Gallic acid degradation in aqueous solutions by UV/H$_2$O$_2$ treatment, Fenton's reagent and the photo-Fenton system

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Abstract

Gallic acid (3,4,5-trihydroxybenzoic acid) is a major pollutant present in the wastewater generated in the boiling cork process, as well as in other wastewaters from food manufacturing industries. Its decay in aqueous solutions has been studied by the action of several oxidation systems: monochromatic UV radiation alone and combined with hydrogen peroxide, Fenton's reagent and the combination Fenton's reagent with UV radiation (photo-Fenton system). The influence of the pH is discussed and the quantum yields are determined in the UV radiation system. Also, the influence of operating variables (initial concentrations of H$_2$O$_2$ and Fe(II), and pH) is established in the Fenton's reaction. The apparent pseudo-first-order rate constants are evaluated in all the experiments conducted in order to compare the efficiency of each one of the processes. Increases in the degradation levels of gallic acid are obtained in the combined processes in relation to the single UV radiation system, due to reactions of the very reactive OH$^\bullet$. These improvements are determined in every process by calculating the partial contribution to the overall decomposition rate of the radical pathways. For the oxidant concentrations applied, the most effective process in removing gallic acid was found to be the photo-Fenton system. The rate constant for the reaction of gallic acid with OH$^\bullet$ was also determined by means of a competition kinetics model, being its value $11.0 \pm 0.1 \times 10^9$ l mol^{-1} s^{-1}.
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Keywords: Gallic acid; Chemical oxidation; Rate constants; OH$^\bullet$

1. Introduction

Several treatments must be frequently applied to wastewaters generated in industrial processes in order to reduce the organic load as well as other contaminants present, before its discharge in public effluents. For the removal of part of this organic load, biological processes are commonly used due to economical reasons. However, in some cases, the presence of biorecalcitrant compounds which are toxic to the microorganisms reprove the use of such as biological treatments, since no chemical oxygen demand removal is obtained.

In these situations, some chemical pre-treatments can achieve reductions of this organic matter prior to the later biological treatment. Among them, procedures based on the use of different oxidants like UV radiation [1], ozone [2],

hydrogen peroxide, etc. have demonstrated a significant efficiency in wastewater treatments.

However, some substances are even refractory to those single oxidation processes, and new alternatives have been developed for the elimination of these contaminants, like the advanced oxidation processes (AOPs) [3], which consist on the combination of single oxidants. These AOPs employ high oxidation-potential sources to produce the primarily oxidant species, the OH$^\bullet$, which react with most organic compounds with rate constants which are in the range 10^7–10^{10} l mol^{-1} s^{-1} [4].

Portugal and Spain are two of the major countries in the production of cork. The manufacture of this material is mainly concentrated in Extremadura Region (southwest of Spain, in the border with Portugal). In order to obtain the wine stoppers, the cork is processed through several stages, such as cleaning, disinfecting and moistening of the raw material. Specifically, the first step is the most important, and consists

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in the immersion of the corkwood in boiling water during an hour. The result of this stage is a dark liquor which contains some corkwood extracts such as phenolic acids, tannic fraction, 2,4,6-trichloroanisol and pentachlorophenol [5].

All these organic substances are considered as water pollutants, and their presence in cork stoppers promote harmful effects on wine quality. So, their accumulation in the boiling water requires a frequent evacuation of this effluent in order to produce a good quality cork with low concentration of these organics. Consequently, some treatment processes are necessary to reduce the contamination of this wastewater in order to be evacuated or reused. However, the presence of these phenolic compounds, most of them with acid nature and low pH, make it unsuitable for biological treatment. Therefore, the chemical treatments before described, by single oxidants or AOPs, seem to be good alternatives for the elimination of the toxic fraction of the cork boiling water. In this way, Silva et al. [6] have reported experimental results on the chemical degradation of this effluent, by using several photo-activated processes.

Gallic acid constitutes one of the most representative compounds in the referred phenolic fraction, which is present in the cork processing wastewater, and therefore, it was selected as a model pollutant of the wastewater generated in the cork boiling process. The chemical oxidation of this substance by means of ozone as the only oxidant was studied previously by Beltran et al. [7]; but no other study on its chemical degradation by different oxidants than ozone has been found in the literature. Due to this lack of information, its oxidation is firstly investigated in the present work by the action of UV radiation alone. This UV oxidation can be summarized by the single reaction:

$$G + h\nu \rightarrow G_{oxid} \tag{1}$$

In addition, the present study includes its oxidation by the AOPs constituted by the combination UV/H_2O_2, Fenton's reagent and photo-Fenton system, which are characterized by the generation of the mentioned OH$^\bullet$. In effect, the generation of OH$^\bullet$ in the AOP UV/H_2O_2 takes place during the direct photolysis of hydrogen peroxide [8]:

