PAPER

Microcystin-LR degradation by solar photo-Fenton, UV-A/photo-Fenton and UV-C/H$_2$O$_2$: a comparative study†

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This work assessed the effectiveness of several methods on degradation of microcystin-LR (MC-LR) by different Advanced Oxidation Processes, like solar photo-Fenton, UV-A/photo-Fenton and UV-C/H$_2$O$_2$. UV-C/H$_2$O$_2$ and UV-A/photo-Fenton processes were carried out in a bench scale photochemical apparatus and the solar photo-Fenton treatment was performed in a CPC photoreactor. MC-LR degradation was monitored by LC-ESI-MS/MS and kinetic parameters were calculated for all systems evaluated. The results demonstrated that UV-C/H$_2$O$_2$ was the most efficient method, showing a reduction of over 90% of initial MC-LR after 5 min of reaction. Solar and photo-Fenton/UVA had a rate decrease of 88 and 76% after the same time, respectively. The kinetic study indicated that the solar photo-Fenton and artificial radiation (UV-A) processes were very similar in their efficiency. The use of sunlight instead of artificial UV radiation significantly reduced the cost of photocatalytic treatment systems; it is also an environmentally friendly method, since it utilizes renewable energy.

Introduction

Population growth and the intensification of agricultural and industrial activities have led to the enhancement of eutrophication in superficial freshwater bodies. Consequently, cyanobacteria blooms became more frequent worldwide. Some cyanobacteria species can produce toxins, called cyanotoxins. Among the most studied hepatotoxins produced by cyanobacteria are the cyclic heptapeptides, also known as microcystins (MCs).[1] MCs are a group of at least 70 molecules and microcystin-LR (MC-LR) is the most common of its congeners (Fig. 1).[2] The first documented human deaths from cyanobacterial hepatotoxins occurred following intravenous exposure in a dialysis clinic in Caruaru city, Brazil, during 1996.
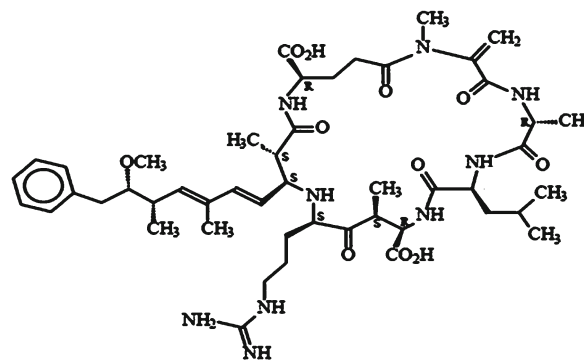

Fig. 1 Structure of microcystin-LR.

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In Brazil, episodes of toxic cyanobacteria blooms, which occurred between 1991–2001, revealed the predominance of production of MCs in water.[3]

Cyanobacterial cells synthesize MCs, which are released into the surrounding water after cell death and lysis. Thus, MCs can enter water treatment plants *via* intra- and extracellular forms.[4] Physical and/or chemical oxidation methods are commonly used in extracellular toxin removal.[5] However, these conventional water treatment methods have been generally proven inadequate for the total removal of dissolved MCs. Therefore, there is an increasing need to develop more effective treatment methods to remove MCs and other cyanotoxins from contaminated water. Advanced Oxidation

Processes (AOPs) are a reasonable alternative for the removal of such toxic organic chemicals.[4] Although they utilize different reacting systems, all these processes are characterized by the production of OH radicals, which are extraordinarily reactive and present low selectivity. The versatility of AOPs is also enhanced by the fact that they can generate OH radicals through multiple processes allowing for specific treatment requirements.[6] Many AOPs have been prominent in the treatment of MCs contaminated water, especially those using sources of radiation (UV, visible or solar light). It is important to remember that the division of UV radiation may be classified as vacuum UV (100–200 nm), UV-C (200–280 nm), UV-B (280–315 nm) and UV-A (315–400 nm). UV-C/H_2O_2, Fenton/photo-Fenton processes, O_3/H_2O_2, O_3/Fe^{2+} and TiO_2 photocatalysis are some of the AOPs already studied for this purpose.[7–12]

UV-C/H_2O_2 process

One of these processes selected in this work was the UV-C/H_2O_2 system, in which hydroxyl radicals are formed according to eqn (1):

$$H_2O_2 + h\nu \rightarrow 2\,^{\cdot}OH \tag{1}$$

This technology has been applied for the MCs degradation in water and has shown good results, with over 90% removal after a few minutes of treatment.[13–16] Despite its advantages, such as no phase transfer problems, no sludge formation and relatively low operational cost, research for its application in MCs degradation is still limited.[13] This fact can be justified since the artificial generation of photons can be costly in the operation of photocatalytic processes for water treatment.[17] However, not all photoassisted processes require light with the same wavelength and energy. While H_2O_2 photolysis needs photons of short wavelength (<310 nm), other AOPs such as TiO_2 photocatalysis and photo-Fenton can take advantage of photons of wavelengths up to 380 nm.[18,19] For this reason, and because of its homogeneous photocatalytic nature, the photo-Fenton process was chosen to be studied and compared in this work.

