Optimization of the mineralization of a mixture of phenolic pollutants under a ferrioxalate-induced solar photo-Fenton process

J.M. Monteagudo*, A. Durán, M. Aguirre, I. San Martín

University of Castilla-La Mancha, Grupo IMAES, Department of Chemical Engineering, Escuela Técnica Superior de Ingenieros Industriales, Avda. Camilo José Cela, 1, 13071 Ciudad Real, Spain

ARTICLE INFO

ABSTRACT

The mineralization of solutions containing a mixture of three phenolic compounds, gallic, p-coumaric and protocatechuic acids, in a ferrioxalate-induced solar photo-Fenton process was investigated. The reactions were carried out in a pilot plant consisting of a compound parabolic collector (CPC) solar reactor. An optimization study was performed combining a multivariate experimental design and neuronal networks that included the following variables: pH, temperature, solar power, air flow and initial concentrations of H_2O_2, Fe(II) and oxalic acid. Under optimal conditions, total elimination of the original compounds and 94% TOC removal of the mixture were achieved in 5 and 194 min, respectively. pH and initial concentrations of H_2O_2 and Fe(II) were the most significant factors affecting the mixture mineralization. The molar correlation between consumed hydrogen peroxide and removed TOC was always between 1 and 3. A detailed analysis of the reaction was presented. The values of the pseudo-first-order mineralization kinetic rate constant, k_{TOC}, increased as initial Fe(II) and H_2O_2 concentrations and temperature increased. The optimum pH value also slightly increased with greater Fe(II) and hydrogen peroxide concentrations but decreased when temperature increased. $^\bullet OH$ and $O_2^{\bullet-}$ radicals were the main oxidative intermediate species in the process, although singlet oxygen ($^1O_2$) also played a role in the mineralization reaction.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Phenolic compounds are considered priority contaminants because of their high toxicity at low concentrations. Their low biodegradability poses serious risks to the environment once they are discharged into natural water [1]. Agro-industrial wastewaters, such as those produced in winemaking, olive-oil extraction or table-olive production, contain significant concentrations of phenolic compounds, contributing to the toxicity of these effluents. It is well known that high concentrations of these compounds prevent mineralization of these effluents by conventional aerobic biological treatment processes [2,3]. Thus, there is currently considerable interest in developing alternative treatment technologies such as advanced oxidation processes (AOPs) for degrading these types of organic pollutants.

AOPs could generate highly reactive intermediate oxidative species such as hydroxyl radicals ($^\bullet OH$), superoxide radical anion ($O_2^{\bullet-}$) or singlet oxygen ($^1O_2$), depending on the operating conditions and chemicals used, as previously reported [4]. The application of solar irradiation to Fenton systems could diminish the energy consumption required for generating these radicals. The addition of oxalic acid to the solar photo-Fenton system promotes the formation of ferrioxalate complexes. This increases the oxidation efficiency of the solar photo-Fenton process because ferrioxalate is a photo-sensitive complex which expands the useful range of the irradiation spectrum up to 550 nm [5,6] and makes the system a more cost-effective and environmentally benign treatment.

In this work, a mixture of three phenolic compounds, gallic, protocatechuic and p-coumaric acids (Fig. 1), typically found in agro-industrial wastes, was chosen as a model phenolic solution to be degraded by a ferrioxalate-induced solar photo-Fenton process.

The degradation of mixtures of phenolic acid solutions has been previously studied using other advanced oxidation processes such as Fenton-like reactions [1], photo-Fenton treatments [7], a TiO₂/UV system [8] or by catalytic wet photo-oxidation photo-Fenton treatments [9]. However, the effect of ferrioxalate complexes on the degradation efficiency of mixtures of various phenolic compounds using solar light has not been studied until now. In this work, a multivariate experimental design according to the response-surface methodology [10] was performed to study the effect of all the variables simultaneously (e.g., pH, air-flow rate and initial concentrations of H_2O_2, Fe(II) and oxalic acid).

The experimental results were fitted using neural networks (NNs) [11,12], which allowed the values of kinetic degradation-rate

* Corresponding author. Tel.: +34 926295300x3888; fax: +34 926295361.
E-mail addresses: josemaria.monteagudo@uclm.es, jmmonte@inqu-cr.uclm.es
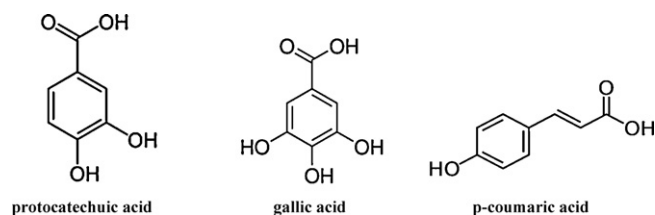(J.M. Monteagudo).

Fig. 1. Molecular structures of selected phenolic compounds.

constants (response functions) to be estimated within the studied range as a function of the process variables. Additionally, a saliency analysis of each variable in the NNs helped to discern their true relevancies. Since the elimination of original phenolic acids does not necessarily imply total mineralization of the solution, the decreases in both acid and TOC concentrations were measured. The remaining H_2O_2, dissolved O_2 and Fe(II) concentrations were also determined. Finally, the contributions of different oxidative intermediate species to the overall mineralization reaction were also quantified. The catalytic behaviour of Fe and the effect of the addition of oxalic were also evaluated.

2. Experimental

2.1. Materials

The mixture solutions of protocatechuic acid (3,4-dihydroxybenzoic acid, Sigma–Aldrich, 97%), gallic acid (3,4,5-trihydroxybenzoic acid, Sigma, 97.5%) and p-coumaric acid (4-hydroxycinamic acid, Sigma, 98%) (Fig. 1) were prepared by dissolving the target compounds in distilled water without further purification. $FeSO_4 \cdot 7H_2O$ (Panreac, analytical grade) and $H_2C_2O_4 \cdot 2H_2O$ (Panreac, 99.5%) were added to the wastewater to form ferrioxalate complexes and used immediately in situ because of their light sensitivity. The initial concentration of all the phenolic compounds was always 20 mg L^{-1}.

In all the experiments, after the addition of Fe(II) and oxalic acid and pH adjustment, a measured amount of commercial hydrogen peroxide (30%, w/v, Merck) was added to the reactor to bring the H_2O_2 initial concentration to between 0 and 400 mg L^{-1}. The pH of the solutions was adjusted with 0.1 M H_2SO_4 and 6 M NaOH solutions as needed prior to degradation. To quantify the oxidation levels by radical reactions, the scavenging of oxidative intermediate species was accomplished with 1,4-benzoquinone, NaN_3 and KI. Before analysis, all samples were withdrawn from the reactor and immediately treated with excess Na_2SO_3 solution to prevent further oxidation (this procedure was performed to prevent an overestimation of the degradation).

2.2. Photochemical reactions in the solar-CPC pilot plant

The compound parabolic collector (CPC) pilot plant (manufactured by ECOSYSTEM, S.A.) comprises a solar reactor (Fig. 2) consisting of a continuously stirred tank (50 L), a centrifugal recirculation pump, and a solar collector unit with an area of 2 m^2 (more details can be seen in elsewhere [4]). Data of incident solar power (W m^{-2}) and accumulated solar energy (W h) were measured by means of a programmable logic controller (PLC) coupled to a radiometer ((Ecosystem, model ACADUS-85).

