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Degradation of tetracycline by photo-Fenton process—Solar irradiation and matrix effects

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Abstract

The degradation of the antibiotic tetracycline (TC) by the photo-Fenton process was evaluated under black-light and solar irradiation. The influences of iron source ($Fe(NO_3)_3$ or ferrioxalate), hydrogen peroxide and matrix (pure water, surface water and a sewage treatment plant effluent—STP) were evaluated. Under black-light irradiation, TC degradation was favored in the presence of $Fe(NO_3)_3$, achieving total degradation after 1 min irradiation, while under solar light the use of ferrioxalate favors the degradation. Nevertheless, no significant difference in total organic carbon removal was observed between these two iron sources, achieving a residual concentration of around 5 mg L^{-1} under black-light and 2 mg L^{-1} under solar light irradiation. No decrease of the degradation efficiency relative to pure water was observed when TC was irradiated in a sample of surface water, under either black-light or solar irradiation. However, lower efficiency was obtained under black-light when TC was present in a sample of STP effluent, indicating the interference of the constituents of this sample on the overall efficiency of the process. On the other hand, under solar irradiation in the presence of ferrioxalate, no influence of the matrix was observed, even in the sample of STP effluent, achieving total degradation of TC in 1.5 min.

Keywords: Advanced oxidation process; Sewage treatment plant; Antibiotic; Ferrioxalate

1. Introduction

The occurrence of a great number of pharmaceutical residues in the environment has been frequently reported in recent literature, receiving increasing attention as emerging contaminants [1]. Different classes of pharmaceuticals such as antibiotics, hormones, anaesthetics and anti-inflammatories have been encountered in the aquatic environment in the concentration range of ng L^{-1} to μg L^{-1}. Although present at trace levels, the continuous introduction into the environment is characterized as a "pseudo-persistence", which may result in toxic effects.

The main source of such compounds is the excretion in urine or faeces, both in unchanged form and as metabolites, due to the incomplete absorption by organisms in human and veterinary medicine. In Brazil, some pharmaceuticals were detected at average concentrations of 0.1–1.0 μg L^{-1} in wastewater from a sewage treatment plant (STP) [2]. Some studies have demonstrated that these substances are persistent in the environment and are not satisfactorily removed in treatment plants, with removals in the range of 12–90%, resulting in contamination of surface and ground waters [2].

Among a wide variety of pharmaceutical compounds, antibiotics are of special concern due to their extensive use in human and veterinary medicine. The presence of traces of this kind of pharmaceutical in the environment can induce the development of antibiotic-resistant pathogens, causing serious problems for human health [3].

Most conventional STPs can usually only partially eliminate these substances [4]. Thus, the search for new alternatives to prevent water contamination is necessary, considering the risks that residual pharmaceuticals can present to human health and to the environment [5].

The advanced oxidation processes (AOP) are considered good alternatives due to their high efficiency in oxidizing a great variety of organic compounds by the generation of highly oxidizing hydroxyl radicals, $^{\bullet}OH$ ($E^0 = 2.720$ V *versus* NHE).

The photo-Fenton process is considered suitable for the treatment of a variety of wastewaters due to its high efficiency,

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simplicity of operation and low cost. The generation of hydroxyl radicals occurs during the decomposition of H_2O_2 in the presence of ferrous ions. Under UV–vis irradiation, the overall efficiency of the process increases due mainly to the regeneration of ferrous ions and formation of additional $^\bullet OH$ (Eqs. (1) and (2)) [6,7]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH \quad k = 76\,M^{-1}\,s^{-1} \tag{1}$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + {}^\bullet OH + H^+ \tag{2}$$

The tetracyclines constitute a group of antibiotics which are obtained naturally by fermentation with some fungi or by semi-synthetic processes. They are effective against different microorganisms and are frequently used in an indiscriminate manner. They are used orally and the absorption by organisms is irregular, varying from 60 to 80%. The rest is eliminated by excretion and ends up contaminating the environment. Residues of tetracycline (TC) have been found in concentrations ranging from 0.11 $\mu g\,L^{-1}$ in surface waters in the United States [8] to 4.2 $\mu g\,L^{-1}$ in surface waters in Germany [9] as well as in STPs, with 0.52 $\mu g\,L^{-1}$ in influents and 0.17 $\mu g\,L^{-1}$ in effluents in the United States [10] and even maximum concentration of 0.977 $\mu g\,L^{-1}$ in effluent [11].

