Co-oxidation of *p*-hydroxybenzoic acid and atrazine by the Fenton's like system Fe(III)/H$_2$O$_2$

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Abstract

The system Fe(III)/H$_2$O$_2$ has been used to oxidise an aqueous solution of *p*-hydroxybenzoic acid (*p*HB) in the absence of light. In the process, typical operating variables such as reagent concentration exert a positive influence in the *p*HB degradation rate. Optimum pH has been found to be around 3. The kinetic study suggests that the mechanism involved in this system differs to some extent from that reported for the classic Fenton's chemistry in pure water. Thus, formation of a complex Fe(III)—*p*HB seems to be a key step to initiate the oxidising mechanism. Stoichiometric measurements of the H$_2$O$_2$ consumption per mole of *p*HB degraded indicate a possible reduction of complexed Fe(III). Simultaneous oxidation of *p*HB (and other similar compounds such as tyrosol (Ty) or *p*-coumaric acid (*p*Cu)) and atrazine have shown a synergistic effect of the first substance to remove the pesticide. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fenton; *p*-Hydroxybenzoic acid; Atrazine; Kinetics; Iron; Hydrogen peroxide

1. Introduction

The oxidation of organic compounds by Fenton's reagent is gaining an increasingly important role in the development of alternative technologies for water and wastewater remediation. Advantages of Fenton's reagent over other oxidising treatments are numerous including, simplicity, suitability to treat a wide range of substances, no special equipment needed, etc. [1]. Nevertheless, in most cases, use of hydrogen peroxide as the oxidant source requires a stoichiometric amount of Fe(II), thereby demanding a high concentration

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Nomenclature

Ar   aromatic ring
k rate constant
C_i concentration of species i
HQ   dihydroxybenzene
$HQ^\bullet$ dihydroxycyclohexadienyl radical
$HQ'^\bullet$ semiquinone radical
Ph   phenol
pHB p-hydroxybenzoic acid
pCu p-coumaric acid
Ty   tyrosol

of this inorganic species. Alternatively, sometimes the ferric form of iron, Fe(III), may be used in lieu of the ferrous iron. Thus, the couple Fe(III)/Fe(II) acts as a catalyst since continuous reduction–oxidation reactions occur. In addition, in other cases, formation of organic Fe(III) complexes also accelerates hydrogen peroxide decomposition [2,3]. Use of Fe(III) instead of Fe(II) contributes to the economy of the process since a reduction step of the sludges produced is avoided. In this sense, the direct reutilisation of the catalyst (after acid re-dissolution) can be accomplished with the subsequent savings in chemicals (reducing agents).

In the system Fe(III)/H_2O_2 the rate of free radical production (or any other oxidant) and, consequently, the rate of contaminant removal, is significantly accelerated by the effective reduction of Fe(III) to Fe(II) or the enhanced decomposition of hydrogen peroxide by Fe(III) complexes. In this sense, photochemical reactions are not the unique route to transform Fe(III) into Fe(II). Thus, for the first case, it has been previously reported that humic substances are capable of reducing ferric iron in the absence of light, moreover, microbial processes are potential sources of Fe(II), [4]. Quinones have also been demonstrated to play a crucial role as electron shuttles in the oxidation of aromatic compounds [5].

In a previous study [6], it has been demonstrated that some phenolic-type compounds typically found in wastewater generated in olive related processing industries, for instance p-hydroxybenzoic acid (pHB), tyrosol (Ty), etc. are catalytically degraded (in the presence of hydrogen peroxide) by small amounts of Fe(II) since, the latter species is regenerated throughout the process. Having in mind the aforementioned properties, the potential synergistic effect of naturally occurring substances such as pHB, Ty or p-coumaric acid (pCu) for the treatment with Fe(III)/H_2O_2 of refractory substances has been investigated.

In this work some studies on the oxidation of pHB, Ty and pCu by the Fenton's like system Fe(III)/H_2O_2 have been carried out. Also, an attempt has been made to gain some knowledge, of the mechanisms developed throughout the process. Atrazine has been selected as a refractory model compound in this oxidation process. Atrazine is characterised by its low biodegradability and slow hydrolysis. Furthermore, it presents a relatively high water solubility, enhancing, therefore, its potential contaminating power [1].

2. Methods

Experiments were carried out in a 2 l glass reactor in the dark, batchwise and in the presence of oxygen. The aqueous solution of reactants was homogenised using a magnetic stirrer to avoid concentration gradients. Systematically, samples were withdrawn and immediately analysed in less than 2 min after sampling. Preliminary experiments were carried out by quenching the samples with sodium thiosulphate. Results were compared to similar runs completed under the same conditions without the addition of any quencher (after removal of H_2O_2 from the media with catalase). Since no differences were obtained, the remaining experiments were conducted in the absence of reducing or scavenging substances.

All chemicals with the exception of atrazine were provided by Aldrich and used without further purification. Commercially available atrazine (55% w/v) was purchased from ERT (Spain). The atrazine emulsion was filtered and the solid residue repeatedly washed with methanol.

Analysis of organics was accomplished by HPLC. The system was equipped with a 1046 Hewlett-Packard UV/VIS detector set at 210 nm. A Waters Nova-Pack C18 column was used. The mobile phase (flowrate 1 ml min^{-1}) utilised to separate the different substances was prepared as follows: 20:80 (v/v) methanol/water at low pH (0.01 M in phosphoric acid) for the analysis of *p*HB or 50:50 (v/v) of the same mobile phase when atrazine was simultaneously analysed. Ty and *p*Cu were detected by using a 10:90 (v/v) and 20:80 (v/v) acetonitrile/water mixture 0.01 M in phosphoric acid, respectively. When atrazine was present, the analysis was carried out in gradient mode. Thus, for the simultaneous analysis of Ty and atrazine a 10:90 (v/v) acetonitrile/water mixture 0.01 M in phosphoric acid was used for 8 min, afterwards this mixture was replaced by a 30:70 (v/v) acetonitrile/water mobile phase. When analysing atrazine and *p*Cu a 20:80 (v/v) acetonitrile/water mixture 0.01 M in phosphoric acid was utilised for 6 min, then, the composition of the mobile phase was changed to a 30:70 (v/v) acetonitrile/water mixture. Samples were injected by means of an automatic 1010 Hewlett-Packard injector. Total peroxide concentration was determined iodometrically. Ferrous ion in the solution was analysed by the 2,4,6-tripyridyl-*s*-triazine (TPTZ) method after hydrogen peroxide removal with the adequate amount of catalase (purchased from Sigma, 1 unit decomposes 1 µmole of H_2O_2 per minute at pH 7 and 25 °C, while the concentration of H_2O_2 falls from 10.3 to 9.2 mM. Used catalase contains 51,100 units per milligram of protein and 47.7 mg of protein per millilitre). Details of the analytical procedure can be found elsewhere [6]. The pH of the reaction media was followed by means of a Radiometer Copenhagen pH-meter (HPM82). This parameter remained practically unchanged throughout the experiments. Therefore, most experiments were conducted in the absence of any buffer solution.

