APPLIED
CATALYSIS
B: ENVIRONMENTAL

# Accelerated photo-oxidation of concentrated *p*-coumaric acid in homogeneous solution. Mechanistic studies, intermediates and precursors formed in the dark

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## Abstract

This study shows that *p*-coumaric acid undergoes accelerated degradation via photo-assisted Fenton reactions. Simulated solar radiation (90 mW/cm$^2$) promotes the full mineralization of a concentrated solution of *p*-coumaric acid (420 mg C/l) in less than 15 min when suitable times for the oxidant addition were used in the presence of very low Fe-ion concentration (4 mg Fe-ion/l). The mineralization of *p*-coumaric acid has been studied as a function of the common variables as pH, concentration of reagents and of the substrate used. The reduction of the total organic compound (TOC) was observed to be a function of the surface-to-volume (*s/v*) ratio on the reaction vessel due to the formation of light induced radicals in the solution surface. Decoloration of these concentrated solutions were observed in <1 min by stopped-flow techniques. The most important reaction intermediates were determined by HPLC, GC–MS and FTIR suggesting a reaction network for the degradation process. The Fenton reagent is shown to form precursor intermediates which are susceptible to degradation under light. Degradation performed via alternate dark and light cycles showed the importance of the dark precursor species. Implications of this observation as an energy saving device during the mineralization process is accounted for in this study. © 1998 Elsevier Science B.V.

*Keywords:* *p*-Coumaric acid mineralization; Accelerated degradation; Catalysis; Photocatalysis; Oxidant intervention; Decoloration

## 1. Introduction

*p*-Coumaric acid is representative of biorecalcitrant compounds found during olive oil and wine processing creating a pollution problem in the Mediterranean coastal regions [1]. *p*-Coumaric acid belongs to a range of compounds that during degradation produces substances which due to their toxicity inhibit biological treatment of the effluents from the food processing industry. Degradation of this compound has been attempted via ozone [2] and more recently by wet oxidation [3]. However, these treatment methods are expensive. An energetically less demanding approach under milder conditions is the object of this study. Until now few studies have been carried out on the spectroscopy and photochemistry of coumaric acids [4,5].

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This study intends to optimize the experimental conditions for p-coumaric acid oxidation via dark Fenton reactions and photo-assisted Fenton processes. It also aims to clear mechanistic studies of the p-coumaric degradation and the nature of the intermediates produced during this process. The oxidizing efficiency in Fenton systems can be greatly enhanced by light since in the dark the reaction has been observed to slow down after conversion of $Fe^{2+}$ to $Fe^{3+}$. Under light, photoreduction of $Fe^{3+}$ to $Fe^{2+}$ takes place with concomitant production of new ·OH radicals [6–9]. The photo-assisted Fenton reaction has been reported to accelerate significantly the degradation rate of many organic pollutants as compared to the more traditional Fenton reactions occurring in the dark [9–16].

This study intends to investigate a) the mineralization of concentrated solutions of p-coumaric acid as found in industrial sites by processes using $Fe^{3+}/H_2O_2$ in the dark and under light irradiation, b) to accelerate this process by a suitable timing of the oxidant addition, c) to explore the main parameters controlling the degradation process, d) to see how the intermediate species formed in the dark activates the decomposition of p-coumaric acid under light irradiation, e) to identify the main reaction intermediates by different analytical techniques and finally f) to minimize the time of illumination when using the photo-assisted Fenton reaction with the consequent saving of energy during the pollutant photo-oxidation.

## 2. Experimental

### 2.1. Materials

p-Coumaric acid (4-hydroxycinnamic acid, A.C.S. [501-98-4]) Aldrich p.a. was used as received. Hydrogen peroxide, catalase and $FeCl_3$ all Fluka p.a. were used without further purification.

### 2.2. Photoreactor and procedures

Photolysis was carried out inside the cavity of a Hanau Suntest solar simulator with a radiant flux of 90 mW/cm² flux and provided with air cooling regulated at ~35°C. The lamp had a λ distribution with about 7% of the emitted photons between 290 and 400 nm. The profile of the photons emitted between 400 and 800 nm followed the lamp spectrum. The photochemical irradiation vessels used were 60 ml cylindrical Pyrex flasks (cutoff λ≈290 nm) each containing 40 ml of reagent solution. The radiant flux was measured with a power meter of Yellow Springs, Colorado, U.S.A. Spectrophotometric analysis for the absorbance of the solutions used during this work was carried out by a Hewlett-Packard 8452 diode-array spectrophotometer.

### 2.3. Analysis in solution and techniques employed

The total organic carbon (TOC) was monitored via a Shimadzu 500 instrument equipped with an ASI automatic sample injector. Detection of $CO_2$ and $O_2$ was performed via a Carlo Erba G. C. provided with a thermal conductivity detector using a Poropak Q and a molecular sieve column, respectively. He was used as a carrier gas. The $O_2$ content of the solution was monitored by a YSI Model 5300 probe (Clark electrode). The end point for the consumption of $H_2O_2$ in the solution was assessed by means of the Merckoquant-test® [13]. This test determines the oxidant concentration between 0 and 25 mg/l. Stopped-flow measurements have been performed via an Applied Photophysics M-2 unit with a 2 mm cell to identify the changes in OD when p-coumaric acid, $Fe^{3+}$ and $H_2O_2$ are mixed at times <1 min.

An HPLC (Varian 9065 Diode Array) was used for identification of reaction intermediates. The peaks observed for the reaction intermediates were referenced with appropriate external standards. Quantification was based on the integrated band component of each compound. Analysis of oxalic and oxaloacetic acid was carried out by means of an H-801 column (Interaction) in an isocratic mode at 60°C. The eluant was $H_2SO_4$ (0.01 M). For the analysis of 4-hydroxybenzyl alcohol and other aromatics, an ODS-2 column was employed in a gradient mode. The eluant was a mixture of $AcONH_4$ (0.03 M) and acetonitrile. GC–MS was also tried for initial identifications. A column FFAP was used with split injection which was found to be suitable for free acids and aromatics in water samples without pretreatment. This instrument was operated in an electron beam mode using a standard library (NIST Mass Spectrum Data Base) containing 65 000 compounds for identification.

Infrared analysis was carried out by means of a Hewlett-Packard Paragon FTIR spectrophotometer. The samples from different degradation times were obtained from concentrating and crystallizing about 160 ml solution during 3 days at 40°C. KBr was used as solid support for the samples.

## 3. Results and discussion

### 3.1. Assessment of the p-coumaric acid degradation through Fenton and photo-Fenton systems

Fig. 1(a) presents the reduction in total organic carbon (TOC) as a function of irradiation time for a solution containing diverse concentrations of p-coumaric acid when Fenton reagent is added consisting of $Fe^{III}$ (2.6 mM) and $H_2O_2$ (10 mM) at pH 2. The open points in Fig. 1 refer to light induced reactions and the full points represent dark reactions. The concentration of p-coumaric acid used in the most concentrated solution 420 mg C/l (3.90 mM) corresponds to the amount of p-coumaric acid found in effluents close to the industrial sites. The $H_2O_2$ has been added hourly and the concentration of this reagent was monitored via the Merckoquant® paper (see Section 2). The mineralization of the p-coumaric acid is seen to be proceeding in a shorter time period at lower concentrations of substrate as expected. The quasi-exponential decay observed during the degradation in the dark or under light irradiation in Fig. 1 indicates a pseudo first order kinetics strongly dependent on the initial concentration of the substrate. The solution was air-saturated during the course of the reaction. A marked inhibitory effect of the initial concentration of p-coumaric acid on the rate of the photo- degradation is observed in Fig. 1(a). Control experiments adding only $H_2O_2$ induced a decrease of ∼33% in the dark after 25 h (TOC values) for the most concentrated solution. Under light irradiation, the degradation was not complete for this solution after 25 h. The addition of $Fe^{3+}$-ions in the absence of $H_2O_2$ did not induce any significant degradation on the most concentrated p-coumaric acid solution in Fig. 1(a).

