

OXIDATION OF *P*-HYDROXYBENZOIC ACID BY FENTON'S REAGENT

PII: S0043-1354(00)00285-2

FRANCISCO J. RIVAS¹*, FERNANDO J. BELTRÁN^{1M}, JESÚS FRADES² and PACO BUXEDA¹

¹Departamento de Ingenieria Quimica y Energética, Universidad de Extremadura, Avenida de Elvas S/N, 06071 Badajoz, Spain and ²Departamento de Ingenieria Quimica Universidad de Castilla la Mancha, Plaza de Manuel Meca s/n 13400 Almadén, Ciudad Real, Spain

(First received 15 November 1999; accepted in revised form 17 May 2000)

Abstract—Fenton's reagent has been shown to be a feasible technique to treat phenolic-type compounds present in a variety of food processing industry wastewaters. A model compound, *p*-hydroxybenzoic acid was oxidised by continuously pumping two solutions of ferrous iron and hydrogen peroxide. Typical operating variables like reagent feeding concentrations and flowrate, temperature and pH were studied.

A mechanism of reactions based on the classical Fenton's chemistry was assumed, and computed concentration profiles of the parent compound, ferrous ion and dihydroxybenzene were compared to experimental results. The model qualitatively predicted the influence of several operating variables, however, calculated results suggested the presence of parallel routes of substrate elimination and/or a initiating rate constant with a higher value. The low efficiency of a well-known hydroxyl radical scavenger (*tert*-butyl alcohol) also supports the contribution of oxidising species different from the hydroxyl radical to substrate removal.

Further evidence of the presence of reactions different from the hydroxyl radical oxidation was observed from comparison of the simultaneous Fenton's or UV/H_2O_2 oxidations of *p*-hydroxybenzoic acid, tyrosol and *p*-coumaric acid. © 2000 Elsevier Science Ltd. All rights reserved

Key words-Fenton, hydroxybenzoic acid, phenolic compounds, wastewater, oxidation

NOMENCLATURE

Ar	aromatic ring
C_i	concentration of species <i>i</i>
C_i^*	concentration of reagent <i>i</i> in the feeding solution
HQ	dihydroxybenzene
HQ.	dihydroxycyclohexadienyl radical
HQ'.	semiquinone radical
k	rate constant
L	chelator of iron
Ph	phenol
pHB	<i>p</i> -hydroxybenzoic acid
O_i	flowrate of reagent <i>i</i> feeding solution
<i>t</i> -BuOH	<i>tert</i> -butyl alcohol
V	reaction volume

INTRODUCTION

Phenolic-type compounds are widely occurring species in wastewater generated in food-processing industries (i.e. olive oil production, tomato transformation, distilleries, etc.). Thus, substances like gallic acid, tannic acid, tyrosol, hydroxybenzoic acid, etc., can be found at concentrations from 400 to 900 ppm of gallic acid (wine distilleries) to values as high as 2500-6000 ppm of tannic acid (table olive elaboration) (López and Ovelleiro, 1978; Kopsidas, 1992). Given the bactericide nature of these chemical structures when found at high concentrations the classic biological treatment cannot be applied and alternative wastewater treatments have to be taken into consideration. Chemical oxidation technologies based on the presence of UV radiation or/and ozone, sonolysis, etc. have been successfully used in contaminated water remediation of a broad spectrum of substances. However, as a rule of thumb, these systems involve prohibitive costs associated to process scaling-up, specially when dealing with highly polluted wastewaters. The application of Fenton's reagent (hydrogen peroxide in combination with a ferrous salt) as a possible way for wastewater purification was not practised until the late 1960s. This oxidation system has been used to treat both individual organic and inorganic substances under laboratory conditions and also real effluents from

^{*}Author to whom all correspondence should be addressed. Tel.: +34-924-289385; fax: +34-924-271304; e-mail: fjrivas@unex.es

different sources like chemical manufacturers, refinery and fuel terminals, engine and metal cleaning, etc. (Bidga, 1996). The process is based on the formation of reactive oxidising species able to efficiently degrade the organic content of the wastewater stream. Nevertheless, the nature of these species is still under discussion and its formulation is a subject of controversy in the past and recent Fenton's-related literature (Bossmann *et al.*, 1998; Pignatello *et al.*, 1999; Walling, 1998; MacFaul *et al.*, 1998; Sawyer *et al.*, 1996).

In the past decades many authors have widely investigated the kinetics and reactions involved in Fenton's chemistry. In spite of the large number of works published on this subject, the influence of crucial parameters (such as pH), role of added substrates and nature of the oxidising species present in the system, are still unclear (Walling, 1998; MacFaul *et al.*, 1998; Sawyer *et al.*, 1996; Yamazaki and Piette, 1991).

In the literature, three main species have been contemplated in Fenton's chemistry. Two of them involve the presence of hydroxyl radicals (classic Fenton's chemistry) either "free" or "caged" radicals (Walling and Amarnath, 1982) and, hence, all the reactions associated to this species. The third oxidant has been postulated to be aquo or organocomplexes of high-valence iron, the ferryl ion (Sawyer *et al.*, 1996).

Proofs based on product distribution, EPR-spin trapping techniques, effect of added substrates, etc., have been used to demonstrate the existence of one or another oxidising intermediate. However, as stated by Yamazaki and Piette (1991), it is quite likely that both hydroxy radicals and ferryl complexes coexist in Fenton's mechanism and, depending on operating conditions (substrate nature, metal–peroxide ratio, scavengers addition, etc.) one of them will predominate.

In any case, it has been demonstrated that Fenton's and Fenton's-like processes are suitable methods to destroy toxic phenolic wastes and nonbiodegradable effluents to render them more suitable for a biological secondary treatment (Chen and Pignatello, 1997).