3. Results and discussion

As reported previously [6] during the semi-continuous Fenton's oxidation of *p*HB, ferrous iron was continuously regenerated by different routes. Therefore, to assess the possibility of this compound presenting some reducing activity, a 10^{-4} M solution of Fe(III) and 10^{-2} M of *p*HB was stirred for several hours in the dark. Measurements of the generated Fe(II)
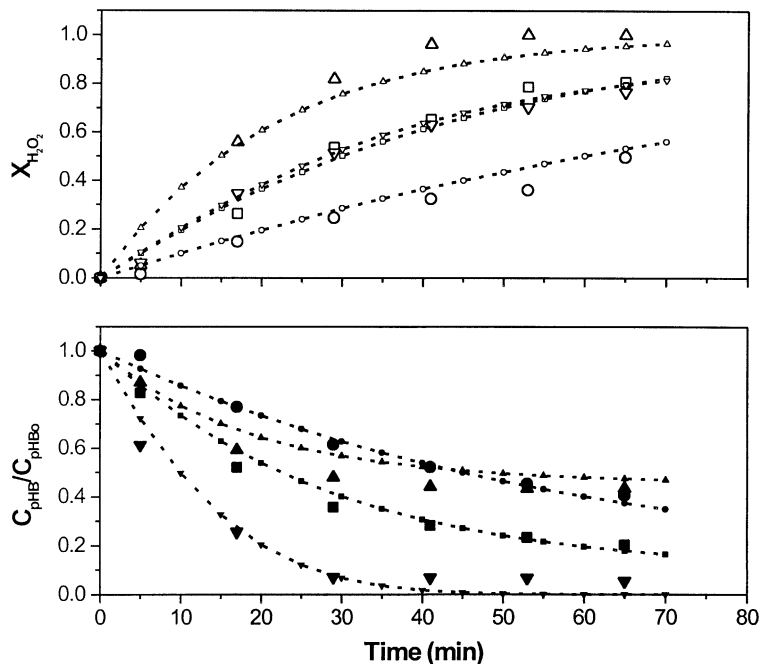
Fig. 1. Oxidation of *p*-hydroxybenzoic acid by Fe(III)/H$_2$O$_2$. Evolution of the normalised *p*-hydroxybenzoic acid concentration (solid symbols) and hydrogen peroxide conversion (open symbols) with time. Conditions: $T = 293$ K; pH $= 3.1$; $C_{pHB0} = 0.01$ M. Symbols: (■), $C_{H_2O_2} = 0.02$ M, $C_{Fe(III)} = 1 \times 10^{-4}$ M; (●), $C_{H_2O_2} = 0.02$ M; $C_{Fe(III)} = 5 \times 10^{-5}$ M; (▲), $C_{H_2O_2} = 0.01$ M, $C_{Fe(III)} = 1 \times 10^{-4}$ M; (▼), $C_{H_2O_2} = 0.04$ M, $C_{Fe(III)} = 1 \times 10^{-4}$ M. Dotted lines with small symbols, theoretical model results.

evolution with time showed no formation of this species above the detection limit of the method employed ($\approx 10^{-7}$ M). Therefore, a previous reduction of Fe(III) and the subsequent development of the classic Fenton's chemistry to oxidise the acid may be precluded in the system *p*HB/Fe(III)/H$_2$O$_2$.

A series of experiments was carried out by mixing solutions of different concentrations of Fe(III) and H$_2$O$_2$ while keeping constant the remaining variables (see Fig. 1). As expected, an increase of the initial ferric ion concentration or hydrogen peroxide concentration resulted in a notable improvement of the *p*HB degradation rate. Thus, after 65 min of reaction, an increase of the Fe(III) fed to the reactor from 5×10^{-5} M up to a value of 1×10^{-4} M led to a final *p*HB conversion roughly from 60 to 80%, respectively. Similarly, changes in the initial hydrogen peroxide concentration from 10^{-2} to 4×10^{-2} M led to a significant enhancement of the *p*HB conversion extent (39 and 93%, respectively, after 30 min of reaction). Also from Fig. 1 it is observed that the initial concentration of reagents strongly influenced the H$_2$O$_2$ depletion rate. In this case, it is noticed that the lower the amount of Fe(III) used, the lower the H$_2$O$_2$ conversion achieved. In contrast, the extent of hydrogen peroxide removal is increased as the initial concentration of this reagent is decreased. Analysis of the Fe(II) formed throughout experiments showed a rapid generation of this species by reduction of Fe(III).

Additionally, an increase of the initial pH of the reaction from 3 to 5 led to the total inhibition of the process when an acetate/acetic acid buffer was used (ionic strength 10^{-2} M). However, some conversion was noticed when the experiment was conducted at the same pH of 5 but in the absence of buffer. As discussed later in the kinetic section, differences found in the presence and absence of the buffer mixture could be explained based on the competitiveness of the "inactive" acetate/acetic chelator to complex Fe(III) preventing, therefore, to some extent the formation of the "active" complex between Fe(III) and pHB.

