Degradation of caffeine by photo-Fenton process: Optimization of treatment conditions using experimental design

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ABSTRACT

The degradation of caffeine in different kind of effluents, via photo-Fenton process, was investigated in lab-scale and in a solar pilot plant. The treatment conditions (caffeine, Fe2+ and H2O2 concentrations) were defined by experimental design. The optimized conditions for each variable, obtained using the response factor (% mineralization), were: 52.0 mg L−1 caffeine, 10.0 mg L−1 Fe2+ and 42.0 mg L−1 H2O2 (replaced in kinetic experiments). Under these conditions, in ultrapure water (UW), the caffeine concentration reached the quantitation limit (0.76 mg L−1) after 20 min, and 78% of mineralization was obtained respectively after 120 min of reaction. Using the same conditions, the matrix influence (surface water – SW and sewage treatment plant effluent – STP) on caffeine degradation was also evaluated. The total removal of caffeine in SW was reached at the same time in UW (after 20 min), while 40 min were necessary in STP. Although lower mineralization rates were verified for high organic load, under the same operational conditions, less H2O2 was necessary to mineralize the dissolved organic carbon as the initial organic load increases. A high efficiency of the photo-Fenton process was also observed in caffeine degradation by solar photocatalysis using a CPC reactor, as well as intermediates of low toxicity, demonstrating that photo-Fenton process can be a viable alternative for caffeine removal in wastewater.

1. Introduction

Most of the consumed pharmaceutical compounds are partially metabolized and excreted by humans and animals, and expelled into wastewaters which are later treated in sewage treatment plants (STPs). Among the pharmaceuticals, caffeine (CAF) is one of the most consumed stimulating substances, being present in foods, beverages and medicines. It has been also used as a chemical marker for surface water pollution caused by domestic wastewater, since the human species almost exclusively consumes and excretes it regularly (Buerge et al., 2003).

Monitoring of influent and effluent in STP and in raw and drinking water has shown that caffeine is one of the compounds present in higher concentration (Chisele, 2006). Caffeine has been found at concentrations of respectively 294 and 1.3 μg L−1 in influent and effluent of STP in Brazil, while concentrations of 1.1–106 and 0.22 μg L−1 were found respectively in raw and drinking water (Chisele, 2006; Sodré et al., 2010).

Advanced oxidation processes (AOPs) have been studied as an alternative for the treatment of urban (Klamerth et al., 2010a,b) and industrial wastewater pre-treatment (Sirtori et al., 2009; Zapata et al., 2010; Pintor et al., 2011) containing different types of contaminants. The AOPs are known to promote the degradation of organic compounds through the action of hydroxyl radicals (·OH) generated in the primary stages of these processes. Among the

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AOPs, the photo-Fenton process has gained attention due to the possibility of using solar energy as radiation source, significantly reducing the demand for energy. Other advantages are the use of low to moderate concentrations of chemicals, which in favorable situations can mineralize completely the organic constituents of aqueous effluents; the use of simple reactors and the possibility of iron reuse.

Several oxidation processes have been evaluated for caffeine degradation (Dalmázio et al., 2005; Broséus et al., 2009; Klamerth et al., 2009; Rosal et al., 2009; Kim and Tanaka, 2010; Klamerth et al., 2010a,b; Rodríguez-Gil et al., 2010). Klamerth et al. (2009) applied the photo-Fenton process and heterogeneous photocatalysis using TiO₂ to degrade caffeine in STP effluent using a solar pilot plant, concluding that the higher degradation rate was obtained applying the photo-Fenton process. In a later study, the same researchers have shown that the application of such process is an alternative to tertiary treatment for a mixture of fifteen emerging contaminants, including caffeine, as strategy for removal of species present in STP effluents (Klamerth et al., 2010a). Although the same authors have proposed conditions considered optimal for degradation of caffeine, a detailed study aiming to evaluate simultaneously the operating parameters involved in the photo-Fenton treatment, such as iron, hydrogen peroxide and caffeine concentration by mathematical models was not presented. In another study, Rodríguez-Gil et al. (2010) evaluated the toxicity of a mixture of compounds (caffeine, ofloxacin, salicylic acid, cotinine and nicotine) in river water matrix using fern spores, during their degradation, mediated by photo-Fenton process. They observed a decrease in the toxicity of the mixture, but noted the permanence of a residual toxicity attributed to the presence of other toxic agents not analyzed, probably of inorganic nature. On the other hand, a study on the toxicity of caffeine and their intermediaries was not presented.