The inset in Fig. 1(a) shows the $CO_2$ generation in the dark and under light as a function of time for the solution mentioned above. After ∼7 h under light irradiation TOC, the $CO_2$ evolution attained ∼85%

of the stoichiometric level for the most concentrated solution (trace 2). This is in fair agreement with the TOC decrease observed in the solution in Fig. 1. After 24 h, only 93% of the stoichiometric $CO_2$ is observed due to septum leaks introduced during the samplings within the reaction period. The dark reaction shows that a plateau has been reached at ∼7 h (trace 2) for this concentrated solution when 50% of the p-coumaric acid has not been mineralized. The residual TOC observed for the dark reactions suggests the formation of long lived intermediate(s). This result is consistent with the $CO_2$ results obtained in the dark.

Fig. 1(b) presents the degradation of a solution p-coumaric (3.95 mM) when $Fe^{III}$ (2.6 mM) as a function of the different concentrations of added $H_2O_2$. Curves 1,2 present the dark and light (open and full points) induced degradation with $H_2O_2$ (3 mM). When the concentration of $H_2O_2$ is increased to 10 mM the results seen in traces 3 (dark) and 4 (light) are in experimental error with the results presented in Fig. 1. A significant acceleration of the degradation is observed in traces 5 (dark) and 6 (light) when $H_2O_2$ (30 mM) is used. The initial degradation observed in the dark seems to produce an intermediate in solution precluding further degradation. The residual p-coumaric acid fraction of 50% is further not seen decreasing when increasing the concentration of $H_2O_2$.

Measurements have also been carried out to test the influence of the gas atmosphere on the degradation kinetics reported in Fig. 1(b). Experiments taking a concentration $H_2O_2$ (10 mM) as shown in traces 1,2 did not show any variation in the decay kinetics when the degradation process was carried out in air, $O_2$ or Ar atmosphere. This result shows that $O_2$ is not an effective oxidant in the presence of the Fenton reagent as reported recently for other compounds [9,10].

Fig. 1(c) presents the effect of the Fe-ion concentration on the degradation of a solution p-coumaric acid (3.90 mM) and $H_2O_2$ (10 mM) for $Fe^{III}$-ion concentrations between 0.07 and 8.10 mM. The different concentrations of Fe-used do not seem to influence to a great extent the degradation in the dark (upper traces) or in the case of light irradiation. When the lowest concentration used (0.07 mM or 4 mg Fe-ion/l) the degradation under light is seen to proceed efficiently. The OECD norms for waste water quality allows 2 mg/l of Fe-ions as an upper limit [2]. The fact that a concentrated solutions of p-coumaric acid are

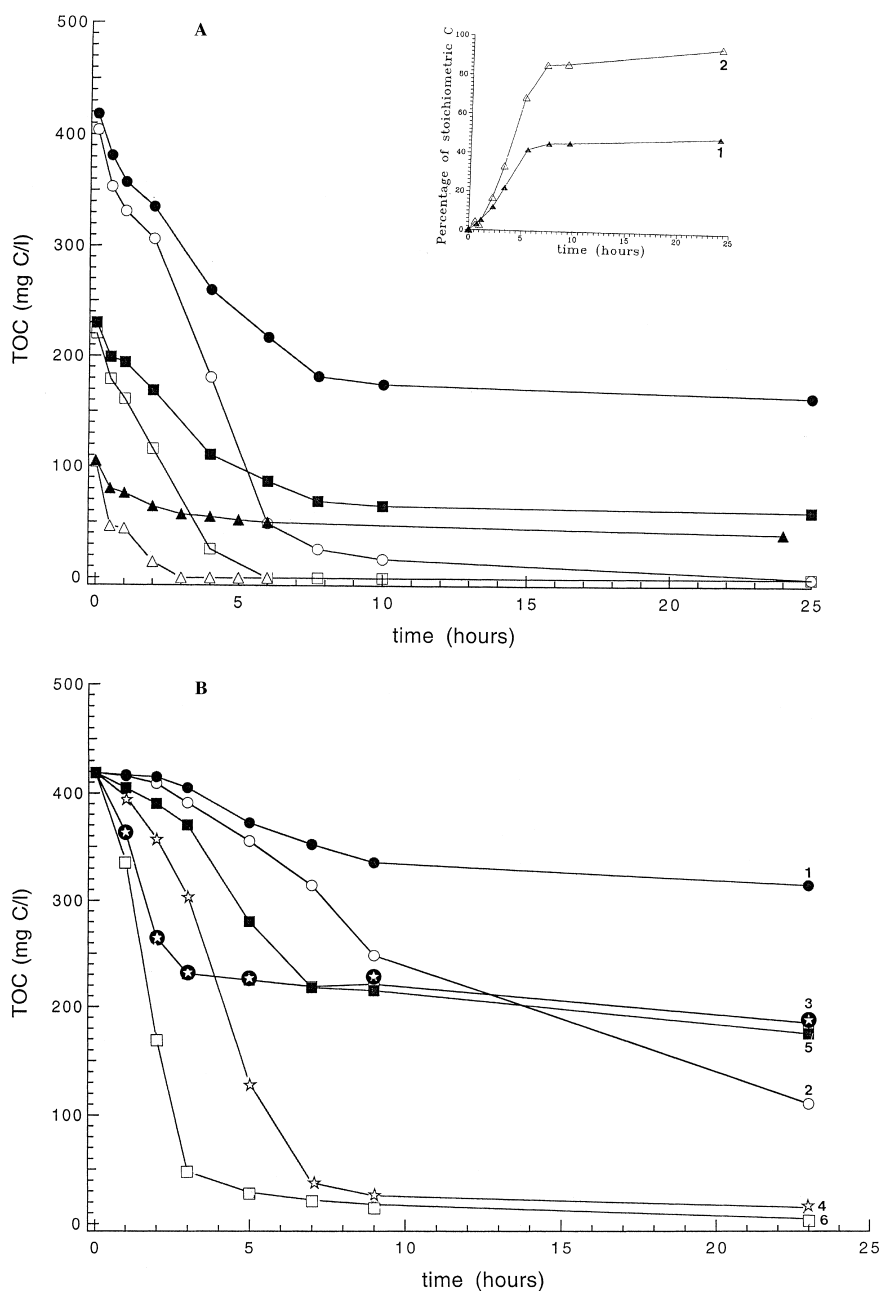Fig. 1. (a) Total organic carbon (TOC) reduction as a function of time for solutions containing $Fe^{III}$(2.6 mM), $H_2O_2$(10 mM, hourly additions) with different concentrations of *p*-coumaric acid (the most concentrated with 3.90 mM) in the dark and under light. The inset shows $CO_2$ evolution for the highest concentration of *p*-coumaric acid used. Dark reactions are noted by full points and light reactions by open points. (b) TOC decrease in the dark (full points) and under light (open points) for a solution *p*-coumaric acid (3.90 mM), $Fe^{III}$(2.6. mM) and $H_2O_2$ added in concentrations: 3 mM (traces 1,2), 10 mM (traces 3,4) and 30 mM (traces 5,6). (c) TOC decrease as a function of time for dark (full points) and light (open points) runs for a concentrated solution of *p*-coumaric acid (3.90 mM), $H_2O_2$ (10 mM) as a function $Fe^{III}$-ion concentrations: 0.07 mM (traces (1,2); 0.54 mM (traces 3,4); 2.7 mM (traces 5,6) and 8.1 mM (traces 7,8). (d) TOC decrease for a diluted solution of *p*-coumaric acid (0.39 mM), $H_2O_2$ (10 mM) showing by full points the degradation in the dark and by open points the degradation under light as function of $Fe^{III}$ concentration: 0.07 mM (traces 1,2), 0.1 mM (traces 3,4) and 2.7 mM (traces 5,6).
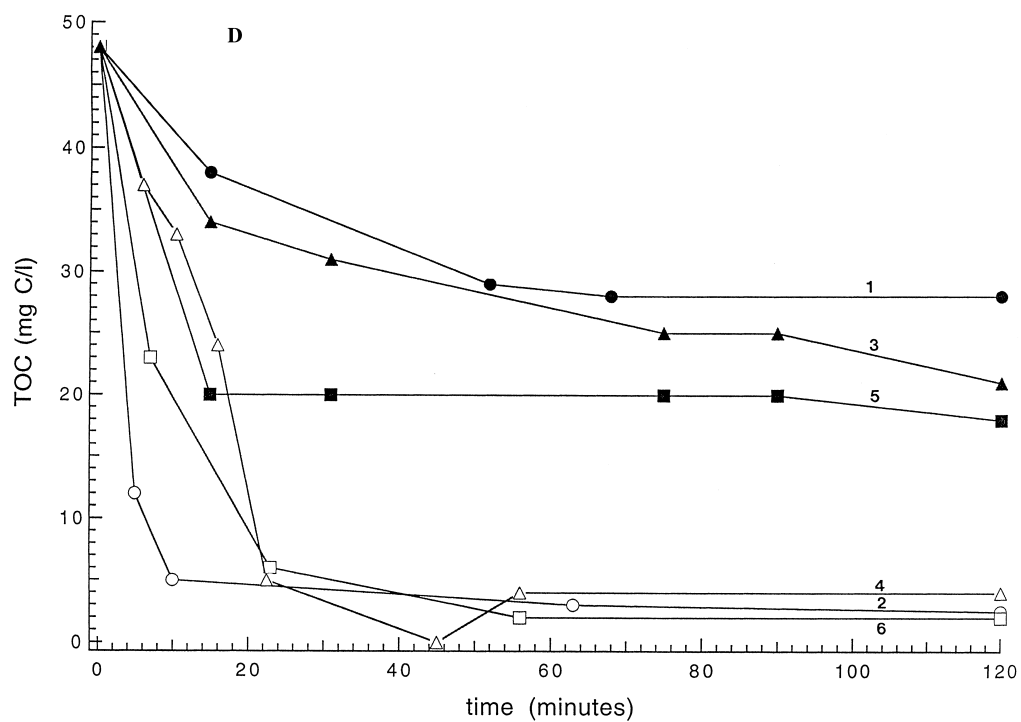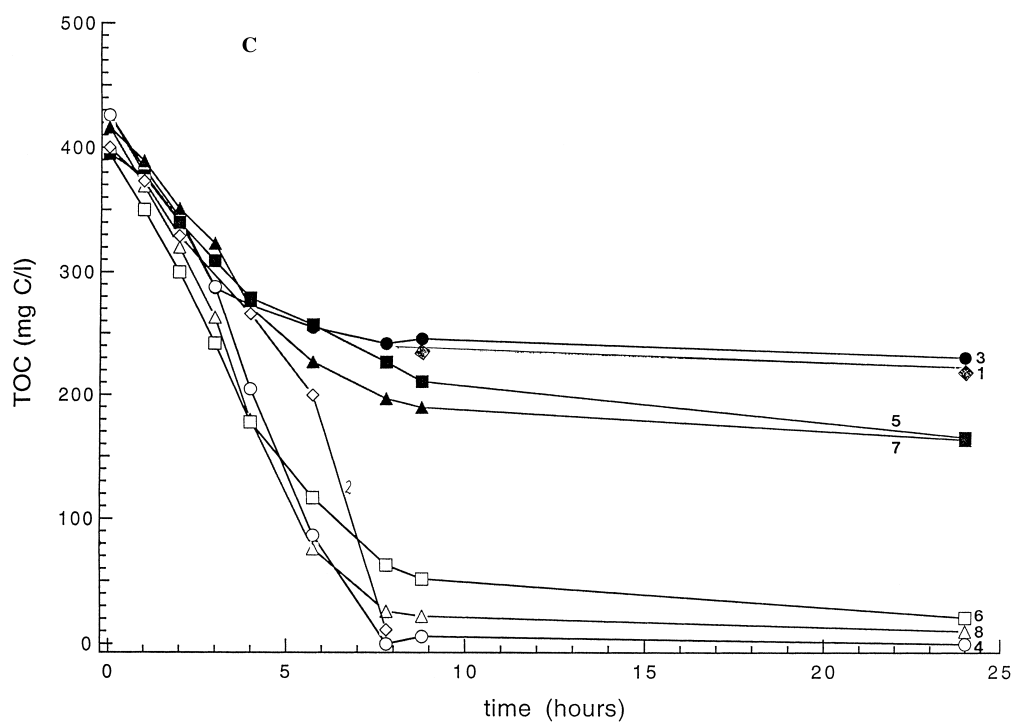
Fig. 1. (Continued)

