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

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HIGHLIGHTS

- ▶ Experimental design was modeled for caffeine degradation by photo-Fenton process.
- ▶ A good agreement between experimental and theoretical results was reached.
- ▶ Under optimized conditions, it was efficiently degraded, even in the most complex media.
- ▶ Less H_2O_2 was required to remove a high organic load.
- ▶ Caffeine degradation did not generate toxic intermediates.

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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, Fe^{2+} and H_2O_2 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} Fe^{2+} and 42.0 mg L^{-1} H_2O_2 (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 H_2O_2 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 (Ghisele, 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 (Ghisele, 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 ($^{\cdot}OH$) 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 TiO_2 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 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, Fe^{2+} and H_2O_2 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. $FeSO_4{\cdot}7H_2O$ (Vetec) was used to prepare aqueous 0.25 M iron stock solution. H_2O_2 (30% w/w), H_2SO_4, NaOH and Na_2SO_3 from Vetec were used as received. Ammonium metavanadate (Vetec) solution was prepared at a concentration of 0.060 M in 0.36 M H_2SO_4, being used for H_2O_2 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 650 000 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 2^k factorial design (all possible combinations of codified values +1 and −1), which 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}), Fe^{2+} (0.6 and 14.5 mg L^{-1}) and H_2O_2 (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, Fe^{2+} and H_2O_2, 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 2^k factorial design (all possible combinations of codified values between +1.0 and −1.0) – 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}), Fe^{2+} (8.6–15.4 mg L^{-1}) and H_2O_2 (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