Since that photo-Fenton treatment of wastewater are affected by several parameters such as the temperature, concentration of iron, hydrogen peroxide and target compound, in addition to the pH of the reaction medium, the working conditions are specific to each case and need therefore to be carefully optimized.

The aim of this study is to apply experimental design to evaluate the role (synergistic or antagonistic effects) of the three variables selected (CAF, Fe²⁺ and H₂O₂ concentrations) and to optimize caffeine photodegradation in ultrapure water (UW). Also assess, under optimized experimental conditions, the kinetic of caffeine removal, dissolved organic carbon (DOC) and toxicity, followed in experiments carried out in UW, not only in lab-scale, but also using a pilot plant based in the use of solar radiation. Furthermore, since residues of caffeine were found in STP and surface water (SW), we also evaluated the application of the photo-Fenton process in lab-scale to degrade caffeine in these complex media, comparing with results obtained in UW.

2. Experimental

2.1. Reagents

The solutions were prepared using UW and analytical grade reagents, FeSO₄·7H₂O (Vetec) was used to prepare aqueous 0.25 M iron stock solution. H₂O₂ (30% w/w), H₂SO₄, NaOH and Na₂SO₃ from Vetec were used as received. Ammonium metavanadate (Vetec) solution was prepared at a concentration of 0.060 M in 0.36 M H₂SO₄, being used for H₂O₂ quantification. The caffeine used in photodegradation experiments was purchased from Sigma–Aldrich and used as received. HPLC grade methanol (Vetec) was used for HPLC analyses.

2.2. Effluent from a sewage treatment plant and of surface water

In order to evaluate the application of photo-Fenton process and matrix effects on caffeine removal, samples of SW and STP effluent were collected during spring 2011. The STP where the collection was done serves about 5% of the population of Uberlândia (18°55′08″S; 48°16′37″W), a city with more than 650000 inhabitants. This plant is based on anaerobic treatment, followed by a flotation system. The sample of STP was collected after a complete treatment. The samples of SW effluent were collected directly of a river whose water, after conventional treatment, is supplied to the city of Uberlândia. Once collected, the samples were kept under refrigeration, for a week at most, so that the experiments were performed. The main parameters determined for both samples are shown in Table 1.

2.3. Experimental design

2.3.1. Factorial design (FD)

The FD was used to investigate the influence of each variable on the response factor. The percentage of mineralization of caffeine, measured by DOC decay after 120 min of reaction in relation to the initial DOC value, was chosen as response factor of the photo-Fenton process. For this, a 2³ factorial design (all possible combinations of codified values +1 and −1), in the case of k = 3 variables consists of eight experiments, was done. All experiments were performed in triplicate. The three variables were codified in two levels: caffeine (5.0 and 50.0 mg L⁻¹), Fe²⁺ (0.6 and 14.5 mg L⁻¹) and H₂O₂ (34.0 and 680.0 mg L⁻¹). The ranges of the variables were chosen according to previous studies (Trovó et al., 2006, 2009; Trovó and Nogueira, 2011). Although caffeine concentration is higher than the found in aqueous environment, it was chosen to permit a reliable evaluation of reaction kinetics and toxicity.