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet \tag{2}$$

On the other hand, the Fenton's system consists of ferrous salts combined with hydrogen peroxide under acidic conditions, which react and form OH$^\bullet$ [9]:

$$H_2O_2 + Fe^{2+} \rightarrow OH^- + OH^\bullet + Fe^{3+} \tag{3}$$
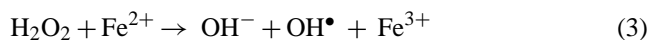
Obviously, in the photo-Fenton system both reactions (2) and (3) participate simultaneously in the production of such as radicals. In all cases, OH$^\bullet$ reacts rapidly and non-selectively with most organic compounds, like gallic acid, by H-abstraction and addition to C–C unsaturated bonds and produce its chemical decomposition:

$$G + OH^\bullet \rightarrow G_{oxid} \tag{4}$$

After studying the chemical oxidation of gallic acid by the single UV radiation and the AOPs mentioned, the aims of the present research are the evaluation of kinetic parameters like quantum yields and rate constants in these processes, as well as the establishment of the partial contributions of the direct and radical reactions pathways to the global processes. This information can be used to propose kinetic models, which allow one to predict the removal of gallic acid within different wastewater streams of the cork boiling processing.

2. Experimental

A 500-ml cylindrical glass reactor was used for all the experiments, which was provided with the necessary elements for the development of the different processes: photochemical decomposition alone and combined with hydrogen peroxide, Fenton's reagent oxidation and photo-Fenton system.

Specifically, for the photochemical experiments, a low pressure mercury vapor lamp (Heraeus TNN 15/32, 15 W) which emitted a monochromatic radiation at 254 nm was used as radiation source. It was located in the reactor in axial position inside a quartz sleeve. An external jacket surrounded the reactor, and a water stream was pumped from a thermostatic bath in order to maintain the temperature at the selected value of 20 °C ± 0.5 °C. As in the later photochemical kinetic study it will be necessary to know the incident radiation intensity into the reactor emitted by the lamp, previous chemical actinometry experiments by using hydrogen peroxide as actinometer were conducted, and the value obtained was 2.03×10^{-6} E s^{-1}.

For every experiment conducted, the reactor was filled with 350 ml of gallic acid aqueous solution at the desired initial concentrations, and the reacting medium was buffered at the selected pH by adding a phosphoric acid/phosphate buffer (0.05 M). The required amounts of ferrous sulfate and hydrogen peroxide were added to the reactor in the Fenton's reagent oxidation experiments and in the photo-Fenton experiments, and only the required amounts of hydrogen peroxide in the UV/H_2O_2 experiments.

Analytical grade gallic acid was used, and the samples obtained during each experiment were analyzed by HPLC using a Waters Chromatograph equipped with a 996 Photodiode Array Detector and a Nova-Pak C18 Column. The mobile phase was composed by a mixture methanol-aqueous solution of phosphoric acid 10^{-2} M (5:95 in volume). The elution flow rate was 1 ml/min and the injection volume was 100 μl in all samples. In the competition kinetics experiments in order to determine the rate constants for the reactions of gallic acid with OH$^\bullet$, the concentration of the reference compound, acetophenone, was also analyzed by HPLC. The rate constant for the reaction between aceotophenone and OH$^\bullet$ has been reported previously [4]. This value is necessary for the application of the competitive kinetic model that will be explained and discussed later.

Table 1
Gallic acid oxidation experiments by UV radiation alone

Experiment	pH	X_{90} (%)	$k_{UV} \times 10^3$ (min^{-1})	$\phi \times 10^3$ (mol E^{-1})
UV-1	2	24.7	3.1	2.9
UV-2	3	41.7	5.9	5.1
UV-3	5	80.4	13.9	10.6
UV-4	7	86.5	21.8	12.9

3. Results and discussion

3.1. Gallic acid photodecomposition by UV radiation alone and combined with H_2O_2

The gallic acid decomposition by UV radiation alone was investigated at 20 °C and different initial pH values (Experiments UV-1 to UV-4 in Table 1) by keeping the initial acid concentration constant at 2.94×10^{-4} M (equivalent to 50 ppm). Fig. 1 shows the results obtained for the gallic acid concentration decay with reaction time: it was interesting to find that the highest decomposition rate was observed at the highest pH (pH 7), and the lowest rate was found at the lowest value (pH 2). As a general conclusion, Table 1 reports the removals obtained X_{90} at a selected time of photo-reaction (90 min).

This result can be explained by taking into account some considerations on the dissociation of acidic organic substances, which have been reported by several authors [10,11] in similar studies. According to this, the dissociated species present higher reactivity towards oxidants, like ozone or UV irradiation, while the non-dissociated species are less reactive. In the present case, the pK_a of gallic acid is 4.0; thus, it can be expected that at pH 2 and 3, a significant fraction of the organic substance is non-dissociated, and the global degradation rate is slow. On the contrary, at pH 5 and 7, most of the compound is dissociated in the aqueous solution, and therefore the photodegradation rate is much higher, which is confirmed by the experimental results obtained.

From Fig. 1, it can be also deduced that the decomposition rate seems to follow a pseudo-first-order reaction; and therefore, the reaction rate could be determined by the integrated first-order kinetics expression:

$$\ln \frac{[G]_0}{[G]} = k_{UV} t \tag{5}$$

According to this Eq. (5), a plot of ln $[G]_0/[G]$ versus time should provide straight lines, and after linear regression analysis, the k_{UV} values listed in Table 1 are deduced, all with correlation coefficients greater than 0.99. It can be observed that these k_{UV} values confirm the trend described above for the decomposition rate with the pH increase.