Fenton and photo-Fenton processes

The photo-Fenton process starts with the classical Fenton's reagent,[20] according to eqn (2).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \,^{\cdot}OH + HO^- \tag{2}$$
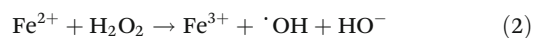
When the system is irradiated with UV or visible light, the photoassisted Fenton's process produces ferric ions as a by-product of the reaction between Fe^{2+} and H_2O_2 and then is photochemically transformed back into ferrous ions as shown by eqn (3) and (4):

$$Fe^{3+} + H_2O_2 \rightarrow FeOOH^{2+} + H^+ \tag{3}$$

$$[Fe(OH)]^{2+} + h\nu \rightarrow Fe^{2+} + \,^{\cdot}OH \tag{4}$$
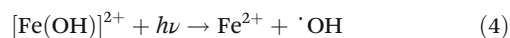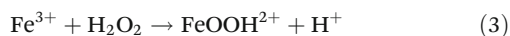
This closed cycle maintains continuous generation.[21] Moreover, because of the soluble iron-hydroxy formation, the photo-Fenton processes seem to be the most apt of all AOPs that can be run under solar irradiation.[22] Many studies have demonstrated the efficiency of degradation of different classes of toxic organic compounds by the solar photo-Fenton process,[21] but until now studies with MC-LR are still scarce. The use of solar radiation is an economically and ecologically viable alternative, since it is an inexhaustible source of energy.[23] Over the past 20 years, several solar photocatalytic reactors for water treatment have been developed and tested.[24] Among solar collector systems, compound parabolic collectors (CPC) are a good option for solar photochemical applications. They can make highly efficient use of both direct and diffuse solar radiation without the need for solar tracking.[25] The objective of this study was to evaluate and compare the effectiveness of degradation of MC-LR by three different photocatalytic AOPs: the photo-Fenton processes, using both artificial light source, UV-A/photo-Fenton (UVA/pF), and solar light, photo-Fenton (solar/pF), and UV-C/H_2O_2 processes.

Materials and methods

Chemicals

Microcystin-LR (MC-LR) standard was kindly provided by the Research Unit of Cyanobacteria of Rio Grande Federal University (UPC/FURG/RS). Solutions with an initial concentration of 50 μg L^{-1} were prepared in Milli-Q water and employed in all experiments. Hydrogen peroxide (Peróxidos do Brasil, reagent-grade, 30% w/v) and $FeSO_4 \cdot 7H_2O$ (Isofar, ACS-grade) were used. Catalase (Sigma, 2200 UA mg^{-1}) was used to stop the photo-Fenton reaction in samples before analysis. The pH was adjusted by using H_2SO_4 and NaOH (1.0 M) solutions (VETEC).

UV-C/H_2O_2 and UV-A/photo-Fenton reactions

The experiments were conducted in a borosilicate bench photoreactor with 250 mL capacity, equipped with a water-cooled system and a magnetic stirrer. Artificial radiation was provided by a medium-pressure mercury vapor lamp (125 W, Philips) placed in the solution through a quartz (UV-C/H_2O_2) and a Pyrex glass jacket (photo-Fenton/UV-A). The radiation intensity was determined by uranyl/oxalate actinometry resulting in 9.7×10^{-5} and 7.1×10^{-7} E s^{-1} for quartz and Pyrex glass jackets, respectively. In the degradation experiments, we used 250 mL of aqueous solution, with optimal values of pH, hydrogen peroxide and Fe^{2+} solution. For all UV-A/photo-Fenton experiments, pH was adjusted to 3.0 using 1.0 M sulphuric acid.