In this work, *p*-hydroxybenzoic acid (C₆H₄OH-COOH), a phenolic model compound found in wastewater from food processing factories and industrial synthetic processes (Nagata *et al.*, 1996) has been oxidised in aqueous solutions by means of the system $Fe^{2+}/Fe^{3+}/H_2O_2$. Experiments were completed in the dark at relatively high concentration of the parent compound (0.01 M) to simulate more realistically the amounts of phenolic compounds present in the aforementioned type of effluents. The potential synergistic or inhibiting effect of other phenolic-type compounds like tyrosol (4-hydroxycinnamic acid) has also been tested. An attempt has been made to gain an insight into the

influence of typical operating variables, the kinetic of the process and intermediates formed during the reaction.

METHODS

Experiments were carried out in the dark, batchwise by continuously feeding two solutions of hydrogen peroxide and ferrous chloride to a solution of p-hydroxybenzoic acid (*p*HB) in the presence of oxygen. The pumping time was in most of the cases 30 min at a flowrate of 0.31 mL min^{-1} , so the reaction volume (1 L) could be considered constant throughout the length of the experiment. The aqueous solution was homogenised by magnetic agitation to avoid concentration gradients. Mass transfer tests were carried out by varying the speed of the magnetic stirrer. Results indicated a perfect mix of the solution under the conditions used. Systematically, samples were withdrawn and analysed to follow different parameters like pHB, intermediates and reagent concentrations (iron and total peroxides). Preliminary experiments on pHB Fenton degradation were carried out by quenching the samples using both sodium thiosulphate and/or tert-butyl alcohol. Results were compared to runs completed at the same conditions without the use of a reducing agent or radical scavenger. Since no differences were obtained, the rest of the experiments were conducted without the addition of these substances

All chemicals (*p*-hydroxybenzoic acid, tyrosol, coumaric acid, catechol, hydroquinone, maleic and oxalic acids, *tert*-butyl alcohol, hydrogen peroxide and ferrous chloride) were purchased from Aldrich and used without further purification.

Analysis of the parent compound and main intermediates formed was carried out by HPLC in isocratic mode immediately after sampling. The system was equipped with a 1046 Hewlett-Packard UV/VIS detector set at 210 nm. A Waters Nova-Pack C18 column was used utilising a 20:80 (v/v) methanol/water mixture (0.01 M in phosphoric acid) as mobile phase with a flowrate of 1 mLmin^{-1} . One μL of sample was injected by means of an automatic 1010 Hewlett-Packard injector. Analysis error was calculated to be in the range $\pm 5\%$. Total peroxides concentration was determined iodometrically. Ferrous ion in the solution was analysed by the 2,4,6, tripyridyl-s-triazine (TPTZ) method (Collins et al., 1959). Thus, 1 mL sample was buffered with 3 mL of a solution containing 2 M acetic acid-2 M sodium acetate, afterwards, 1 mL of TPTZ reagent (10⁻³ M) was added and the final volume brought to 10 mL with ultrapure water. Absorbance of the solution was measured at 593 nm (extinction coefficient 22,600 M^{-1} cm⁻¹).

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 showing variations of less than 13% in the worst of the cases. Therefore, experiments were conducted in the absence of any buffer solution.

Intermediate identification was carried out as follows: 1 L of the treated aqueous solution (90% conversion of the parent compound) was first acidified with hydrochloric acid (pH < 2) and extracted two times with 100 mL of methylene chloride. The organic phase was then dried with anhydrous sodium sulphate and concentrated in a rotary evaporator to less than 2 mL. In each analysis 1 μ L of sample was injected into a Hewlett-Packard HP 5890 gas chromatograph coupled to a 5972 Mass Spectrometer operated in Scan mode. A 30 m-0.25 µm film thickness HP-5MS cross-linked 5% phenyl methyl silicone column was used. The oven temperature programme was set at 323 K for 2 min ramped up to 583 K (8 K min⁻¹) and kept for 15 min at this temperature. The carrier gas was helium.

RESULTS AND DISCUSSION

Influence of operating conditions

Two series of experiments were completed by varying the concentration of both ferrous cation (0–0.01 M) and hydrogen peroxide (0–4 M) feeding solutions to ascertain the effect of these parameters on *p*HB conversion. As expected, an increase in concentration of any Fenton's reagent constituents led to higher conversions in *p*HB removal (see Figs 1 and 2). However, an optimum value (around 5×10^{-3} M) for Fe²⁺ concentration was noticed, experiencing no appreciable enhancement of the process rate with a further increase in the ferrous ion amount fed to the *p*HB solution (see Fig. 1).



Fig. 1. Degradation of *p*-hydroxybenzoic acid in aqueous solution by Fenton's reagent. Evolution of the normalised remaining concentration of *p*HB with time. Influence of ferrous iron concentration in the feeding solution ($C_{\text{Fe}^{2+}}^*$). Conditions: T = 293 K, pH=3.2, $C_{p\text{HBo}} = 0.01$ M, $C_{\text{H}_2\text{O}_2}^* = 2.65$ M, pumping time = 30 min, flowrate = 0.31 mL min⁻¹. Dotted lines: model calculations assuming $k_{i2} = 76 \text{ M}^{-1} \text{ s}^{-1}$.



Fig. 2. Degradation of *p*-hydroxybenzoic acid in aqueous solution by Fenton's reagent. Evolution of the normalised remaining concentration of *p*HB with time. Influence of hydrogen peroxide concentration in the feeding solution $(C^*_{\rm H_2O_2})$. Conditions: T=293 K, pH=3.2, $C_{p\rm HBo}=0.01$ M, $C^*_{\rm Fe^{2+}}=0.01$ M, pumping time=30 min, flowrate = 0.31 mL min⁻¹. Dotted lines: model calculations assuming $k_{i2}=76$ M⁻¹ s⁻¹.

From these results, it can be inferred that under the conditions used in this work, the limiting reactant seems to be in most of the cases hydrogen peroxide, since Fe²⁺ is likely regenerated throughout the process, and thereby, playing a catalytic role in the mechanism. This catalytic effect was analytically confirmed since, on the one hand, ferrous ion concentration found in the bulk of the reaction at any time was practically coincident to the theoretical amount pumped into the reactor and, on the otherhand, hydrogen peroxide was immediately consumed after being injected, experiencing none or negligible regeneration. This could also be corroborated since no further conversion in pHB was observed when the H₂O₂ feeding pump was stopped, in spite of the presence of significant amounts of Fe^{2+} in solution.