degraded as seen in Fig. 1(c), strongly suggests that the degradation of diluted solutions of $p$-coumaric acid should proceed well with Fe-ions added in concentrations of 2 mg/l within the discharge limits acceptable for treated waste water and does not create a problem for the sludge discharge [15]. For $p$-coumaric acid concentrations in levels corresponding to the $p$-coumaric pollutant contamination found in large water bodies (40–45 mg C/l or $\sim$0.4 mM) experiments were carried out and the degradation results are reported in Fig. 1(d). It is readily seen that fast degradation under light occurs in $\sim$20 min and a TOC value of 3–4 mg C/l is reached for the solutions used independently of the different initial Fe-ion concentration added. Even lower concentrations of $Fe^{2+}$-ions were observed to catalyzed a kinetically accepted degradation of $p$-coumaric dilute solutions (within the minute range). These low TOC values attained after are in experimental error with values corresponding to the total C-removal in the Shimadzu instrument used. In the dark, a plateau at about 50% of the initial C-content was reached after 2 h reaction. In separate experiments $Fe^{3+}$-, $Fe^{2+}$-ions and $Fe^{3+}$: $Fe^{2+}$=1: 1 were used in three different experiments with a total concentration of 2.7 mM in each case. No

difference in the degradation kinetics was observed in runs similar to the ones reported in Fig. 1(d).

Fig. 2 shows the decoloration of a $p$-coumaric acid solution as followed by stopped-flow measurements. The decrease in the peak of $p$-coumaric acid as a function of $\lambda$ is shown at 3, 9, 15, 20, 30 and 60 s in the captions to this Figure. The inset shows the reduction in the optical density with time from OD=1.8 to $\sim$1.0 within 60 s. Therefore, the decoloration is fast and is observed to be complete after the addition of the initial $H_2O_2$. The base line (trace 6) corresponds to the absorption of the $Fe^{3+}$-ion of the Fenton reagent added in solution. Figs. 3 and 4 shows that the main absorber during $p$-coumaric degradation is the $Fe^{3+}$-ion and that the absorption due to $p$-coumaric acid disappears after a short reaction time.

## 3.2. Accelerated degradation of p-coumaric acid. Timing of the oxidant addition

Fig. 3 presents the TOC decrease of dark degradation (full circles) and light activated reactions (open circles) for a concentrated solution of $p$-coumaric acid when the addition of $H_2O_2$ (40 µl $H_2O_2$) was carried out immediately after the consumption of the oxidant
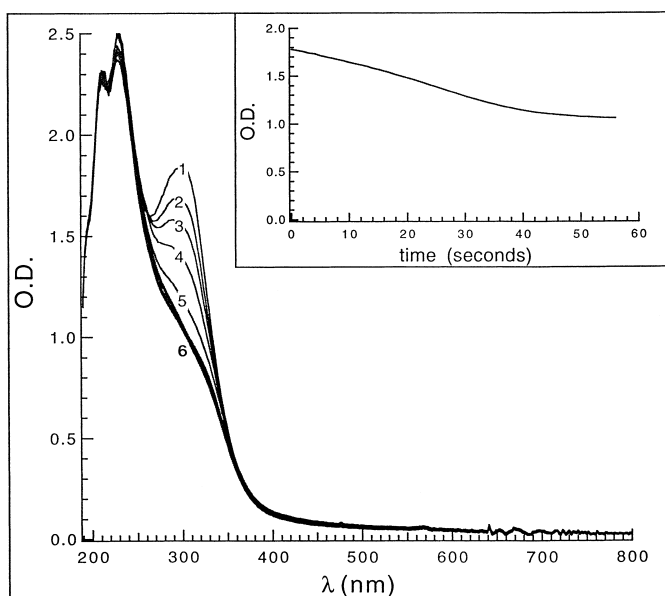