2.3. Analysis

Analysis of the original phenolic compounds' concentrations was carried out by high-performance liquid chromatography with UV detection (HPLC–UV; Agilent Technologies 1100) in
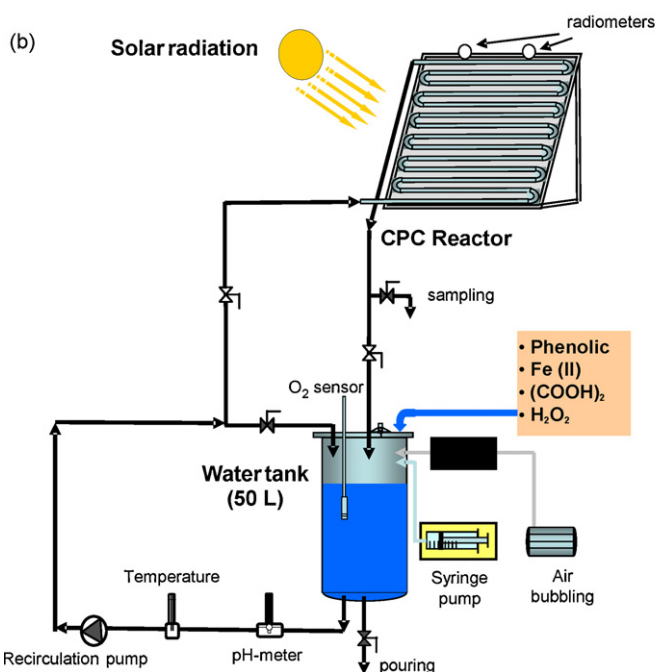

Fig. 2. Experimental setup based on a CPC pilot plant. Reactor volume: 16 L; (a) photo; (b) schematic.

isocratic mode immediately after sampling. An Eclipse XDB-C18 column (5 μm, 4.6 mm × 250 mm) was used with an 18:82 (v/v) methanol/water mixture at an acidic pH (2% acetic acid) as the mobile phase (detection wavelength, $\lambda = 280$ nm). Ferrous concentration was obtained by photometric measurement with 1,10-phenanthroline (according to ISO 6332) using a UV–vis spectrophotometer (Zuzi 4418PC). The degree of mineralization was monitored by TOC variation determined with a TOC-5050 Shimazdu analyzer (standard deviation <0.2 mg L^{-1}). The TOC contribution of the added oxalic acid had a relatively low significance as ferrioxalate is easily photolyzed, leading to the mineralization of oxalate. H_2O_2 in solution was determined by titration through an aqueous solution of potassium permanganate (0.02 M) using an automatic Titrino SET/MET 702 (Metrohm). The dissolved O_2 concentration was measured using a Lange LXV416 Luminescent Dissolved Oxygen (LDO) sensor.

Table 1
The 5-factor Central Composite Design Matrix. Ferrioxalate-induced solar photo-Fenton process.

Coded levels	Natural levels				
	$[H_2O_2]_o$ (mg L^{-1})	$[Fe(II)]_o$ (mg L^{-1})	$[H_2C_2O_4]_o$ (mg L^{-1})	Air flow (m^3 h^{-1})	pH
$(+\alpha)$	400.00	20.00	60.00	1.60	6.00
$(-\alpha)$	0.00	0.00	0.00	0.00	2.00
$(+1)$	284.09	14.20	42.61	1.14	4.84
(-1)	115.91	5.80	17.39	0.46	3.16
(0)	200.00	10.00	30.00	0.80	4.00

Central composite design: 46 experiments; reference [13]
Additional experiments
  47: Optimal conditions
  48: Optimal conditions + 1,4-benzoquinone
  49: Optimal conditions + NaN$_3$
  50: Optimal conditions + KI
Response functions: k_{PA}, k_{GA}, k_{CA} (W^{-1} h^{-1}) and k_{TOC} (W^{-1} h^{-1})

Selected optimal conditions and best obtained results

$[H_2O_2]_o$ (mg L^{-1})	400
$[Fe(II)]_o$ (mg L^{-1})	20
$[H_2C_2O_4]_o$ (mg L^{-1})	60
Air flow (m^3 h^{-1})	No air injection
pH	4
k_{PA}	1.21 W^{-1} h^{-1}
k_{GA}	1.99 W^{-1} h^{-1}
k_{CA}	2.32 W^{-1} h^{-1}
k_{TOC}	0.0959 W^{-1} h^{-1}
%Original compounds elimination	100% coumaric (2 W h; ≈2 min)
	100% gallic (3.3 W h; ≈3 min)
	100% protocatechuic (4.7 W h; ≈4 min)
%TOC removal	94% (240 W h; 194 min)

[Phenolic compounds] = 20 mg L^{-1}; temperature typical range: ≈25–39 °C; solar power typical range: ≈30–41 W m^{-2}.

2.4. Experimental design

A central-composite experimental design (CCED) consisting of 46 experiments was applied to investigate the effects of five variables (initial concentrations of H_2O_2, Fe(II) and oxalic acid, pH and air-flow rate) in the ferrioxalate-induced solar photo-Fenton process (see Table 1; complete details of the CCED were as previously described [13]). Here the initial concentration of each phenolic compound (20 mg L^{-1}) was a constant and thus not considered as a factor. In this case, an increase in the initial concentration of phenolic compounds increases the degradation efficiency according to a pseudo-first-order kinetic, as indicated below.

The design consisted of three series of experiments [13]: (i) a 2^k factorial design (all possible combinations of the coded values +1 and −1), which in the case of $k = 5$ variables consisted of 32 experiments; (ii) axial or star points (coded values $\alpha = 2^{k/4} = \pm2.378$) consisting of $2k = 10$ experiments; and (iii) replicates of the central point (4 experiments). Four additional experiments (47–50) were carried out under optimal conditions to complete the degradation study and determine the role of different oxidative species in the process (Table 1).

Incident solar power and temperature were not controlled during the experiment, but they were measured during the reaction and their average values were included in the fitting.

In all the experiments, both the elimination of the original substances and the disappearance of the solutions' TOC followed pseudo-first-order kinetics with respect to the target compound and TOC concentrations, respectively, as follows:

$$r = -\frac{dC}{di} = kC \tag{1}$$

where r is the reaction rate; C is the concentration (mg L^{-1}) of the original phenolic compound or the total organic carbon at an accumulated solar energy i (W h) received by the water solution; and k (W^{-1} h^{-1}) is the pseudo-first-order rate constant of the elimination of original compound (namely, either k_{PA}, k_{GA} or k_{CA}, for protocatechuic, gallic or p-coumaric acid, respectively) or of the solution mineralization (namely k_{TOC}) for the photochemical reaction.

Eq. (1) can be integrated between $i = 0$ and $i = i$, yielding:

$$\ln \frac{Co}{C} = ki \tag{2}$$

where Co is the initial concentration of original substances or TOC. According to this expression, a plot of the first term versus i must yield a straight line satisfying Eq. (2) with slope k.

2.5. Neural network strategy

In this work, a linear basis function was used (a linear combination of input variables, X_j, and weight factors, W_{ij}; see Table 2). Each neural network was solved with two neurons and used a simple exponential activation function [11,12]. The strategy was based on a back-propagation calculation. Parameters were found using the Solver tool in Excel using the Marquardt non-linear fitting algorithm [14]. Further details can be found in our previous report [13]. Finally, a measure of the saliency of the input variables was made based on the connection weights of the NNs. This allowed for an analysis of the relevance of each variable with respect to the others (expressed as a percentage).

3. Results and discussion

3.1. Comparative previous studies

An initial comparative study on the mineralization of solutions composed of the mixture of the three phenolic compounds cited above in different systems is shown in Table 3. The mineralization of phenolic solutions via direct photolysis using single solar

Table 2

Equation and parameters of neural network fittings for the degradation of a mixture of protocatechuic, gallic and p-coumaric acids. Ferrioxalate-induced solar photo-Fenton process.