Some experiments were also conducted to determine the influence of different temperatures and pH on the effectiveness of the process. Thus, an increase of the starting pH from 3 to 7 made the process to come to a halt. These results are in agreement with the majority of studies reported on Fenton's chemistry. The usual optimum working pH when using this system is in the range 3–5. However, neutral pH has also been found to be the most appropriate to oxidise some chemical species like polynuclear aromatic hydrocarbons, nitrobenzene, amines, etc., (Beltrán *et al.*, 1998).

Broadly speaking, it is assumed that the poor conversions achieved at neutral pH are related to reduction in stability of both Fe^{2+} and H_2O_2 when increasing pH from acidic conditions. Moreover, at neutral pH ferrous iron is readily oxidised by atmospheric oxygen and ferric iron precipitates preventing the regeneration of Fe^{2+} . However, other factors may affect the influence of pH, specially the presence of organic and/or inorganic species able to stabilise or promote by complexation the autooxidation of ferrous ion (Yamazaki and Piette, 1991).

The range of temperatures from 284 to 314 K was also investigated, although no influence of this parameter was noticed under the operating conditions used in this work. Few studies in the literature have dealt with the effect of temperature in Fenton's systems, although values of activation energy for the classic initial step to generate the hydroxyl radical (probably the limiting step) have been reported to be just a few kilocalories (Hardwick, 1956). Also, Lin and Lo (1997) showed low activation energies for the chemical oxygen demand (COD) depletion when treating a desizing wastewater. In this case, however, they experienced an optimum value of temperature around 303 K.

Some intermediates formed in the process were identified by HPLC and GC/MS. Among them maleic and oxalic acids, catechol and hydroquinone were analysed throughout the experiments using high-performance liquid chromatography. Corresponding peaks were identified by comparison of retention time of standards prepared in the laboratory.

Generation of dihydroxybenzenes (catechol and hydroquinone mainly) is supposed to occur through decarboxylation of the parent compound (*p*-hydroxybenzoic acid) or/and decarboxylation of the hydroxylated species of *p*HB (dihydroxybenzoic acid). This mechanism has already been proposed for the case of similar structures like phenoxyacetic acid (Pignatello, 1992) or phenylacetic acid (Barbeni *et al.*, 1987). The oxidising species involved in the decarboxylation process is a matter of controversy and will be treated in the kinetic section of this study.

In Fig. 3 the evolution with time of by-product concentrations analysed by HPLC is presented. From this figure it is seen that a maximum in catechol and hydroquinone concentrations was noticed when roughly a 70% *p*HB removal was achieved. Maleic and oxalic acids accumulated in the reaction media due to their refractory nature to Fenton's reagent (Bidga, 1996) or the generation of more reactive intermediates that consume the oxidising species formed in the system.

Mechanism of pHB acid elimination by Fenton's reagent

In this work a simplistic mechanism based on the work of Chen and Pignatello (1997) on the ironcatalysed oxidation of phenol by hydrogen peroxide has been assumed; nevertheless, to avoid mathematical complexity some reactions have been discarded. Among them radical–radical recombination has been neglected given the low probability of these reactions to occur. Also, the reaction of free hydroxyl radicals with phenol has been assumed to proceed by aryl addition generating the corresponding dihydroxybenzene, hence, parallel routes leading to different products were not considered. Furthermore, given the low working pH in this study (pH < 4.8) reactions of the peroxyl radical have also been ruled out.



Fig. 3. Degradation of *p*-hydroxybenzoic acid in aqueous solution by Fenton's reagent. Evolution of intermediate concentration. Conditions: T=293 K, pH=3.2, $C_{pHBo}=0.01$ M, $C_{H_2O_2}^*=2.0$ M, $C_{Fe^{2+}}^*=0.01$ M, pumping time = 30 min, flowrate = 0.31 mL min⁻¹.

Although the primary step in the mechanism corresponds to the classic initiating reaction (generation of hydroxyl radicals) proposed by Haber and Weiss (1934), formation of ferryl species should not be discarded as discussed later in this section. The values of the rate constants have been taken from Chen and Pignatello (1997) unless the opposite is stated. (Units are $M^{-1}s^{-1}$ and s^{-1} for second-order reaction rates and first-order reaction rates, respectively.)

The following set of reactions has been considered:

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+OH^-+HO.$$
 $k_{i2} = 76$ (1)
 $Fe^{3+}+H_2O_2 \rightarrow Fe^{2+}+H^++HO_2^{\bullet}$ $k_{i3} = 0.02$ (2)

$$H_2O_2 + HO_{\bullet} \to HO_2^{\bullet} + H_2O \quad k_{p1} = 2.7 \times 10^7$$
 (3)

$$Fe^{2+}+HO_{\bullet} \rightarrow Fe^{3+}+OH^{-}$$
 $k_{p2}=4.3 \times 10^{8}$ (4)

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \quad k_{rl} = 10^4 \quad (5)$$

$$Fe^{2+}+HO_{2}^{\bullet}+H^{+}\rightarrow Fe^{3+}+H_{2}O_{2}$$
 $k_{01}=1.2 \times 10^{6}$ (6)

$$Fe^{3+} + O_2^- \rightarrow Fe^{2+} + O_2 \quad k_{r2} = 1.5 \times 10^8$$
 (7)

$$Fe^{2+} + O_2^{-+}2H^+ \rightarrow Fe^{3+} + H_2O_2 \quad k_{02} = 10^7$$
 (8)

ł

$$\mathrm{HO}_{2}^{\bullet} \rightarrow^{\bullet}\mathrm{O}_{2}^{-} + \mathrm{H}^{+} \quad k_{\mathrm{d}} = 8 \times 10^{5} \tag{9}$$

$$\mathbf{O}_2^- + \mathbf{H}^+ \to \mathbf{HO}_2^\bullet \quad k_{\rm dr} = 5 \times 10^{10} \tag{10}$$

$$OH-Ar-COOH + HO \rightarrow OH-Ar + H_2O + CO_2$$

 $k_h = 1.14 \times 10^{10}$

$$OH-Ar \cdot Fe^{3+} \rightarrow OH-Ar + Fe^{2+}$$
$$k_{r3} = 4.4 \times 10^4$$
(12)