Fig. 2. Stopped-flow measured decoloration (OD=optical density) of $p$-coumaric acid (0.2 mM) under light for a solution containing $Fe^{III}$(2.6 mM) and $H_2O_2$ (10 mM) under light irradiation as a function of time. Traces 1, 2, 3, 4, 5, 6 taken at reaction times: 3, 6, 9, 15, 20, and 30 s, respectively. Trace 6 (base line) represents the absorption due to $Fe^{III}$-ions. The inset represents the OD as a function of reaction time.
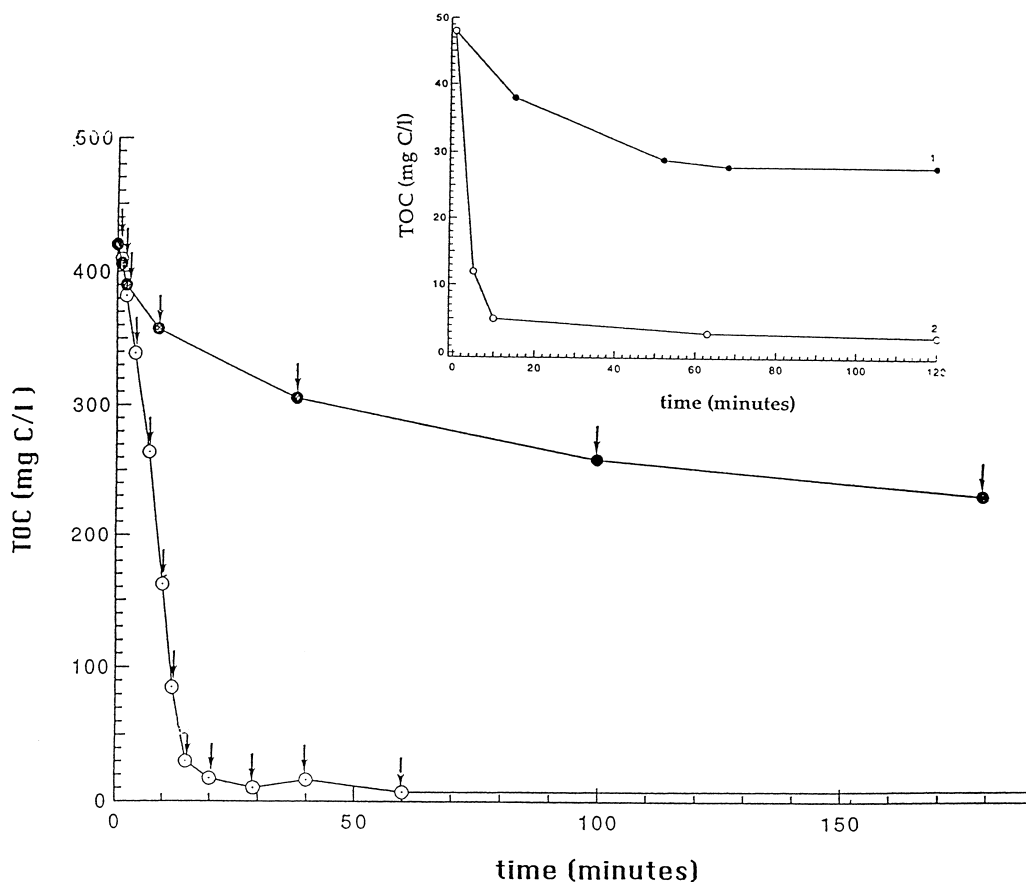
Fig. 3. Total organic carbon (TOC) vs. time during dark and light reactions when $H_2O_2$ is added immediately after the consumption of the previous addition into a solution of $p$-coumaric acid (3.90 mM) and $Fe^{3+}$ (2.6 mM) at pH 2.8. The inset shows the degradation of a diluted solution containing $p$-coumaric (0.43 mM).

from the previous addition as monitored by the Merckoquant® peroxide test. The arrows in the two curves in Fig. 3 show the timing for the oxidant addition. Under these experimental conditions, it is possible to optimize the dynamics of oxidant addition. The initial TOC value was reduced during light induced processes practically zero in ∼20 min. The increased production of OH· radical has been reported recently in the literature [9–12,16–18].

When adding $H_2O_2$ on an hourly basis as shown in Fig. 1(a)–(d) the same degradation level of $p$-coumaric acid was reached within 7 h. In both cases, the stoichiometric amount of $CO_2$ evolved in parallel to the decrease in the TOC showing that no long lived intermediates are formed in solution. Fig. 3 shows that

the abatement of $p$-coumaric acid involves rapid depletion of the oxidant in solution within the initial stage(s) of the degradation. The inset in Fig. 3 shows that the degradation of a dilute solution of $p$-coumaric acid with initial TOC ∼48 mg C/l proceeds faster than at the higher concentrations shown in Fig. 3. The $H_2O_2$ was added in the same amounts and with the same timing. The additions were monitored by the peroxide test.

The $p$-coumaric disappearance could not be followed directly by HPLC since the time of elution in the HPLC spectrogram was ∼20 min and therefore longer than abatement time of $p$-coumaric itself. Therefore, reaction intervals affected the reaction kinetics but did not affect the oxidation stoichiometry.
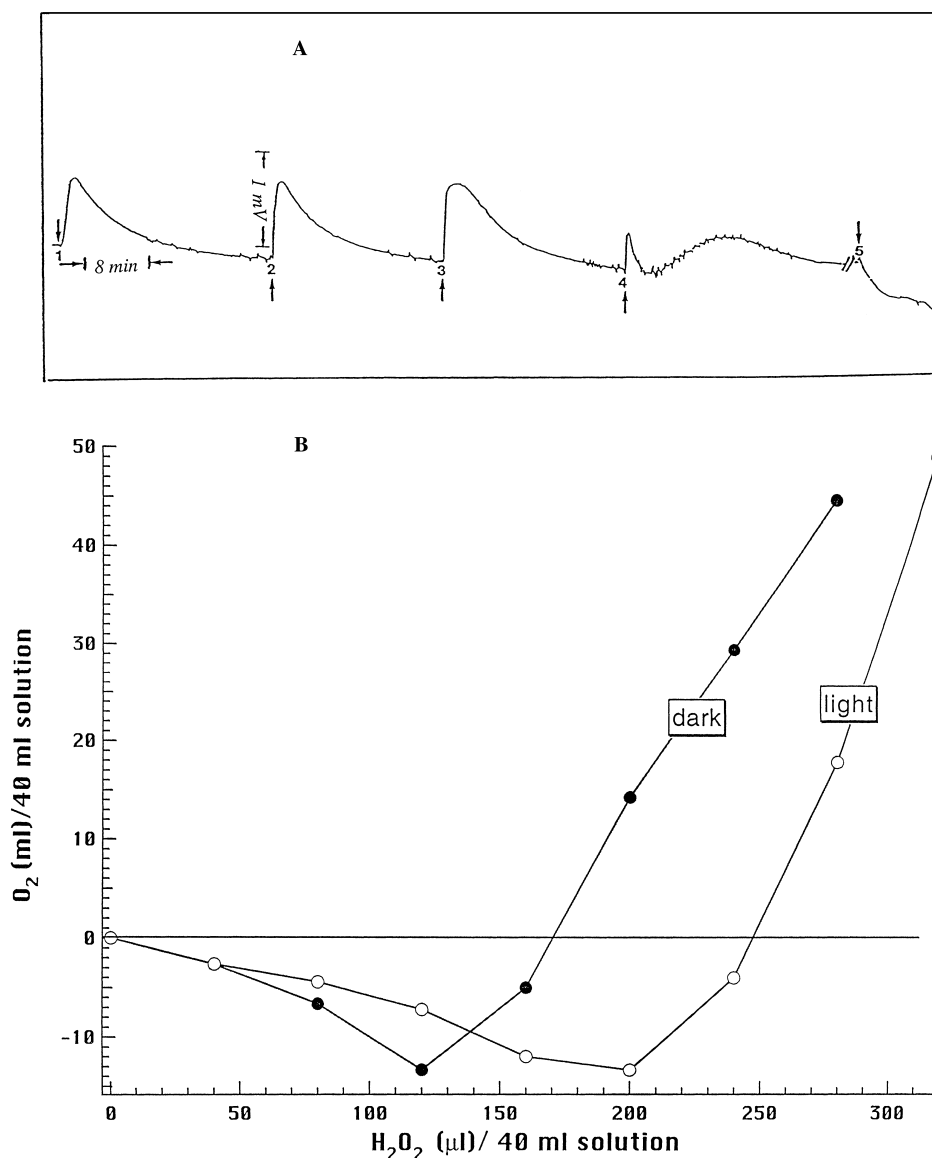
Fig. 4. (a) Voltage cycles vs. time detected via a Clark electrode after additions of $H_2O_2$ (10 mM aliquots at the times indicated by the arrows) to a solution containing *p*-coumaric acid (3.95 mM) and $Fe^{3+}$ (2.6 mM). (b) Oxygen content in a solution of *p*-coumaric acid (3.95 mM) and $Fe^{+3}$ (2.6 mM) in the liquid and gas phase in the dark or under light. $H_2O_2$ is added in 10 mM aliquots (see arrows).