Neural network fitting

Equation[a] for original phenolic compounds elimination/solution mineralization

$k_{Phenolic}/k_{TOC}[W^{-1} h^{-1}] =$

$N_1 \times (1/(1 + 1/EXP([H_2O_2]_o \times W_{11} + [Fe(II)]_o \times W_{12} + [pH] \times W_{13} + [H_2C_2O_4]_o \times W_{14} + [temperature] \times W_{15} + [solar power] \times W_{16} + [air flow] \times W_{17}))) + N_2 \times (1/(1 + 1/EXP([H_2O_2]_o \times W_{21} + [Fe(II)]_o \times W_{22} + [pH] \times W_{23} + [H_2C_2O_4]_o \times W_{24} + [temperature] \times W_{25} + [solar power] \times W_{26} + [air flow] \times W_{27})))$

Weight factors	Parameter	Values of neurons and factors			
		k_{PA}	k_{GA}	k_{CA}	k_{TOC}
N_1	**Neuron**	0.6192	0.5453	−1.1544	0.1657
W_{11}	$[H_2O_2]_o$	−3.6852	−0.3443	13.9432	−1.8714
W_{12}	$[Fe(II)]_o$	8.8412	−1.5008	−7.5193	−1.0137
W_{13}	pH	−5.5533	1.9073	−4.9493	3.6041
W_{14}	$[H_2C_2O_4]_o$	−4.7111	−3.5312	−1.9440	0.1063
W_{15}	Temperature	2.4865	2.6142	12.6372	1.4176
W_{16}	Solar power	6.0071	4.1272	4.4460	−0.4558
W_{17}	Air flow	−2.1070	−7.6931	−10.2456	−0.2924
N_2	**Neuron**	−0.5547	0.1758	1.7255	−0.2064
W_{21}	$[H_2O_2]_o$	−10.8808	−2.2232	6.8822	−1.9142
W_{22}	$[Fe(II)]_o$	14.8622	12.0293	−1.7084	−1.0916
W_{23}	pH	−9.8064	−9.6928	−2.9757	3.6283
W_{24}	$[H_2C_2O_4]_o$	−8.7109	10.9436	0.0780	−0.9872
W_{25}	Temperature	0.9074	5.0484	5.2980	0.6723
W_{26}	Solar power	10.6592	−8.4971	0.2279	−0.3716
W_{27}	Air flow	−0.9654	−1.6283	−4.5313	−0.0416

Saliency analysis of the input variables for the neural network (%)

Neural network output	Parameters						
	$[H_2O_2]_o$	$[Fe(II)]_o$	pH	$[H_2C_2O_4]_o$	Temperature	Solar power	Air flow
k_{PA} ($W^{-1} h^{-1}$)	15.47	27.22	17.51	15.20	4.77	0.85	18.99
k_{GA} ($W^{-1} h^{-1}$)	3.01	15.47	14.07	19.06	11.06	19.34	17.99
k_{CA} ($W^{-1} h^{-1}$)	28.38	10.69	11.30	1.93	23.55	19.64	4.52
k_{TOC} ($W^{-1} h^{-1}$)	23.02	12.82	37.84	6.97	12.42	1.94	5.00

[a] Parameter values in equations must be previously normalized to the (0.1) interval.

light was very inefficient (11%) due to the maximum absorbance wavelengths of compounds (290, 293 and 307 nm for gallic, protocatechuic, and p-coumaric acids, respectively). The wavelength of solar radiation received by the earth is above 290 nm. The use of solar light in the presence of only Fe(II) did not improve the TOC (12%) removal due to the fact that oxidative intermediate species (mainly hydroxyl radicals) are not generated under irradiation of ferrous ions in the absence of H_2O_2 or oxalic acid.

When the degradation reaction was carried out under solar light irradiation and the addition of oxalic acid alone, TOC removal was increased from approximately 11–40% when compared to the single solar system. This could be due to the formation of phenolic–oxalate complexes (data not shown), which absorb more radiation and thus break down the aromatic ring of the target molecules. This effect has been previously demonstrated by

Table 3

Mineralization data of solutions composed by a mixture of three phenolic compounds (gallic, p-coumaric and protocatechuic acids). A previous comparative study is shown. .

System	TOC removal (%)
Solar	11.24
Solar/Fe(II)	12.11
Solar/oxalic	40.21
H_2O_2[a]	37.16
Solar/H_2O_2	48.01
Solar/H_2O_2/Fe(II)	70.21
Solar/H_2O_2/Fe(II)/oxalic	84.24

Experimental conditions: $[H_2O_2]$: 200 ppm; $[Fe(II)]$: 10 ppm; $[oxalic]$: 30 ppm; pH: 4; air flow: 0.8 m³ h. Accumulated solar energy: 30 W h; reaction time: 24 min.

[a] Reaction time: 24 min.

the authors [4] in the case of solutions composed of a single protocatechuic acid plus oxalic acid. However, this achieved mineralization degree (40%) indicated that the intermediate compounds formed were possibly more difficult to break down. Besides, in this solar/oxalic system, hydroxyl radicals or other oxidative intermediate species were not generated.

The mineralization results shown in Table 3 also confirmed the small effect of H_2O_2 as a single oxidant (37% TOC removal), since the direct reaction of peroxide with molecules of protocatechuic and p-coumaric acids did not occur (data not shown). The percentages of decomposition of the original compounds by single H_2O_2 system after 90 min of reaction were as follows: 93% gallic acid; 14% protocatechuic acid and 14% p-coumaric acid. On the other hand, when the phenolic solution was irradiated with solar light in the presence of H_2O_2 alone, the removal rate of TOC was 48% (11% by the action of direct solar photolysis as indicated above and 37% by the action of hydrogen peroxide). In this case, no synergistic effect took place and hydroxyl radicals were not generated since the photolysis of hydrogen peroxide needs 200–300 nm irradiation solar light wavelength is higher 290 nm.

The solar treatment using Fenton reagent (H_2O_2 + Fe(II)) alone or oxalic-assisted Fenton reagent increased the mineralization efficiency compared to the solar/H_2O_2 system, as expected. In these prior experiments, the maximum TOC removal efficiency (84%) was obtained with the ferrioxalate-assisted solar photo-Fenton system. The increased degradation efficiency could be due to the continuous regeneration of Fe^{2+} via photoreduction of Fe^{3+} with solar UV-A light according to Eq. (3) and extra generation of free radicals (mainly •OH) by ferrioxalate photochemistry [13]. These Fe(III) ions are formed by the oxidation of ferrous iron (added as $FeSO_4$) by dissolved oxygen (Eq. (4)), where superoxide radical anions ($O_2^{•-}$)
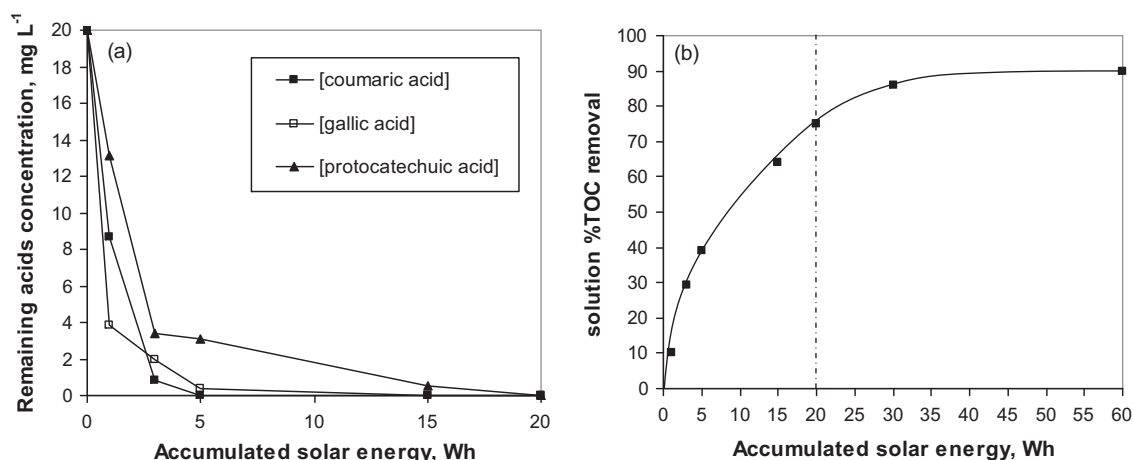
Fig. 3. (a) Degradation of original compounds; (b) evolution of %TOC removal of acids from the mixture solution. Ferrioxalate-induced solar photo-Fenton process. [phenolic compounds]$_o$: 20 mg L^{-1}; pH: 4; [H$_2$O$_2$]$_o$: 200 mg L^{-1}; [Fe(II)]$_o$: 10 ppm; [H$_2$C$_2$O$_4$]$_o$: 30 mg L^{-1}; air flow: 0.80 N m^3 h^{-1}; average temperature: 34 °C; average solar power: 33 W m^{-2}.

are also generated.

$$Fe(III)(OH)^{2+} + h\nu \rightarrow Fe(II) + {}^{\bullet}OH \tag{3}$$

$$Fe(II) + O_2 \rightarrow Fe(III) + O_2{}^{\bullet -} \tag{4}$$

Taking into account the results from this previous study, a central-composite experimental design was applied to optimize the ferrioxalate-induced photo-Fenton process under solar light, as this solar-activated catalytic system could offer an economical and practical alternative for the destruction of this type of contaminants.