 $OH-Ar + HO \rightarrow (OH)_2 - Ar \cdot k_{Ph} = 7.3 \times 10^9$ (13)

$$(OH)_2 - Ar \cdot + Fe^{3+} \rightarrow (OH)_2 - Ar + Fe^{2+}$$

 $k_{r4} = 4.4 \times 10^4$ (14)

$$(OH)_2 - Ar + Fe^{3+} \rightarrow OH - Ar - O + Fe^{2+}$$

 $k_{r5} = 4.4 \times 10^2$ (15)

OH-Ar-O. + Fe³⁺
$$\rightarrow$$
 benzoquinone + Fe²⁺
 $k_{r6} = 4.4 \times 10^4$

(17)

$$OH-Ar-OH + HO \rightarrow (OH)_3 - Ar + products$$

 $k_{HQ} = 1.0 \times 10^9$

where Ar stands for the aromatic ring.

The value of $k_{\rm h}$ was determined in experiments of UV/H₂O₂ according to the method described elsewhere (Beltrán *et al.*, 1995). Accordingly, given the similarities of reactions (12), (14) and (16) the values of $k_{\rm r3}$ and $k_{\rm r4}$ were assumed to be in the same order of magnitude as $k_{\rm r6}$. The value of $k_{\rm HQ}$ was taken from Farhataziz and Ross (1977).

From the mechanism of reactions (1)–(17) the corresponding mass balances of molecular species in a perfectly mixed reactor yield the following system of differential equations:

Ferrous iron:

$$\frac{\mathrm{d}C_{\mathrm{Fe}^{2+}}}{\mathrm{d}t} = \frac{\mathcal{Q}_{\mathrm{Fe}^{2+}}C_{\mathrm{Fe}^{2+}}^{*}}{V} - (k_{i2}C_{\mathrm{H}_{2}\mathrm{O}_{2}} + k_{\mathrm{O1}}C_{\mathrm{HO}_{2}} + k_{\mathrm{O2}}C_{\mathrm{O}_{2}^{-}})C_{\mathrm{Fe}^{2+}} + (k_{i3}C_{\mathrm{H}_{2}\mathrm{O}_{2}} + k_{\mathrm{r1}}C_{\mathrm{HO}_{2}} + k_{\mathrm{r2}}C_{\mathrm{O}_{2}^{-}} + k_{\mathrm{r3}}C_{\mathrm{Ph}\bullet} + k_{\mathrm{r2}}C_{\mathrm{O}_{2}^{-}} + k_{\mathrm{r3}}C_{\mathrm{Ph}\bullet} + k_{\mathrm{r4}}C_{\mathrm{HQ}\bullet} + k_{\mathrm{r5}}C_{\mathrm{HQ}} + k_{\mathrm{r6}}C_{\mathrm{HQ}\bullet})C_{\mathrm{Fe}^{3+}}$$

$$(18)$$

• Ferric iron:

$$\frac{dC_{Fe^{3+}}}{dt} = (k_{i2}C_{H_2O_2} + k_{O1}C_{HO_2\bullet}.$$

$$+k_{O2}C_{O_2^-\bullet})C_{Fe^{2+}} + (k_{i3}C_{H_2O_2}$$

$$+k_{r1}C_{HO_2\bullet} + k_{r2}C_{O_2^-\bullet}.$$

$$+k_{r3}C_{Ph\bullet} + k_{r4}C_{HQ\bullet} + k_{r5}C_{HQ}$$

$$+k_{r6}C_{HQ\bullet}.)C_{Fe^{3+}}$$
(19)

• Hydrogen peroxide:

$$\frac{\mathrm{d}C_{\mathrm{H}_{2}\mathrm{O}_{2}}}{\mathrm{d}t} = \frac{\mathcal{Q}_{\mathrm{H}_{2}\mathrm{O}_{2}}C_{\mathrm{H}_{2}\mathrm{O}_{2}}^{*}}{V} - (k_{\mathrm{i}2}C_{\mathrm{Fe}^{2+}} + k_{\mathrm{i}3}C_{\mathrm{Fe}^{3+}})C_{\mathrm{H}_{2}\mathrm{O}_{2}} + (k_{\mathrm{O}1}C_{\mathrm{HO}_{2}} + k_{\mathrm{O}2}C_{\mathrm{O}_{2}}^{-})C_{\mathrm{Fe}^{2+}} \quad (20)$$

• Phenol:

$$\frac{\mathrm{d}C_{\mathrm{Ph}}}{\mathrm{d}t} = k_{\mathrm{r3}}C_{\mathrm{Ph}\bullet}C_{\mathrm{Fe}^{3+}} - k_{\mathrm{Ph}}C_{\mathrm{Ph}}C_{\mathrm{OH}} \qquad (21)$$

• Hydroquinone:

$$\frac{\mathrm{d}C_{\mathrm{HQ}}}{\mathrm{d}t} = k_{\mathrm{r4}}C_{\mathrm{HQ}\bullet}C_{\mathrm{Fe}^{3+}} - \left(k_{\mathrm{r5}}C_{\mathrm{Fe}^{3+}} + k_{\mathrm{HQ}}C_{\mathrm{HO}\bullet}\right)C_{\mathrm{HQ}} \qquad (22)$$

• *p*-Hydroxybenzoic acid:

$$\frac{\mathrm{d}C_{p\mathrm{HB}}}{\mathrm{d}t} = -k_{\mathrm{h}}C_{\mathrm{HO}\bullet}C_{p\mathrm{HB}} \tag{23}$$

where Q_i stands for the flowrate of the reagent *i* feeding solution with C_i^* concentration, Ph is phenol, HQ dihydroxybenzene, HQ• the dihydroxycyclohex-

adienyl radical and HQ'. semiquinone radical in equation (16).