A more exact kinetic parameter in the photooxidation reaction of an organic compound described by Eq. (1) is the quantum yield ϕ, which is defined as the number of molecules reacted (or decomposed) per photon of light absorbed [12]. Under conditions where this organic G is the principal absorber, like gallic acid in the present case, the reaction model, which was deduced and described in detail in a previous publication [13] has been used in the present work for the evaluation of ϕ. The only difference is that in the present case a monochromatic radiation source was used instead of a polychromatic UV radiation that was used in that mentioned previous research. This model leads to the following final expression:

$$[G] = [G]_0 - \frac{\phi}{V} \int_0^t W_{abs} \, dt \tag{6}$$

where W_{abs} is the radiation flow rate absorbed by the solution at any reaction time t, and V is the reactor volume. The procedure for the Wabs determination is also described in the aforementioned previous paper [13]. For this purpose, a radiation source model, which describes the distribution of radiant energy within the reactor was used, being the Line Source Spherical Emission Model [14] the selected model.

Once Wabs was determined at any reaction time, the term $\int W_{abs} \, dt$ was calculated numerically since it cannot be solved analytically because the flow rate absorbed varied with the reaction time. Thus, for every [G] the experimental data (Wabs, t) were fitted to a polynomial expression by least squares regression and the resulting function was integrated. With the integral terms evaluated, and according to Eq. (6), a plot of the gallic acid concentration [G] versus the corresponding term $\int W_{abs} \, dt$ should lead to a straight line, of intercept $[G]_0$ and negative slope ϕ/V. From this slope, the overall quantum yield ϕ of the photoreaction can be immediately evaluated.

Following a regression analysis, the slopes ϕ/V were determined, which provided the true overall quantum yields ϕ, which are also included in Table 1: they range from 2.9×10^{-3} mol E^{-1} at pH 2 to 1.29×10^{-2} mol E^{-1} at pH 7. Again, it is observed the increase of this kinetic parameter
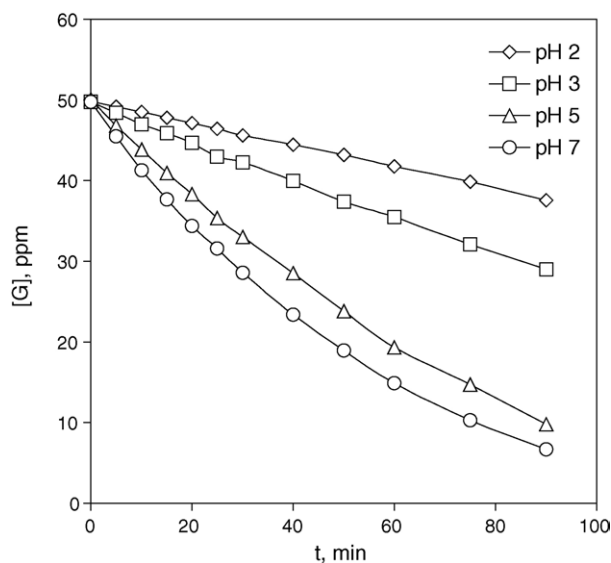

Fig. 1. Gallic acid concentration decay in oxidation experiments by UV radiation alone at 20 °C. Influence of pH.

Table 2
Gallic acid oxidation experiments by the combination UV/H$_2$O$_2$

Experiment	pH	H$_2$O$_2$ × 10^3 (M)	X$_{90}$ (%)	k_{UP} × 10^3 (min^{-1})	k_R × 10^3 (min^{-1})
UVH-1	5	1	89.6	16.3	2.4
UVH-2	5	2	100[a]	22.2	8.3
UVH-3	3	1	90.3	16.9	11.0

[a] Total degradation obtained at 75 min of reaction.

when the pH is increased, as was already obtained for the pseudo-first-order rate constant k_{UV}.

The obtained quantum yields values show that the photodecomposition of gallic acid seems to be a slow process, and therefore, although UV irradiation can be used for disinfection purposes, the elimination of this pollutant substance might need the presence of a second oxidant in an AOP system.

Due to this moderate efficiency in the decomposition of gallic acid by a single UV radiation, photodegradation experiments of this substance with the same initial concentrations (50 ppm) and temperature (20 °C) were later conducted at pH 5 in the presence of hydrogen peroxide (with initial concentrations of $1 × 10^{-3}$ and $2 × 10^{-3}$ M) in the combined UV/H$_2$O$_2$ process. These experiments are depicted in Table 2 (Experiments UVH-1 and UVH-2), while Fig. 2 shows the decrease obtained in the gallic acid concentration as a function of irradiation time. It can be clearly observed the positive influence of this combined system UV + H$_2$O$_2$ in comparison to the single photodegradation (Experiment UV-3 performed at the same pH and temperature which is showed in Fig. 2 as well); and also, the positive influence of the H$_2$O$_2$ initial concentration on the process, with an increasing disappearance rate when this initial concentration is increased.
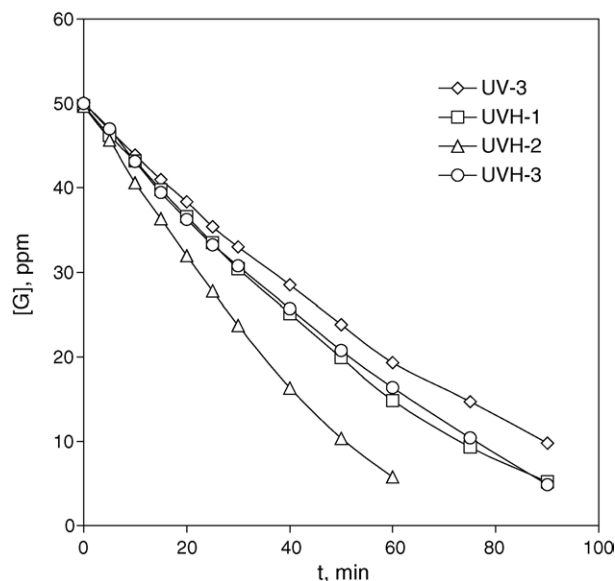