3.2. Solar pilot plant experiments

All the experiments presented in this section were based on the degradation of solutions containing a mixture of gallic, protocatechuic and p-coumaric acids, in a ferrioxalate-assisted photo-Fenton system irradiated under solar light. In all of these experiments, both the disappearance of each target compound and the total organic carbon removal followed pseudo-first-order kinetics with respect to the phenolic compounds and TOC concentrations, respectively, as indicated above. To simultaneously study the effect of pH, air-flow rate and initial concentrations of H$_2$O$_2$, Fe(II) and oxalic acid on the response functions (k_{PA}, k_{GA} or k_{CA} and k_{TOC}), a central-composite design was performed. The experimental design matrix, coded and natural levels, and variable ranges are presented in Table 1. This table also shows the selected optimal operating conditions for the process; the best results obtained for k_{PA}, k_{GA} or k_{CA} and k_{TOC}; and the original compounds' elimination and TOC removal percentages. Solar power and temperature were not controlled during the experiment, but they were measured during the reaction and their average values were included in the fitting.
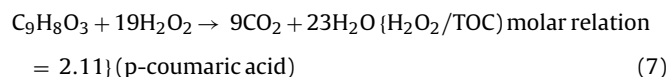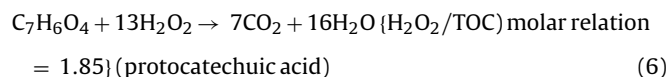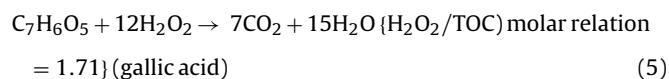
Experimental results and NN predictions of these constants were in good agreement, with an average error lower than 15% in all cases (data not shown). The equation and fitting parameters for k_{PA}, k_{GA} or k_{CA} and k_{TOC} are shown in Table 2. N_1 and N_2 are general factors related to the first and the second neuron, respectively. W_{11} to W_{17} are the contribution parameters to the first neuron and represent the influence of each of the variables ([H$_2$O$_2$]$_o$, [Fe(II)]$_o$, pH, [H$_2$C$_2$O$_4$]$_o$, average temperature, average incident solar power and air-flow rate, respectively) on the process. W_{21} to W_{27} are the contributions to the second neuron corresponding to the same variables.

The results of a saliency analysis on the input variables for each neural network are also shown in Table 2. From these results, it was

possible to deduce the effects of each parameter on the studied variables; these values are reported as percentages. It was confirmed that over the studied range, pH and initial concentrations of H$_2$O$_2$ and Fe(II) were the most significant factors affecting the solution mineralization.

Fig. 3 shows that the three phenolic acids of the mixture solution, protocatechuic, gallic and p-coumaric acids, oxidized rapidly into intermediates under the ferrioxalate-assisted solar photo-Fenton process. As can be seen, gallic acid degradation was more rapid than that of the other two compounds at the beginning of the reaction, possibly due to the fact that it was the only compound to be decomposed by direct reaction with molecules of H$_2$O$_2$, as indicated above. However, the total elimination of original p-coumaric acid was reached first (5 W h), while 15 and 20 W h were necessary for the total decomposition of gallic acid and protocatechuic acid, respectively. These differences may be due to the fact that free radicals first attack the open C=C double bond of the p-coumaric molecule. Besides, p-coumaric acid absorbs at a wavelength (307 nm), higher than protocatechuic acid (293 nm) or gallic acid (290 nm), thereby using a major part of available solar radiation capable of inducing photolytic reaction and contributing to the molecule's oxidative degradation. Typically, original compound elimination was quicker at the beginning and decelerated towards the end of the reaction. As can be seen in Fig. 3, in these conditions, complete decomposition of target compounds was reached in approximately 20 W h (≈17 min). In that moment, 75% TOC removal was achieved.

The molar correlation between consumed hydrogen peroxide and removed TOC was between approximately 1 and 3 in all experiments (Fig. 4). This is in agreement with the following mineralization global reactions:

$$C_7H_6O_5 + 12H_2O_2 \rightarrow 7CO_2 + 15H_2O \{H_2O_2/TOC\}\text{ molar relation}$$
$$= 1.71\} \text{ (gallic acid)} \tag{5}$$

$$C_7H_6O_4 + 13H_2O_2 \rightarrow 7CO_2 + 16H_2O \{H_2O_2/TOC\}\text{ molar relation}$$
$$= 1.85\} \text{ (protocatechuic acid)} \tag{6}$$

$$C_9H_8O_3 + 19H_2O_2 \rightarrow 9CO_2 + 23H_2O \{H_2O_2/TOC\}\text{ molar relation}$$
$$= 2.11\} \text{ (p-coumaric acid)} \tag{7}$$

These results revealed that some molecules of H$_2$O$_2$ were consumed by unproductive reactions during the process. Thus, the reactions that were either carried out at pH 6 (experiment 41) or
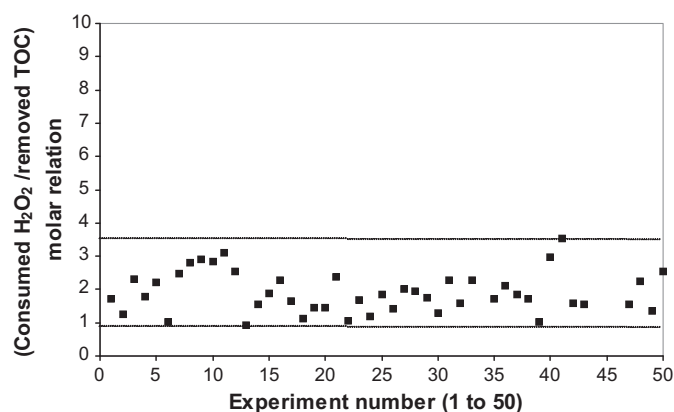
Fig. 4. Molar correlation between consumed H_2O_2 and removed TOC at different conditions, in all 50 experiments studied.

without oxalic addition (experiment 40) presented the higher values of this correlation, which indicates that some amount of H_2O_2 is being unproductive in these conditions (data not shown).