3.1. Kinetic considerations

Experiments carried out at different initial pHB acid concentration in the range 10^{-3} to 2.5×10^{-2} M showed a dependency on this parameter other than a simple first order kinetics with respect to the parent compound concentration (see Fig. 2). A first approach to model the process was accomplished by considering the basic chemistry of the system Fe(III)/H_2O_2 in organic free water, notice that for simplification purposes aquocomplexes
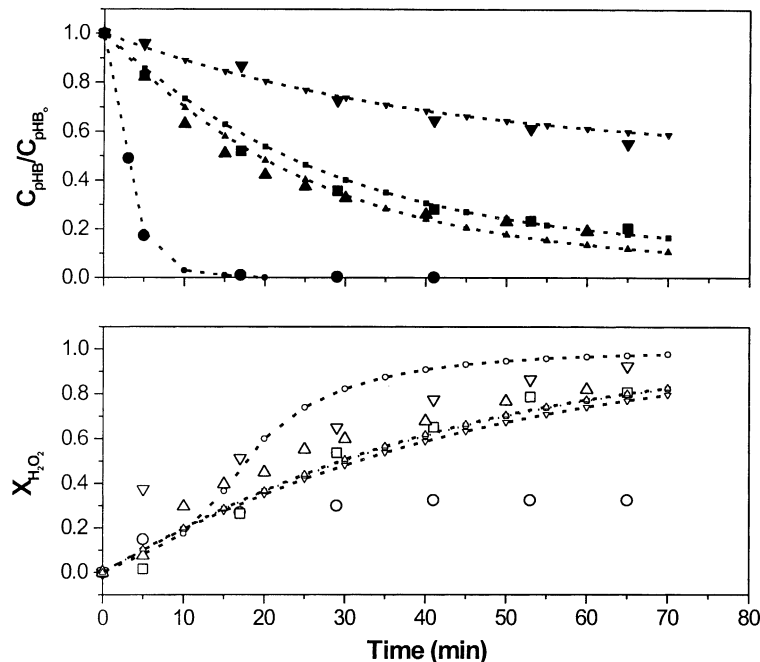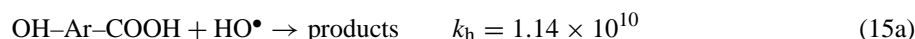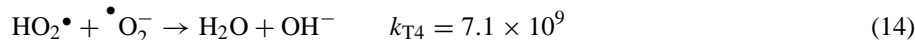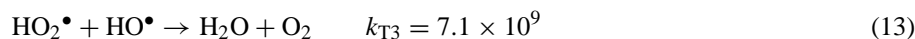

Fig. 2. Oxidation of p-hydroxybenzoic acid by Fe(III)/H_2O_2. Evolution of the normalised p-hydroxybenzoic acid concentration (solid symbols) and hydrogen peroxide conversion (open symbols) with time. Conditions: $T = 293$ K; pH = 3.1. Symbols: (■), $C_{pHB0} = 0.01$ M, $C_{H_2O_2} = 0.02$ M, $C_{Fe(III)} = 1 \times 10^{-4}$ M; (●),$C_{pHB0} = 0.001$ M, $C_{H_2O_2} = 0.02$ M, $C_{Fe(III)} = 1 \times 10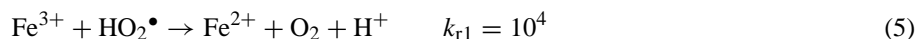^{-4}$ M; (▲),$C_{pHB0} = 0.01$ M, $C_{H_2O_2} = 0.023$ M, $C_{Fe(II)} = 1 \times 10^{-4}$ M; (▼),$C_{pHB0} = 0.025$ M, $C_{H_2O_2} = 0.02$ M, $C_{Fe(III)} = 1 \times 10^{-4}$ M. Dotted lines with small symbols, theoretical model results.

are not introduced [6–8]. Therefore, the following set of reactions was contemplated (units in mole, litre and second):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet \qquad k_{i2} = 76 \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^\bullet \qquad k_{i3} = 0.02 \tag{2}$$

$$H_2O_2 + HO_2^\bullet \rightarrow HO_2^\bullet + H_2O \qquad k_{p1} = 4.3 \times 10^8 \tag{3}$$

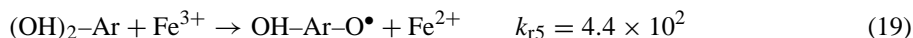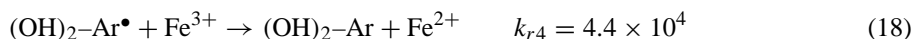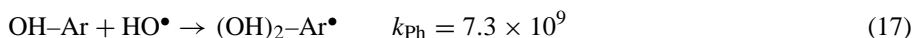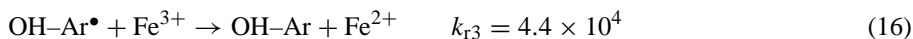$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + OH^- \qquad k_{p2} = 4.3 \times 10^8 \tag{4}$$

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+ \qquad k_{r1} = 10^4 \tag{5}$$

$$Fe^{2+} + HO_2^\bullet + H^+ \rightarrow Fe^{3+} + H_2O_2 \qquad k_{01} = 1.2 \times 10^6 \tag{6}$$

$$Fe^{3+} + {}^\bullet O_2^- \rightarrow Fe^{2+} + O_2 \qquad k_{r2} = 1.5 \times 10^8 \tag{7}$$

$$Fe^{2+} + {}^\bullet O_2^- + 2H^+ \rightarrow Fe^{3+} + H_2O_2 \qquad k_{02} = 10^7 \tag{8}$$

$$HO_2^\bullet \rightarrow {}^\bullet O_2^- + H^+ \qquad k_d = 8 \times 10^5 \tag{9}$$

$${}^\bullet O_2^- + H^+ \rightarrow HO_2^\bullet \qquad k_{dr} = 5 \times 10^{10} \tag{10}$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \qquad k_{T1} = 8.3 \times 10^5 \tag{11}$$

$$2HO^\bullet \rightarrow H_2O_2 \qquad k_{T2} = 5.2 \times 10^9 \tag{12}$$

$$HO_2^\bullet + HO^\bullet \rightarrow H_2O + O_2 \qquad k_{T3} = 7.1 \times 10^9 \tag{13}$$

$$HO_2^\bullet + {}^\bullet O_2^- \rightarrow H_2O + OH^- \qquad k_{T4} = 7.1 \times 10^9 \tag{14}$$

