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Article

Degradation of the Herbicide Paraquat by Photo-Fenton Process: Optimization by Experimental Design and Toxicity Assessment

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Este trabalho descreve a influência e otimização dos reagentes de Fenton (concentração de Fe^{2+} e H_2O_2) na eficiência da mineralização do herbicida paraquat (PQT, 50 mg L^{-1}) em água, após 60 min (equivalendo a 642 kJ L^{-1} de radiação UVA acumulada) de tratamento por processo foto-Fenton em escala de laboratório, usando planejamento composto central (CCD). Sob condições otimizadas, experimentos cinéticos foram feitos, avaliando a remoção do PQT, sua mineralização e toxicidade em escala de laboratório, usando irradiação artificial, e em planta piloto sob irradiação solar. A mesma eficiência de remoção e mineralização do PQT foram obtidas em ambos os reatores utilizados. A toxicidade das amostras, estimada em termos de mortalidade de *Artemia salina*, diminui simultaneamente com o decaimento da concentração de PQT, sugerindo a formação de intermediários de menor toxicidade. Dessa maneira, o processo foto-Fenton/solar pode ser considerado uma alternativa viável para o tratamento de águas residuais contendo PQT.

This study describes the influence and optimization of Fenton's reagent (concentration of Fe^{2+} and H_2O_2) on the efficiency of mineralization of the herbicide paraquat (PQT, 50 mg L^{-1}) in water, after 60 min (equivalent to 642 kJ L^{-1} of accumulated UVA radiation) treatment by photo-Fenton process in laboratory scale, using central composite design (CCD). Under optimized conditions, kinetic experiments were done, evaluating the PQT removal, its mineralization and toxicity in laboratory scale, using artificial irradiation, and in a pilot plant under solar irradiation. The same removal efficiency and mineralization of PQT were obtained in both reactors. The toxicity of the samples, estimated in terms of mortality of *Artemia salina*, decreases simultaneously with the decay of concentration of PQT, suggesting the formation of intermediates of lower toxicity. In this way, the solar photo-Fenton process can be considered as a viable alternative for the treatment of wastewater containing PQT.

Keywords: pesticides, detoxification, pilot plant, wastewater treatment, solar light intensity

Introduction

Since 2008 Brazil has overtaken the United States in pesticides consumption, becoming the largest consumer.[1] The herbicide paraquat dichloride (PQT, Figure 1) has been widely used for application in post-emergence of weeds and also as desiccant.[2] Its residence time in soils can vary from 1.4 to 7.2 years depending on the concentration, soil characteristics (organic matter), temperature and rainfall.[3] In river water samples, it has been observed that PQT is not easily microbiologically degraded, since, even after 56 days of incubation, more than 80% of the initial concentration remains unchanged, suggesting to PQT considerable recalcitrance.[4] In addition, PQT is polar, showing high solubility in water, as well as a low octanol-water partition coefficient (log $K_{ow} = -4.5$), which provides a great mobility in some soils, arriving easily until the next water supplies.[5] It has been found in the range of 2-12 µg L^{-1} in groundwater,[6] and, for example, at average concentration of 0.78 µg L^{-1} in surface waters in Spain.[7]

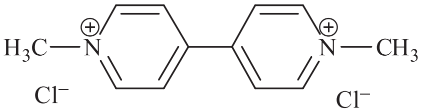

Figure 1. Chemical structure of paraquat dichloride.

In acute toxicity studies performed by US Environmental Protection Agency using laboratory animals, PQT has been shown to be highly toxic by inhalation route, having

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been classified in toxicity category I (the highest of four levels). The high toxicity of this compound has also been observed in studies involving the use of bacteria, small crustaceans, algae and aquatic plants.[8-12] Thus, its presence in the environment can cause adverse effects in aquatic and terrestrial organisms. Therefore, it is desirable for the development and optimization of viable technologies with a focus on disposal of such waste.