3.2.1. Optimal conditions

Table 1 shows the selected optimal conditions and the best obtained results of the degradation of the solution formed by the three phenolic compounds in the ferrioxalate-induced solar photo-Fenton process. Under the optimal conditions, (which can be seen in Fig. 5), the reaction times necessary for the total elimination
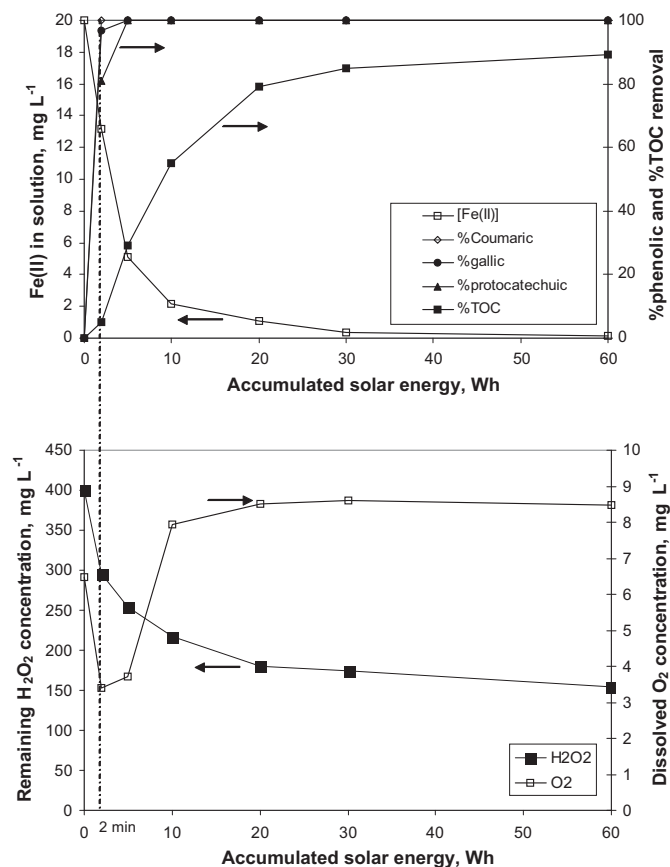
Fig. 5. Original compounds elimination and mineralization of the mixture solution in a ferrioxalate-induced solar photo-Fenton process. Evolution of Fe(II), H_2O_2 and dissolved O_2 in solution. *Optimal conditions:* $[H_2O_2]_o = 400\,mg\,L^{-1}$; $[Fe(II)]_o = 20\,mg\,L^{-1}$; $[H_2C_2O_4]_o = 60\,mg\,L^{-1}$; [phenolic compounds]$_o = 20\,mg\,L^{-1}$; no air flow; average temperature: 29 °C; average solar power: 35 W m^{-2}.

of the original compounds were 2 min or ≈2 W h for p-coumaric acid; 3.5 min or ≈3.3 W h for gallic acid; and 5 min or ≈4.7 W h for protocatechuic acid. An 89% mineralization degree of the phenolic solution was achieved in 60 W h and 94% TOC removal was achieved in 240 W h (data not shown; 194 min reaction time). Solution TOC showed steady degradation in the first stage (up to 20 W h accumulated solar energy), while its degradation rate slowed down at the end of the reaction. This behaviour indicated the formation of hard-to-degrade by-products during the reaction. It would be of interest to further study the character of such by-products formed during the reaction, but it was outside the scope of this work (which only attempted to demonstrate the mineralization of a mixture of various phenolic compounds in the ferrioxalate-catalyzed solar system in the presence of H_2O_2).

In the first stage of the reaction, when accumulated solar energy was 5 W h, the elimination of the original compounds was 100% but the mineralization degree was only 30%, indicating that the original phenolic compounds rapidly oxidized into intermediates that were more difficult to degrade. During this first stage, H_2O_2 concentration rapidly decreased from 400 to 250 mg L^{-1}, followed by a second, slower depletion stage. The consumption of H_2O_2 could be due to any of the following reactions:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + {}^\bullet OH \tag{8}$$

$$H_2O_2 \rightarrow O_2 + H_2O \tag{9}$$

$$H_2O_2 + {}^\bullet OH \rightarrow HO_2{}^\bullet + H_2O \tag{10}$$

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + O_2 + 2H_2O \tag{11}$$

$$H_2O_2 + HO_2{}^\bullet \rightarrow O_2{}^\bullet + {}^\bullet OH + H_2O \tag{12}$$
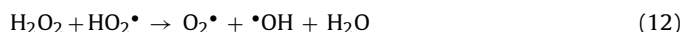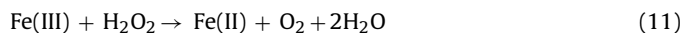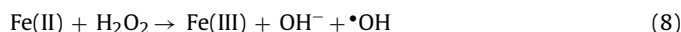
Additionally, when ferrioxalate complex $[Fe(III)(C_2O_4)_3]^{3-}$ is irradiated from the ultraviolet to the visible range in the presence of H_2O_2, reactions (13)–(16) take place, with H_2O_2 also being consumed by Eq. (16):
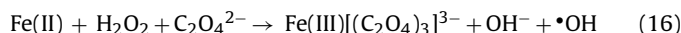
$$Fe(III)[(C_2O_4)_3]^{3-} + h\nu \rightarrow Fe(II) + 2C_2O_4{}^{2-} + C_2O_4{}^{\bullet-} \tag{13}$$
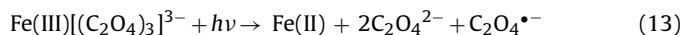
The oxalyl radical anion, $C_2O_4{}^{\bullet-}$, quickly decomposes to the carbon dioxide radical anion, $CO_2{}^{\bullet-}$:

$$C_2O_4{}^{\bullet-} \rightarrow CO_2{}^{\bullet-} + CO_2 \tag{14}$$

This reducing agent can produce Fe(II) via reaction [15]:

$$CO_2{}^{\bullet-} + Fe(III)[(C_2O_4)_3]^{3-} \rightarrow Fe(II) + CO_2 + 3C_2O_4{}^{2-} \tag{15}$$
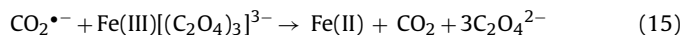
When ferrioxalate is irradiated in the presence of H_2O_2, one $^\bullet OH$ for every Fe(II) is generated:

$$Fe(II) + H_2O_2 + C_2O_4{}^{2-} \rightarrow Fe(III)[(C_2O_4)_3]^{3-} + OH^- + {}^\bullet OH \tag{16}$$

In this initial stage of the reaction, the dissolved O_2 concentration rapidly decreased until a minimum value was reached and then increased until a plateau value was achieved. This indicated a less significant role of O_2 during the mineralization stage. The decrease of dissolved O_2 could be due to the reaction of oxygen with the oxalyl radical anion, $C_2O_4{}^{\bullet-}$, according to Eq. (17), and with intermediate organoradicals, by Eq. (18), in agreement with other researchers [15,16]. After this period, the dissolved oxygen concentration increased, likely due to ferrioxalate photochemistry reactions (Eqs. (13), (19)–(21)), by H_2O_2 decomposition (Eq. (9)) and by catalytic reactions of Fe(III) with either H_2O_2 or $HO_2{}^\bullet$ according to Eqs. (11) and (22), respectively. Both oxygen depletion and formation reactions occurred throughout the process. Depending on the availability of the reagents, one of the reactions becomes dominant at different stages of the overall reaction.

$$C_2O_4{}^{\bullet-} + O_2 \rightarrow O_2{}^{\bullet-} + 2CO_2 \tag{17}$$

$$R^\bullet + O_2 \rightarrow RO_2{}^\bullet + H_2O \rightarrow ROH + HO_2{}^\bullet \tag{18}$$

$$C_2O_4^{\bullet-} + [Fe(C_2O_4)_3]^{3-} \rightarrow Fe(II) + 3C_2O_4^{2-} + 2CO_2 \qquad (19)$$

$$O_2^{\bullet-} + H+ \rightarrow HO_2^{\bullet} \qquad (20)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (21)$$

$$Fe(III) + HO_2^{\bullet} \rightarrow Fe(II) + O_2 + H^+ \qquad (22)$$
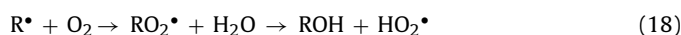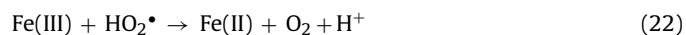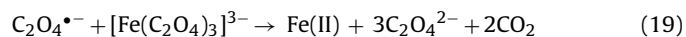
Fe(II) in solution decreased rapidly at the beginning of the reaction as a consequence of its oxidation into Fe(III) by dissolved oxygen (according to Eq. (4)), by reaction of decomposition of H_2O_2 (Fenton reaction) and by Eq. (16).