$$OH\text{–}Ar\text{–}COOH + HO^\bullet \rightarrow products \qquad k_h = 1.14 \times 10^{10} \tag{15a}$$
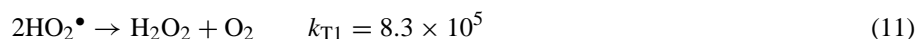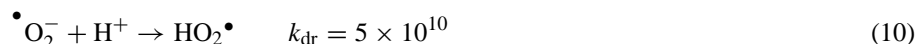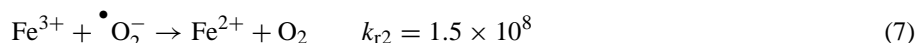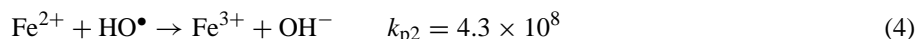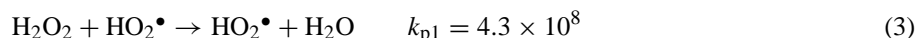
In this mechanism of reactions, the direct attack of the hydroxyl radical to the parent compound (reaction 15a) has been assumed to be a termination step. After having applied the hypothesis of the steady-state to radicals, the system of first order differential equations derived from the mechanism was numerically solved for the molecular species present in the reaction media. The fourth order Runge–Kutta method was used for that purpose. Computed results of pHB acid depletion profiles ($C_{Fe(III)} = 1 \times 10^{-4}$ M, $C_{H_2O_2} = 0.02$ M, pH = 3.1, $C_{pHB} = 0.01$ M) with time showed a poor 1.5% conversion after 70 min treatment (actual conversion is roughly 80%, see Fig. 1 square symbols).

In a previous paper [6] a kinetic model based on the work of Chen and Pignatello [5] was proposed for the Fe(II)/H_2O_2 oxidation of pHB. In this mechanism, some reactions that regenerated Fe(II) from the oxidised form were assumed. Thus, given the high Fe(II) concentration found during the experiments, steps (15b), instead of (15a), to (21) were added to the mechanism:

$$OH\text{–}Ar\text{–}COOH + HO^\bullet \rightarrow OH\text{–}Ar^\bullet + H_2O + CO_2 \qquad k_h = 1.14 \times 10^{10} \tag{15b}$$

$$\text{OH–Ar}^\bullet + \text{Fe}^{3+} \rightarrow \text{OH–Ar} + \text{Fe}^{2+} \qquad k_{r3} = 4.4 \times 10^4 \tag{16}$$

$$\text{OH–Ar} + \text{HO}^\bullet \rightarrow \text{(OH)}_2\text{–Ar}^\bullet \qquad k_{Ph} = 7.3 \times 10^9 \tag{17}$$

$$\text{(OH)}_2\text{–Ar}^\bullet + \text{Fe}^{3+} \rightarrow \text{(OH)}_2\text{–Ar} + \text{Fe}^{2+} \qquad k_{r4} = 4.4 \times 10^4 \tag{18}$$

$$\text{(OH)}_2\text{–Ar} + \text{Fe}^{3+} \rightarrow \text{OH–Ar–O}^\bullet + \text{Fe}^{2+} \qquad k_{r5} = 4.4 \times 10^2 \tag{19}$$

$$\text{OH–Ar–O}^\bullet + \text{Fe}^{3+} \rightarrow \text{benzoquinone} + \text{Fe}^{2+} \qquad k_{r6} = 4.4 \times 10^4 \tag{20}$$

$$\text{OH–Ar–OH}^\bullet \rightarrow \text{(OH)}_3\text{–Ar} + \text{products} \qquad k_{HQ} = 1.0 \times 10^9 \tag{21}$$
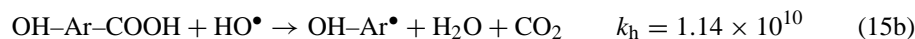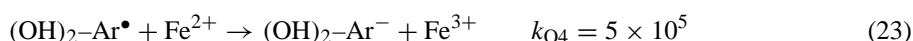
Again, the system of differential equations was numerically solved by means of the fourth order Runge–Kutta method. In this case, the model overestimated the removal rate of pHB. Thus, after just 5 min of reaction, computed results showed an 82% conversion of the parent compound ($C_{\text{Fe(III)}} = 1 \times 10^{-4}\,\text{M}$, $C_{\text{H}_2\text{O}_2} = 0.02\,\text{M}$, pH = 3.1, $C_{p\text{HB}} = 0.01\,\text{M}$), much higher than the 17% actual conversion experimentally found (see Fig. 1 square symbols).

In any case, it has been shown that the set of reactions (1)–(21) could well simulate the pHB Fenton's degradation in semi-continuous mode under different operating conditions [6]. However, since the presence of impurity traces in commercially available reagents may lead to different results when studying the Fenton's process [5], in this work, for comparison and modelling purposes, a new Fe(II)/H$_2$O$_2$ oxidation run has been conducted in batch mode (see Fig. 2, up triangles) instead of semi-continuous mode. Also, as the model overestimates the actual pHB conversion, it may be hypothesised that: (1) complexation of the different forms of iron and organics might influence to some extent the initiating reactions of the Fenton's mechanism; (2) the model lacks some important reactions (i.e. oxidation of ferrous iron by organic radicals).

In this sense, it has been reported that some Fe(II)/Fe(III) organic chelators catalyse hydrogen peroxide decomposition [3]. Therefore, it may be suggested that the initiating rate constants k_{i2} and/or k_{i3} have a higher value than the accepted ones taken for organic free water. Contrarily, other ligands stabilise the metal cation, preventing the catalytic decomposition of H$_2$O$_2$. In the latter case, their dissociation is the rate-limiting step in the development of the Fenton's mechanism [9]. Furthermore, in this work, decolouration of the Fe(II)-TPTZ complex (analytical method used to determine ferrous iron) by H$_2$O$_2$ has been shown to proceed much more slowly than expected for a theoretical rate constant of this reaction in the range 53–76 M^{-1} s^{-1} in organic free water.