Solar photo-Fenton reaction

The solar photo-Fenton reactions were carried out in a compound parabolic collector (CPC) system. The CPC is composed of a solar collector unit with six borosilicate glass tubes (1000 mm length, OD 32 mm, transmissivity 0.900 < τ < 0.915, λ > 350 nm), a continuously stirred tank (6 L), a recirculation pump and connecting tubes. The aluminum reflectors are fixed on a base that can be adjusted for 25° inclination for

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maximum use of solar radiation. The collector area is 1.25 m^2 and the total volume treated was 5 L. The reactor was operated in a recirculation system, with an average flow of 0.4 L min^{-1}. The studies were conducted in Curitiba (25°25′S/49°16′E) during spring months. Sunlight exposure occurred between 11:00 am and 2:00 pm. The average intensity of UVA radiation was measured with a CosmoLUX® UVATEST-3000 radiometer and remained constant at 2.4 mW cm^{-2}.

At the beginning of all the photo-Fenton experiments, the solutions studied were added directly to the photoreactor, and a sample was taken after 15 min of homogenization (initial concentration C_0). Then the pH was adjusted with sulphuric acid and another sample was taken after 15 min to confirm the pH. Afterwards, the iron salt was also added (FeSO$_4$·7H$_2$O) and was mixed for 15 min before sampling. Finally, an initial dose of hydrogen peroxide was added and samples were taken to evaluate MC-LR degradation. Photo-Fenton experiments were carried out at pH 3.0. The initial concentrations of Fe^{2+}/H$_2$O$_2$ were defined by factorial design, which will be presented in detail in the next section.

Analytical methods

MC-LR degradation was determined by LC-ESI-MS/MS analyses performed on a system consisted of a liquid chromatograph (Agilent 1100 Series, Palo Alto, CA) coupled to a triple quadrupole mass spectrometer API 4000 (Applied Biosystems, Foster City, CA) with positive mode electrospray ionization (ESI). The samples were injected directly into the HPLC. A column 3 µm Luna C18 (2) 100A, 150 × 2.0 mm (Phenomenex) was used for all analysis. Two mobile phases were used: A (10% acetonitrile/90% water with 5 mM ammonium acetate and 0.1% formic acid) and B (90% acetonitrile/10% water with 5 mM ammonium acetate and 0.1% formic acid), in an isocratic elution with composition 55% A and 45% B. The column temperature was 25 °C and the flow rate was 0.2 mL min^{-1}. The injection volume was 100 µL. The limit of quantification of the chromatographic analysis was 0.1 µg L^{-1} and was validated according to methodology previously described.[26] Residual hydrogen peroxide and Fe^{2+}/Fe^{3+} ion concentrations were determined by UV-Vis spectroscopy, using methods based on ammonium metavanadate[27] and o-phenanthroline reactions,[28] respectively.

Results and discussion

Experimental design

Initially, the effect of relevant experimental variables on the efficiency of the AOPs was evaluated using a 2^2 factorial design complemented with a central point, in accordance with the percentage of MC-LR degraded (C/C_0). In the photo-Fenton processes, [Fe^{2+}] and [H$_2$O$_2$] were evaluated; in UV-C/H$_2$O$_2$ reactions, pH values and [H$_2$O$_2$]. The complete design matrix, variables range and MC-LR degradation values for these processes are shown in Table 1. Subsequently, photocatalytic reactions were performed under the previously optimized experimental

Table 1 Factorial design 2^2 matrix for the study of MC-LR degradation under the solar/photo-Fenton, UV-A/photo-Fenton and UV-C/H$_2$O$_2$ processes^a

Variable	Level		
	+	0	−
pH	4.0	5.0	8.0
[H$_2$O$_2$] (mg L^{-1}) UV-C/H$_2$O$_2$	25	50	75
[H$_2$O$_2$] (mg L^{-1}) photo-Fenton processes	50	75	100
[Fe^{2+}] (mg L^{-1})	5	10	15

	UVC/H$_2$O$_2$				Solar/pF	UVA/pF
Exp.	pH	[H$_2$O$_2$]	%MC-LR degradation	[Fe^{2+}]	[H$_2$O$_2$]	%MC-LR degradation	%MC-LR degradation
1	−	−	78 ± 1.2	−	−	47 ± 1.8	41 ± 2.2
2	+	−	74 ± 2.2	+	−	12 ± 2.0	8 ± 2.9
3	−	+	91 ± 2.0	−	+	61 ± 2.0	58 ± 1.7
4	+	+	84 ± 1.1	+	+	89 ± 1.9	76 ± 2.1
5	0	0	84 ± 0.9	0	0	89 ± 2.0	77 ± 2.3

^{a} Solar photo-Fenton (solar/pF), photo-Fenton/UVA (UVA/pF).

