19.782 J cm^{-2}. Addition of H_2O_2: 10.604 J cm^{-2}.

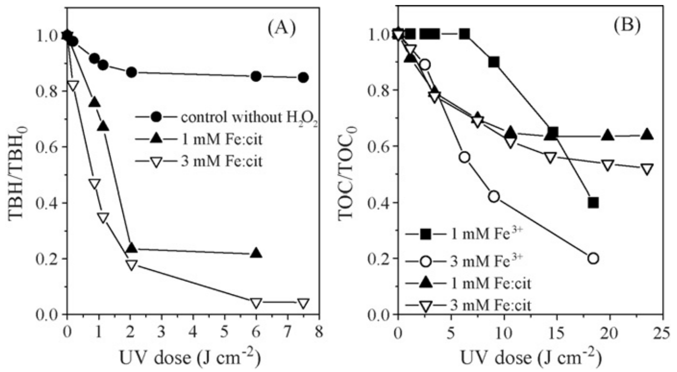

Fig. 5. Influence of the increase in the initial Fe:cit concentration on TBH oxidation (A). Influence of iron concentration on TOC removal (B). Initial conditions: [TBH] = 0.5 mM; [$Fe(NO_3)_3$] = [citric acid] = 1.0 and 3.0 mM; [H_2O_2] = 10 mM; pH = 2.5 ($Fe(NO_3)_3$) and pH = 6.0 (Fe:cit).

was observed, reaching 96% oxidation after 65 min (6 J cm^{-2}) (Fig. 5A). On the other hand, a similar behavior for TOC removal was observed initially for the 1.0 and 3.0 mM solutions (Fig. 5B). However, after a longer irradiation time, the solution containing 3.0 mM Fe:cit presented better degradation results, reaching 48% TOC removal. The precipitation in this solution was only observed at the end of the experiment (19.8 J cm^{-2}), while in the presence of 1.0 mM, it occurred at 10.6 J cm^{-2}.

The increase in the initial concentration of $Fe(NO_3)_3$ (pH 2.5) from 1.0 to 3.0 mM considerably improved the degradation efficiency since the mineralization had already started at the beginning of the irradiation. Using 3.0 mM $Fe(NO_3)_3$, 44% TOC removal was obtained after 42 min (6.3 J cm^{-2}), while for this UV dose, no mineralization was observed in the 1.0 mM $Fe(NO_3)_3$ solution. These results can be explained by an increase in the reaction kinetics due to the higher iron concentration [23], which was also observed in a faster consumption of H_2O_2 (Table 1) certainly promoting a higher generation of hydroxyl radicals and consequently inducing an enhancement of the mineralization rate. In these terms, a considerable improvement in mineralization was obtained when the iron concentration was increased from 1 to 3 mM achieving 60% and 82%, respectively, after a 18.4 J cm^{-2} UV dose. However, this higher TOC removal of 82% was only obtained at pH 2.5. When using Fe:cit, the degradation can be carried out at neutral pH, which is advantageous to environmental applications. Considering that the iron citrate complex is decomposed during irradiation leading to iron precipitation after long irradiation times (80 min, 7.5 J cm^{-2}), a new sample of citric acid solution (0.187 mmol in 190 mL) was added to the TBH solution when the plateau of the mineralization was reached (7.5 J cm^{-2}) in order to improve the mineralization and avoid precipitation. After the H_2O_2 was totally consumed (UV dose of 10.6 J cm^{-2}), a further addition was made to the solution (1.7 mmol in 170 mL). As can be seen in Fig. 6, the addition of citric acid and H_2O_2 improved the TBH degradation and TOC removal by only 15% after 208 min (19.8 J cm^{-2}).

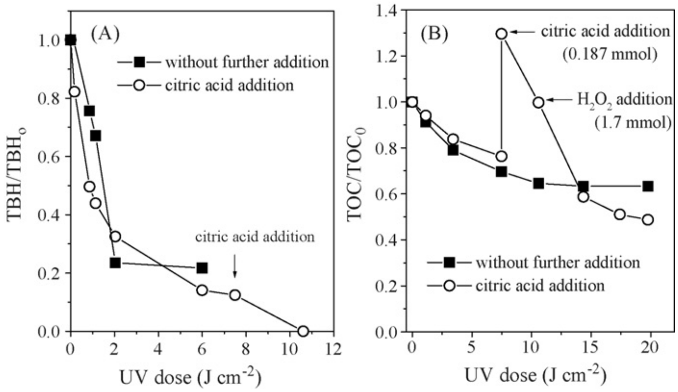

Fig. 6. Effect of the new additions of citric acid on TBH degradation (A) and TOC removal (B) under solar irradiation. Initial conditions: [TBH] = 0.5 mM; [$Fe(NO_3)_3$ = citric acid] = 1.0 mM; [H_2O_2] = 10 mM; pH = 6.0. Addition of 0.187 mmol citric acid at 7.5 J cm^{-2} and 1.7 mmol H_2O_2 at 10.6 J cm^{-2}.

4. Conclusion

It was verified that ferric citrate complex can be effectively applied to the solar photo-Fenton process up to pH 7.5 achieving 78% TBH degradation and 20% mineralization after 45 min. Furthermore, the presence of Fe:cit drastically increases the efficiency of solar TBH degradation in comparison to what is achieved using $Fe(NO_3)_3$ (1.0 mM) at low pH values (2.5). Between 20% and 85% mineralization can be obtained depending on the pH, which would be very satisfactory when combining the photo-Fenton process with biological treatment avoiding pH adjustment steps. However, residual carbon content is observed even after long irradiation times, especially at higher pH values, either with an increase in the initial Fe:cit concentration or a further addition of citric acid and H_2O_2, which results in only a 15% enhancement of the mineralization at pH 6. Toxicity and biodegradability studies will determine the need for further mineralization after TBH degradation (7.5 J cm^{-2}), which will be the subject of future work.

Acknowledgements

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