Consequently, considering all the above statements, a second attempt to model the system was accomplished by (1) testing the influence of k_{i2} and k_{i3} on the pHB conversion and (2) Adding some potential Fe(II) oxidation steps by organic radicals that might occur. Thus, reactions (22) and (23) were added with rate constants in the range of those reported for similar steps in the literature [5].

$$\text{OH–Ar}^\bullet + \text{Fe}^{2+} \rightarrow \text{O–Ar}^- + \text{Fe}^{3+} \qquad k_{O4} = 5 \times 10^5 \tag{22}$$

$$\text{(OH)}_2\text{–Ar}^\bullet + \text{Fe}^{2+} \rightarrow \text{(OH)}_2\text{–Ar}^- + \text{Fe}^{3+} \qquad k_{O4} = 5 \times 10^5 \tag{23}$$

The final set of first order differential equations obtained, to be solved, was as follows:

- Ferrous iron

$$-\frac{dC_{Fe^{2+}}}{dt} = (k_{i2}C_{H_2O_2} + k_{O1}C_{HO_2}{}^\bullet + k_{O2}C_{O_2^-}{}^\bullet + k_{O3}C_{HQ}{}^\bullet + k_{O4}C_{HQ'}{}^\bullet)C_{Fe^{2+}}$$
$$+ (k_{i3}C_{H_2O_2} + k_{r1}C_{HO_2}{}^\bullet + k_{r2}C_{O_2^-}{}^\bullet + k_{r3}C_{Ph}{}^\bullet$$
$$+ k_{r4}C_{HQ}{}^\bullet + k_{r5}C_{HQ} + k_{r6}C_{HQ'}{}^\bullet)C_{Fe^{3+}} \tag{24}$$

- Ferric iron

$$-\frac{dC_{Fe^{3+}}}{dt} = (k_{i2}C_{H_2O_2} + k_{O1}C_{HO_2}{}^\bullet + k_{O2}C_{O_2^-}{}^\bullet k_{O3}C_{HQ}{}^\bullet + k_{O4}C_{HQ'}{}^\bullet)C_{Fe^{2+}}$$
$$+ (k_{i3}C_{H_2O_2} + k_{r1}C_{HO_2}{}^\bullet + k_{r2}C_{O_2^-}{}^\bullet + k_{r3}C_{Ph}{}^\bullet + k_{r4}C_{HQ}{}^\bullet$$
$$+ k_{r5}C_{HQ} + k_{r6}C_{HQ'}{}^\bullet)C_{Fe^{3+}} \tag{25}$$

- Hydrogen peroxide

$$-\frac{dC_{H_2O_2}}{dt} = (k_{i2}C_{Fe^{2+}} + k_{i3}C_{Fe^{3+}})C_{H_2O_2} + (k_{O1}C_{HO_2}{}^\bullet + k_{O2}C_{O_2^-}{}^\bullet)C_{Fe^{2+}}$$
$$+ k_{T1}C_{OH^\bullet}^2 + k_{T2}C_{HO_2^\bullet}^2 \tag{26}$$

- Phenol

$$\frac{dC_{Ph}}{dt} = k_{r3}C_{Ph}{}^\bullet C_{Fe^{3+}} - k_{Ph}C_{Ph}C_{OH^\bullet} \tag{27}$$

- Hydroquinone

$$\frac{dC_{HQ}}{dt} = k_{r4}C_{HQ}{}^\bullet C_{Fe^{3+}} - (k_{r5}C_{Fe^{3+}} + k_{HQ}C_{HO^\bullet})C_{HQ} \tag{28}$$

- pHB

$$-\frac{dC_{pHB}}{dt} = k_h C_{HO^\bullet}C_{pHB} \tag{29}$$

Figs. 1–3 (results corresponding to pHB, square symbols, in Fig. 3) shows the experimental and computed results for pHB removal and H_2O_2 conversion with time for runs completed under different operating conditions. As observed from these figures, depletion profiles are acceptably well simulated by the model (for both Fe(II)/H_2O_2 and Fe(III)/H_2O_2 systems). Nevertheless, a higher value of k_{i3} (roughly 50 times higher), if compared to the one reported for organic free water ($k_{i3} = 0.02\,M^{-1}\,s^{-1}$ in pure water) was obtained by the optimisation subroutine of the computer programme. It has to be pointed out that, in this work, both k_{i2} and k_{i3} are pseudoempirical constants that include complexation equilibriums and hydrogen peroxide decomposition with complexed and uncomplexed Fe(II) and Fe(II), respectively.

Thus, as stated previously, the presence of some chemical structures such as gallic acid, picolinic acid, etc. leads to formation of Fe(III) complexes able to catalyse and accelerate the hydrogen peroxide decomposition [2]. pHB possesses a structure similar to that of these compounds, prompting the thought that this substance may be capable of acting as a chelator
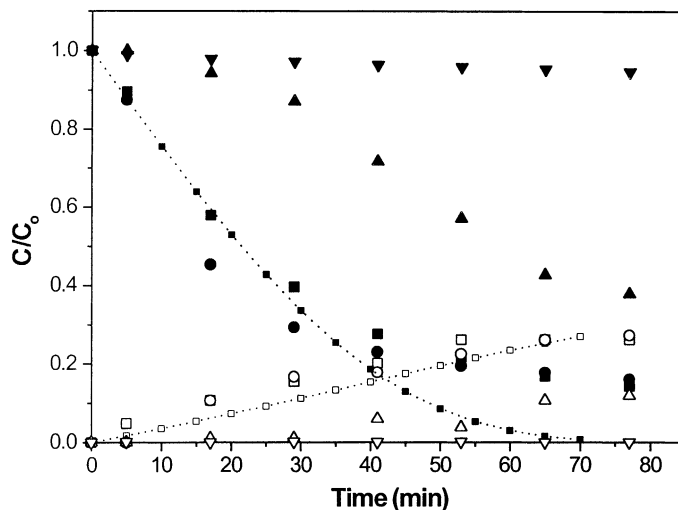
Fig. 3. Oxidation of phenolic compounds by Fe(III)/H$_2$O$_2$. Evolution of the normalised phenolic substance concentration (solid symbols) and hydrogen peroxide conversion (open symbols) with time. Conditions: $T = 293$ K; pH = 3.6; $C_{\text{Atrazine}} = 10^{-4}$ M; $C_{\text{Ph0}} = 0.001 FIG$ M; $C_{\text{H}_2\text{O}_2} = 0.01$ M; $C_{\text{Fe(III)}} = 2.5 \times 10^{-5}$ M. Symbols: (■), p-hydroxybenzoic acid (lines, model calculations); (●), tyrosol (initial pH = 5.6); (▲), coumaric acid; (▼), atrazine.