2.3.2. Central composite design (CCD)

The CCD was applied to optimize the concentration of caffeine, Fe²⁺ and H₂O₂, as well as to evaluate the correlation among these three variables. The same response factor defined in FD was chosen. Central composite design is a star type project that consists of three series of experiments: (i) a 2³ factorial design (all possible combinations of codified values +1 and −1) for k = 3 variables, consists of eight experiments; (ii) axial or star points (+1.7 and −1.7), and 0 for three variables (six experiments); and (iii) replicates of the central point (0) (five experiments). Thus, for this design, it was necessary to do nineteen experiments, in which the three variables were codified in five levels, varying within the following ranges: caffeine (33.2–66.8 mg L⁻¹), Fe²⁺ (8.6–15.4 mg L⁻¹) and H₂O₂ (17.2–50.8 mg L⁻¹). The range of the variables was chosen after carried out the FD. For FD and CCD, the equations used to quantitatively describe each system and draw the response surface and contour plots were built using STATISTICA 6.0. Statistical validation was obtained using the ANOVA test at 95% confidence level.

2.4. Photodegradation procedures

2.4.1. Lab-scale experiments

The photodegradation experiments were performed in lab-scale using a 400 W high pressure mercury vapor lamp as irradiation source. The photocatalytic reactor consists of an annular recipient of borosilicate glass with a 1 cm optical path jacket through it circulates the material to be degraded. The lamp was positioned at the center of the reactor, as described and schematically presented by Oliveira et al. (2012). The average dose of UVA radiation measured for the lamp is 1100 W m⁻² (Machado et al., 2003), which
presents a photonic flux of $3.3 \times 10^{-6}$ einstein s$^{-1}$ between 295 and 710 nm (Machado et al., 2008). The measurements were done using a Solar Light PMA 2100 photometer/radiometer, equipped with an UVA detector (320–400 nm) and a radiometric/photometric setup built with components furnished by Ocean Optics, Inc. (Machado et al., 2008).

The irradiated volume of the reactor was 0.280 L and a total volume of 4 L of the caffeine solution was recirculated, by pumping at a flow rate of 2.14 L min$^{-1}$ after the addition of iron solution, pH adjustment between 2.5 and 2.8 (the optimum pH range for the Fenton reaction) and addition of H$_2$O$_2$. The lamp was only turned on when the reactor was filled with solution. For FD and CCD design, aliquots (20 mL) of the photolyzed solutions were collected after 120 min of reaction, while for the kinetic experiments, samples (70 mL) were collected at each 20 min intervals up to 120 min. The initial conditions used in FD and CCD design are described in Sections 2.3.1 and 2.3.2.

The kinetic experiments with UW, SW and STP effluent were carried out under previously selected optimum conditions (52.0 mg L$^{-1}$ caffeine, 10.0 mg L$^{-1}$ Fe$^{2+}$ and 42.0 mg L$^{-1}$ H$_2$O$_2$). The consumed H$_2$O$_2$ was replaced when necessary. After sampling and before analysis, a calculated volume of 2.0 M Na$_2$SO$_3$ solution was added to the samples, according to the stoichiometry between H$_2$O$_2$ and Na$_2$SO$_3$, and H$_2$O$_2$ concentration, ensuring the removal of the remaining H$_2$O$_2$, stopping the Fenton reaction, and the interference of traces of H$_2$O$_2$ in toxicity assays. For these assays the pH was adjusted in the range between 6 and 8 after adding the Na$_2$SO$_3$ solution. The solution temperature was controlled using a thermostatic bath (Tecnal TE-184), keeping close to 25 ± 2 °C.

2.4.2. Experiment in the pilot plant: use of solar radiation

The experiment using solar radiation was carried out during autumn, under clear sky conditions, using a solar pilot plant. The solar irradiance was measured using a radiometer (PMA 2100 Solar Light Co.) in the UVA region (320–400 nm), with the sensor placed at the same angle as that of the reactor, and an average solar irradiance of 49.7 ± 3.9 W m$^{-2}$ was obtained. It consists of a compound parabolic collector (CPC) with an irradiated surface of 1.62 m$^2$ (irradiated volume: 12 L) and a reservoir with maximum capacity of 120 L (Duarte et al., 2005; Machado et al., 2008). A volume of 50 L of the caffeine solution was recirculated under turbulent flow (33.3 L min$^{-1}$) into the CPC absorber tubes in a closed recirculating system. The photoreactor hydraulic circuit consists of a continuously stirred tank and a 0.50 HP centrifugal recirculation pump. At the beginning of the experiment, with the collectors covered, the same initial conditions defined for the reagents in kinetic experiments under lab-scale reactor were used. The cover was then removed and samples were collected at intervals of 20 min up to 180 min. The same treatment using Na$_2$SO$_3$ solution, previously described, was done to stop the Fenton reaction.