Since the traditional biological treatments are not effective in the PQT removing, an alternative can be the use of advanced oxidation processes (AOPs) due to their recognized efficiency in the treatment of recalcitrant organic matter, through the efficient generation of $HO^{\bullet}$ radicals.[13-15] From the variety of existing AOPs, particular attention has been given to photo-Fenton process and heterogeneous photocatalysis due to the possibility of use of solar radiation,[16] reducing the energetic costs. The photo-Fenton process has the advantage to be a homogeneous process, avoiding an additional step of removal of catalyst, usual when dealing with a heterogeneous process. Another advantage is the fact that homogeneous processes favor a greater contact between reagent species, with favorable implications for process performance.

The use of different AOPs for degradation of PQT has been reported, such as immobilized TiO_2 and/or in suspension, combined with UV irradiation,[17-21] UV-ozonation,[22,23] Fenton's reaction,[24] activated carbon modified with iron and combined with hydrogen peroxide, and electrochemical methods.[25,26] However, a study by applying experimental design and response surface methodology that provides conclusions which result in the optimization of Fenton's reagents for PQT degradation was not reported until now. In addition, a kinetic study on the degradation of PQT by photo-Fenton process and toxicity assessment was also not published. Therefore, the aim of the present work was to evaluate the role of each variable (Fe^{2+} and H_2O_2 concentration) on the percentage of mineralization of a commercial formulation of PQT (Helmoxone™) at lab-scale, and, under optimized conditions, monitor the kinetic of PQT removal, mineralization, toxicity and the carbon oxidation state (COS) during photo-Fenton treatment not only at lab-scale but also in a solar pilot plant.

Experimental

Reagents

All solutions were prepared using ultrapure water. $FeSO_4.7H_2O$ (Vetec) was used to prepare aqueous 0.25 mol L^{-1} Fe^{2+} stock solution; H_2O_2 (30% m/m), H_2SO_4, NaOH and Na_2SO_3, all from Vetec, were used as received. A solution of ammonium metavanadate (Vetec) was prepared at a concentration of 0.060 mol L^{-1} in 0.36 mol L^{-1} H_2SO_4 and used for H_2O_2 quantification.

All experiments were carried out using the commercial formulation (276 g L^{-1} of PQT, $C_{12}H_{14}Cl_2N_2$ = 257 g mol^{-1}), diluted to obtain 50 mg L^{-1} PQT in solution. Although the PQT concentration is higher than that found in aquatic environments, it was chosen to permit an adequate evaluation of the toxicity. An analytical standard of PQT for chromatographic analysis was purchased from Sigma-Aldrich. High performance liquid chromatography (HPLC) analyses were done using HPLC grade methanol (Vetec).

Experimental design

The central composite design (CCD) was applied to optimize the concentration of the variables (Fe^{2+} and H_2O_2), able to induce a high percentage of mineralization of commercial formulation by the photo-Fenton process, as well as to evaluate the interactions among these two variables. The percentage of mineralization, measured by total organic carbon (TOC) decay after 60 min of reaction in relation to the initial TOC value, was chosen as the response factor of the photo-Fenton process. CCD 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 = 2 variables consists of four experiments; (*ii*) axial or star points (+1.4 and –1.4), and 0 for two variables (four experiments); and (*iii*) replicates of the central point (0) (five experiments). Thus, for this design, it was necessary to do thirteen experiments, in which the two variables were codified in five levels, varying within the following ranges: Fe^{2+} (7.2-12.8 mg L^{-1}) and H_2O_2 (39.8-232.2 mg L^{-1}). The ranges of the variables were chosen according to previous studies.[27-30] For CCD, the equations used to quantitatively describe each system and draw the response surface and contour plots were built using STATISTICA 6.0 software. Statistical validation was obtained using the analysis of variance (ANOVA) test at 95% confidence level.

Photodegradation procedures

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 an irradiated surface of 3.89×10^{-2} m^2. The lamp was positioned at the center of the reactor, as described and schematically presented by Oliveira *et al*.[31] The average irradiance of UVA radiation measured for the lamp[32] is 1100 W m^{-2}, which presents a photonic flux of 3.3×10^{-6} einstein s^{-1} between 295 and 710 nm.[33] 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,[33] built with components furnished by Ocean Optics, Inc.