of Fe(III), thus accelerating the decomposition of hydrogen peroxide and further generation of Fe(II) and the hydroperoxide radical through reactions (30)–(32), [10]. Prevention of Fe(III) precipitation at high pH (>7) in the presence of pHB confirmed this hypothesis.

$$(30)$$

$$(31)$$

$$(32)$$
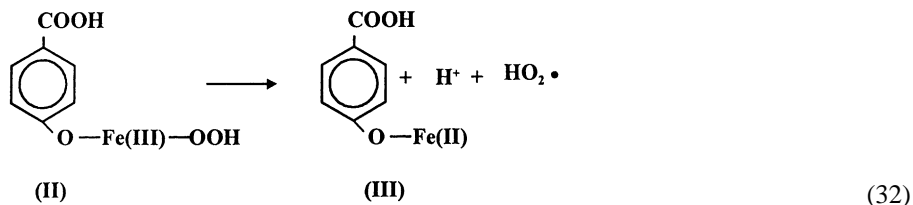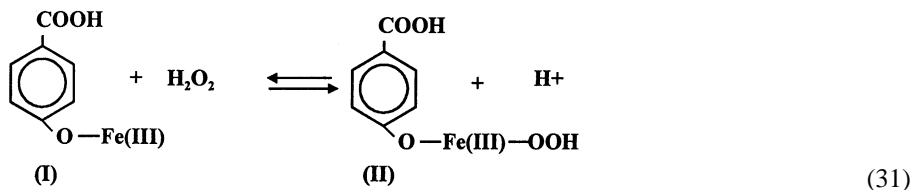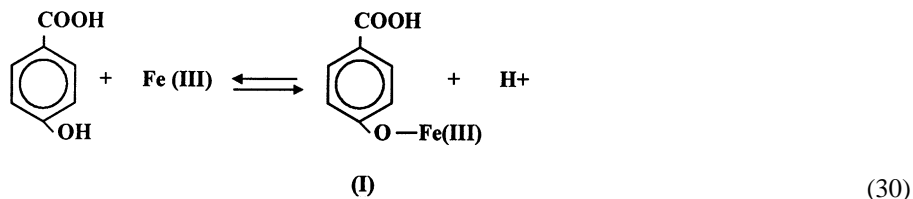
Broadly speaking, the hydroperoxyl radical formed in (32) is a rather inactive species, the kinetic constants of its reactions with organic substrates are relatively low except for the case of some specific compounds [11]. However, the complex **III** (or non-complexed Fe(II)), in excess of hydrogen peroxide, may react with a molecule of this species to form the active oxidant, either the free or "caged" hydroxyl radical (considered in this work) and/or the ferryl group (reactions (33) and/or (34)).

$$ \text{(33)} $$

$$ \text{(34)} $$
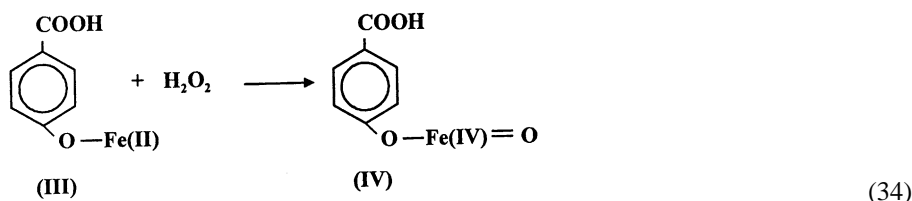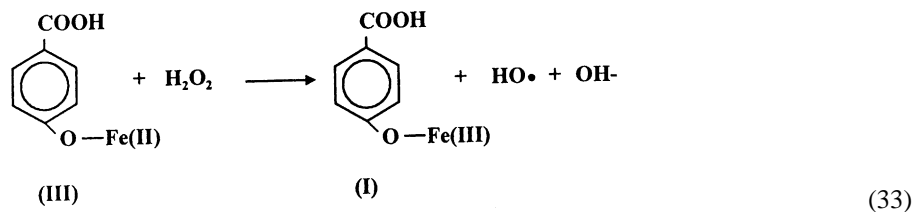
Furthermore, given the concentration of the parent compound, it is logical to assume that the first steps of the process are the hydroxylation of *p*HB and first intermediates, so consumption of hydroxyl radicals (or any other oxidising species) is practically devoted to degradation (or derivatisation) of these substances. This is the explanation for which the model does not account for further steps. If no intermediates are taken into account, reactions (30)–(34) lead to a stoichiometric coefficient of 2, measured as the ratio mole of H_2O_2 consumed per mol of acid degraded. Experimental determinations of this stoichiometric coefficient showed a scattered dispersion of this parameter in the range 1.5–2.5, although for most operating conditions the value oscillated quite close to 2.0.

Although *p*HB and H_2O_2 evolution profiles were acceptably modelled by the proposed kinetic mechanism, Fe(II) formation was underestimated if compared to experimental results. Thus, computed results were 5–10 times lower than analysed concentrations. Obviously, the model is incomplete and many reactions that may be occurring are not accounted for. However, given the extreme complexity of the Fenton's system, the mechanism does a good job when simulating the behaviour of the main species involved in the process, *p*HB and H_2O_2.

In any case, as experimentally found, Fe(II) was generated almost in stoichiometric amounts from Fe(III), therefore it can be assumed that Fe(III) reduction reactions predominate over Fe(II) oxidation reactions. Consequently, in a second attempt, the mechanism of reactions was again tested by discarding reactions (22) and (23) and adjusting k_{i2} and k_{i3} to fit experimental and computed results. Model results were comparable to those achieved with the complete set of reactions (1)–(23). In this case, the value of k_{i3} was found to be similar to the one obtained in the previous case (considering reactions (22) and (23)). This suggests, therefore, the existence of the complex *p*HB-Fe(III) and its role in catalysing H_2O_2

decomposition faster than the ferric aquocomplexes do. However, in this second attempt, the value of k_{i2} obtained was significantly lower than the accepted value in ultrapure water. Thus, values of k_{i2} in the range $2–5\,M^{-1}\,s^{-1}$ were numerically obtained. These results would be explained if complex **III** were stabilised in such a way as to prevent the fast oxidation of Fe(II) by H_2O_2, similarly to the effect of TPTZ and other ligands. In this case k_{i2} would represent the rate of the limiting step, for instance the dissociation of **III** to give the free Fe(II) cation. Nevertheless, this seems to be quite unlikely given the chemical structure of the chelator. Advantages of the latter model are based on the good fitting achieved between experimental and computed Fe(II) evolution with time. Hence, as experimentally found, with this mechanism Fe(II) rapidly accumulates in the reaction media.