2.5. Chemical analyses

Before chemical analyses, the samples were filtered through membranes with pore diameter of 0.45 μm. Mineralization was followed measuring the DOC decay using a TOC analyser (Shimadzu TOC-VCPH/CPN) equipped with an ASI-V auto sampler. Hydrogen peroxide was quantified spectrophotometrically using ammonium metavanadate, as described by Nogueira et al. (2005).

The kinetic experiments were also carried out by HPLC analyses aiming to evaluate the caffeine removal from UW, SW and STP effluent, as well as the toxicity for experiments using UW in lab-scale and in the solar pilot plant. The caffeine removal was quantified using a VWR-Hitachi L-2130 chromatograph equipped with a Lycrhisper C-18 column (5 μm, 250 × 4.6 mm) and an UV–Vis detector (Merck-Hitachi L-4250) set at 273 nm. The retention time for caffeine was between 8.6 and 8.8 min, with a quantitation limit of 0.76 mg L$^{-1}$. In each assay, 20 μL of the sample was eluted using a mixture of 30% methanol and 70% UW, at a flow rate of 1 mL min$^{-1}$.

The toxicity assays were done evaluating the immobilization of Artemia salina. The artemia were bred in an aqueous culture medium whose salinity resembled the conditions for the survival and development of these microcrustaceans. Test plates containing ten A. salina crustaceans in the presence of 9.5 mL of the sample solution and 0.5 mL of saline medium were incubated for 48 h at 20 °C in the dark. No food was given to these crustaceans between hatching and test steps. Acute toxicity was assessed by noting the effects of the test-compounds on the mobility of A. salina. The crustaceans were considered immobile if after 48 h incubation they remained at the bottom of the test container and did not start swimming within 15 s of observation. Acute toxicity is expressed as percentage of immobilization compared to a non-toxic control, where an artemia immobilization of 10% is accepted after 48 h of exposure.

3. Results and discussion

3.1. Photo-Fenton experiments: experimental design

In order to apply efficiently AOPs to remove contaminants in wastewater, the optimization of experimental conditions is crucial. Firstly, a FD was applied to investigate the role (individual or combined synergistic or antagonistic effects) of the three selected variables (caffeine, Fe$^{2+}$ and H$_2$O$_2$ concentration), named in Pareto chart as 1, 2 and 3, respectively, on the response functions and set the trend of each variable as high (+1) or low (−1). The Pareto chart (Fig. 1), obtained for the results (Table 1 – Supplementary results) suggests that all variables plays as important role in mineralization.

The analysis of Fig. 1 suggests that a higher mineralization of caffeine is obtained when the levels of caffeine (50.0 mg L$^{-1}$) and Fe$^{2+}$ (14.5 mg L$^{-1}$) were kept elevated. On the other hand, a negative value was obtained for hydrogen peroxide, indicating that a low level of H$_2$O$_2$ (34.0 mg L$^{-1}$) must be used to reduce the negative effect on caffeine mineralization. Although the 2:3 (Fe$^{2+}$:H$_2$O$_2$) interaction also plays a negative role on the percentage of mineralization, there was no need to change any tendency of the main effects. This is due to the positive effects of the individual variables caffeine and iron, and to the 1:3 (CAF:H$_2$O$_2$) synergistic interaction (Fig. 1). This result agrees with a previous study in which was
demonstrated that iron concentration plays a very important role in the degradation of 4-chlorophenol mediated by photo-Fenton reaction (Trovó et al., 2006). On the other hand, for the two levels evaluated for H$_2$O$_2$ (3.40 and 680.0 mg L$^{-1}$), the higher H$_2$O$_2$ concentration plays a negative role on the percentage of mineralization. Detrimental effects were also observed when high H$_2$O$_2$ concentrations were employed in diclofenac degradation mediated by photo-Fenton process, probably due to self-decomposition (Eq. (1)) and scavenging of hydroxyl radicals by an excess of H$_2$O$_2$ (Eq. (2)) (Trovó and Nogueira, 2011).