The irradiated volume of the reactor was 0.280 L and a total volume of 4 L of commercial formulation 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_2O_2. The lamp was only turned on when the reactor was filled with solution.

For CCD experiments, aliquots of the photolyzed solutions (20 mL) were collected only after 60 min of reaction, while for the kinetic experiment, samples (70 mL) were collected at 20 min intervals up to 120 min. The initial conditions used in CCD design are described in the section of the experimental design.

The kinetic experiments were carried out using initially 50.0 mg L^{-1} PQT, 11.8 mg L^{-1} Fe^{2+} and 188.1 mg L^{-1} H_2O_2, the last replaced in 60 and 100 min of reaction due to its consumption. After sampling and before analysis, a calculated volume of 2.0 mol L^{-1} Na_2SO_3 solution was added to the samples, according to the stoichiometry between H_2O_2 and Na_2SO_3, and H_2O_2 concentration. This procedure ensures the removal of the remaining H_2O_2, interrupting the Fenton reaction. Also, it eliminates the interference caused by traces of H_2O_2 in toxicity assays and avoids the sulfite interference on the chemical oxidation demand (COD) measurements.[34]

For the toxicity assays, the pH value was adjusted in the range between 6 and 8 after adding the Na_2SO_3 solution. The solution temperature was controlled using a thermostatic bath (Tecnal TE-184), keeping close to 25 ± 2 °C. Control experiments were performed using the same experimental setup previously described for the kinetic photo-Fenton experiments.

Experiments in a pilot plant: use of solar radiation

Experiments using solar radiation were 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 attached with the same inclination of the reflective surface of the reactor.[35] Under this condition, an average solar irradiance of 36.4 ± 5.4 W m^{-2} was obtained between 9:45 and 11:45 am in May/2012.

The solar reactor is 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.[35] A volume of 50 L of the PQT solution was circulated 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 pump. At the beginning of the experiment, with the collectors covered, the same initial conditions defined for the reagents in kinetic experiments using lab-scale reactor were used. The cover was then removed and samples were collected at intervals of 20 min up to 120 min. The same treatment previously described, using Na_2SO_3 solution, was done to stop the Fenton reaction.

In this experiment, new additions of H_2O_2 were done at 60, 80 and 100 min of reaction.

Measurements of the accumulated UVA energy

It is important to mention that due the differences of the reactors, like as the average irradiance, surface area, total volume of solution, the accumulated UVA energy ($Q_{UVA,n}$, kJ L^{-1}) was calculated for each time of sampling in each reactor to allow a good comparison of the results. Equation 1 allows to estimate the amount of accumulated UVA energy ($Q_{UVA,n}$) received on any surface *per* unit of volume, for a solution inside the reactor, in a time interval Δt.[36]

$$Q_{UVA,n} = Q_{UVA,n-1} + \Delta t_n \overline{UVA}_{G,n}\left(\frac{A_r}{V_t}\right) \qquad (1)$$

where t_n is the sampling time, V_t is the total reactor volume, A_r the illuminated collector surface area and $UVA_{G,n}$ the average solar or artificial UVA radiation, measured during the period Δt_n ($t_n - t_{n-1}$).

Table 1 presents the accumulated UVA energy for each reactor corresponding to the sampling times of 20, 40, 60, 80, 100 and 120 min. A significant difference in the accumulated UVA energy was obtained for both reactors. An accumulated UVA energy 10 times higher than that provided by solar radiation to the pilot plant is provided by the mercury lamp to the lab-scale reactor. In the X-axis of Figures 3 and 4, the sampling time was maintained for comparison with control experiments done in the dark, in function of the reaction time.