Fig. 2. Gallic acid concentration decay in oxidation experiments by the UV/H$_2$O$_2$ system. Influence of initial H$_2$O$_2$ and pH. Experimental conditions given in Table 2.

These trends are confirmed with the evaluation of the pseudo-first-order rate constants k_{UP} for this combined process, whose deduced values are also depicted in Table 2. Thus, values of $1.63 × 10^{-2}$ and $2.22 × 10^{-2}$ min^{-1} were deduced for the combination UV/H$_2$O$_2$ (Experiments UVH-1 and UVH-2); and $1.39 × 10^{-2}$ min^{-1} was obtained for the single UV radiation process (Experiment UV-3) at the same operating conditions.

These findings demonstrate that gallic acid decay is enhanced in relation to the single photoreaction by the OH$^\bullet$ generated by the presence of hydrogen peroxide. In effect, the whole mechanism of this combined process is constituted by the direct photoreaction (Eq. (1)), which is supplemented by the radical reaction between the organic compound and the OH$^\bullet$ (Eq. (4)), these OH$^\bullet$ being produced during the direct photolysis of hydrogen peroxide (Eq. (2)).

Another experiment of gallic acid oxidation by the combination UV/H$_2$O$_2$ was also performed with an initial concentration of H$_2$O$_2$ of $1 × 10^{-3}$ M but at pH 3 (Experiment UVH-3 in Table 2) with the aim of establishing the potential effect of the operating variable pH on the pollutant destruction in this AOP. Its concentration decay versus reaction time is also represented in Fig. 2, and the corresponding resultant value of the pseudo-first-order rate constant k_{UP} is also given in Table 2. As it is seen, similar degradation results are obtained for both experiments (UVH-3 and UVH-1), which seems to be in apparent contradiction with the results obtained in the single photochemical process by the UV radiation alone, where there was a direct effect of the pH on the oxidation rate.

The explanation of this result can be found by considering the global mechanism of the UV/H$_2$O$_2$ combined process, which leads to two opposite effects. On one hand, the direct photolysis (Eq. (1)) is enhanced when the pH is increased, as it has been discussed previously. But, at the same time, together with reactions (2) and (4), it must be taken into account the self-decomposition reaction of hydrogen peroxide, which also participates in this combined process:

$$2H_2O_2 \rightarrow H_2O + O_2 \tag{7}$$

As Chu [12] pointed out, this reaction (7) is strongly dependent on the pH: its rate increases when the pH is increased, and then, dominates over reaction (2), with a lower production of OH$^\bullet$. In addition, molecular O$_2$ presents a lower oxidizing power than the OH$^\bullet$.

In conclusion, the increase in the pH enhances the direct photolysis rate and increases its contribution to the global photochemical process, with a higher decomposition rate of the organic substance. But simultaneously, it also enhances the self-decomposition of hydrogen peroxide, which leads to a lower generation of OH$^\bullet$, and subsequently with a decrease in the contribution of the radical pathway to the global oxidation reaction, resulting in a lower degradation rate of the organic pollutant. The final result in a particular case depends on the partial contribution of both pathways to the global pro-

Table 3
Gallic acid oxidation experiments by Fenton's reagent and the photo-Fenton system

Experiment	$[G]_0 \times 10^4$ (M)	$[H_2O_2]_0 \times 10^3$ (M)	$[Fe^{2+}]_0 \times 10^5$ (M)	pH	X_5 (%)	X_{40} (%)	k_F (min^{-1})
F-1	5.9	2.5	2.5	3	49	79	0.127
F-2	5.9	1	2.5	3	26	64	0.070
F-3	5.9	1	5	3	56	76	0.149
F-4	2.9	1	2.5	3	47	79	0.258
F-5	5.9	1	2.5	2	19	54	0.040
UVF-1	5.9	1	2.5	3	26	93	0.072[a]
UVF-2	5.9	1	5	3	49	100[b]	0.132[a]

[a] In the photo-Fenton experiments k_F corresponds to k_{UF}.
[b] Total degradation obtained at 34 min of reaction.

cess (direct photolysis and radical reaction, which is directly affected by the self-decomposition of hydrogen peroxide). Then, in the present case, both reactions seem to present a similar importance, and therefore, the decay rate of gallic acid by the combined UV/H$_2$O$_2$ system is not affected by the pH in the range studied.