3.3. Effect of Fe(II), pH, oxalic acid addition, H_2O_2 and temperature

As can be seen from the saliency analysis shown in Table 2, pH is the most significant parameter affecting the mineralization rate. The equation shown in Table 2 allows a simulation analysis of the effect of any of the studied variables on the value of k_{TOC}. Fig. 6 shows (as an example) in three dimensions, the effect of pH and the addition of oxalic acid on the value of the rate constant of mineralization of phenolic mixture solution, k_{TOC}, as simulated by the NNs at three different values of initial concentration of Fe(II). The operating conditions were the following: $[H_2O_2]_o = 200\,mg\,L^{-1}$; $[Fe(II)]_o = 2, 10$ and $20\,mg\,L^{-1}$; $[H_2C_2O_4]_o = 60\,mg\,L^{-1}$; pH 4; air flow $= 0.8\,m^3\,h^{-1}$; [GA; CA; PA] $= 20\,mg\,L^{-1}$; average temperature $= 25\,°C$; average solar power $= 37\,W\,m^{-2}$. The results revealed that the addition of oxalic acid to the Fe(II)/H_2O_2 system irradiated with sunlight positively affected the value of k_{TOC} over the studied range and that the pH could increase the reaction rate or cause inhibition effects depending on the operating conditions. Thus, k_{TOC} increased with the pH until reaching a maximum value, when an optimum pH was used. Both the maximum value of k_{TOC} (from 0.043 to 0.064 $W^{-1}\,h^{-1}$) and the optimum pH (from 3.5 to 4.5) increased as the initial Fe(II) concentration increased (from 2 to 20 ppm). This fact indicates that Fe(II) can significantly accelerate the mineralization reaction by the formation of more hydroxyl radicals according to Eqs. (3), (8), (16) and superoxide radicals by Eqs. (4) and (17). When the pH was greater than 4.5, the process efficiency decreased because the coagulation of Fe(III) complexes reduced the catalytic effect of Fe(II) to decompose H_2O_2. At a more acidic pH, below 3.5, protonation of H_2O_2 to form $H_3O_2^+$, which hardly reacts with Fe(II) ions, may also be responsible for the decrease in the formation of $^{\bullet}OH$ radicals. On the other hand, oxalic acid positively affected the photocatalytic reaction due to the faster generation of Fe^{2+} ion by photolysis of ferrioxalate and additional oxidative intermediate species.

Fig. 7 shows (as an example) the effect of pH and the addition of oxalic on the mineralization rate constant of the phenolic mixture solutions in the ferrioxalate-assisted solar photo-Fenton process at different initial H_2O_2 concentrations. The influence of these two variables was similar to that attained while varying the initial Fe(II) amount. Both the maximum value of k_{TOC} (from 0.043 to 0.068 $W^{-1}\,h^{-1}$) and the optimum pH (from 3.5 to 4.9) increased as the initial H_2O_2 concentration increased over the studied range (from 100 to 400 $mg\,L^{-1}$). It is well known that an increase in H_2O_2 concentration in a photo-Fenton reaction produces a higher amount of $^{\bullet}OH$ radicals provided that its concentration is below the excess concentration that produces the radicals' scavenger effect.

As can be seen in Fig. 8 (for example), the values of k_{TOC} are presented as a function of the variables pH and initial oxalic concentration for three different values of the process' average temperature. The effect of oxalic addition on mineralization was the same as indicated above while an optimal value of pH also produced a higher mineralization rate. However, in this case, the optimal value of pH decreased (from 4.5 to 3.5) when the tem-
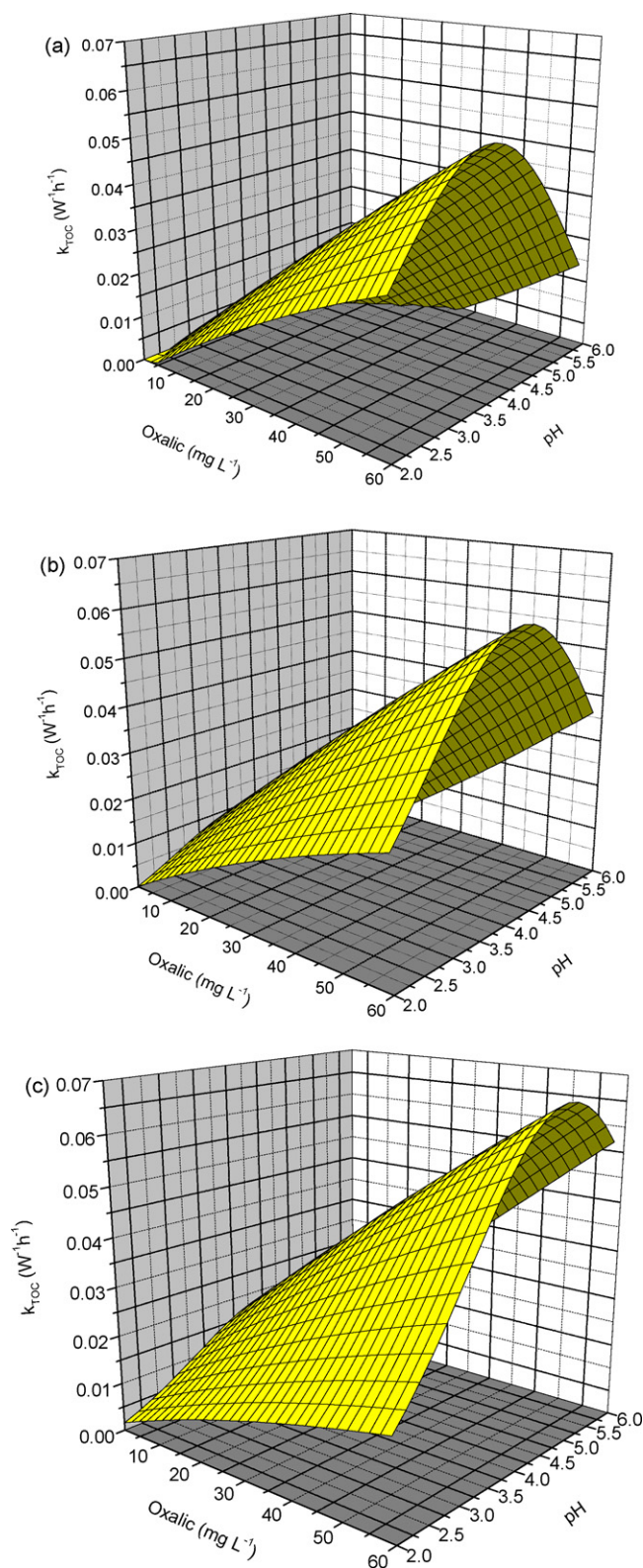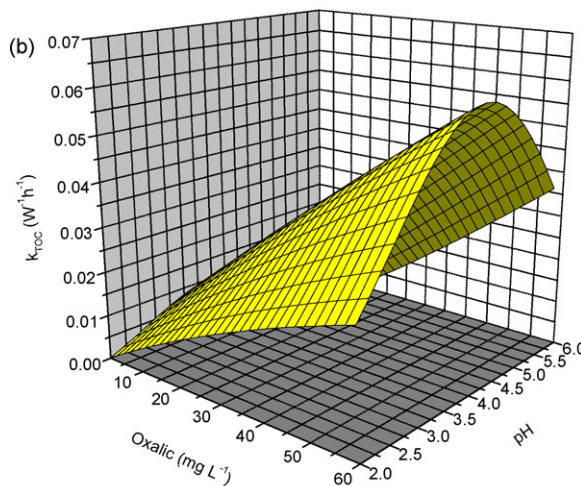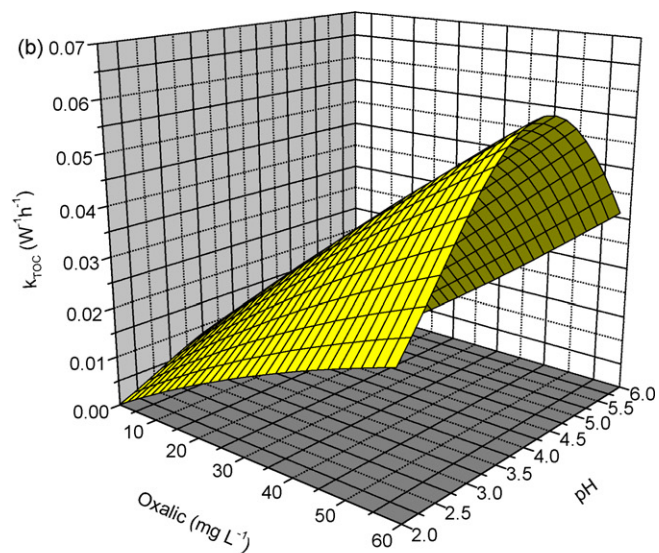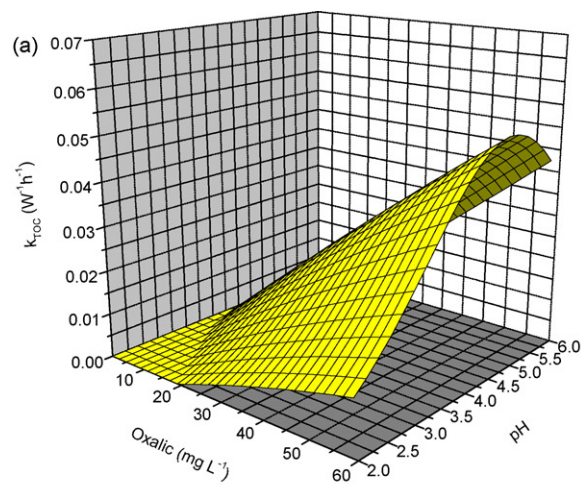