If the steady-state hypothesis for radical species is assumed, the set of first-order differential equations (18)–(23) may be solved numerically by means of the fourth-order Runge–Kutta method.

Application of the mechanism: kinetic considerations

Figures 1 and 2 depict the theoretical (dotted lines) and experimental (symbols + solid lines) profiles of the remaining *p*HB acid dimensionless concentration with time for the series of experiments carried out at different concentrations of the reagents fed to the reactor. Qualitatively, the applied mechanism is able to predict the influence of these operating parameters (i.e. concentration of feeding solutions); however, the model overestimates the experimental results, specially for the first 15–20 min of reaction.

At the sight of the S-shaped theoretical profile concentrations, it is reasonable to assume that either the value of the rate constant for the initiating step (k_{i2}) possesses a higher value or the mechanism involves a parallel reaction which generates an additional oxidant different from the hydroxyl radical (for instance a high-valence iron complex). A sensitivity analysis of the rate constants used in the mechanism demonstrated that the value of k_{i2} is the most influencing parameter in the shape of calculated profiles.

The low value of k_{i2} was already questioned by Bossmann *et al.* (1998) when compared to the rate constant of the ligand exchange between aquocomplexes of Fe²⁺ and hydrogen peroxide (equation (24)):

$$\left[\operatorname{Fe}(\mathbf{L})_{x}(\mathbf{H}_{2}\mathbf{O})_{y}\right]^{2+} + \operatorname{H}_{2}\operatorname{O}_{2} \xrightarrow{k = 2 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}} \times \left[\operatorname{Fe}(\mathbf{H}_{2}\mathbf{O}_{2})(\mathbf{L})_{x}(\mathbf{H}_{2}\mathbf{O})_{y-1}\right]^{2+} + \operatorname{H}_{2}\operatorname{O}$$
(24)

where L is any inorganic or organic ligand of Fe^{2+} .

Subsequently, the complex containing the H_2O_2 as a chelator undergoes an inner-sphere two-electron transfer reaction to form the ferryl ion:

$$\left[\operatorname{Fe}(\mathrm{H}_{2}\mathrm{O}_{2})(\mathrm{L})_{x}(\mathrm{H}_{2}\mathrm{O})_{y-1}\right]^{2+} \xrightarrow{k_{\mathrm{i}_{1}}} \times \left[\operatorname{Fe}(\mathrm{OH})_{2}(\mathrm{L})_{x}(\mathrm{H}_{2}\mathrm{O})_{y-1}\right]^{2+}$$
(25)

where k_{i1} presents a value in the range 10^2-10^4 s⁻¹ depending on the nature of chelators of the ferrous ion (Yamazaki and Piette, 1991; Bossmann *et al.*, 1998). The intermediate Fe⁴⁺ complex in equation (25) may generate free hydroxyl radicals through the following reaction:

$$\left[\operatorname{Fe}(\mathrm{OH})_{2}(\mathrm{L})_{x}(\mathrm{H}_{2}\mathrm{O})_{y-1}\right]^{2+} + \mathrm{H}_{2}\mathrm{O}$$
$$\rightarrow \left[\operatorname{Fe}(\mathrm{L})_{x}(\mathrm{H}_{2}\mathrm{O})_{y}\right]^{3+} + \mathrm{HO} \cdot + \mathrm{HO}^{-}$$
(26)

In contrast to the hypothesis of the ferryl ion formation, other authors claim that the variation in the value of k_{i2} to generate the hydroxyl radical is due to the presence of organic ligands. Thus, according to Sedlak and Hoigné (1993), k_{i2} would have a value of $3.1 \pm 0.6 \times 10^4$ M⁻¹s⁻¹ when oxalate ions are in the reaction media. Other substances able to increase the value of k_{i2} would be gallic acid, catechol, dihydroxybenzoic acid, etc. (Sun and Pignatello, 1993). Given that the structure of these compounds is able to increase the value of k_{i2} , it is likely that the parent compound (pHB) itself acts as a chelator of ferrous iron accelerating the rate of the initial step (see equation (27)). In this case a complex similar to that proposed by Walling and Amarnath (1982) using mandelic acid may be formed:



The stoichiometric coefficient for the complex would likely be $Fe(pHB)_2^{2+}$ in the same manner as found for a similar structure like picolinic acid (Sawyer *et al.*, 1996).

The mechanism of reactions was tested by varying the value of k_{i2} from 76 to an average value between 10^2 and $10^4 M^{-1} s^{-1}$. In this case, either the assumption of a higher value of k_{i2} or taking into consideration the formation of Fe⁴⁺ (k_{i1}) as an additional oxidant (reactions (24) and (25)), would likely lead to similar results, since it has been reported previously that both the hydroxyl radical and the ferryl ion present a similar reactivity and stoichiometry (Yamazaki *et al.*, 1998; Walling, 1998) although they differ in selectivity.

Figure 4 shows the theoretical (dotted lines) and experimental (symbols) concentration profiles of *p*HB depletion with time for the experiments presented in Fig. 2. It can be observed that the model is significantly improved if compared to results obtained when utilising a value of k_{i2} of 76 M⁻¹s⁻¹. It is also noticeable that the higher the value of the hydrogen peroxide concentration fed, the higher the effect of the k_{i2} value on theoretical profiles.

To validate the kinetic model Fig. 5 also presents the computed values obtained when varying several operating variables other than hydrogen peroxide concentration fed to the reactor. Thus, as observed from this figure the kinetic model does a good job when changing the flowrate of reagents injected, the initial concentration of the parent compound and the concentration of ferrous iron fed. Moreover, radical concentrations simulated by the mechanism are in the order of magnitude expected, for instance $\approx 10^{-13}$ M for free hydroxyl radicals and $\approx 10^{-11}$ – 10^{-7} M (depending on nature) for organic radicals.