Considering that residues of tetracycline have been found in surface water and STPs, the aim of the present work is to evaluate the efficiency of tetracycline degradation mediated by the photo-Fenton process in complex and real media such as STP effluent and surface water. The study includes an evaluation of the influence of source of iron ($Fe(NO_3)_3$ or ferrioxalate) and initial H_2O_2 concentration under black-light and solar irradiation.

2. Materials and methods

2.1. Reagents

All the solutions were prepared using Millipore Milli-Q water and analytical grade reagents. $Fe(NO_3)_3{\cdot}9H_2O$ (Mallinkrodt) was used to prepare aqueous 0.25 M iron stock solution. H_2O_2 30% (w/w) (Synth) was used. Ammonium metavanadate (Vetec) solution was prepared at a concentration of 0.060 M in 0.36 M H_2SO_4. Potassium ferrioxalate ($K_3Fe(C_2O_4)_3{\cdot}3H_2O$) was prepared and purified as described previously [12] using iron nitrate and potassium oxalate (Mallinkrodt). 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 1 week. Oxalic acid (Mallinkrodt), methanol and HPLC grade acetonitrile (Tedia Brazil) were used in HPLC analysis. The tetracycline hydrochloride ($C_{22}H_{24}O_8N_2{\cdot}HCl$) (Fig. 1) used in photodegradation experiments was obtained from a commercial source.

2.2. Effluent from sewage treatment plant and surface water

In order to evaluate matrix effects on TC degradation, samples of STP effluent and surface water were collected during February 2006. This STP is based on activated sludge treatment and services a population of almost 200,000 inhabitants of the city of Araraquara. The sample was collected after complete treatment. The sample of surface water was collected from a reservoir, whose water supplies the city of Taquaritinga (following conventional treatment). After collection, both samples were kept refrigerated until the experiments were performed. The main parameters determined for both samples are shown in Table 1. An appropriate amount of TC was dissolved in 500 mL of both samples, the pH was adjusted to 2.5, and the samples were irradiated under artificial or solar light after addition of iron and H_2O_2.

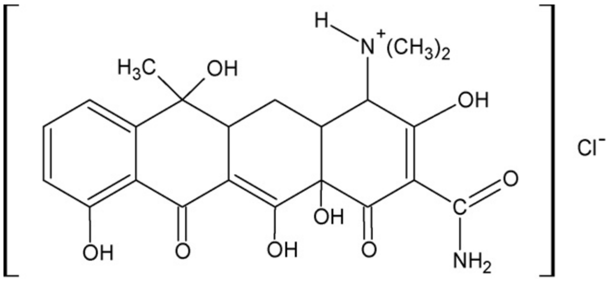

Fig. 1. Chemical structure of tetracycline hydrochloride.

2.3. Photodegradation procedures

2.3.1. Black-light irradiation

The experiments using artificial irradiation were carried out in an upflow reactor previously described by Nogueira and Guimarães [13]. The irradiation source was a 15 W black-light lamp, with maximum emission at 365 nm. The irradiance, measured using a radiometer (PMA 2100 Solar Light Co.) in the UVA region (320–400 nm), was 19 $W\,m^{-2}$. The irradiated volume of the reactor was 280 mL, and a total volume of 500 mL of TC solution was recirculated at a flow rate of 80 $mL\,min^{-1}$ using a peristaltic pump (Masterflex 7518-12) after addition of iron solution, pH adjustment to 2.5 with H_2SO_4 and addition of an appropriate volume of H_2O_2. The lamp was only

Table 1
Main parameters determined for the samples of surface water and STP effluent

Parameters	Sample	
	Surface water	STP
Total carbon ($mg\,L^{-1}$)[a]	16.1	63.0
Inorganic carbon ($mg\,L^{-1}$)[a]	10.3	52.4
Total organic carbon ($mg\,L^{-1}$)[a]	5.8	10.6
pH[b]	6.3	8.0
Turbidity (nephelometric units)[b]	<1.00	134
BOD ($mg\,O_2\,L^{-1}$)[b]	13.0	30.0
COD ($mg\,O_2\,L^{-1}$)[b]	n.a.	136
Dissolved O_2 ($mg\,L^{-1}$)[b]	5.20	5.0
Total chloride ($mg\,L^{-1}$)[b]	3.10	54.4
Dissolved Fe ($mg\,L^{-1}$)[b]	0.25	2
Nitrate ($mg\,L^{-1}$)[b]	0.23	0.73
Total dissolved solids ($mg\,L^{-1}$)[b]	44.50	510.0

n.a.: not available.