In this combined photo-decomposition process, it is relevant to establish the relative contribution to the global degradation rate of these two main pathways. They can be evaluated by a simple mechanism already proposed [15], in which the overall reaction rate r_T is assumed to be the addition of the rate corresponding to the previous mentioned reactions, direct photolysis r_U and radical reaction r_R, in the form:

$$-r_T = -\frac{[dG]}{dt} = -(r_U + r_R) = (k_{UV} + k_R)[G] = k_{UP}[G] \tag{8}$$

According to Eq. (8), the rate constants for the radical reaction k_R are easily deduced by subtracting the k_{UV} value obtained for the experiment without H$_2$O$_2$ from the k_{UP} values. Thus, the subtraction of 13.9×10^{-3} min^{-1} (Experiment UV-3 at pH 5) leads to 2.4×10^{-3} and 8.3×10^{-3} min^{-1} for k_R in Experiments UVH-1 and UVH-2, respectively, showing that the direct photolysis had a greater contribution to the overall reaction than the radical reaction, especially at lower initial hydrogen peroxide concentrations.

More specifically, the contribution to the overall reaction rate of the direct photolysis was 85.2% compared to the 14.8% of the radical pathway in Experiment UVH-1, although in Experiment UVH-2 with more H$_2$O$_2$, it was 62.6% while the radical pathway contributed the remaining 37.4%. On the other hand, for experiments performed at pH 3, the subtraction of $k_{UV} = 5.9 \times 10^{-3}$ min^{-1} obtained in Experiment UV-2 leads to a $k_R = 11.0 \times 10^{-3}$ min^{-1} for Experiment UVH-3, indicating a higher contribution of the radical reaction at this pH; that is, a 65% versus a 35% of the direct photolysis.

3.2. Gallic acid decomposition by Fenton's reagent and the photo-Fenton system

The gallic acid degradation by OH$^\bullet$, with these radicals being generated by the Fenton's reagent was investigated in a next step. As is commented in Section 1, this is a very fre-

quent system used for the generation of OH$^\bullet$ through reaction (3), which later attack the organic compound and produce its chemical decomposition (Eq. (4)).
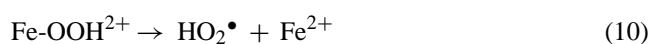
Table 3 compiles the experiment performed, by varying the initial concentrations of gallic acid, hydrogen peroxide and ferrous ions, as well as the pH. The gallic acid removals obtained at two selected reaction times (5 and 40 min) are also depicted in this Table 3, X_5 and X_{40}, respectively. From that Table 3, a direct effect of the initial hydrogen peroxide concentration is observed (Experiments F-1 and F-2); that is, an increase in the removal of the organic pollutant is obtained when this operating variable is increased: thus, removals of 49% versus 26% at 5 min, and 79% versus 64% at 40 min are deduced when $[H_2O_2]_0$ is varied from 2.5×10^{-3} to 1×10^{-3} M. A similar effect is observed for the increase in the ferrous ions initial concentration (Experiments F-2 and F-3), where an increase in the removal is obtained at these selected times of reaction. Finally, higher degradation rates are observed when the initial gallic acid concentration is lower (Experiments F-2 and F-4, respectively) as could be expected. Some of these direct effects have also been reported by other authors in similar studies with this reaction system [16–18].

Fig. 3 shows the gallic acid decay curves with reaction times in the experiments performed at pH 3 (Experiments F-1 to F-4). It is clearly seen that a more significant decrease in the concentration of gallic acid occurred in the first reaction minutes, with a lower rate of decrease in the following minutes. This concentration evolution can be explained by taking into account the whole reaction mechanism for the Fenton's system. In effect, all the experiments are performed in excess of hydrogen peroxide as compared to ferrous ions (see Table 3), and therefore, the OH$^\bullet$ are produced rapidly through reaction (3), which is followed by a fast oxidation of the organic substance through reaction (4).

However, when most of the Fe(II) has been consumed, the Fe(III) generated in reaction (3) reacts with the remaining hydrogen peroxide by forming the peroxo complex:

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}OOH^{2+} + H^+ \tag{9}$$
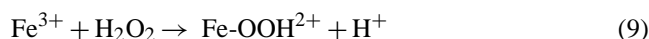
which later decomposes very slowly into Fe(II):

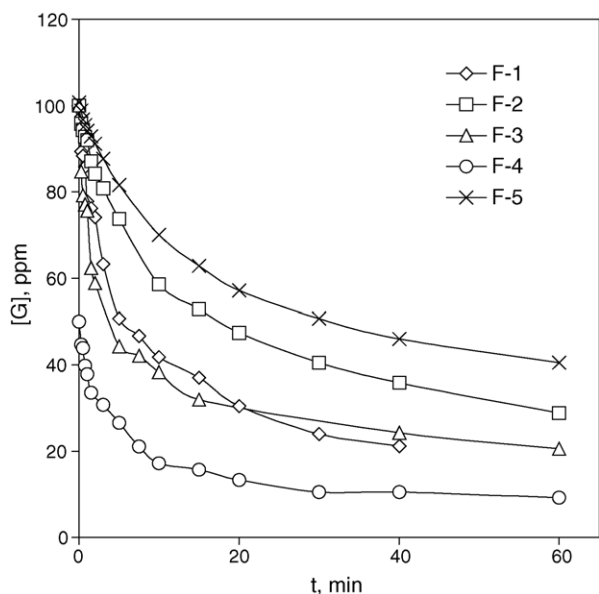$$Fe\text{-}OOH^{2+} \rightarrow HO_2^\bullet + Fe^{2+} \tag{10}$$

Fig. 3. Gallic acid concentration decay in oxidation experiments by Fenton's reagent. Influence of initial operating variables. Experimental conditions given in Table 3.