Fig. 6. Mineralization of a mixture of phenolic solutions in the ferrioxalate-induced solar photo-Fenton process; effects of initial concentrations of oxalic and pH. [phenolic compounds]$_o$ = 20 mg L^{-1}; air-flow rate = 0.8 N m^3 h^{-1}; average temperature = 25 °C; average solar power = 35 W m^{-2}. (a) [Fe(II)]$_o$ = 2 mg L^{-1}; (b) [Fe(II)]$_o$ = 10 mg L^{-1}; (c) [Fe(II)]$_o$ = 20 mg L^{-1}.
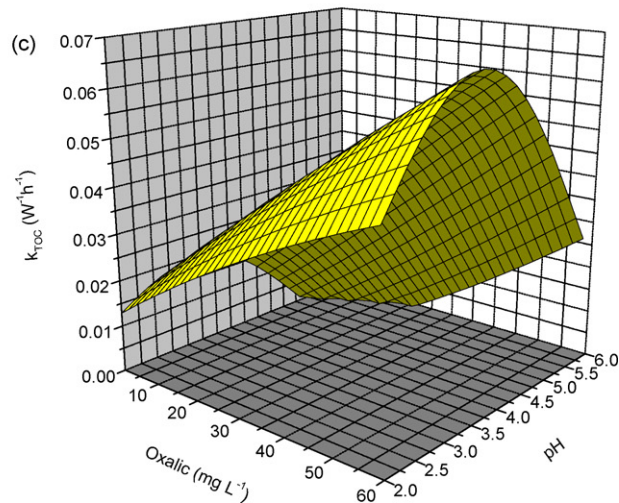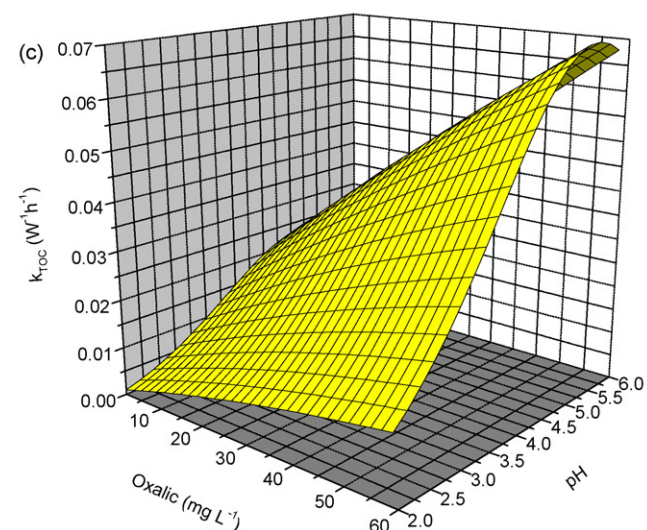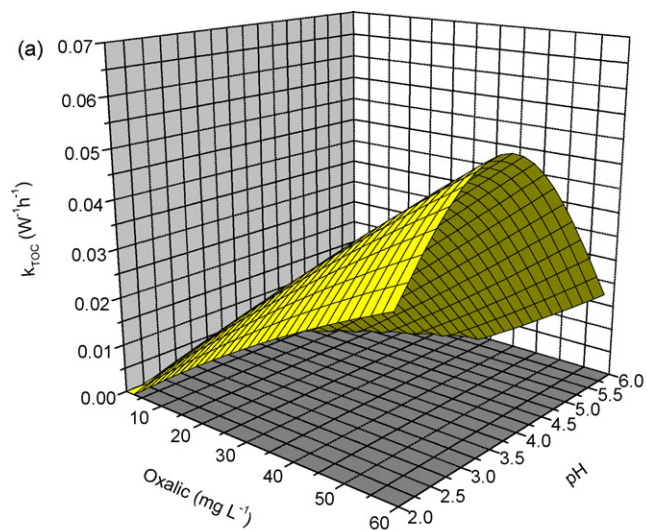
Fig. 7. Mineralization of a mixture of phenolic solutions in the ferrioxalate-induced solar photo-Fenton process; effects of initial concentrations of oxalic and pH. [phenolic compounds]$_o$ = 20 mg L^{-1}; air-flow rate = 0.8 N m^3 h^{-1}; average temperature = 25 °C; average solar power = 35 W m^{-2}. (a) [H$_2$O$_2$)]$_o$ = 100 mg L^{-1}; (b) [H$_2$O$_2$)]$_o$ = 200 mg L^{-1}; (c) [H$_2$O$_2$)]$_o$ = 400 mg L^{-1}.

Fig. 8. Mineralization of a mixture of phenolic solutions in the ferrioxalate-induced solar photo-Fenton process; effects of initial concentrations of oxalic and pH. [H$_2$O$_2$)]$_o$ = 200 mg L^{-1}; [phenolic compounds]$_o$ = 20 mg L^{-1}; air-flow rate = 0.8 N m^3 h^{-1}; average solar power = 35 W m^{-2}. (a) Average temperature = 22 °C; (b) average temperature = 29 °C; (c) average temperature = 36 °C.
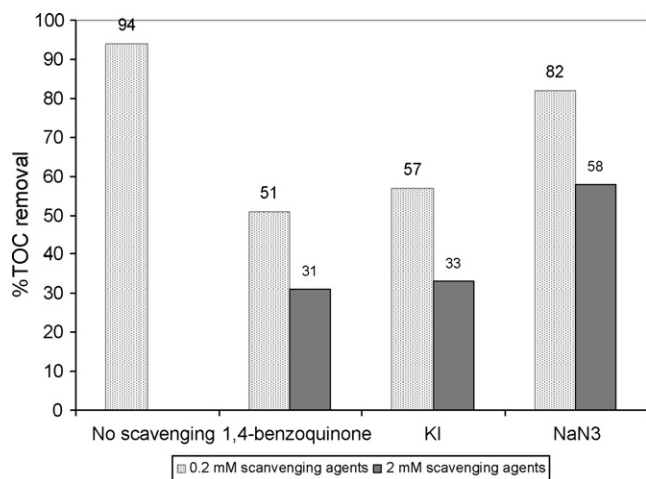
Fig. 9. Role of different oxidative species in the mineralization of a mixture composed by p-coumaric, gallic and protocatechuic acids under a ferrioxalate-induced solar photo-Fenton process in the presence of 0.2 and 2 mM scavenging agents 1,4-benzoquinone, KI and NaN$_3$. *Experimental conditions*: [H_2O_2] = 400 mg L^{-1}; [Fe(II)] = 20 mg L^{-1}; [$H_2C_2O_4$] = 60 mg L^{-1}; pH = 4; [phenolic compounds] = 20 mg L^{-1}; average temperature = 25 °C; average solar power = 35 W m^{-2}.

perature increased from 22 to 36 °C. This may be due to the higher self-decomposition rate of H_2O_2 into water and oxygen (unproductive reaction) at higher temperatures. Since basic pH also favors this reaction of H_2O_2 decomposition, the decrease of pH increased the mineralization efficiency.