[a] Determined in our laboratory.

[b] Obtained from the STP facility.

turned on when the reactor was completely filled with the solution. The concentration of TC used in all experiments was 49 μmol L^{-1} (24 mg L^{-1}), which corresponds to 13 mg L^{-1} of TOC. Although the concentrations of TC found in aqueous environments are lower than this value, this concentration was chosen due to the difficulty in working at trace levels with HPLC and to permit TC quantification during irradiation since the detection limit determined for the analysis was 0.31 mg L^{-1}.

2.3.2. *Solar irradiation*

The experiments under solar irradiation were carried out in Araraquara, Brazil (22° S 48 °W) during summer between 10 a.m. and 14 p.m. The volume of 500 mL of TC solution was exposed to direct sunlight in a transparent glass vessel (6 cm high and 13 cm diameter) with magnetic stirring. The irradiance and UV dose were measured using the radiometer described previously, with the sensor positioned horizontally. The irradiance measured during the experiments varied from 15 to 20 W m^{-2}.

2.4. *Chemical analysis*

The total organic carbon (TOC) concentration during experiments was measured using a carbon analyzer (TOC 5000A-Shimadzu). Prior to TOC determination, the samples of surface and STP waters were filtered through 0.45 μm membranes.

Before determination of TC concentration, the samples were extracted using solid phase extraction Oasis cartridges (60 mg) from waters. A solution of 0.01 mol L^{-1} oxalic acid in methanol was used for conditioning of the cartridges and elution of the sample. Recovery tests for TC were carried out at three concentration levels (5, 15 and 25 mg L^{-1}), resulting in an average recovery of 77% with a 2% coefficient of variation ($n = 3$). These tests were undertaken in the presence and absence of iron and no significant differences were obtained.

The concentration of TC was measured by reversed phase HPLC using a Varian ProStar 230 chromatograph and a Luna 5μ C-18 (250 mm × 4.60 mm) column from Phenomenex. The detection was performed by UV absorption at a wavelength of 355 nm, using a UV–Vis ProStar 310 detector. The mobile phase used as eluent was 0.01 mol L^{-1} oxalic acid:methanol:acetonitrile (72:8:20) at a flow rate of 1 mL min^{-1}.

The residual hydrogen peroxide during TC degradation was measured by a spectrophotometric method using ammonium metavanadate (Shimadzu mini-1240 UV spectrophotometer) as described by Nogueira et al. [14].

3. Results and discussion

The concentrations of iron and hydrogen peroxide are important parameters in the photodegradation process. An excess or a lack of these additives can significantly reduce the efficiency. Furthermore, the use of lower concentrations reduces the costs. It has been previously observed that the degradation of organic compounds is improved when the concentration of iron is increased [13]. However, considering the maximum concentration of iron allowed in wastewater by Brazilian law (15 mg L^{-1} or 0.27 mmol L^{-1}), only concentrations below this value were studied in this work (0.1 and 0.2 mmol L^{-1}) to avoid the iron precipitation step which would considerably increase the costs of treatment.

The black-light irradiation of TC in the presence of 0.2 mmol L^{-1} $Fe(NO_3)_3$ and 10 mmol L^{-1} H_2O_2 was very efficient, resulting in total degradation of TC after only 1 min. However, 72% TOC removal was obtained only after 60 min, indicating the formation of intermediates which are further degraded. When the concentration of iron was decreased to 0.1 mmol L^{-1}, total degradation of TC was observed after 5 min, with a TOC removal of 47% after 60 min, indicating the limitation of degradation reactions due to the low iron concentration. The following experiments were carried out using 0.2 mmol L^{-1} iron.

3.1. *Influence of the iron source and H_2O_2 concentration on the degradation of TC under black-light and solar irradiation*

The source of iron is an important parameter to evaluate in photo-Fenton processes since previous works have demonstrated that it can considerably influence the degradation of different compounds, especially under solar light irradiation. It was observed that degradation of the herbicides tebuthiuron and diuron can be considerably accelerated in the presence of ferrioxalate in relation to $Fe(NO_3)_3$ under solar irradiation [15,16]. In the present work these two iron sources were also applied in the degradation of TC under black-light and solar irradiation.