To photo-oxidize 0.158 millimoles of *p*-coumaric acid (Fig. 3) about 2.2 millimoles $H_2O_2$ were required. This is an oxidant pollutant ratio of 14.1 indicating the approximate mineralization stoichiometry
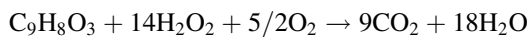
$$C_9H_8O_3 + 14H_2O_2 + 5/2O_2 \rightarrow 9CO_2 + 18H_2O \tag{1}$$

The turnover number of *p*-coumaric acid in terms of mg of acid degraded per mg $H_2O_2$ per hour was 2.3. In dark runs after six injections ($\sim$100 min) a plateau is reached. This is due to the formation of a persistent intermediates under the experimental conditions used. A similar situation has been observed recently by Pignatello [8] during the degradation of 2,4-D.

Experiments by HPLC were not successful when following the peak of *p*-coumaric acid during the degradation process in the Suntest irradiator unless the progress of the reaction is stopped by catalase addition. The time of elution of *p*-coumaric acid in the HPLC was ~20 min. This is four times longer (see below Fig. 6) than the time of complete disappearance of *p*-coumaric acid reported in Fig. 3.

Fig. 4(a) presents the response of a Clark electrode when $H_2O_2$ (10 mM) was added at the arrow positions in a flask containing a 40 ml solution of *p*-coumaric acid and the $Fe^{3+}$-ion. Experiments were carried out in the dark. The increased voltage after each of the first four additions reflected the $O_2$ depletion within the reaction time. The signals during the first four cycles were seen to come back to the base line. Only after the fifth cycle the signals were seen to vary in direction meaning that $O_2$ evolution is taking place.

Fig. 4(b) shows the evolution of $O_2$ in the dark and under light irradiation for a solution as used for Fig. 4(a). Only after addition of 120 µl of $H_2O_2$ was the evolution of $O_2$ observed in the gas phase in the dark. Fig. 4(b) shows that under light irradiation $O_2$ consumption takes place. But this is observed at a higher level of added $H_2O_2$ compared to reactions taking place in the dark. This observation confirms the improved efficiency for the photo-assisted Fenton vs. dark Fenton reaction during *p*-coumaric acid degradation [9,16,17].

### 3.3. Concentration-time profile during p-coumaric photo-oxidative degradation as detected by HPLC and FTIR

Fig. 5 presents the concentration-time profile for the Fenton photo-assisted oxidation of *p*-coumaric
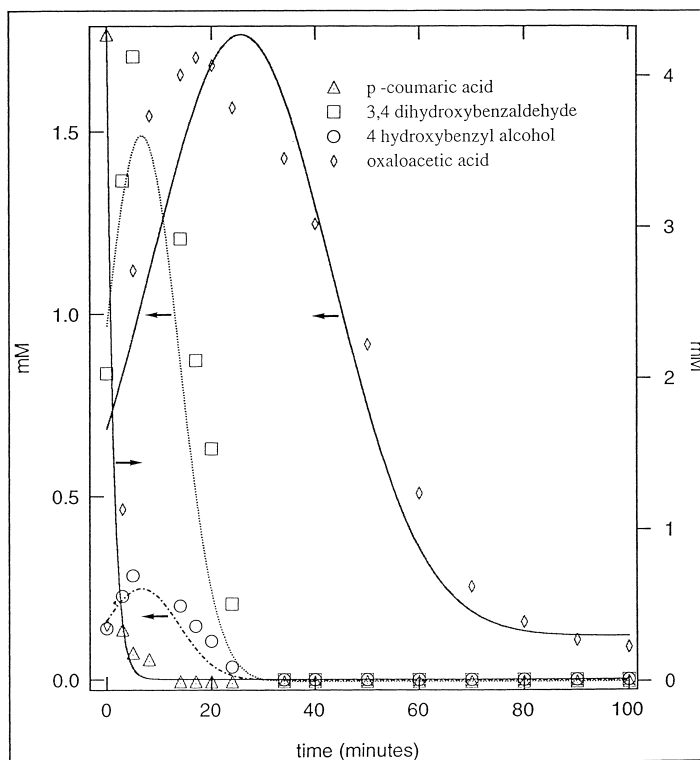


Fig. 5. Concentration profile of aromatic and aliphatic compounds as a function of time during the photolysis of a solution of *p*-coumaric acid (3.95 mM), $Fe^{3+}$(2.6 mM) and $H_2O_2$(150 mM).

acid. These intermediates are found during photo-assisted Fenton reactions for the same system as presented in Fig. 3. Catalase (3 mg/40 ml) was added at each of the experimental points shown in Fig. 3 since the action of the residual $H_2O_2$ in solution had to be inhibited in order to avoid further oxidation during the time of the analysis. Fig. 5 shows the $p$-coumaric acid concentration disappearing within the first 6 min of reaction. The aromatic intermediates detected during the degradation by HPLC were: 4-hydroxybenzyl alcohol, 3,4-dihydroxybenzaldehyde and oxaloacetic acid. The evolution profile of these intermediates as a function of time is shown in Fig. 5. Oxalic acid is also produced but it cannot be adequately shown in the time scale used in Fig. 5. Its evolution will be reported below in Fig. 6(a) and (b). By HPLC aromatics as mentioned above along with compounds originating from the aromatic ring cleavage like oxaloacetic and oxalic acid could be observed within the degradation period.

Fig. 6(a) shows the concentration time profile for a solution containing $p$-coumaric acid and $FeCl_3$ as reported in the previous figure reacting in the dark or under light for 16 h in the presence of different concentrations of $H_2O_2$. The oxidant concentrations were applied in such concentration to the solution so as to act as initial reagent in the system at the beginning of each run. The precursor role of oxaloacetic acid for oxalic acid in solution is shown in Fig. 6(a). The decomposition of the oxalic acid due to an iron-complex does not seem to take place. In effect, after a peak is reached for oxalic acid production in the dark at concentrations of $H_2O_2 \geq 20$ mM, no decrease in the concentration of the oxalic acid in solution was observed in the dark up to an $H_2O_2$ level of 160 mM. In all cases, the initial $H_2O_2$ added had disappeared in solution after 16 h. Under light irradiation, the concentration of oxalic acid reaches $\sim$1.3 mM. The oxalic acid concentration decreased at higher $H_2O_2$ concentrations. This profile reflects the activity of the Fe-complex in the decomposition of the oxalic acid under light irradiation. The appreciable difference in the concentrations of oxalic acids in the dark and under light ($\Delta \approx 1$ mM) with $H_2O_2$ (160 mM) confirms the active role of the iron-complex in the decomposition of the oxalic acid.

Fig. 6(b) shows the decomposition of the oxalic acid and oxaloacetic acid when a solution containing

STOICHIOMETRIC CONTROL OF THE REACTION
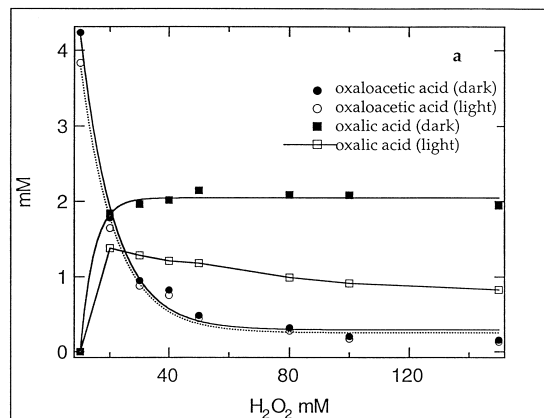


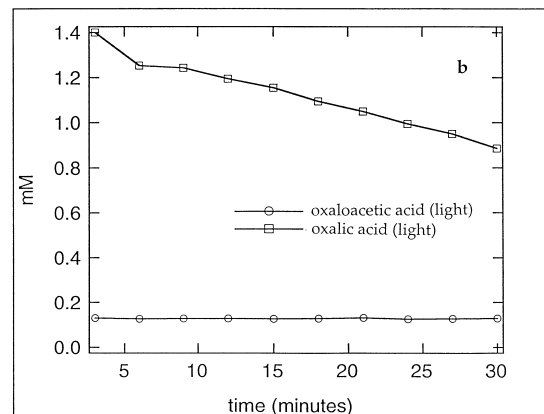COUMARIC ACID, DARK REACTION UNDER ILLUMINATION



Fig. 6. (a) Concentration profile of oxaloacetic acid and oxalic acid in the dark and under light after 16 h irradiation as a function of the $H_2O_2$ concentration used. (b) Concentration profile for oxaloacetic acid and oxalic acid under light when irradiation was applied after a 16 h reaction in darkness on $p$-coumaric acid (3.95 mM) $Fe^{3+}$(2.6 mM) and $H_2O_2$ (150 mM) solution.