Analysis

Before chemical analyses, except for TOC determination, the samples were filtered through membranes with pore

Table 1. Accumulated UVA energy *per* unit of volume (Q_{UVA}) for the experiments carried out at lab-scale and in a solar pilot plant

time / min	Q_{UVA} / (kJ L^{-1})	
	Lab-scale	Solar pilot plant
20	214	21.7
40	428	42.8
60	642	65.9
80	856	92.1
100	1070	119.5
120	1284	146.9

diameter of 0.45 µm. Mineralization, conversion of the organic matter to carbon dioxide and water, of PQT present in a commercial formulation was followed measuring the TOC decay using a TOC analyzer (Shimadzu TOC-VCPH/CPN) equipped with an ASI-V auto sampler. The determination consists of two analyses: first the total carbon (TC) of the sample is determined after catalytic oxidation at high temperature, while the total inorganic carbon (TIC) is determined by equilibrium shift after addition of phosphoric acid to the sample. In both analyses, the CO_2 released is determined by infrared spectroscopy.

The TOC concentration includes the carbon content of the target compound, the intermediates generated during the experiment and the excipient of the commercial product. It is calculated by the difference between TC and TIC. Hydrogen peroxide was quantified spectrophotometrically using ammonium metavanadate, monitoring the absorption of the red-orange peroxovanadium cation, at 450 nm (equation 2).[37]

$$VO_3^- + 4H^+ + H_2O_2 \rightarrow VO_2^{3+} + 3H_2O \qquad (2)$$

Kinetic experiments were also carried out by HPLC analyses aiming to evaluate the PQT removal, as well as the toxicity and COS. The PQT concentrations were determined by reversed phase HPLC, using a VWR-Hitachi L-2130 chromatograph with UV-Vis detector (Merck-Hitachi L-4250) and a C_{18} column (Lychrispher, 5 µm, 250 × 4.6 mm). The separation occurred using a mixture of 3 mmol L^{-1} HCl and methanol (25:75, v/v) in isocratic mode, at a flow rate of 1 mL min^{-1}. The detection was performed by UV absorption at 257 nm. The injection volume was 20 µL. Under these conditions, the retention time for PQT was between 2.6 and 2.8 min, with a limit of quantitation of 1.0 mg L^{-1}.

COD, quantity of oxygen required to chemically oxidize organic matter without the intervention of microorganisms, was estimated by absorbance measurement at 420 nm by means a standard photometric method (5220 D).[38] This parameter was determined after digestion of the organic matter with dichromate solution in closed reflux vessels at 150 °C for 2 h.

COS of the solutions treated by photo-Fenton process was estimated according to equation 3, where TOC and COD are expressed in mg C L^{-1} and mg O_2 L^{-1}, respectively. COS is between +4 for CO_2, the most oxidized state of C, and –4 for CH_4, the most reduced state of C.[34]

$$COS = 4 - 1.5x\left(\frac{COD}{TOC}\right) \qquad (3)$$

The toxicity tests were done evaluating the immobilization of *Artemia salina*, as described by Trovó *et al.*[30]

Results and Discussion

Optimization of Fenton's reagents for the mineralization of PQT in a commercial formulation using experimental design

Before evaluating the degradation kinetics of PQT, CCD was held with the purpose of evaluating the role of each reagent, optimizing their concentration, so as to ensure maximum efficiency for photo-Fenton reaction. Table 2 shows the experimental planning in CCD as well as the response obtained in each experiment in terms of mineralization of PQT present in a commercial formulation.

Equation 4 was obtained using statistical analysis of the experimental data presented in Table 2.

$$TOC\,(\%) = -218.55 + 44.01[Fe^{2+}] - 2.30[Fe^{2+}]^2 + 0.20[H_2O_2] - 0.002[H_2O_2]^2 + 0.05[Fe^{2+}][H_2O_2] \qquad (4)$$

The effect of each process independent variable can be directly correlated to its coefficient.[27,30]

From equation 4, although negative quadratic coefficients have been obtained for Fe^{2+} (–2.30) and H_2O_2 (–0.002), the expressive positive linear coefficients for Fe^{2+} (+44.01) and H_2O_2 (+0.20), and the positive coefficient found for the interaction between Fe^{2+} and H_2O_2 (+0.05), suggest that the mineralization is favored increasing their concentrations. The overall effect can be observed in Figure 2, that presents a diagram that represents the polynomials related to photo-Fenton reaction, constructed from the results presented in Table 2. An analysis of the surface (Figure 2) suggests that a high percentage of mineralization can be obtained using 11.8 mg L^{-1} Fe^{2+} and 188.1 mg L^{-1} H_2O_2.