Although Fe(II) is regenerated in the process, the low rate of both reactions (9) and (10) explain the lower gallic acid overall decomposition rate at advanced reaction times. Moreover, other radicals, like perhydroxyl radicals, are formed through reaction (10), as well as through the following reaction, which also takes place:

$$H_2O_2 + OH \rightarrow HO_2^\bullet + H_2O \qquad (11)$$
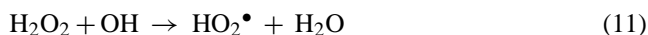
These radicals reduce the oxidation power of the system, because the oxidation potential relative to chlorine of hydroxyl and perhydroxyl radicals are 2.06 and 1.25 V, respectively [19]. Finally, there are several competition reactions that also consume OH$^\bullet$, like reaction with Fe(II) [20]:

$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^- \qquad (12)$$

Or reactions with the intermediates products formed from the organic compound decomposition when the process advances, which hinder the decay of the parent compound [18]. In conclusion, there are several factors that negatively contribute to the decrease of the gallic acid global decomposition rate at higher times of reaction, as the experimental results demonstrate.

On the other hand, as it has been widely reported, the optimal range of pH for Fenton's reaction is between 3 and 3.5 [9,19]. Therefore, the pH selected for most of the experiments in this work was 3. In order to test the effect of this operating variable when it was decreased, another experiment (Experiment F-5 in Table 3) was carried out at the same operating conditions than Experiment F-2, but at pH 2. From the comparison of the removals obtained in both experiments, it is seen a lower removal at pH 2 than at pH 3: 19% versus 26%

after 5 min of reaction, and 54% versus 64% at 40 min of reaction.

This decrease in the degradation at lower pHs can be explained by taking into account that at lower pHs, like pH 2, the scavenging effect of OH$^\bullet$ by hydrogen ions becomes important [21], and the regeneration of Fe(II) by the reaction of Fe(III) with H_2O_2 (Eqs. (9) and (10)) is inhibited by a higher concentrations of protons. Moreover, this lower efficiency at pH <3 is also due to the formation of the complex specie [Fe(II) $(H_2O)_6]^{2+}$ which reacts more slowly with H_2O_2 than [Fe(II) $(OH)(H_2O)_5]^+$, and therefore, produces less amount of OH$^\bullet$ [22]. In conclusion, the generation rate of OH$^\bullet$ is slower at lower pH.

Following the suggestions of several authors [18,23], the Fenton's reaction is well represented by using pseudo-first-order kinetics for the initial times, although some authors like Guedes et al. [17] proposed second-order kinetics for the first period. The evaluation of these initial decay rates allows us to quantify the differences among the several oxidation processes used in this study for the degradation of gallic acid: UV and UV/H_2O_2 systems; Fenton's reagent, and the photo-Fenton system that will be discussed later. After regression analysis, the values obtained for these rate constants k_F are also summarized in Table 3. These values for the pseudo-first-order rate constants confirm the trends above discussed for the influence of the operating variables, including the decrease in the removal rate obtained in the Experiment F-5, which was carried out at pH 2. Also, the comparison with the previous systems, UV radiation alone and the combination UV/H_2O_2, reveals a more efficiency of the Fenton's reagent in the removal of this organic pollutant (see k_{UV} and k_{UP} values in Tables 1 and 2).

Once the pseudo-first-order rate constants k_F were determined, a kinetic study was carried out in order to evaluate the specific rate constants k_{OH} for the reaction between gallic acid and these OH$^\bullet$ generated in the Fenton's reaction, which value has not been reported in the literature so far. For this purpose, the competition kinetics model described in detail in a previous paper was followed [15]. This procedure has also previously been used with success by several authors for the oxidation of organic pollutants by several oxidants like ozone, UV radiation and OH$^\bullet$ as in the present case [24,25].

This procedure consisted in the simultaneous degradation of mixtures of two organic compounds by any of the mentioned oxidants, with the first organic compound acting as the reference compound, whose rate constant with the oxidant is known; and the second one being the target compound, whose rate constant for the reaction with the oxidant must be determined. In the present study, OH$^\bullet$ (generated by the Fenton's reaction) were the oxidant agent, the target compound was gallic acid and the reference compound was acetophenone. As was previously mentioned, the kinetic rate constant for its reaction with OH$^\bullet$ is well known [4]: 6×10^9 l mol^{-1} s^{-1}.