The degradation of TC in the presence of either $Fe(NO_3)_3$ or ferrioxalate was compared using different H_2O_2 concentrations under black-light irradiation. It was observed that degradation of TC is more efficient when using $Fe(NO_3)_3$ in relation to ferrioxalate, independently of H_2O_2 concentration (Fig. 2A). Total degradation of TC was observed between 1 and 1.5 min in the presence of $Fe(NO_3)$, while this result was observed only after 8 min in the presence of ferrioxalate. However, similar TOC removals were obtained after 60 min with an average residual concentration of around 4 mg L^{-1} for both iron sources and all H_2O_2 concentrations tested except 1 mmol L^{-1}. It is important to mention that when ferrioxalate is used, 50% of the TOC concentration corresponds to oxalate, which is also photolysed during irradiation, as can be seen in Fig. 2B.

The influence of initial H_2O_2 concentration in the range 1–10 mmol L^{-1} was evaluated for both iron sources. The results demonstrate that TC degradation is independent of H_2O_2 initial concentration in the range of 1–5 mmol L^{-1}. However, further increase of H_2O_2 to 10 or 20 mmol L^{-1} hinders the degradation of TC (Fig. 2A). This increase corresponds to H_2O_2/Fe ratios of 50 and 100, which are relatively high. Some studies have reported that a H_2O_2/Fe ratio higher than 10 can result in excess peroxide in solution and consequently in scavenging of hydroxyl radicals, hindering the efficiency of degradation, according to the Eq. (3) [17]:

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2{}^{\bullet} \qquad (3)$$

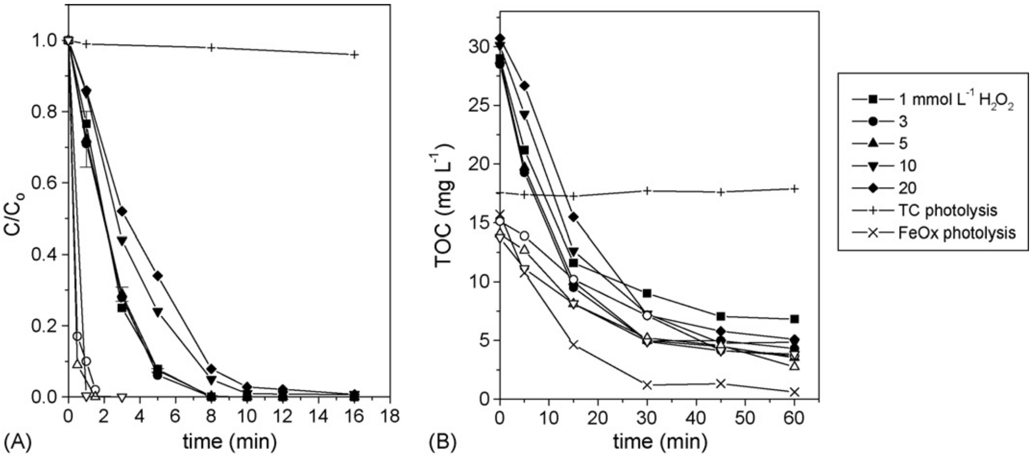

Fig. 2. Influence of the iron source and H_2O_2 concentration on the degradation of TC (A) and TOC removal (B) during black-light irradiation. Initial concentrations: [TC] = 24 mg L^{-1}; [FeOx] = [Fe(NO$_3$)$_3$] = 0.20 mmol L^{-1}. FeOx (solid symbols) and Fe(NO$_3$)$_3$ (open symbols).

When considering the TOC removal, a slight improvement in the initial degradation is observed when increasing the concentration to 3 or 5 mmol L^{-1} (Fig. 2B), which suggests that 1 mmol L^{-1} is not sufficient to promote the same degree of mineralization as with 3 mmol L^{-1}, due to the total consumption of H_2O_2 in 15 min, while at 3 mmol L^{-1} total consumption was reached only after 30 min. The next experiments were carried out using 3 mmol L^{-1} H_2O_2 and 0.2 mmol L^{-1} of iron.

In a previous study of TC degradation by heterogeneous photocatalysis [18], it was observed that total oxidation of TC was achieved only after 2 h and a 10% mineralization after 4 h, for an initial concentration of TC of 50 mg L^{-1} under UV irradiation (125 W Hg lamp). According to the authors, the low TOC removal is due to the formation of recalcitrant intermediates. Although the TC concentration used in the present study is lower, a much shorter period of time was necessary for the total degradation by photo-Fenton process compared to heterogeneous photocatalysis.