An experiment was performed in order to check the optimized values, predicted by the mathematical model. The theoretical result, calculated using equation 4, shows a very good agreement with the experimental results

Table 2. Central composite design and experimental results for mineralization of PQT in a commercial formulation after 60 min (642 kJ L^{-1} of UVA radiation) of photo-Fenton process

Experiment	Concentration (codified value)		Consumption of H_2O_2 / %	Mineralization / %
	Fe^{2+} / (mg L^{-1})	H_2O_2 / (mg L^{-1})		
1	8.0 (–1)	68.0 (–1)	100	17.6
2	8.0 (–1)	204.0 (+1)	56.4	14.8
3	12.0 (+1)	68.0 (–1)	98.8	27.2
4	12.0 (+1)	204.0 (+1)	100	54.1
5	7.2 (–1.4)	136.0 (0)	78.9	22.8
6	12.8 (+1.4)	136.0 (0)	100	50.1
7	10.0 (0)	39.8 (–1.4)	98.2	16.8
8	10.0 (0)	232.2 (+1.4)	96.7	51.5
9	10.0 (0)	136.0 (0)	100	51.5
10	10.0 (0)	136.0 (0)	100	49.8
11	10.0 (0)	136.0 (0)	100	47.3
12	10.0 (0)	136.0 (0)	100	55.6
13	10.0 (0)	136.0 (0)	100	52.8
Standard deviation of central points (experiments 9-13)				3.1

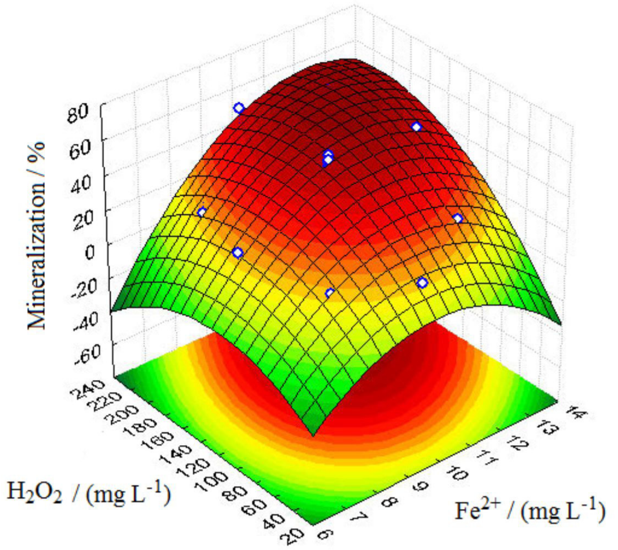

Figure 2. Response surface of quadratic models for the mineralization of PQT in a commercial formulation after 60 min (642 kJ L^{-1} of UVA radiation) of photo-Fenton process.

obtained for the optimal concentration of Fe^{2+} and H_2O_2 (Table 3), assuming a standard deviation of ± 3.1% 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 in reactions mediated by photo-Fenton process.

Table 3. Optimized values for the studied variables and comparison between experimental and theoretical results

Variable	Concentration / (mg L^{-1})	Mineralization / %	
		Theoretical	Experimental
Fe^{2+}	11.8	58.4	64.6
H_2O_2	188.1		

Kinetics of PQT degradation and toxicity assessment

Using the optimized conditions defined by the analysis of the response surface from the results obtained at lab-scale, the degradation profile of PQT and its mineralization in a commercial formulation (Figure 3), as well as assessment of the toxicity and COS (Figure 4) during photo-Fenton process at lab-scale and in a solar pilot plant was obtained.