conditions. In order to evaluate the efficiency of each of the tested processes we compared the values of MC-LR degradation after 5 min of reaction that will be discussed in detail in the next session. In the photo-Fenton processes, no significant difference was observed between the upper values (exp. 4) and the central point (exp. 5). Hence, for reasons of economy, 10 mg L^{-1} [Fe^{2+}] and 75 mg L^{-1} [H$_2$O$_2$] were used. For a better visualization, the results are shown as geometric representations in Fig. 2. A central point was assayed in triplicate, showing a mean standard deviation (SD) of 2%. The pH was always kept at 3.0. In accordance with the spectrophotometric analysis, the total iron concentration was maintained constant throughout the process. It is known that the higher the initial concentration of Fe^{2+}, the greater is the stimulus for the H$_2$O$_2$ decomposition and consequently higher production of ˙OH radicals.[20] However, when we used the highest concentrations of Fe^{2+} (15 mg L^{-1}) and H$_2$O$_2$ (100 mg L^{-1}) there was no significant increase in process efficiency compared to the central point. This probably occurred because the excess Fe^{2+} competes with the organic matter in solution for ˙OH radicals.[20,29] Also, high concentrations of H$_2$O$_2$ can lead to their recombination with hydroxyl radicals. Furthermore, in the presence of excess H$_2$O$_2$, the concentration of Fe^{2+} in the medium is low in relation to Fe^{3+}, since the reaction between Fe^{3+} and H$_2$O$_2$ is much slower than the decomposition of H$_2$O$_2$ in the presence of Fe^{2+}. In Fenton processes, the production of hydroxyl radicals and consequently the efficiency of organic matter removal are much more dependent on a favorable relationship between [Fe^{2+}] and [H$_2$O$_2$] than the individual concentrations of each of these parameters.[21,30] The main effects calculated demonstrate this interaction (Fe^{2+} × H$_2$O$_2$: +10.0 ± 2.0). In general, it is estimated that when the concentration of Fe^{2+} exceeds H$_2$O$_2$, the reaction tends to have an effect of chemical coagulation. If the reverse is true, the reaction will likely oxidize.[20] For this reason, it is recommended to maintain the
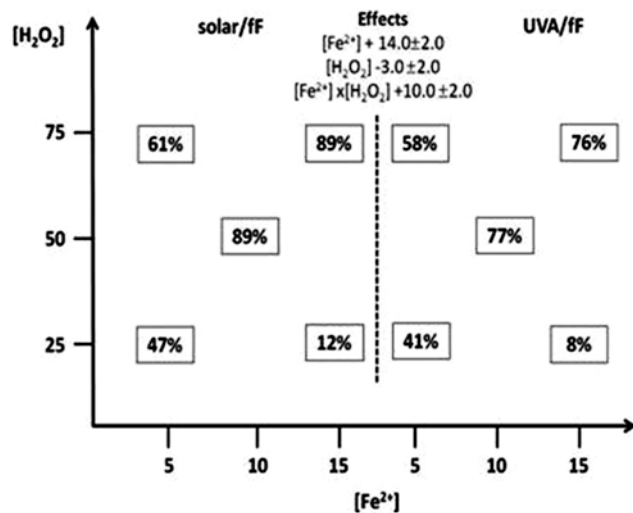
Fig. 2 Geometric representation of 2^2 factorial design for MC-LR degradation during photo-Fenton experiments ([MC-LR]: 50 μg L^{-1}); reaction time: 5 min.

Fe^{2+}/H_2O_2 ratio at the lowest possible value.[31] In this study, the ratio was 0.13. In the UV-C/H_2O_2 process, it was observed that the pH variation has little influence on the degradation rate of microcystin-LR, showing slightly better results at pH 4.0.

This information can be confirmed by calculations of main effects (Fig. 3). Therefore, we chose to perform the experiments at pH 5.0, which is the natural pH of the MC-LR solution. The little influence of the pH range can be explained by the behavior of the molecule of MC-LR under different pH conditions. MC-LR contains two ionizable carboxyl groups and one ionizable amino group (Fig. 1) that are not part of peptide bonds that make up the cyclic peptide structure and the pK_a values of these groups are 2.09, 2.19 and 12.48, respectively.[32,33] Thus, in the pH ranges used in this study (4.0 to 8.0), the dominant species of MC-LR are $(COO^-)_2(NH_2^+)$, with an overall charge of −1. Previous studies demonstrated similar results, in which acidic and neutral conditions were appropriate for degradation of MC-LR[15] whereas the degradation rate decreased in strong alkaline media (pH 11–12).[13] Regarding the H_2O_2 concentration, the best results were obtained with the highest values (75 mg L^{-1}), demonstrating that in the variation range studied, there was a proportional increase in the degradation rate as the concentration increased (Fig. 3). In similar studies, the same relation was observed.[13] However, at higher concentrations, the additional H_2O_2 did not contribute to a significant increase in the process. This fact can be explained by the scavenging effect of excess H_2O_2 in solution. It competes with MC-LR by reaction with ˙OH, thus reducing its rate of degradation and efficiency of the process.