Fig. 4. Degradation of *p*-hydroxybenzoic acid in aqueous solution by Fenton's reagent. Evolution of the normalised remaining concentration of *p*HB with time. Influence of hydrogen peroxide concentration in the feeding solution $(C^*_{H_2O_2})$. Conditions: T=293 K, pH=3.2, $C_{pHBo}=0.01$ M, $C^*_{Fe^{2+}}=0.01$ M, pumping time=30 min, flowrate= 0.31 mL min⁻¹. Dotted lines: model calculations assuming $k_{i2}=10^3$ M⁻¹ s⁻¹.



Fig. 5. Degradation of *p*-hydroxybenzoic acid in aqueous solution by Fenton's reagent. Evolution of the normalised remaining concentration of *p*HB with time. General conditions: T=293 K, pH=3.2, $C_{pHBo}=0.01$ M, $C_{Fe^{3+}}^*=0.01$ M, $C_{H_2O_2}^*=2.65$ M, pumping time=30 min, flowrate=0.31 mL min⁻¹. Dotted lines: model calculations assuming $k_{i2}=10^3$ M⁻¹s⁻¹. Specific conditions: \bigcirc \blacktriangle , pumping time=10 min, flowrate=0.92 mL min⁻¹; \odot \checkmark , $C_{pHBo}=0.0033$ M; \odot \blacklozenge , $C_{H_2O_2}=2.65$ M; \odot \blacksquare , pumping time=60 min, flowrate=0.15 mL min⁻¹.

Figure 6 shows the evolution of Fe^{2+} , dihydroxybenzene and peroxides concentration with time for both experimental and model calculations. It should be pointed out that calculated results in the figure representing peroxide concentration just correspond to hydrogen peroxide. From Fig. 6 it can be inferred that the value of k_{i2} does not significantly affect the concentration profiles of Fe^{2+} , dihydroxybenzene and phenol (results not shown in the latter case). However, the theoretical accumulation of hydrogen peroxide in the bulk of reaction is reduced when k_{i2} is increased to a value of 10^3 (see Fig. 6B). Discrepancies between experimental peroxide concentration and theoretical evolution of H_2O_2 concentration suggest the generation of organic peroxides



Fig. 6. Degradation of *p*-hydroxybenzoic acid in aqueous solution by Fenton's reagent. Evolution of dihydroxybenzene (HQ), hydrogen peroxide and total peroxides (ROOH) and ferrous iron concentration with time. Conditions: as in Fig. 1 ($C_{\text{Fe}^{2+}}^* = 0.01 \text{ M}$). Dotted lines: model calculations. (A) $k_{i2} = 76 \text{ M}^{-1} \text{ s}^{-1}$. (B) $k_{i2} = 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

according to the following mechanism (MacFaul et al., 1998):

$$> CH_{\bullet} + O_2 \rightarrow > CHOO_{\bullet}$$
 (28)

$$> CHOO_{\bullet} + > CH_2 \rightarrow CHOOH + > CH_{\bullet}$$
 (29)

It is noteworthy that reaction (29) constitutes a different route of substrate elimination and should not be ruled out in certain cases as for example cyclohexene elimination (MacFaul *et al.*, 1998).

Dihydroxybenzoic acid, phenol and polyphenols like catechol, hydroquinone, resorcinol and 1,2,3 benzenetriol were detected by GC/MS and their presence was attributed to simple decarboxylation/ hydroxylation reactions of either *p*HB or intermediates formed from the former. Other species like 2,2-dimethyl 2,3-dihydro 7-benzofuranol or 5-methyl 2-furancarboxaldehyde, also identified by GC/MS, were likely generated through more complicated mechanisms involving organic radical-radical termination, internal rearrangement, etc. Table 1 shows the intermediates detected and identified by GC/MS.

In this work hydroxylated species from *p*HB (dihydroxy and trihydroxybenzoic acids) were detected only at trace levels. Contrarily, Nagata *et al.* (1996) found the hydroxylated species of hydroxybenzoic acid as the principal intermediates detected when a sonochemical treatment was applied. These results may be explained if: (a) under the conditions used in this work the main oxidising species is not HO[•] or (b) dihydroxybenzoic acid undergoes decarboxylation so rapidly that its concentration does not reach the levels of other intermediates.

Fable 1.	Intermediates identified in the Fenton's oxidation	of
	phenolic-type compounds by GC/MS	

Identified compound	Substrate ^a
Phenol	1
1-Methyl-4-(1-methylethyliden) cyclohexene	1
1,2 Benzenediol	1
Hydroquinone	1
Catechol	1
1,2,3 Benzenetriol	1
Dihydroxybenzoic acid	1
3,4 Dihydroxybenzaldehyde	1
2,3, Dihydro 2,2, dimethyl 7-benzofuranol	1
5-Methyl 2-furancarboxaldehyde	1
Resorcinol	1
2-Furancarboxylic acid	2
3,4 Furandicarboxylic acid	3
2,3, Dihydrobenzofurane	2
4-Hydroxybenzaldehyde	2
2,4-bis (1,1 dimethylethyl) phenol	2
4 Methylphenol	2

^a 1—*p*-hydroxybenzoic acid;

2-p-hydroxybenzoic acid + tyrosol + p-coumaric acid;

3-p-coumaric acid.

Although the decarboxylation process does not preclude the involvement of free hydroxyl radicals, Siegel and Lanphear (1979) concluded that benzoyl-formic acid (with a structure similar to pHB) decarboxylated to benzoic acid through oxidation with a highly reactive iron species.