The PQT concentration reached the limit of quantitation (1.0 mg L^{-1}) at lab-scale after 20 min (214 kJ L^{-1} of UVA radiation) while 40 min (42.8 kJ L^{-1} of UVA radiation) were necessary when the solar pilot plant was used (Figure 3a). Similar behavior was also observed during the mineralization of PQT by photo-Fenton treatment (Figure 3b). A rapid decay of mineralization at lab-scale was obtained in relation to the solar pilot plant. This can be attributed to the higher accumulated UVA energy at lab-scale (Table 1). However, after 120 min of photo-Fenton treatment, a similar efficiency was reached for both reactors (89.4 at lab-scale and 84.1% at solar pilot plant), even assuming a standard deviation of ± 3.1% for mineralization (Table 2). In addition, a lower accumulated UV energy at solar pilot plant (146.9 kJ L^{-1} of UVA radiation) was necessary to obtain the same efficiency in relation lab-scale (1284 kJ L^{-1} of UVA radiation). Nogueira *et al.*[39] evaluated the influence of the solar light intensity on the TOC removal and observed that the degradation rate

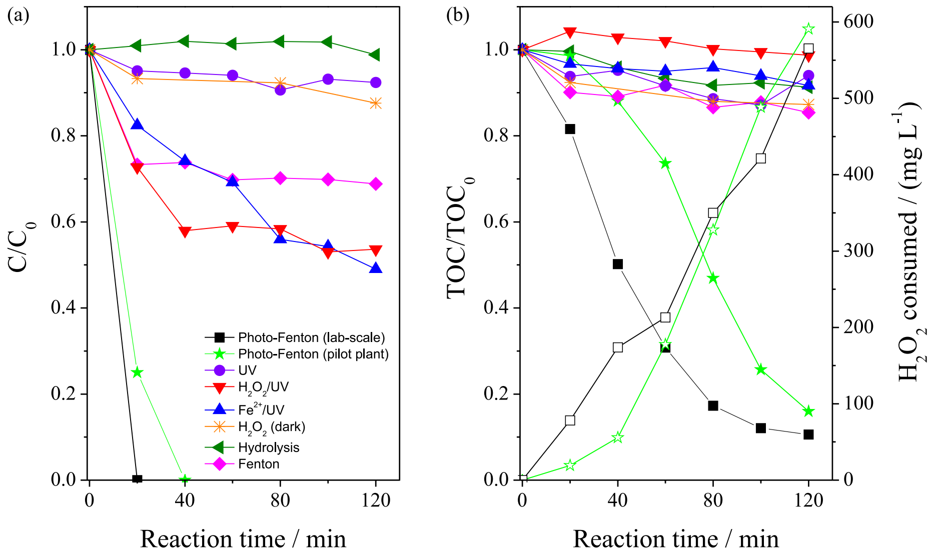

Figure 3. Profiles of (a) PQT and (b) TOC removal (solid symbols) and consumption of H_2O_2 (open symbols) during the degradation of PQT present in a commercial formulation by photo-Fenton process at lab-scale and in a solar pilot plant, compared to control experiments (lab-scale). Initial conditions: [PQT] = 50 mg L^{-1} (TOC = 59 mg C L^{-1}), [Fe^{2+}] = 11.8 mg L^{-1}, [H_2O_2] = 188.1 mg L^{-1} and pH = 2.5-2.8. New additions of H_2O_2 were done at 60 and 100 min lab-scale (642 and 1070 kJ L^{-1} of UVA radiation) and 60, 80 and 100 min at solar pilot plant (65.9, 92.1 and 119.5 kJ L^{-1} of UVA radiation, respectively) during the photo-Fenton process.