3.2. Atrazine removal, synergistic effects of phenolic compounds oxidation

Three phenolic compounds usually found in some foodstuff industry wastewaters [12] have been used to co-oxidise atrazine in aqueous solutions. Thus, as observed from Fig. 3, *p*HB (model calculations have also been added for this experiment), Ty (4-hydroxyphenethyl alcohol) and *p*Cu (4-hydroxicinnamic acid) were degraded by the system Fe(III)/H_2O_2 at acceptable rates. Contrarily, this system was shown to be totally inefficient for atrazine elimination unless light is used [13]. As seen in Fig. 3, the reactivity order of the phenolic compounds studied in this work with the system Fe(III)/H_2O_2 was Ty > *p*HB acid > *p*Cu. However, when Fe(II) was used instead of Fe(III) the observed reactivity was altered [6]. In the latter case, the reactivity order was as follows: *p*HB > Ty > *p*Cu, suggesting some differences between both oxidising systems.

Experiments of simultaneous oxidation of atrazine phenolic compounds are presented in Figs. 4–6. As observed from these figures, some interesting points are noticed:

- The three substances tested were capable of significantly reducing the content of atrazine in the aqueous solution. For instance, when Ty or *p*Cu were used an atrazine conversion of 75–80% was achieved, whereas a higher conversion > 90% was obtained when *p*HB was present. An attempt to simulate the process, when using *p*HB, was made by considering reactions (1)–(23) plus the removal of atrazine by hydroxyl radicals with an average rate constant of $5 \times 10^9\,M^{-1}\,s^{-1}$ [14,15]. As observed from Fig. 4, the model properly simulates the removal profiles of *p*HB, H_2O_2 and atrazine until the phenolic compound disappears (this effect can also be noticed in Fig. 2 for the experiment represented by closed circles). From this point, hydrogen peroxide and atrazine conversions are overestimated by the model, confirming the hypothesis of the intimate relationship between *p*HB presence and generation of oxidising species. It is likely that after the total elimination of *p*HB (no possibility of complexation) the value of k_{i3} decreases to the normal value found for organic free water. In the inset of Fig. 4 it is seen how the computed profiles of hydroxyl and perhydroxyl radicals achieve a maximum, their concentrations gradually decreasing after 80 min.
- At the conditions used in these experiments, hydrogen peroxide consumption was roughly 40–50% of the initial concentration. Fe(II) accumulated at the end of the process achieving almost a stoichiometric concentration regarding the initial Fe(III) added to the reaction media.
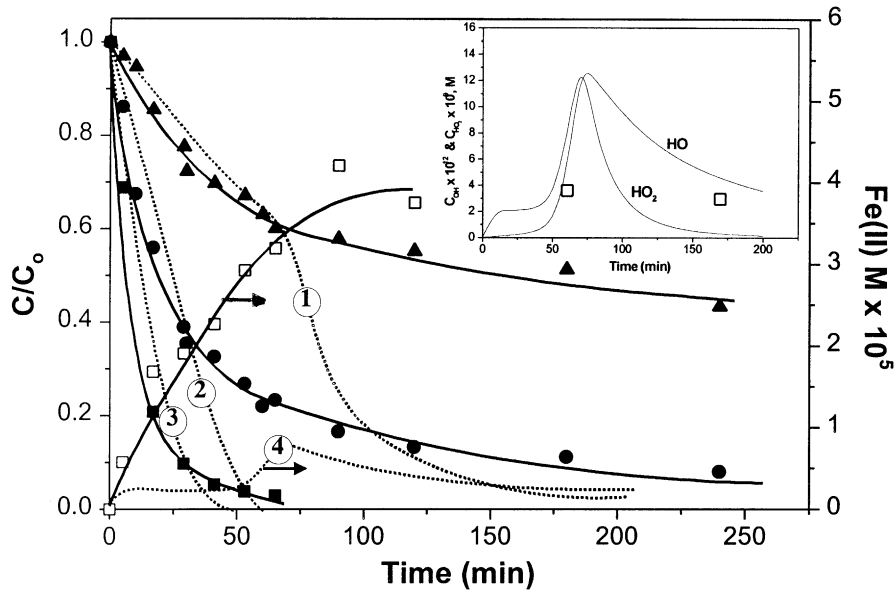
Fig. 4. Co-oxidation of *p*-hydroxybenzoic acid and atrazine by Fe(III)/H$_2$O$_2$. Generation of Fe(II) and evolution of the normalised *p*HB, atrazine and hydrogen peroxide concentration with time. Conditions: $T = 293$ K; pH = 3.3; $C_{\text{Atrazine}} = 10^{-4}$ M; $C_{p\text{HB0}} = 0.001$ M; $C_{\text{H}_2\text{O}_2} = 0.01$ M; $C_{\text{Fe(III)}} = 5 \times 10^{-5}$ M. Symbols: (■), *p*-hydroxybenzoic acid (2); (●), atrazine (3); (▲), H$_2$O$_2$ (1); (□), Fe(II) (4). Dotted lines, model calculations. Inset, evolution of hydroxyl and perhydroxyl radicals.
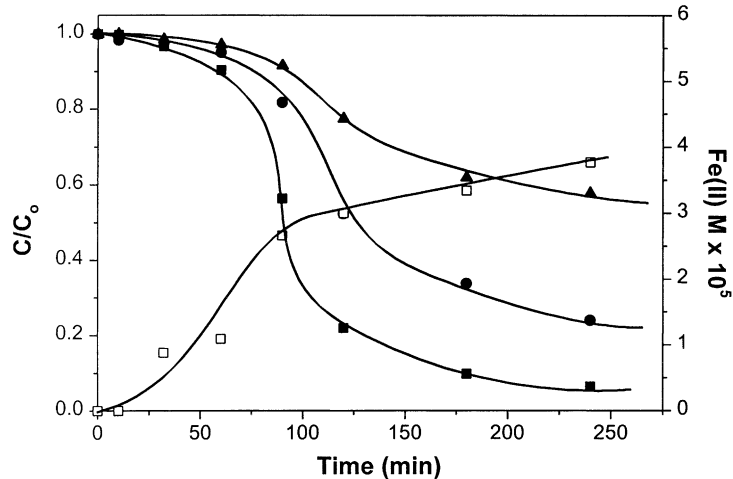