The great advantage of the photo-Fenton process, besides the simplicity of operation, is the possibility of using solar light as source of irradiation. The use of solar light considerably reduces the costs of the process, especially for the treatment of high volumes such as effluents from STPs. Many studies have demonstrated the high efficiency of ferrioxalate when using solar light irradiation, which is mainly related to its high absorption in the UV–vis region and its high quantum yield of Fe(II) generation [19]. Thus the influence of iron source on TC degradation was also evaluated under solar irradiation. Under solar light, a different behavior was observed than that observed under black-light—the degradation is improved in the presence of ferrioxalate, achieving 100% degradation in only 0.5 min (0.054 J cm^{-2} UV dose), while in the presence of Fe(NO$_3$)$_3$ 3 min (0.270 J cm^{-2} UV dose) were necessary for total degradation (Fig. 3A). This result denotes the importance of ferrioxalate in solar photo-Fenton process. However, no significant difference in TOC removal was observed when comparing the two

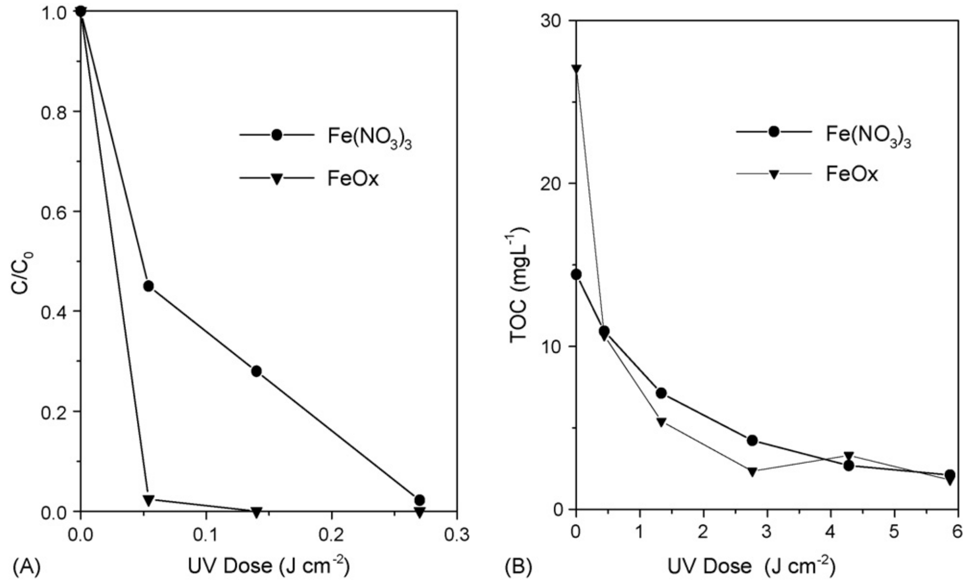

Fig. 3. Influence of the iron source on the degradation of TC (A) and TOC removal (B) under solar light irradiation. Initial concentrations: [TC] = 24 mg L^{-1}; [FeOx] = [Fe(NO$_3$)$_3$] = 0.20 mmol L^{-1}; [H_2O_2] = 3.0 mmol L^{-1}.

iron sources, achieving a residual concentration of 2 mg C L^{-1} in 60 min irradiation (5.870 J cm^{-2} UV dose) (Fig. 3B).

3.2. Matrix effects on TC degradation under black-light and solar irradiation

Most of the studies involving evaluation of advanced oxidation processes, including photo-Fenton, are carried out using solutions of the target compound made with distilled or frequently ultra pure water. Considering that pharmaceutical residues have been detected in surface waters and in effluent from STPs, in this work the degradation of TC was also evaluated in these two matrices under solar and black-light irradiation. The organic matter present in aqueous samples can interfere in different manners with the degradation of target compounds. While it has been reported that humic acids can favor the degradation of pharmaceuticals [20,21] in UV/H_2O_2 degradation by photosensitization, they can also inhibit the degradation through competition for hydroxyl radicals generated or by radiation attenuation [22]. The presence of carbonates can also strongly decrease the degradation efficiency by scavenging of hydroxyl radicals [23].