MC-LR degradation in the different processes

In order to simulate an approximate average value of the MC-LR concentration commonly found in water blooms of cyanobacteria, an initial concentration of 50 μg L^{-1} was used. To evaluate the efficiency of each process described previously,
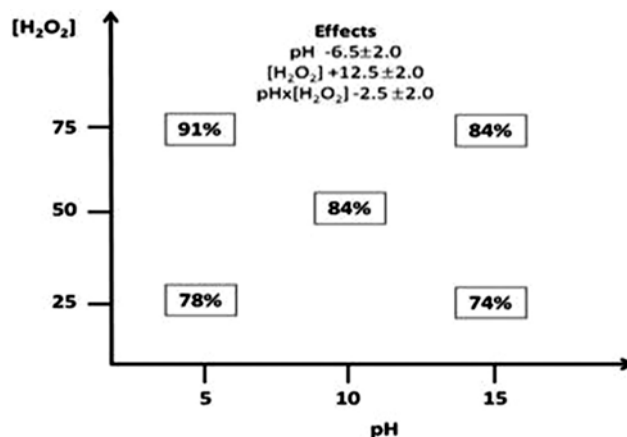

Fig. 3 Geometric representation of a 2^2 factorial design for MC-LR degradation during UV-C/H_2O_2 experiments. ([MC-LR]$_0$: 50 μg L^{-1}); reaction time: 5 min.

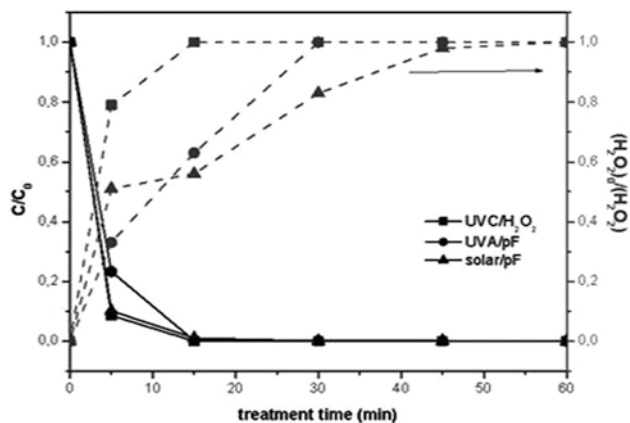the experiments were carried out under the optimized conditions by factorial design.

The comparison of the different processes studied, using MC-LR degradation (C/C_0), showed that the UV-C/H_2O_2 system was slightly better with 91% reduction of the initial MC-LR concentration after 5 min of treatment, at which point about 80% H_2O_2 had been consumed. At the same time, the UVA/fP process showed a decrease of 89.4% of the initial MC-LR concentration and a 52% H_2O_2 consumption, followed by the solar/pF process, with 76.7% MC-LR reduction and 37% consumption of H_2O_2 (Fig. 4).

Experiments using only H_2O_2, H_2O_2, UV-C, UV-A or solar light were performed. No considerable MC-LR degradation was observed with H_2O_2, UV-A and solar light. With UV-C only about 20% degradation was observed after 60 min treatment. Previous studies have shown similar results.[13,14,34,35] It would be also important to analyze the reduction of TOC after treatment, but due to low concentrations of MC-LR used in the work and the infrastructure available, it was not possible to perform these analyses. In order to achieve a better comparison between the processes studied were used kinetic parameters, such as rate constants (k) and half-lives ($t_{1/2}$), that is, the time required to decrease the concentration of the reactant to half the amount present before the reaction. In this study, the photocatalytic disappearance of MC-LR followed apparent *pseudo*-first order kinetics in all processes. Kinetic parameters were obtained by plotting ln (C/C_0) *versus* irradiation time (t). Experimental data were fitted to a first-order kinetic model according to eqn (5) and the half-life times ($t_{1/2}$) according to eqn (6). These results are summarized in Table 2.