\[
\begin{align*}
H_2O_2 + H_2O_2 & \rightarrow 2H_2O + O_2 \\
H_2O_2 + \text{HO}^- & \rightarrow H_2O + \text{HO}_2
\end{align*}
\]

Considering that with a higher initial concentration of caffeine a large amount of DOC is treated, the absolute DOC removal (mass of carbon removed) is higher for the same percentage of mineralization. So the mass of organic carbon removed was calculated in each removal (10.4 mg C L$^{-1}$) is higher for the same percentage of mineralization. Detrimental effects were also observed when high H$_2$O$_2$ concentrations were employed in diclofenac degradation mediated by photo-Fenton process, probably due to self-decomposition (Eq. (1)) and scavenging of hydroxyl radicals by an excess of H$_2$O$_2$ (Eq. (2)) (Trovó and Nogueira, 2011).

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H_2O_2 + \text{HO}^- & \rightarrow H_2O + \text{HO}_2
\end{align*}
\]

In a previous analysis of the results obtained with CCD it was observed that Fe$^{2+}$ does not play a significant role on the percentage of mineralization in the evaluated concentration range (8.6–15.4 mg L$^{-1}$). So, based on these results and given that Brazilian legislation limits the iron concentration for discharge of effluents in 15 mg L$^{-1}$ (0.27 mmol L$^{-1}$), our limit was fixed in 10.0 mg L$^{-1}$. The effect of each independent variable of the process should be directly attributed to its coefficients (Trovó et al., 2006). From Eq. (3), the low negative quadratic coefficient values for caffeine and H$_2$O$_2$, and positive coefficient values for caffeine and H$_2$O$_2$ suggest that the mineralization is favored in the presence of high concentrations of caffeine and H$_2$O$_2$. The overall effect can be observed in Fig. 2, which shows the diagram that represents the polynomials (fixing the concentration of Fe$^{2+}$ at 10 mg L$^{-1}$) for the photo-Fenton reaction, built up with the results obtained with CCD (Table 2 – Supplementary results). These response surfaces (Fig. 2) described by Eq. (3), suggest that higher percentages of mineralization can be obtained using 52.0 mg L$^{-1}$ caffeine, 10.0 mg L$^{-1}$ Fe$^{2+}$ and 42.0 mg L$^{-1}$ H$_2$O$_2$.

An experiment was performed in order to check the optimized values, predicted by the mathematical model. The theoretical result (65.0% mineralization), calculated using Eq. (3) and the optimal concentrations of caffeine and H$_2$O$_2$, agree very well with the experimental one (66.0% mineralization) using the same conditions, even assuming a standard deviation of ±2.0% for mineralization (value obtained from five replicates in the central point of CCD). This demonstrates that the surface response methodology can be useful as a tool to optimize the degradation of organic matter mediated by photo-Fenton process.

Control experiments were performed for an initial caffeine concentration equal to 52.0 mg L$^{-1}$, in the absence of Fe$^{2+}$ and H$_2$O$_2$ (direct photolysis); in the absence of Fe$^{2+}$ and presence of H$_2$O$_2$ (42.0 mg L$^{-1}$) and UV light (H$_2$O$_2$/UV), hydrolysis (at pH 2.5), and also without UV light irradiation (dark Fenton experiment) (10.0 mg L$^{-1}$ Fe$^{2+}$ and 42.0 mg L$^{-1}$ H$_2$O$_2$). These assays were done aiming to elucidate the role of Fe$^{2+}$ and UV radiation on advanced oxidation of aqueous solutions containing caffeine, and to assure that the results found during the photocatalytic assays were consistent and not due to hydrolysis, Fenton and/or direct photolysis. In general, no appreciable mineralization was observed after 120 min in control experiments except in the Fenton reactions conducted in the dark, where 13.5% of mineralization was reached (data not shown). However, when compared with the result obtained by photo-Fenton (66.0% of mineralization) (data not shown), it is evident that an improvement in caffeine mineralization must occur when the Fenton processes are combined with electromagnetic radiation.