$p$-coumaric/$Fe^{3+}$/$H_2O_2$ reacted in the dark for 16 h and was subsequently photolyzed for 30 min by way of a Suntest irradiator. Fig. 6(b) shows that the accumulated oxalic acid decomposed in contact with light. It also shows that oxaloacetic acid in solution does not intervene in oxalic acid decomposition when present in solution at concentrations of $\sim$0.1 mM under light irradiation. The bulk of the oxaloacetic acid was already destroyed within the 16 h in agreement with the results presented above in Fig. 6(a).
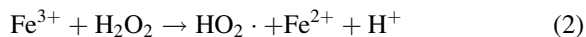
In a separate experiment a solution of oxalic acid (1.5 mM) and oxaloacetic acid (1.1 mM) were photolyzed together for 20 min under Suntest illumination in the presence of $Fe^{3+}$-ions and $H_2O_2$. The run was carried out until the total consumption of $H_2O_2$ took place. In a second experiment these two acids were photolyzed separately under similar conditions. When the acids were photolyzed together total degradation of the compounds in solution was observed. When the oxaloacetic acid is photolyzed alone, only traces of oxalic acid were found. But only a very slow degradation of oxalic acid is observed under light irradiation. Oxalic acid is seen to accelerate the degradation of the mixture undergoing decomposition since it does not appear in Fig. 5. These observations helped us to understand the accumulation and slow degradation of oxalic acid in Fig. 6(a) Fig. 6(b) under light irradiation when oxaloacetic acid (or another organic substrate) is not more available in solution.

The evolution of the intermediates during the degradation process has been detected by HPLC and are reported in Fig. 5 and Fig. 6. The results obtained suggest a reaction network for the oxidation of *p*-coumaric acid via the photo-assisted Fenton reactions. This is shown in Scheme 1.
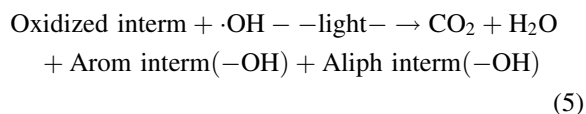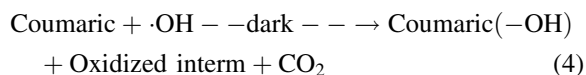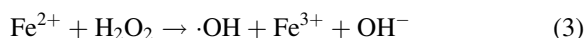
Under acidic conditions, it is seen that *p*-coumaric acid reacts to form p-vinyl phenol as suggested in [3] since decarboxylation sets in from the beginning as shown previously in Fig. 5. Acid catalyzed water addition to p-vinyl phenol subsequently allows the formation p-(1-hydroxyethyl) phenol. The decomposition of the latter compound seems to lead to the phenol-4-ethyl cation detected by GC–MS. This compound was unequivocally identified as an intermediate on irradiated samples irradiated for less than 20 min. Further oxidation of the aromatic alcohol would lead to 3,4-dihydroxybenzaldehyde as shown in Scheme 1. After ∼10 min the reaction of 4-hydroxybenzyl alcohol and 3,4-dihydroxybenzaldehyde was observed to reach the maximum concentration (Fig. 5). The ratio observed between the oxaloacetic acid intermediate and the initial *p*-coumaric acid concentration was 2.3. The HPLC results obtained suggest that at a low pH the 3,4 dihydroxybenzaldehyde cleaves, due to the Fenton reaction, to oxaloacetic acid, oxalic acid, formic acid (traces) and $CO_2$. After the ring opening, formation of small quantities of aliphatic acids ($C_3$–$C_6$)
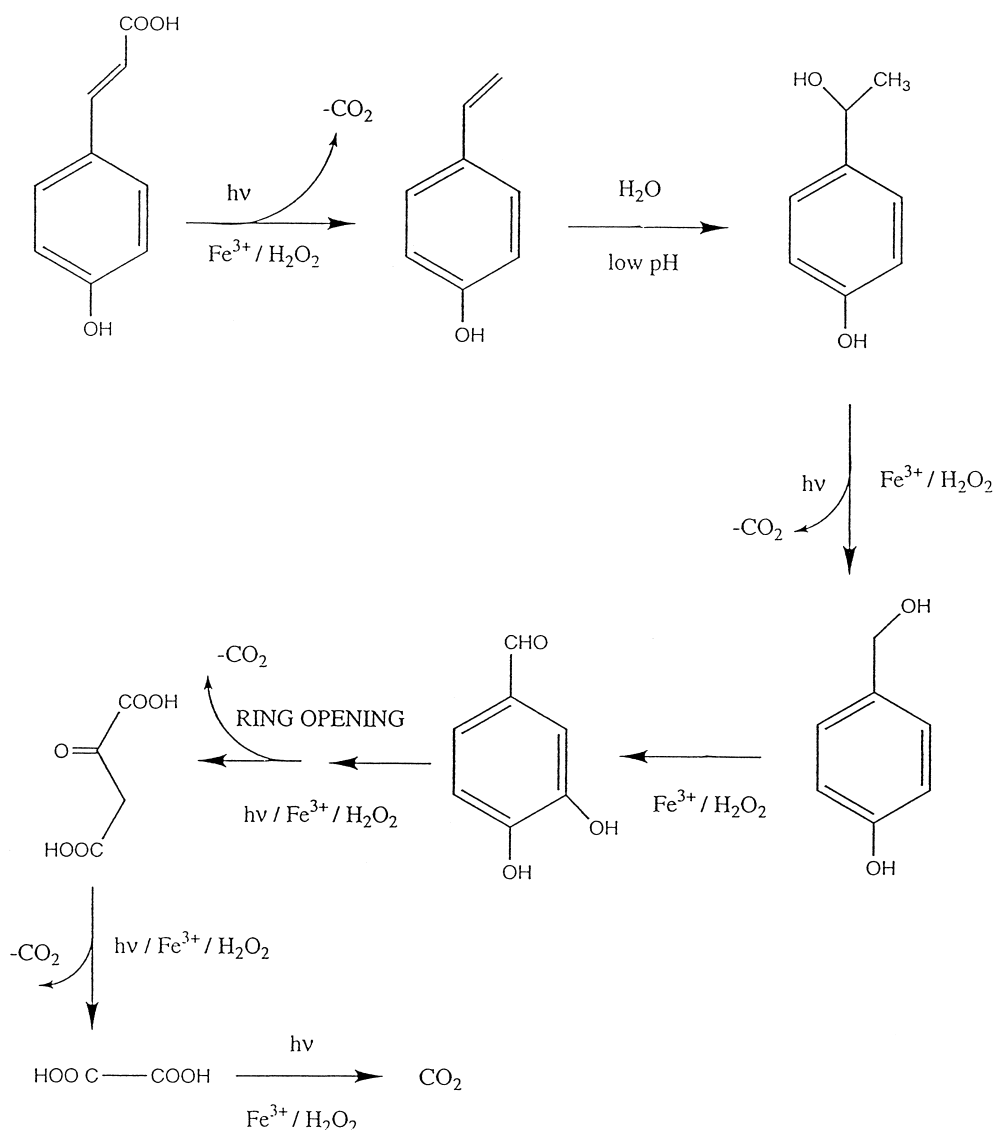
were observed, but at concentrations <0.1 mM. Nevertheless, their appearance in the HPLC spectrogram provides the link to the full mineralization of *p*-coumaric acid shown in Fig. 5. The evolution of $CO_2$ occurs from the beginning and was observed during the whole degradation time. The rapid formation of the oxaloacetic acid in Fig. 5 can only be explained by the cleavage of the aromatic ring [1–3]. Andreozzi et al. [2] supported this mechanism reporting that during the aqueous ozonization of *p*-coumaric acid at pH∼2, the free radical mechanism played only a minor role. In the latter case the *p*-coumaric degradation was seen to occur through direct oxidation of the substrate showing that the formation of the high concentration of the intermediate, oxaloacetic acid (Fig. 5) could be rationalized in terms of *p*-coumaric acid reacting with the Fenton reagent with subsequent decarboxylation of the intermediates in solution like p-vinyl phenol and p-(1-hydroxyethyl) phenol.