The application of this model is described in detail in the above mentioned publication [15] and leads to the final

expression:

$$\ln\left(\frac{[G]_0}{[G]}\right) = \frac{k_{OH-G}}{k_{OH-R}}\ln\left(\frac{[R]_0}{[R]}\right) \tag{13}$$

where k_{OH-G} and k_{OH-R} represent the rate constants for the reaction between $OH^\bullet$ and the target (gallic acid) and reference compound (acetophenone), respectively. According to this Eq. (13), a plot of $\ln([G]_0/[G])$ against $\ln([R]_0/[R])$ should be a straight line whose slope is the ratio of rate constants. As k_{OH-R} is known, k_{OH-G} can then be determined.

Two experiments were performed at 20 °C and pH 3 with different initial concentrations of both compounds (1×10^{-4} and 5×10^{-5} M) and with $[H_2O_2]_0 = 2.5 \times 10^{-3}$ M and $[Fe^{2+}]_0 = 5 \times 10^{-5}$ M. The experimental points obtained were plotted according to Eq. (13), and after least squares regression analysis, the slopes k_{OH-G}/k_{OH-R} were determined, these values being 1.86 and 1.80 for both experiments. Then, from the k_{OH-R} value above mentioned (6×10^9 l mol s^{-1}), it is finally deduced for k_{OH-G} in these experiments 11.2×10^9 and 10.8×10^9 l mol^{-1} s^{-1}, respectively. Thus, a mean value of $11.0 \pm 0.1 \times 10^9$ l mol^{-1} s^{-1} can be finally proposed for the reaction between gallic acid and $OH^\bullet$, which lies in the range of 10^7–10^{10} l mol^{-1} s^{-1}, values reported by Buxton et al. [4] for similar reactions between organic compounds and $OH^\bullet$.

The Fenton's reaction could be significantly enhanced if UV radiation is involved in the process, in the so-called photo-Fenton system. For the investigation of this effect, two gallic acid oxidation experiments (Experiments UVF-1 and UVF-2) were conducted by the simultaneous action of UV radiation and Fenton's reagent at 20 °C and pH 3 with an initial concentration of gallic acid of 5.9×10^{-4} M. The removals obtained at 5 and 40 min of reaction, as well as the pseudo-first-order rate constants k_{UF} for the initial times of reaction are reported in Table 3. Moreover, Fig. 4 shows the degradation curves with reaction time for these experiments together with their corresponding experiments for the Fenton's reaction without UV radiation, which were carried out at the same operating conditions, that is pH 3 and same initial concentrations of gallic acid, hydrogen peroxide and ferrous ion (Exptserimen F-2 and F-3, respectively).

From Table 3 and Fig. 4 it is interesting to note that a similar oxidation rate is observed in the initial reaction times during both processes (Fenton's and photo-Fenton systems), with similar removals at short reaction times (X_5). However, a significant improvement is obtained in the photo-Fenton system for the overall removal of gallic acid at higher reaction times (X_{40}): 93% versus 64% in Experiments UVF-1 and F-2, and total elimination in Experiment UVF-2 at 40 min versus 76% in Experiment F-3. These findings suggest an increasing contribution of the radical pathway when the photo-Fenton system advances, due to an additional generation of $OH^\bullet$.

Again, the reaction mechanism of this process explains this improvement in the overall removal. Thus, in addition to reactions (1) and (3), corresponding to the direct pho-
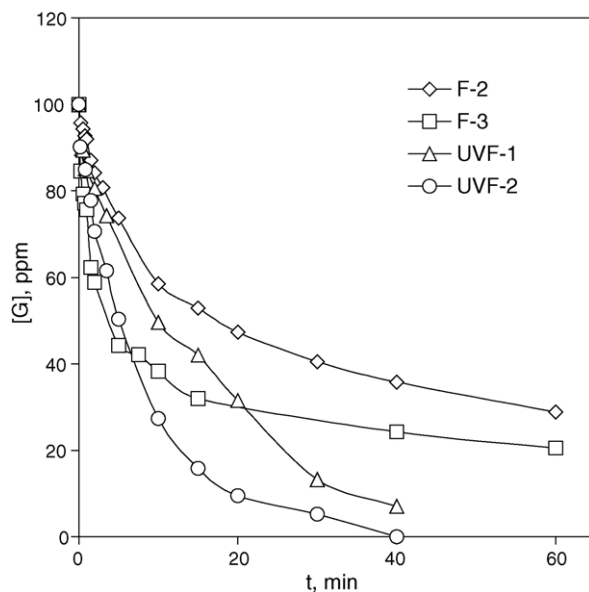

Fig. 4. Comparison between gallic acid concentration decay in the oxidation by Fenton's reagent and the photo-Fenton system. Experimental conditions given in Table 3.

todecomposition and the generation of $OH^\bullet$ by the Fenton's reagent, respectively, it must be now considered the $OH^\bullet$ generation reaction due to the photolysis of H_2O_2 which is represented by Eq. (2). Moreover, the Fenton's reaction can be made catalytic in presence of UV radiation, because in aqueous solutions, the generated Fe(III) undergoes spontaneous hydrolysis with water and form several species, mainly the monohydroxy complex Fe(OH)$^{2+}$. This specie is capable to produce Fe(II) and $OH^\bullet$ directly [26] through the photo-sensitization reaction:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^\bullet \tag{14}$$

and constitutes a supplementary source of $OH^\bullet$. Additionally, the generation of Fe(II) in this Eq. (14) indirectly induces the Fenton's reaction, providing more $OH^\bullet$ through reaction (3).