$$\ln C/C_0 = -kt \quad (5)$$

$$t_{1/2} = \ln 2/k \quad (6)$$

It is well known that the Fenton reactant consists of an aqueous solution of H_2O_2 and ferrous ions providing hydroxyl radicals. When the process is supplemented with UV/visible radiation, it is called photo-Fenton. Assuming that both photo-

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Fig. 4 Degradation of microcystin-LR (—) *vs.* treatment time and H_2O_2 consumption (– –) by solar photo-Fenton (solar/pF), UV-A/photo-Fenton (UVA/pF) and UV-C/H_2O_2. ([MC-LR]$_0$ = 50 µg L^{-1}; [H_2O_2]$_0$ = 75 mg L^{-1}; [Fe^{2+}]$_0$ = 10 mg L^{-1}; pH UV-C/H_2O_2 = 5.0; pH pF = 3.0).

Table 2 Degrading kinetic parameters of microcystin-LR (MC-LR) with different processes[a]

	Process		
	UVC/H_2O_2	Solar/pF	UVA/pF
k (min^{-1})	0.691 ± 0.01	0.174 ± 0.006	0.152 ± 0.005
$t_{1/2}$ (min)	1.0 ± 0.02	3.98 ± 0.1	4.56 ± 0.1
R	0.9941	0.9987	0.9973

[a] Solar photo-Fenton (solar/pF), photo-Fenton/UVA (UVA/pF). k (rate constant), $t_{1/2}$ (half-life), R (coefficient of determination).

Fenton and UV-C/H_2O_2 processes had the same behavior and the initial MC-LR is so low, the reaction between ˙OH radicals and MC-LR is diffusion controlled and the degradation is typically limited by the generation of hydroxyl radicals.[36] The comparison of kinetic parameters was the most appropriate way to assess the effectiveness of the MC-LR degradation methods. These parameters include kinetic and radiation influences, and reactor design effects on the global reaction rate, allowing for an overall comparison between the different AOPs tested.[37] According to the literature, the AOPs generally follow the rate law for first-order reactions, where there is a direct proportionality between the reaction rate and concentration of reactants.[38] As expected, the UV-C/H_2O_2 process was the most efficient, as it completely removed MC-LR after 10 min, followed by solar photo-Fenton with the CPC reactor and the photo-Fenton/UVA. The efficiency of the process UV-C/H_2O_2 relies on some factors intrinsic to the molecule of hydrogen peroxide. One is its high solubility in water, discarding mass transfer problems typically associated with gas (*i.e.*, ozone). Moreover, it is a very efficient source of hydroxyl radicals, producing two molecules of ˙OH for every molecule of H_2O_2 when irradiated at 254 nm.[39] But due to the low coefficient of molar absorptivity (ε_{254} = 18.6 mol^{-1} cm^{-1}), high concentrations are necessary in the reaction of the oxidant.[6,39] Nevertheless, at

higher concentrations, the additional H_2O_2 did not significantly increase the degradation rate. In the presence of high H_2O_2 concentration, more ˙OH production would be expected, but scavenging of H_2O_2 becomes significant.[13] However, the main consideration in this work is that the solar/pF process showed to be very efficient on MC-LR degradation. The good performance is justified by its sensitivity to light up to wavelengths of 540 nm. Sunlight is an adequate polychromatic irradiation source, compared to shorter wavelength UV lamp sources since soluble iron-hydroxy and especially iron–organic acid complexes absorb even part of the visible light spectrum, not only ultraviolet radiation.[22] Moreover, the CPC reactors are very simple systems, cost-effective, easy to use and require low capital investment.[25] For this reason, the photo-Fenton process seems to be the most apt of all AOPs driven by sunlight and different classes of toxic organic compounds have been treated using this technology.[40–43]

Conclusions

Three AOPs (UV-C/H_2O_2, UV-A/photo-Fenton and solar/photo-Fenton) have been studied and compared for the MC-LR degradation, with a view to the *pseudo*-first order kinetic constants and half life times. The results discussed here demonstrated the high degradation capacity of these AOPs toward aqueous solutions containing MC-LR. Although the UVC/H_2O_2 process has been slightly better, especially remarkable are the results obtained with the solar/photo-Fenton process, which permitted total MC-LR degradation after 15 min treatment. Thus, the highlight of this work is to point out the possibility of using the solar photo-Fenton process as a good alternative for MC-LR water removal, since the use of solar energy is renewable, reduces the cost and is environmentally friendly.

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