3.2. Application of the photo-Fenton process to caffeine degradation under optimized condition in UW, SW and STP effluent in lab-scale and in solar pilot plant

The degradation of caffeine by photo-Fenton reactions in lab-scale was evaluated in aqueous solutions of different qualities (UW, SW and STP effluents) to verify the matrix effects on caffeine degradation (Fig. 3). In UW and SW, the caffeine concentration was below the quantitation limit after 20 min of reaction, while for STP effluent 40 min were necessary, demonstrating that the sample composition influences in caffeine removal (data not shown). Similar behavior was also observed during the degradation of tetracycline by photo-Fenton processes using black light irradiation (Bautz and Nogueira, 2007).

The lower efficiency of caffeine removal on STP effluent can be explained by the high concentrations of DOC and dissolved inorganic carbon (DIC) (Table 1). The first competes with caffeine by hydroxyl radicals, while the second acts as hydroxyl radicals scavenger (Eqs. (4) and (5)) (Klamerth et al., 2010a; Trovó and Nogueira, 2011). Even after pH reduction from 6.0 to 2.5 and magnetic stirring during 30 min, a residual DIC of 8.7 mg L$^{-1}$ remained in solution, which may have contributed to diminish the efficiency of caffeine removal.

\[
\text{HO}^- + \text{HCO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_3^-
\]
3.5 mg C L\(^{-1}\), which corresponds to a value close to 10% of the initial DOC content, while STP effluent contributes with 139.3 mg L\(^{-1}\), almost forty times the DOC concentration in SW (Table 1). The difference of mineralization in a same matrix (UW) can be attributed to the characteristics of the different reactors used, like as the high potency of the mercury vapor lamp in the lab-scale reactor, once the residence time in lab-scale reactor is lower than in solar pilot plant. However, an increasing in the time of reaction up to 180 min resulted in the same mineralization efficiency in both reactors (Fig. 3). Although a lower mineralization rate has been attained to a high organic load, it is worthy of mention that under the same operating conditions less H\(_2\)O\(_2\) was required for mineralizing the DOC as the initial organic load increased (4.82, 3.83 and 2.34 mg H\(_2\)O\(_2\) consumed mg\(^{-1}\) DOC mineralized for UW, SW and STP at lab-scale, respectively, and 6.89 for UW at the solar pilot plant) (Fig. 3). The higher consumption of H\(_2\)O\(_2\) in the pilot plant when compared to the lab-scale to obtain the same mineralization efficiency (Fig. 3) can be explained by the occurrence of inefficient reactions (Eqs. (1), (2) and (6)), and therefore, when the organic load is low, fewer hydroxyl radicals are required and hydrogen peroxide is not used efficiently (Fig. 3). No toxicity to A. salina was observed for the initial solution of caffeine (10%), as well as to its degradation products (5%) in both systems (at lab-scale and solar pilot plant) (data not shown), demonstrating that the photo-Fenton process can be a safe alternative to the treatment of wastewater containing this compound.

Fe\(^{3+}\) + H\(_2\)O\(_2\) → Fe\(^{2+}\) + H\(^{+}\) + HO\(_2\)  

(6)

4. Conclusions

The association between experimental design and response surface methodology yielded reliable statistical results for the mineralization of caffeine mediated by photo-Fenton process. Predictions made using response functions are in good agreement with the experimental results, showing the reliability of the methodology used. Although a lower rate of caffeine removal and mineralization of caffeine have been observed in STP samples, the results presented in this study demonstrate that the photo-Fenton process can be successfully applied in the degradation of caffeine, even when present in complex samples such as SW and STP effluents.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2012.06.022.

References