3.4. Role of different oxidative intermediate species

The main active species responsible for the mineralization of phenolic mixture solutions were determined. Several additional comparative experiments (see Table 1; experiments: 47–50) were carried out under the ferrioxalate-induced solar photo-Fenton process in the selected optimal conditions. In these reactions, various oxidative intermediate species were generated, such as hydroxyl radical ($^{\bullet}OH$), hydroperoxyl ($HO_2^{\bullet}$), singlet oxygen ($^1O_2$) and superoxide radical anion ($O_2^{\bullet-}$). Thus, the degradation process was developed both in the absence and in the presence of appropriate quenchers of these species [17] under the same conditions. The scavenging agents used were as follows: 1,4-benzoquinone ($C_6H_4O_2$, a quencher of superoxide radical anion), sodium azide (NaN$_3$, a quencher of singlet oxygen) and potassium iodide (KI, a quencher of hydroxyl radicals). The role of these species is shown in Fig. 9. As can be seen, the increase in concentration of the scavenging agents from 0.2 to 2 mM increased the inhibition effect of the mineralization reaction (%TOC removal decreased). This indicates the participation of these species in the reaction. Superoxide and hydroxyl radicals were the main species contributing to the mineralization of phenolic mixture solutions. In both cases, the reduction in %TOC removal was from 94% to approximately 31–33%. The significant role of $O_2^{\bullet-}$ was due to its generation by Eq. (4) and by the reaction between $CO_2^{\bullet-}$ (generated by ferrioxalate photochemistry) and oxygen according to Eq. (23). On the other hand, the addition of NaN$_3$ had a smaller effect on %TOC removal, reducing the degree of mineralization from 94% to 58.4%. This indicated that $^1O_2$ also played a role in the degradation reaction. This singlet oxygen was formed when oxygen molecules absorbed photons and were activated [18].

$$CO_2^{\bullet-} + O_2 \rightarrow O_2^{\bullet-} + CO_2 \qquad (23)$$

4. Conclusions

Solutions composed by mixtures of three phenolic compounds, gallic, p-coumaric and protocatechuic acids, can be efficiently photo-degraded using the ferrioxalate-induced solar photo-Fenton process. Under optimal conditions, total elimination of original compounds and 94% TOC was achieved in 5 and 194 min, respectively. pH and initial concentrations of H_2O_2 and Fe(II) were the most significant factors affecting the mixture mineralization. The molar correlation between consumed hydrogen peroxide and removed TOC was always between 1 and 3. The values of k_{TOC} increased as initial Fe(II) and H_2O_2 concentrations as well as temperature increased. The optimum pH value also increased with Fe(II) and hydrogen peroxide but decreased at higher temperatures. $^{\bullet}OH$ and $O_2^{\bullet-}$ radicals were the main oxidative intermediate species in the process, although singlet oxygen ($^1O_2$) also played a role the in mineralization reaction.

Acknowledgement

References

[1] Y. Du, M. Zhou, L. Lei, Role of the intermediates in the degradation of phenolic compounds by Fenton-like process, J. Hazard. Mater. 36 (2006) 859–865.
[2] M. Rodríguez, S. Malato, C. Pulgarín, S. Contreras, D. Curcó, J. Giménez, S. Esplugas, Optimizing the solar photo-Fenton process in the treatment of contaminated water. Determination of intrinsic kinetic constants for scale-up, Solar Energy 79 (2005) 360–368.
[3] R.F.P. Nogueira, M.R.A. Silva, A.G. Trovó, Influence of the iron source on the solar photo-Fenton degradation of different classes of organic compounds, Solar Energy 79 (2005) 384–392.
[4] J.M. Monteagudo, A. Durán, M. Aguirre, I. San Martín, Effect of light source on the catalytic degradation of protocatechuic acid in a ferrioxalate-assisted photo-Fenton process, Appl. Catal. B: Environ. 96 (2010) 486–495.
[5] H. Yao-Hui, T. Shu-Ting, H. Yi-Fong, C. Chuh-Yung, Degradation of commercial azo dye reactive Black B in photo/ferrioxalate system, J. Hazard. Mater. 140 (2007) 382–388.
[6] C. Yong, W. Feng, L. Yixin, D. Nansheng, B. Nikolai, G. Evgeni, Photodegradation of glyphosate in the ferrioxalate system, J. Hazard. Mater. 148 (2007) 360–365.
[7] W. Gernjak, T. Krutzler, A. Glaser, S. Malato, J. Caceres, R. Bauer, A.R. Fernández-Alba, Photo-Fenton treatment of water containing natural phenolic pollutants, Chemosphere 50 (2003) 71–78.
[8] E. Kusvuran, A. Samil, O.M. Atanur, O. Erbatur, Photocatalytic degradation kinetics of di- and tri-substituted phenolic compounds in aqueous solution by TiO$_2$/UV, Appl. Catal. B: Environ. 58 (2005) 211–216.
[9] S. Azabou, W. Najjar, A. Gargoubi, A. Ghorbel, S. Sayadi, Catalytic wet peroxide photo-oxidation of phenolic olive oil mill wastewater contaminants: Part II. Degradation and detoxification of low-molecular mass phenolic compounds in model and real effluent, Appl. Catal. B: Environ. 77 (2007) 166–174.
[10] G.E.P. Box, W.G. Hunter, J.S. Hunter, Statistics for Experimenters: An Introduction to Design, Data Analysis and Model Building, Wiley, New York, 1978.
[11] D.P. Morgan, C.L. Scofield, Neural Networks and Speech Processing, Kluwver Academic Publishers, London, 1991.
[12] R. Nath, B. Rajagopalan, R. Ryker, Determining the saliency of input variables in neural network classifiers, Comput. Oper. Res. 24 (1997) 767–773.
[13] J.M. Monteagudo, A. Durán, I. San Martin, M. Aguirre, Effect of continuous addition of H$_2$O$_2$ and air injection on ferrioxalate-assisted solar photo-Fenton degradation of Orange II, Appl. Catal. B: Environ. 89 (2009) 510–518.
[14] D.W. Marquardt, An algorithm for least-squares estimation of nonlinear parameters, J. Soc. Ind. Appl. Math. 11 (1963) 431–441.
[15] K.A. Hislop, J.R. Bolton, The photochemical generation of hydroxyl radicals in the UV–vis/ferrioxalate/H$_2$O$_2$ system, Environ. Sci. Technol. 33 (1999) 3119–3126.
[16] A. Aris, P.N. Sharrat, Influence of initial dissolved oxygen concentration on Fenton's reagent degradation, Environ. Technol. 27 (2006) 1153–1161.
[17] W. Li, S. Zhao, B. Qi, Y. Dua, X. Wang, M. Huo, Fast catalytic degradation of organic dye with air and MoO$_3$:Ce nanofibers under room condition, Appl. Catal. B: Environ. 92 (2009) 333–340.
[18] S. Malhotra, M. Pandit, J.C. Kapoor, D.K. Tyagi, Photo-oxidation of cyanide in aqueous solution by the UV/H$_2$O$_2$ process, J. Chem. Technol. Biotechnol. 80 (2005) 13–19.