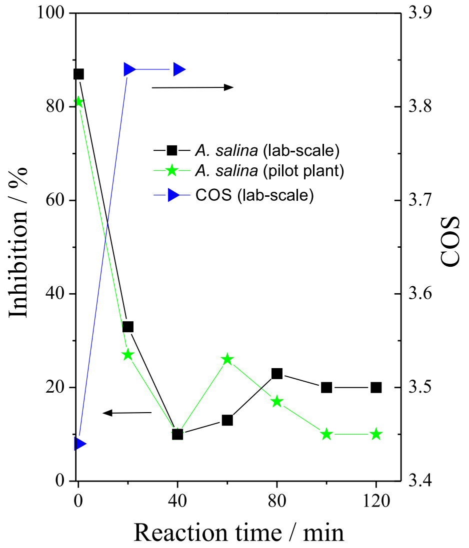

Figure 4. Profiles of evolution of toxicity (at lab-scale and in a solar pilot plant) and COS (at lab-scale) during the degradation of PQT in a commercial formulation by photo-Fenton process. Initial conditions: [PQT] = 50 mg L^{-1} (TOC = 59 mg C L^{-1}), [Fe^{2+}] = 11.8 mg L^{-1}, [H_2O_2] = 188.1 mg L^{-1} and pH = 2.5-2.8. New additions of H_2O_2 were done at 60 and 100 min lab-scale (642 and 1070 kJ L^{-1} of UVA radiation) and 60, 80 and 100 min at solar pilot plant (65.9, 92.1 and 119.5 kJ L^{-1} of UVA radiation, respectively).

increases linearly with the light intensity for values up to 15 W m^{-2}, but above this value, the degradation is best described by a square root relationship, which justifies the results obtained in this work. Although a 400 W high pressure mercury vapor lamp (average irradiance of 1100 W m^{-2}) was used as irradiation source at lab-scale, the same efficiency was obtained in a solar pilot plant with an average solar irradiance of 36.4 ± 5.4 W m^{-2}. The consumption of hydrogen peroxide agrees with the results of mineralization (Figure 3b). After 120 min (146.9 and 1284 kJ L^{-1} of UVA radiation, respectively under solar irradiation and in lab-scale) of photo-Fenton treatment, 565 and 591 mg L^{-1} of H_2O_2 were consumed at lab-scale and solar pilot plant experiments, respectively (Figure 3b). The H_2O_2 consumption profile shows a linear correlation with the reaction time (α = 4.7 and 4.9 mg H_2O_2 min^{-1} at lab-scale and in a solar pilot plant, respectively). For this same sequence, under the operating conditions, 10.8 and 12.4 mg H_2O_2 were consumed for each mg of TOC mineralized (Figure 3b).

Control experiments at lab-scale were also performed for an initial PQT concentration equal to 50 mg L^{-1} in the: (*i*) absence of Fe^{2+} and H_2O_2 (direct photolysis at pH 6.3, natural pH of the solution); (*ii*) dark, without Fe^{2+} and in the presence of H_2O_2 (188.1 mg L^{-1}); (*iii*) presence of UV irradiation and 188.1 mg L^{-1} H_2O_2 at pH 6.3, without Fe^{2+}; (*iv*) hydrolysis at pH 2.5; (*v*) presence of UV irradiation and 11.8 mg L^{-1} Fe^{2+} at pH 2.5, without H_2O_2; and (*vi*) presence of 11.8 mg L^{-1} Fe^{2+} and 188.1 mg L^{-1} H_2O_2 in the dark (Figure 3). A lower removal of PQT and mineralization was obtained for all control experiments, when compared to the photo-Fenton process, evidencing its high efficiency and assuring that the results found are consistent and not due to hydrolysis, thermal Fenton process, and/or direct or due to hydrogen peroxide photolysis (Figure 3).

COSs for the samples in reactions mediated at lab-scale, and toxicity at lab-scale and using a solar pilot plant, were also analyzed during PQT degradation aiming to evaluate the toxicity behavior and COS variation during application of the photo-Fenton process under optimum conditions. The assessment of the toxicity during the degradation of pesticides is critical when a process is studied as an alternative to wastewater treatment, or when this same process is regarded as the first stage in a treatment process coupled to a subsequent biological process.[40]