In conclusion, the decay in the gallic acid concentration when is degraded by the photo-Fenton system resulted in two possible pathways: direct photolysis (Eq. (1)) and radical reaction (Eq. (4)). These $OH^\bullet$ are generated through three possible sources: photolysis of hydrogen peroxide (Eq. (2)), the original Fe(II)/H_2O_2 reaction (Eq. (3)), and Fe(III) sensitization (Eq. (14)), which probably is the dominant mechanism for producing $OH^\bullet$ at advanced reaction times, when the initial stage is finished.

It is also interesting to determine the hydroxyl radical pathways contribution to this global process, which can be evaluated again by using an expression similar to Eq. (8):

$$-r_T = -\frac{[dG]}{dt} = -(r_U + r_R) = (k_{UV} + k_R)[G] = k_{UF}[G] \tag{15}$$

where r_U represents the contribution of the direct photochemical reaction, and r_R the contribution corresponding to the

radical pathway, with the radicals now generated through the several reactions already described. Therefore, and according to the previous considerations, this reaction rate r_R (and subsequently its rate constant k_R) is expected to be higher than in the former system UV/H_2O_2 for experiments performed with similar initial concentration of hydrogen peroxide, where the radicals were only generated through one source (reaction (2)).

Thus, and following Eq. (15), the rate constant $k_U = 5.9 \times 10^{-3}$ min^{-1} corresponding to Experiment UV-2 (which was performed at pH 3 and with single UV radiation) is subtracted from the values of k_{UF} given in Table 3 for Experiments UVF-1 and UVF-2, also carried out at pH 3. This procedure provides the values of $k_R = 0.066$ min^{-1} for Experiment UVF-1 and 0.126 min^{-1} for Experiment UVF-2, which clearly confirm the previous hypothesis of the much higher expected values for k_R in the photo-Fenton system in comparison to that of the UV/H_2O_2 combination, that was $k_R = 11 \times 10^{-3}$ min^{-1} for Experiment UVH-3 (also performed at the same pH 3).

Finally, and similarly to the UV/H_2O_2 process, the partial contributions of the photochemical and radical pathways can be established in this photo-Fenton system: thus, the contribution of the direct photochemical reaction is much smaller, with values of 8.2% and 4.5% in Experiments UVF-1 and UVF-2, respectively, while the corresponding contributions of the radical pathways are 91.8% and 95.5%, respectively. This predominant contribution can be attributed to the synergic effect of the different reactions generating OH$^\bullet$, which at the same time increase the efficiency of the photo-Fenton system. Another reason could be that most of the energy emitted by the radiation source is mainly absorbed by hydrogen peroxide and Fe(III), leading to more generation of OH$^\bullet$, instead of being absorbed by the organic compound for a direct photochemical decomposition reaction.

4. Conclusions

From the results obtained in this work, it can be concluded that the influence of the pH in the range 2–7 on the photodegradation of gallic acid in ultrapure water by a monochromatic UV radiation alone at 20 °C was positive, with increasing decay rates when the pH is increased. The pseudo-first-order rate constant varied from 3.1×10^{-3} to 21.8×10^{-3} min^{-1}, and the quantum yields varied from 2.9×10^{-3} to 12.9×10^{-3} mol E^{-1} for pH 2 and 7, respectively. In the combined UV/H_2O_2 process, the enhancement in the photodegradation rate promoted by the presence of OH$^\bullet$ was clearly demonstrated, and the contribution of the radical pathway resulted in a 15% and a 37% for the lower and higher initial hydrogen peroxide concentration experiments.

In the Fenton's reagent system, a higher rate of decay was observed in the first minutes of reaction and the pseudo-first-order rate constants for this initial period varied from 0.040 to 0.258 min^{-1}, depending on the pH and initial concentra-

tions of gallic acid, hydrogen peroxide and ferrous ion. Later, when the reaction advanced, the rate of gallic acid decay decreased, and the removal obtained at 40 min of reaction varied from 54% to 79%, depending again on the initial operating conditions. A competition kinetics model, which used acetophenone as reference compound, allowed us to evaluate the rate constant for the reaction between gallic acid and OH$^\bullet$, which obtained value was $11.0 \pm 0.1 \times 10^9$ l mol^{-1} s^{-1}.

The photo-Fenton system provided similar removals of gallic acid at initial reaction times than the Fenton's reaction, but a significant increase at advanced reaction times, due to the generation of OH$^\bullet$ through several reactions. Thus, the contribution of the radical pathway to the global decomposition resulted in values higher than 90%, while the direct photodecomposition reaction contributed less than 10%. Finally, a global comparison of the efficiency of the several chemical oxidation systems used (UV irradiation, UV/H_2O_2, Fenton's reagent and photo-Fenton system) was conducted and the results obtained revealed that the most efficient method in the total removal of gallic acid was the photo-Fenton system.

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