Fig. 5. Co-oxidation of tyrosol and atrazine by Fe(III)/H$_2$O$_2$. Generation of Fe(II) and evolution of the normalised tyrosol, atrazine and hydrogen peroxide concentration with time. Conditions: $T = 293$ K; pH = 3.3; $C_{\text{Atrazine}} = 10^{-4}$ M; $C_{\text{Ty0}} = 0.001$ M; $C_{\text{H}_2\text{O}_2} = 0.01$ M; $C_{\text{Fe(III)}} = 5 \times 10^{-5}$ M. Symbols: (■), tyrosol; (●), atrazine; (▲), H$_2$O$_2$; (□), Fe(II).
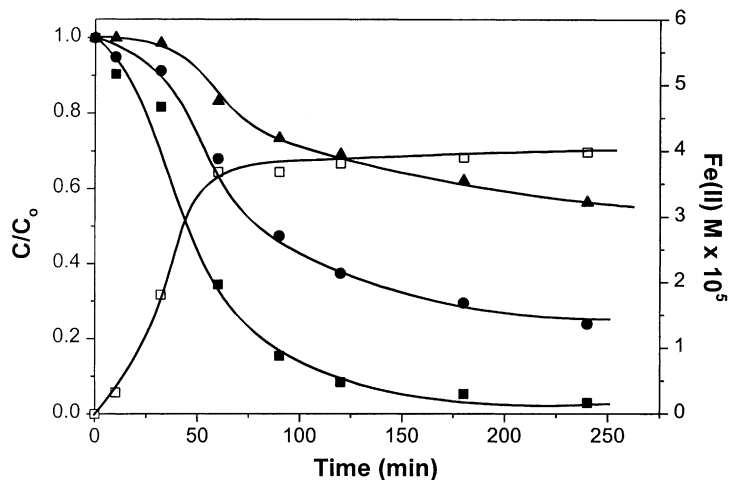
Fig. 6. Co-oxidation of p-coumaric acid and atrazine by Fe(III)/H_2O_2. Generation of Fe(II) and evolution of the normalised p-coumaric acid, atrazine and hydrogen peroxide concentration with time. Conditions: $T = 293$ K; pH $= 3.3$; $C_{Atrazine} = 10^{-4}$ M; $C_{pCu0} = 0.001$ M; $C_{H_2O_2} = 0.01$ M; $C_{Fe(III)} = 5 \times 10^{-5}$ M. Symbols: (■), p-coumaric acid; (●), atrazine; (▲), H_2O_2; (□), Fe(II).

- In all cases, depletion profiles of both the phenolic substance and atrazine were similar, even for those experiments where an initial lag period was experienced. Also, for high conversions of the phenolic compound, Fe(II) concentration reached the stationary state and the atrazine degradation rate decreased. As stated previously, these experimental facts suggest that the oxidant species involved in the system is intimately related to the presence of the phenolic substance.
- From Figs. 4–6, the most effective chelator of Fe(III) to reduce atrazine concentration seems to be pHB. Similar structures such as gallic acid have been shown to accelerate the degradation of some pesticides and insecticides through the same process [2,9]. Nevertheless, given the well-known influence of operating conditions (reagent concentrations, pH, etc.) a more exhaustive study should be carried out to ascertain the optimum operating conditions to be used [2,9].

Some preliminary studies on the Fe(II)/Fe(III)/H_2O_2 oxidation of wastewater from olive oil mills have demonstrated that the Fenton or Fenton's like systems are capable of achieving high chemical oxygen demand conversions in just 1 to 2 h, depending on conditions [16]. This type of effluent is known to contain high amounts of substances of polyphenolic structure. Concentration of phenols in olive related industries may reach values in the range 0.01–0.05 M (measured as pure phenol) depending on the manufacturing process [17]. Additionally, it is noteworthy to point out the high level of mineralisation achieved by the Fenton's process. Thus, values above 50% of total carbon removal have been reported when treating strong contaminated (initial COD roughly $14\,\mathrm{g\,l^{-1}}$) olive processing wastewater [17]. Dilution of wastewater from olive oil processing industries with atrazine-contaminated water has resulted in the total degradation of the pesticide by using either the classic Fenton's

reagent or the system Fe(III)/H_2O_2. The rapid elimination of atrazine by Fenton's treatment has been reported [1]. However, as inferred from this work and other reported studies, this pesticide may also be removed by the system Fe(III)/H_2O_2 if the appropriate substances are present. From results herein showing the suitability of using foodstuff wastewaters as promoters of the oxidation of pesticides in water, a more rigorous study is being carried out.

4. Conclusions

From the present work the following conclusions can be drawn:

- *p*HB, Ty and *p*Cu can be effectively degraded by the system Fe(III)/H_2O_2 in the absence of light from either the near UV or UV region.
- In the process, formation of a complex between the phenolic compound and Fe(III) seems to be a key limiting step in the reaction mechanism developed.
- A stoichiometric factor close to 2 mole of hydrogen peroxide consumed per mole of *p*HB degraded suggests a first reduction of L-Fe(III) to L-Fe(II) (first H_2O_2 molecule used) and further reaction of complexed L-Fe(II) with a second H_2O_2 molecule.
- Atrazine, a refractory pesticide to the system Fe(III)/H_2O_2 is also degraded if the simultaneous oxidation of the pesticide and any phenolic compound (*p*HB, Ty, *p*Cu) is carried out.
- The presence of these polyphenolic substances together with the low pH of wastewaters from some types of foodstuff-related processes suggest the feasibility of a joint treatment of these effluents diluted with pesticide-contaminated waters or the use of the first type of effluents as "inexpensive co-catalyst" to effectively degrade pesticides.

Preliminary experiments completed by using olive oil mill wastewater and atrazine-contaminated water have shown the high efficiency of the system Fe(III)/H_2O_2 to reduce both the chemical oxygen demand of the wastewater and the pesticide content. A more rigorous study is being completed by also assessing the biodegradability of the final effluent.

Acknowledgements

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