The solution containing 50 mg L^{-1} of PQT showed a high value of COS (+ 3.44), suggesting that the compound has a high COS (Figure 4). However, this value does not show correspondence with the theoretical value. The experimental COD value obtained for the experimental TOC initial concentration of commercial formulation is equivalent to only 14.0% of the theoretical value (157 mg O_2 L^{-1}). This low experimental COD value obtained in relation the experimental initial TOC (59 mg C L^{-1}) contributes to generate a high experimental COS (equation 3), higher than the theoretical value (COS = 0.0008). This lower value measured for COD is probably due to the presence of two pyridine rings on PQT structure, a refractory species to APHA method for determination of COD.[34]

Applying the photo-Fenton process at lab-scale, the PQT concentration reached the limit of quantitation (1.0 mg L^{-1}) with 18% of TOC removal (Figure 3) and an increase in COS from +3.44 to +3.84 (Figure 4), in only 20 min of reaction (214 kJ L^{-1} of UVA radiation), after consumption of 78 mg L^{-1} H_2O_2. In this same period, the acute toxicity, calculated by the inhibition of mobility of *A. salina*, decreased from 87 to 33% (Figure 4), which is related with the PQT concentration reduction (Figure 3a). With the increase of the reaction time up to 40 min (428 kJ L^{-1} of UVA radiation), a consumption of 174 mg L^{-1} H_2O_2, a TOC removal of 50% (Figure 3b), the same COS value of +3.84 and a decrease in the toxicity from 33 to 10% (Figure 4) were reached. Although the COS values obtained do not show correspondence with the theoretical data, the application of photo-Fenton process contributed to the formation of intermediates more oxidized and a lower toxicity than the verified for the initial sample containing only PQT. After 60 min (642 kJ L^{-1} of UVA radiation) of reaction and consumption of 213 mg L^{-1} H_2O_2, 69% of TOC removal (Figure 3b) and a toxicity of 13% (Figure 4) were obtained. It was not possible to calculate the COS value after 60 min (642 kJ L^{-1} of UVA radiation) of reaction, once that the COD values obtained were null. For an irradiation time up to 120 min (1284 kJ L^{-1} of UVA radiation) and consumption of 565 mg L^{-1} H_2O_2, 89% of TOC removal (Figure 3b) and a toxicity of 20% were reached (Figure 4). Similar behavior was obtained to toxicity when the experiment was carried out in a solar pilot plant, however with a lower accumulated UVA energy (Figure 4 and Table 1). The residual toxicity, between 10-20% in both reactors (Figure 4) is probably due the formation of carboxylic acids, as already observed for *Daphnia magna* and *Vibrio fischeri* during degradation of sulfamethoxazole and amoxicillin.[41,42]

On the other hand, Santos *et al*.[24] observed a decrease in the biodegradability and no toxicity reduction during PQT degradation by the Fenton's process after 25 h using the initial conditions: 100 mg L^{-1} PQT, 28 mg L^{-1} Fe^{2+} and 221 mg L^{-1} H_2O_2. Probably this difference, compared to our best results, may be due to different initial concentration of PQT and reagents, the removal of TOC reached and/or the concentration of intermediates generated in solution.

In general, it can be observed that after short periods of photo-Fenton process (between 20 and 40 min), the toxicity tends to decrease with the PQT concentration reduction and intermediates more oxidized were obtained (Figure 4). So, after these times, probably a biological process could be coupled with the photo-Fenton one, reducing the operational costs of the oxidative treatment. Similar behavior has been observed for other compounds/wastewaters, during the application of Fenton and photo-Fenton processes.[43-46]

Conclusions

Based on the experimental results obtained, it is possible to conclude that experimental design and response surface methodology are powerful tools to optimize, in a short set of experiments, the concentration of Fenton reagents, obtaining a high percentage of mineralization of PQT in a commercial formulation. Under optimized conditions, the same efficiency was obtained for both reactors. These results demonstrates that the photo-Fenton process can be applied as an alternative to the wastewater treatment containing this herbicide in large scale and using solar radiation, once that the toxicity decreased significantly with the paraquat concentration reduction and intermediates more oxidized were obtained. In addition, the use of solar radiation is completely advantageous, mainly in tropical countries like Brazil since the energetic costs of the process are reduced to zero.

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