The degradation of TC when present in surface water and in STP effluent under black-light irradiation is compared to the results obtained in pure water (Fig. 4). The degradation of TC in surface water showed very similar behavior to that obtained in pure water, with almost total degradation of TC observed in 0.5 min (Fig. 4A). The low TOC concentration of this sample, 5.8 mg L^{-1} (Table 1), may have contributed to the small interference of this matrix on the degradation of TC when compared to the results obtained in pure water. No significant difference was observed in the removal of TOC when comparing TC degradation in pure water or surface water, achieving 70% after 45 min irradiation with a residual concentration of 4 mg L^{-1}. On the other hand, when evaluating the degradation of TC present in STP effluent under black-light irradiation, a lower efficiency was observed, achieving only 58% degradation in 0.5 min and 80% in 3 min, indicating that the higher complexity of this sample interferes with TC degradation. Furthermore, no TOC removal was observed in the first 15 min for the STP effluent sample, in contrast to the degradation in pure and surface water (Fig. 4B). Only after 30 min was some TOC removal observed.

Besides the high TOC content of the STP effluent sample, at 10.6 mg L^{-1}, almost twice the TOC concentration of the surface water, another important characteristic is the concentration of inorganic carbon. With a pH of 8, this sample presented a high inorganic carbon content of 52.4 mg L^{-1} in relation to organic carbon (10.6 mg L^{-1}) (Table 1), which decreased to 26.0 mg L^{-1} after pH adjustment to 2.5. The high carbonate content of this sample may have scavenged hydroxyl radicals according to Eqs. (4) and (5) [17]:

$$^{\bullet}OH + HCO_3^{-} \rightarrow H_2O + CO_3^{\bullet -} \quad (4)$$

$$^{\bullet}OH + CO_3^{2-} \rightarrow HO^{-} + CO_3^{\bullet -} \quad (5)$$

Therefore, considering that the higher content of organic and inorganic carbon of this sample could compete for or scavenge $^{\bullet}OH$, the initial concentration of H_2O_2 was increased to 10 mmol L^{-1}. However, this increase resulted in even lower efficiency of TC degradation relative to 3 mmol L^{-1}, as can be seen in Fig. 4A. The lower efficiency at higher H_2O_2 concentration leads to the consideration that other sample constituents may have interfered with TC degradation in STP effluent under these conditions.

It is important to point out that the concentration of soluble iron in both the surface water sample (0.25 mg L^{-1} = 4.46 × 10^{-3} mmol L^{-1}) and STP effluent (2 mg L^{-1} = 0.036 mmol L^{-1}) (Table 1) is low in relation to the concentration of iron added (0.200 mmol L^{-1}) and do not change significantly the concentration of iron for the photo-Fenton process.

However, under solar light irradiation and the use of ferrioxalate as source of iron, the same TC degradation efficiency was observed in all matrices showing no interference even of STP, resulting in total degradation of TC after 0.14 J cm^{-2} (1.5 min irradiation) (Fig. 5A). The irradiation of TC present in surface water in the absence of iron and hydrogen peroxide showed that no significant photolysis occurs in this sample under solar irradiation (Fig. 5A). Considering TOC removal, a sharp decrease was

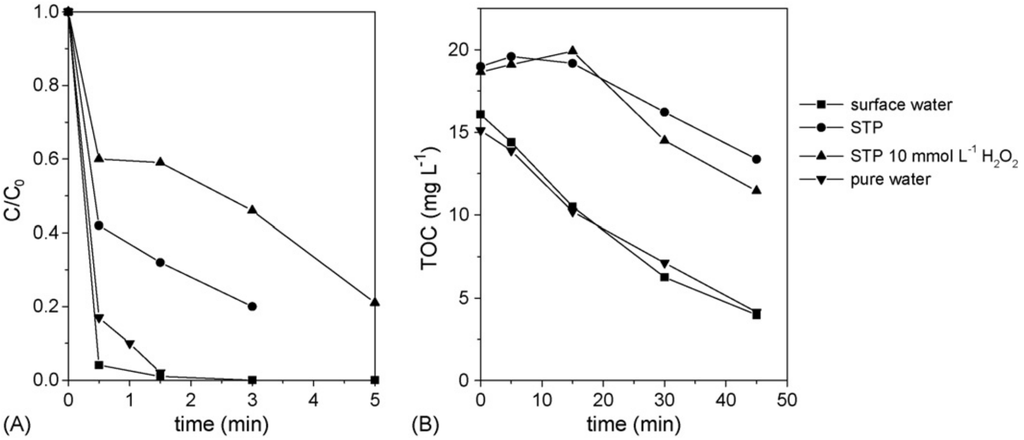

Fig. 4. Influence of matrix on the degradation of TC (A) and TOC removal (B) under black-light irradiation in the presence of iron nitrate. Initial concentrations: [TC] = 24 mg L^{-1}; [$Fe(NO_3)_3$] = 0.20 mmol L^{-1}; [H_2O_2] = 3.0 mmol L^{-1}, except for STP 10 mmol L^{-1}.