To cast light on the nature of the oxidising species involved, some experiments were conducted in the presence of an *apparent* hydroxyl radical scavenger, tert-butyl alcohol (t-BuOH). Two values of t-BuOH concentration were examined, 0.01 and 0.05 M. An induction period at the beginning of the process was experienced (see Fig. 7), increasing the length of this period as the t-BuOH amount in the media was increased. Again theoretical calculations (just by considering HO. as the unique reactive species) overestimated the experimental results, even when utilising a value of k_{i2} of $10^3 M^{-1} s^{-1}$. From these results some considerations can be postulated. On the one hand, some authors (Rahhal and Richter, 1988) have claimed that the inefficiency of t-BuOH to prevent substrate oxidation in Fenton's systems is attributable to the absence of HO. However, in this study some inhibition was noticed, indicating that t-BuOH and the generated oxidising species reacted to some extent. On the other hand, other works published in the literature (Yamazaki and Piette, 1991) have pointed out that the Fenton reaction is scavenged by t-BuOH no matter the nature of the oxidising agent. In addition, it could be suggested that radicals formed from the oxidation of *t*-BuOH could reduce Fe^{3+} to Fe^{2+} promoting the system. However, since primary radicals are not oxidized by ferric iron, Fenton's reagent oxidation of t-BuOH gives a dimer as essentially the sole product, and therefore regeneration of ferrous iron is not possible (Walling



Fig. 7. Degradation of *p*-hydroxybenzoic acid in aqueous solution by Fenton's reagent. Evolution of the normalised remaining concentration of *p*HB with time. Influence of added tert-butyl alcohol (*t*-BuOH). Conditions: as in Fig. 1 ($C_{\text{Fe}^{2+}}^* = 0.01 \text{ M}$). Dotted lines: model calculations $(k_{i2} = 10^3 \text{ M}^{-1} \text{ s}^{-1})$.

and Amarnath, 1982). Once more, these contradictory statements seem to corroborate the hypothesis of the existence of different oxidising species, namely HO., Fe IV, ROO., etc.; one of those prevails depending on external operating conditions and specially the nature of the substrate to be oxidised. The shape of the curves obtained for the experiments completed in the presence of *t*-BuOH indicates that at the first stages of the process an oxidising species that is not scavenged by *t*-BuOH is being formed, although the primary step of the process is likely the attack of the hydroxyl radical to *p*HB.

Finally, to confirm the existence of additional pathways of organic substrate removal, a series of experiments was carried out by utilising several substrates of polyphenolic nature similar to that of *p*-hydroxybenzoic acid. As a first step, the second-order kinetic constants of *p*HB, tyrosol and *p*-coumaric acid in their reaction with the hydroxyl radical were calculated utilising the system UV/H₂O₂ in excess of H₂O₂ (Beltrán *et al.*, 1995). Values of 11.4, 6.7 and $5.7 \times 10^9 \text{ M}^{-1} \text{s}^{-1}$ were determined for the aforementioned rate constants corresponding to *p*HB, tyrosol and *p*-coumaric acid–hydroxyl radical reactions, respectively.

Figure 8 shows the evolution of the three compounds studied when treated separately by Fenton's reagent (solid symbols). As can be observed from this figure, the reactivity follows the trend $pHB > Tyrosol \approx p$ -coumaric acid. Therefore, according to the rate constant values, the higher the reactivity with the hydroxyl radical the faster Fenton's reaction. However, if pHB acid, tyrosol and p-coumaric acid are oxidised simultaneously (same initial concentration) different results are obtained. From Fig. 8 (open symbols) a shift in reactivity can



Fig. 8. Degradation of *p*-hydroxybenzoic acid, tyrosol and *p*-coumaric acid in aqueous solution by Fenton's reagent. Evolution of the normalised remaining concentration with time. Conditions: T = 293 K, pH = 3.2, $C_0 = 0.0033$ M, $C_{\text{Fe}^{2+}}^* = 0.01$ M, $C_{\text{H}_2\text{O}_2}^* = 2.65$ M, pumping time = 30 min, flowrate = 0.31 mL min⁻¹. Experiments carried out separately (solid symbols) and simultaneously (open symbols).

be observed as follows: p-coumaric acid > pHB > tyrosol.

A plausible explanation to these "anomalous" results is, as stated previously, the presence of oxidising agents other than the hydroxyl radical that present a different selectivity towards the model compounds studied. Similarly, Pignatello and coworkers (Pignatello et al., 1999) gave evidence of an additional pathway of cyclohexane loss when comparing experiments carried out by the photo-Fenton system and other reactions that only produce hydroxyl radicals, for instance UV/H₂O₂. The change in the kinetic deuterium isotope effect (KDIE) that they experienced, was attributed to high-valent oxoiron complexes. However, the classic Fenton's reaction in the dark showed no differences when compared to the UV/H2O2 system.

A simultaneous oxidation experiment of pHB, tyrosol and p-coumaric acid using the system UV/ H₂O₂ (hydrogen peroxide in excess to discard the photolysis contribution) showed a similar order of reactivity to that found for the simultaneous Fenton's treatment (not shown). These results confirm the existence of reactive species formed from the original substrates (organic radicals) which would react with a different selectivity depending on the nature of the substance to be oxidised. This synergising effect has already been observed in previous works when using similar radical generating systems like wet air oxidation (Kolaczkowski *et al.*, 1997). pounds from aqueous solutions. *p*-Hydroxybenzoic acid removal has been investigated by using the iron II catalysed decomposition of hydrogen peroxide. The study of typical operating variables of this system resulted in the following statements:

- Fe^{2+} seems to play a catalytic role in the process, being regenerated throughout the experiments. As a consequence, hydrogen peroxide is the limiting reactant and an optimum value of the Fe^{2+}/H_2O_2 ratio may, thereby, be found.
- Activation energy of the process must be low, since an increase in reaction temperature from 284 to 314 K did not result in appreciable changes in the *p*HB acid conversion rate.
- A remarkable inhibition of the reaction was noticed when pH was increased from acidic (pH = 3.2) to neutral conditions (pH = 7).
- Among the intermediates identified, the presence of phenol, catechol, hydroquinone and trihydroxybenzene suggests a decarboxylation step in the mechanism.