Fig. 7 shows the degradation via Fenton processes in the light and in dark processes as TOC consumed (mg C/l) when the solution were reacted in a Suntest lamp (see Section 2). The degradation results are shown for a surface to volume ratio (*s*/*v*) equal to 1.34. This occurs when 40 ml solution is added in the 60 ml Pyrex glass flask. Additional results under light irradiation show the results for surface-to-volume ratio (*s*/*v*) 2.06 when 20 ml solution and (*s*/*v*) 5.90 when 10 ml are photolyzed in the reaction flask. Fig. 7 shows reactions leading to TOC reduction occurring in solutions where the s/v ratio allows for the formation of a higher concentration of radicals on the solution surface. From this result and the known radical mechanism of Fenton reactions [4–6,9] Figs. 1–6 suggest a reaction mechanism

$$Fe^{3+} + H_2O_2 \rightarrow HO_2 \cdot + Fe^{2+} + H^+ \tag{2}$$

with $Fe^{2+}$-ion producing $\cdot OH$ radicals

$$Fe^{2+} + H_2O_2 \rightarrow \cdot OH + Fe^{3+} + OH^- \tag{3}$$

$$\begin{aligned} Coumaric + \cdot OH - -dark - - \rightarrow Coumaric(-OH) \\ + \text{Oxidized interm} + CO_2 \end{aligned} \tag{4}$$

$$\begin{aligned} \text{Oxidized interm} + \cdot OH - -light- \rightarrow CO_2 + H_2O \\ + \text{Arom interm}(-OH) + \text{Aliph interm}(-OH) \end{aligned}$$
$$\tag{5}$$

$$\text{Aliph interm}(-OH) + \cdot OH \rightarrow CO_2 + H_2O \tag{6}$$

Scheme 1.

Fig. 8 presents the near-infrared spectroscopy (FTIR) for the photodegradation of a solution of _p_-coumaric acid/$Fe^{3+}$/$H_2O_2$. The analysis of the FTIR samples as carried out at times that were different to the times taken to report the HPLC data shown in Fig. 5. The change in the sharp band at 3381 $cm^{-1}$ associated to the stretching -OH vibration of the _p_-coumaric acid indicates that after 40 min aliphatic carboxylic acids and some trace compounds are formed, as shown in Fig. 6 [19,20]. The band at

2963 $cm^{-1}$ associated with the aromatic CH-stretching of the ring is seen to decrease by up to 3 h. This observation is confirmed by the concomitant disappearance (during the reaction time) of the vibrations due to double substitution in the ring para-positions at 1628, 1602 and 1590 $cm^{-1}$. The bands at 2838, 2714 and 2579 $cm^{-1}$ reflecting the OH- and CO-stretching overtones and combinations are only noticeable up to 20 min while the ring still exists in solution. The carboxylic acid giving rise to the C=O stretching at
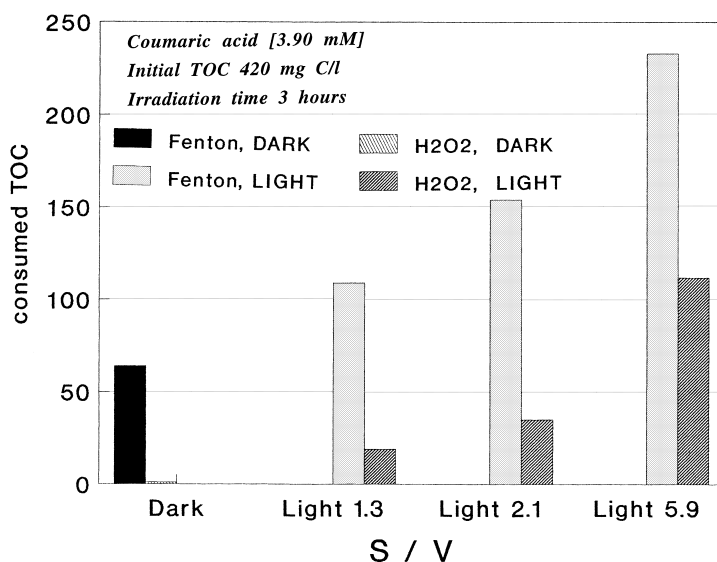
Fig. 7. Influence of the surface-to volume ratio on the TOC decrease after 3 h reactions under the conditions specified in the captions.

$1673$ cm$^{-1}$ disappears after 40 min confirming the ring cleavage suggested from the concentration profile with time of the intermediates in Fig. 5. Other vibrations of the C=O group in different space directions at 1448, 1327 and 945 cm$^{-1}$ are also seen to disappear in less than 40 min. Finally, the vibrations of the vinyl group at 1512, 1104, 979 and 834 cm$^{-1}$ were not seen after 20 min. This is possible when the original ring structure of the p-coumaric acid has already disappeared. The FTIR technique gives further evidence supporting Scheme 1.

### 3.4. Implication of the degradation intermediates formed during reactions in the dark. Energy saving devices

Fig. 9 presents the degradation for a solution of p-coumaric acid/Fe$^{3+}$/H$_2$O$_2$ with the same make up as the solution used in Fig. 3. The addition of H$_2$O$_2$ was carried out hourly. The photodegradation is seen to proceed at a much lower rate than reported previously in Fig. 3. The effect of a 20 min irradiation in a Suntest simulator on a solution after a 20 h pretreatment in the dark [8] is seen next.

Five different experimental conditions are explored in Fig. 9, namely 1) catalase added under Ar in the presence of H$_2$O$_2$ showed further 10% reduction of the TOC when light was applied, 2) when the catalase was added in the presence of air the residual TOC was observed to decrease by 40% showing the favorable effect of the O$_2$ under light, 3) when no catalase was added, the residual H$_2$O$_2$ was capable of reducing by 60% the TOC of a solution kept 20 h in the dark, 4) under air, the residual H$_2$O$_2$ was seen to induce up to 80% reduction in TOC under illumination and finally 5) when H$_2$O$_2$ (10 mM) was added in air total destruction of the residual p-coumaric acid was observed. The results obtained in traces 1) through 5) confirm the important role of the gas atmosphere during the destruction of the active intermediates formed in dark reactions. The inset in Fig. 9 shows the decrease in the absorption spectrum between the initial and final solutions since color removal is an important part of pollutant removal in waste water treatment.