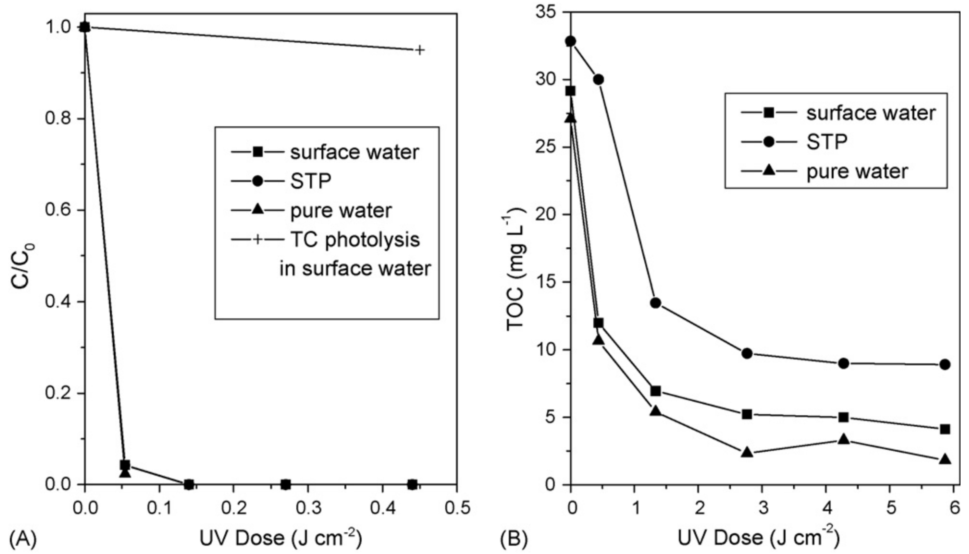

Fig. 5. Influence of matrix on the degradation of TC (A) and TOC removal (B) under solar light irradiation in the presence of ferrioxalate. Initial concentrations: [TC] = 24 mg L^{-1}; [FeOx] = 0.20 mmol L^{-1}; [H_2O_2] = 3.0 mmol L^{-1}.

observed in the first 15 min irradiation (1.3 J cm^{-2}) for all samples. The use of solar light and ferrioxalate strongly improved the TOC removal in the STP sample, where the decay showed similar behavior as for surface water, although with higher absolute values. These results suggest that the organic matter in the STP sample may have attenuated the radiation, hindering the photolysis of aqueous $Fe(OH)^{2+}$ under black-light irradiation, and consequently the ferrous ion regeneration and $^{\bullet}OH$ generation, hindering the degradation, which may be insignificant under solar light considering the higher absorption of ferrioxalate in the UV–vis region.

4. Conclusions

The photo-Fenton process under artificial or solar irradiation is very efficient for the degradation of tetracycline in aqueous solution, achieving total degradation after approximately 1 min irradiation. Under black-light irradiation, higher efficiency is obtained using iron nitrate than when ferrioxalate is used. In contrast, the solar degradation is favored by the use of ferrioxalate as source of iron at the same hydrogen peroxide concentration. When TC was dissolved in a sample of surface water instead of pure water, similar results were obtained indicating no significant interference of this matrix on the degradation process. On the other hand, the degradation of TC in the sample of STP effluent showed lower efficiency under black-light irradiation and $Fe(NO_3)_3$. However, very high efficiency was obtained under solar irradiation and by the use of ferrioxalate, achieving total degradation of TC after 1 min irradiation. The results shown in this work indicate that the photo-Fenton process under solar irradiation can be applied for the degradation of tetracycline present in surface water or even more complex samples such as STP effluent, a matrix where it has often been found recently. The fast degradation of tetracycline by photo-Fenton process is a very promising treatment. Since pharmaceuticals are often encountered in STP effluents, this procedure offers a good alternative for the treatment of such samples, since it permits the treatment of large volumes of effluents using low concentrations of reagents and solar light, preventing the contamination of aquatic environments.

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