Although the chemistry of Fenton's systems involves a rather complex mechanism, an attempt has been made to fit experimental results to a simplistic kinetic model. In the model the most important reactions of the classic Fenton's chemistry (generation of hydroxyl radicals) have been considered. From the application of the kinetic model some inferences were deduced:

- Although the model rightly predicts the quantitative effect of the operating parameters checked, it overestimates the experimental results, specially at the beginning of the process. The S-shaped theoretical concentration profiles obtained suggest a higher value of the reaction rate that generates the oxidising species involved in *p*HB removal. An increase in one order of magnitude in this kinetic constant resulted in the improvement of model predictions.
- The anomalous low efficiency of *tert*-butyl alcohol (hydroxyl radical scavenger) to prevent *p*HB acid oxidation prompts the thought that other oxidising species are implicated in the system.
- Oxidation of *p*HB, tyrosol and *p*-coumaric acid conducted by using the Fenton's reagent and the UV/H₂O₂ system gives a different order of reactivity whether experiments are carried out with individual compounds or simultaneously. This result indicates the formation of organic radicals involved in the mechanism.

CONCLUSIONS

Fenton's reagent seems to be an appropriate method to efficiently remove phenolic-type com*Acknowledgements*—This work has been supported by the junta de Extremadura and Fondo Social Europeo (Project IPR98EC001).

REFERENCES

- Barbeni M., Minero C., Pelizetti E., Borgarello E. and Serpone N. (1987) Chemical degradation of chlorophenols with Fenton's reagent. *Chemosphere* 16, 2225–2237.
- Beltrán F. J., González M., Rivas F. J. and Alvarez P. (1998) Fenton reagent advanced oxidation of polynuclear aromatic hydrocarbonsin water. *Water Air and Soil Pollut.* **105**, 685–700.
- Beltrán F. J., Ovejero G. and Rivas F. J. (1995) Oxidation of polynuclear aromatic hydrocarbons in water. 3 UV radiation combined with hydrogen peroxide. *Ind. Eng. Chem. Res.* 35, 883–890.
- Bidga R. J. (1996) Fenton's chemistry: an effective advanced oxidation process. *Environ. Technol.* 34–39.
- Bossmann S. H., Oliveros E., Göb S., Siegwart S., Dahlen E. P., Payawan L., Straub M., Wörner M. and Braun A. M. (1998) New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced Fenton reactions. J. Phys. Chem. A. 102, 5542–5550.
- Chen R. and Pignatello J. J. (1997) Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds. *Environ. Sci. Technol.* **31**, 2399–2406.
- Collins P. F., Dihel H. and Smith G. F. (1959) 2,4,6-Tripyridyl-s-triazine as a reagent for iron. Determination of iron in limestone, silicates and refractories. *Anal. Chem.* **31**, 1862–1867.
- Farhataziz and Ross A. B. (1977) Selected specific rates of reactions of transients from water in aqueous solution. III Hydroxyl radical and perhydroxyl radical and their radical ions. *Nat. Stand. Ref. Data Ser. Nat. Bur. Stand.* (US) NSRDS-NBS **59**, 1–113.
- Haber F. and Weiss J. (1934) The catalytic decomposition of hydrogen peroxide by iron salts. *Proc. Roy. Soc. A* 134, 332–351.
- Hardwick T. J. (1956) The rate constant of the reaction between ferrous ions and hydrogen peroxide in acid solution. *Can. J. Chem.* 35, 428–436.
- Kolaczkowski S., Beltrán F. J., McLurgh D. B. and Rivas F. J. (1997) Wet air oxidation of phenol: factors that may influence global kinetics. *Trans. Inst. ChemEng. Part B.* 75, 257–265.
- Kopsidas G. C. (1992) Wastewater from the preparation of table olives. *Water Res.* 26, 629–631.
- Lin S. H. and Lo C. C. (1997) Fenton process for treatment of desizing wastewater. *Water Res.* **31**, 2050–2056.

- López F. and Ovelleiro J. L. (1978) Wine distillery wastewater remediation (Depuración de las aguas residuales de las destilerías de alcohol vínico). *Ingenier. Quíím.* 109, 167–178.
- MacFaul P. A., Wayner D. D. M. and Ingold, K. U. (1998) A radical account of oxygenated Fenton chemistry. Acc. Chem. Res. 31, 159–162.
- Nagata Y., Hirai K., Bandow H. and Maeda Y. (1996) Decomposition of hydroxybenzoic acid and humic acids in water by ultrasonic irradiation. *Environ. Sci. Technol.* **30**, 1133–1138.
- Pignatello J. J. (1992) Dark and photoassisted Fe³⁺ catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environ. Sci. Technol.* 26, 944–951.
- Pignatello J. J., Liu D. and Huston P. (1999) Evidence for an additional oxidant in the photoassisted Fenton reaction. *Environ. Sci. Technol.* 33, 1832–1839.
- Rahhal R. and Richter H. W. (1988) Reduction of hydrogen peroxide by the ferrous iron chelate of diethylenetriamine-N, N, N',N", N"-pentaacetate. J. Am. Chem. Soc. 110, 3127–3133.
- Sawyer D. T., Sobkowiak A. and Matsushita T. (1996) Metal [MLx=Fe, Cu, Co, Mn]/hydroperoxide induced activation of dioxygen for the oxygenation of hydrocarbons: oxygenated Fenton chemistry. Acc. Chem. Res. 29, 409–416.
- Sedlak D. L. and Hoigné J. (1993) The role of copper and oxalate in the redox cycling of iron in atmospheric waters. *Atmos. Environ.* 27A, 2173–2185.
- Siegel B. and Lanphear J. (1979) Iron catalyzed oxidative decarboxylation of benzoylformic acid. J. Am. Chem. Soc. 101, 2221–2222.
- Sun Y. and Pignatello J. J. (1993) Activation of hydrogen peroxide by iron (III) chelates for abiotic degradation of herbicides and insecticides in water. J. Agric. Food Chem. 41, 322–327.
- Walling C. (1998) Intermediates in the reactions of Fenton type reagents. Acc. Chem. Res. 31, 155–157.
- Walling C. and Amarnath K. (1982) Oxidation of mandelic acid by Fenton's reagent. J. Am. Chem. Soc. 104, 1185–1189.
- Yamazaki I. and Piette L. H. (1991) EPR Spin trapping study on the oxidizing species formed in the reaction of the ferrous ion with hydrogen peroxide. J. Am. Chem. Soc. 113, 7588–7593.