Fig. 10 shows the degradation of a p-coumaric/Fe$^{3+}$/H$_2$O$_2$ solution with the same make up as used previously in Fig. 9. Trace 1) refers to the a dark degradation process where after 10 h pretreatment long lived intermediates are formed accounting for ~50% of the initial TOC. The oxidant was added on an hourly basis as in Fig. 1. Trace 2 shows the TOC decrease when dark and light periods are used as marked by the arrows along this trace. Six light
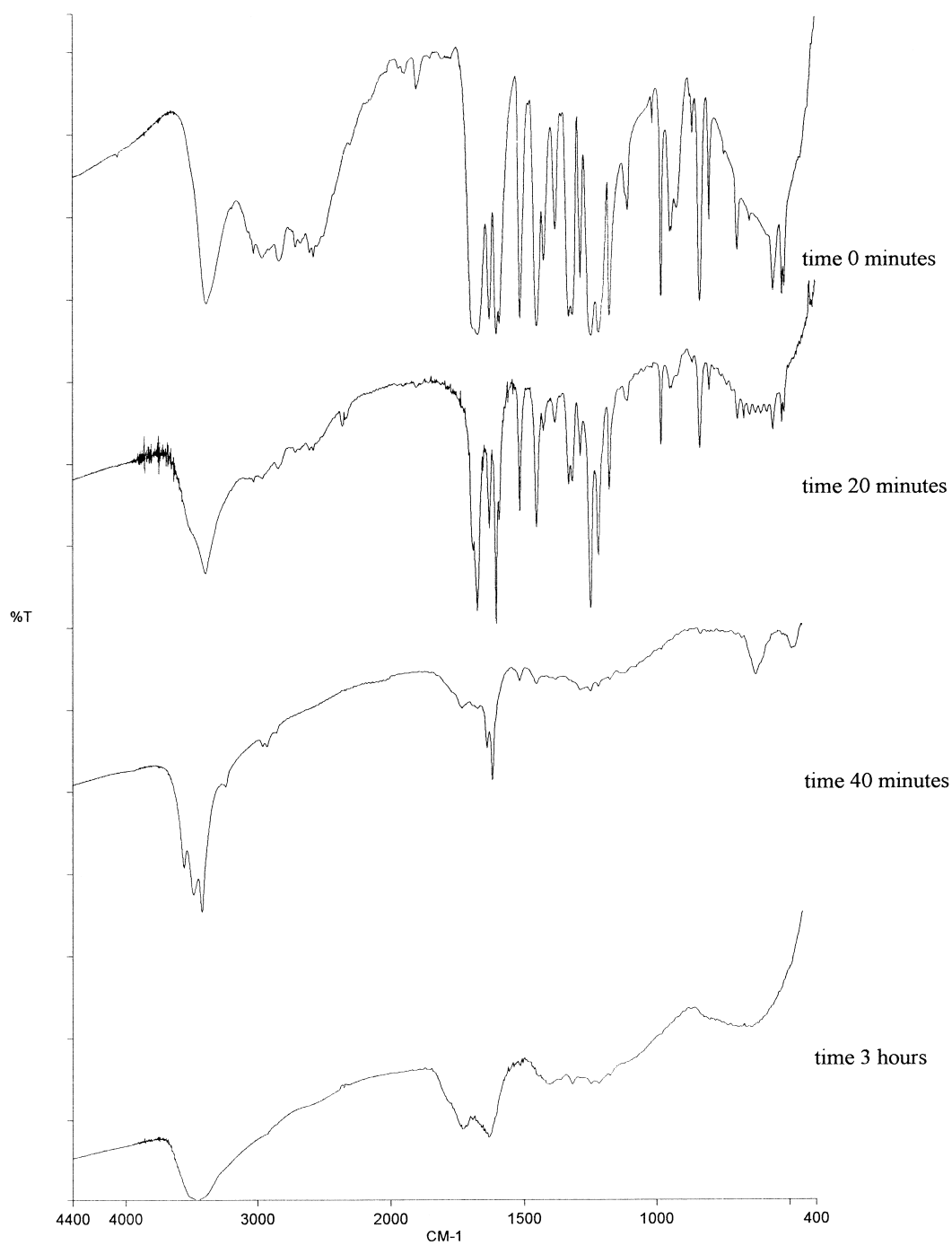
Fig. 8. Fourier-transform infrared spectra (FTIR) during the photolysis of the solution. For other details see text.
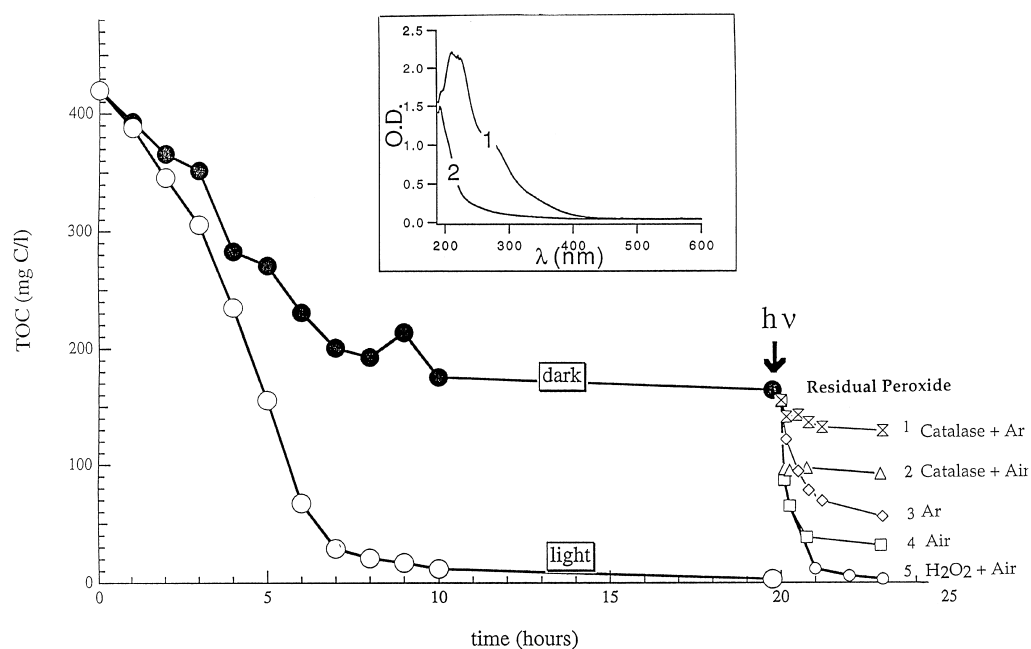
Fig. 9. TOC change vs. time for a solution with the same make up as in Fig. 5. After 20 h, reaction in the dark light is applied. The residual degradation under different conditions is marked in the captions. The inset shows 1) the optical absorption after 20 h in the dark and 2) after photolysis for 20 min in air (see trace 4).
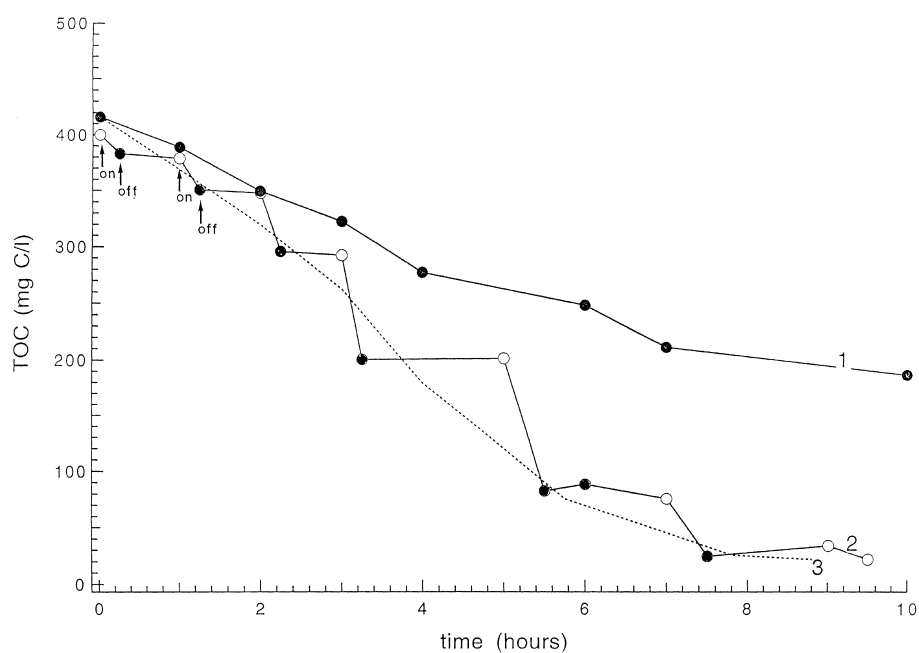


Fig. 10. Degradation of a solution like the one used Fig. 9 under the following conditions: 1) in the dark, 2) with light periods (open circles) and dark (full circles) and 3) continuous irradiation by a Suntest simulator.

periods were applied within a ten hour reaction period for a total of 90 min. Therefore, light irradiation during 15% of the total reaction time degraded the concentrated *p*-coumaric solution in a way equivalent to continuous illumination as seen by the dotted point line (trace 3). This last observation indicates the usefulness of the precursor formed the dark for significative savings in the electrical energy during *p*-coumaric acid degradation via Fenton photo-assisted reactions. This observation is relevant to practical applications when expensive photons come into consideration.

## 4. Conclusions

In conclusion, the accelerated photocatalytic oxidation of *p*-coumaric acid, a compound found in olive oil and wine processing is presented in this study. The degradation of solutions containing high concentration and low concentration of *p*-coumaric acid found respectively at production sites or in large water estuaries has been shown possible. Photo-assisted Fenton reactions were observed to be more efficient than solutions where $H_2O_2$ only was added under illumination. By HPLC and FTIR techniques, it has been possible to work out a reaction network for the degradation mechanism. The relevance of the precursor species formed in the dark subsequently undergoing light induced decomposition in solution is reported in detail.

## Acknowledgements

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