

Fenton's Oxidation of Food Processing Wastewater Components. Kinetic Modeling of Protocatechuic Acid Degradation

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The oxidation of protocatechuic acid (PA), a typical phenol-type compound present in food processing wastewater, has been carried out by means of Fenton's reagent. Both the H₂O₂ and Fe(II) initial concentrations increase the PA degradation rate. Temperature also enhances the PA conversion when raised from 283 to 313 K, a further increase to 323 K results in a lower PA removal. Increasing the PA initial concentration leads to a decrease of conversion values but an opposite effect in terms of removal rate. pH values in the range 3–4 resulted in the total inhibition of the oxidation process. Similar PA depletion rates were experienced regardless of the oxidation state of the catalyst (ferrous or ferric iron). Additionally, an attempt based on the classic Fenton's chemistry plus some other stages accounting for the Fe(II) regeneration from Fe(III) and the inefficient H₂O₂ decomposition was conducted to model the process.

KEYWORDS: Fenton's reagent; protocatechuic acid; kinetics; phenolic compounds; water treatment; hydrogen peroxide.

INTRODUCTION

The increasing restrictions relating to the quality and quantity of aqueous discharges into natural aquatic systems or into the public sewage system are triggering the need for efficient and inexpensive wastewater treatment technologies. To the present, biological processes have traditionally been used to deal with moderately contaminated effluents showing acceptable levels of biodegradability. In contrast, the generation of highly polluted and/or biotoxic liquid wastes involves, in most of cases, the accumulation of these effluents in artificial ponds to reduce/minimize the problem by natural routes (evaporation, anaerobic activity, etc.). Typical examples of the latter situation are the accumulation of leachates from municipal landfill sites or the generation of extremely contaminated wastes from the farming and agricultural industries. Thus, in the latter case, the problem is sometimes aggravated by the seasonal character of the activities. Manufacturing processes such as those related to tomato byproducts, olive oil extraction, table olive production, distilleries, etc., are characterized by the generation of aqueous streams with a considerable COD (chemical oxygen demand) level and the presence of bactericide compounds of the phenol and polyphenol groups (*1*). Implementation of biological treatments in these situations is unthinkable.

The aforementioned phenol-type substances range from simple molecules such as phenolic acids to large, highly polymerized compounds such as tannins. Species such as gallic, protocatechuic, and hydroxybenzoic acids or tyrosol can be listed as some of the simplest molecules.

Because phenols show bactericidal properties when found in relatively high concentrations (*2*), alternative prebiological purification technologies are required. Thus, Fenton's reagent has been shown to efficiently degrade a wide number of contaminants in a nonspecific way. The success of this technology relies on its implementation simplicity and economy and the acceptable insensitivity to external disturbances (i.e., changes in influent composition, temperature, flow rate, etc.). However, the behavior of this system varies from case to case, i.e., the efficiency depends not only on the reactivity of the target compounds toward the oxidizing species generated but also on the capability of Fe(II) regeneration, complexation of iron forms, inefficient decomposition of hydrogen peroxide in parallel routes, etc.

In this work, protocatechuic acid (PA) has been used as a model substance typically found in food processing wastewater matrixes. The biological effect of this compound is a matter of controversy. Thus, some authors have claimed that it acts as an antioxidant preventing chemical-induced carcinogenesis, whereas others assert that it induces oxidative stress and promotes tumor formation. In the latter case, the mechanism is

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similar to Fenton's reagent, protocatechuic acid potentiating Fe(II)-induced lipid peroxidation of the cells (3).

Oxidation of PA has been previously studied by using other advanced oxidation processes such as photo-Fenton (4), O_3/UV or H_2O_2/UV methods (5), etc. However, a thorough analysis of Fenton's reagent features has not been completed until now. In this work, the main operating variables affecting Fenton's reagent performance have been studied. Additionally, an attempt has been conducted to model the process by means of a pseudoempirical model.

MATERIALS AND METHODS

Experiments were conducted under typical laboratory light in a jacketed cylindrical 2-L (reaction volume) glass vessel. The procedure was executed in discontinuous mode by initially adding an aliquot of concentrated hydrogen peroxide to a solution already containing the target compound and the required amount of Fe(II) ($FeCl_2 \cdot 4H_2O$, Sigma-Aldrich, 99.995%) or Fe(III) ($FeCl_3 \cdot 6H_2O$, Panreact, >97%). pH was adjusted by a buffer solution made of $H_3PO_4/NaOH$ (ionic strength 0.1 M). The variation of this parameter was negligible at the end of the reaction. Temperature was kept constant by using a thermostatic bath that continuously recirculated water through the reactor jacket.

Analysis of the parent compound (Sigma-Aldrich, 97%) was carried out by HPLC (HP 1100) in isocratic mode immediately after sampling. A Waters Nova-Pack C18 column was used with a 35:65 (v/v) methanol/water mixture (pH 2.5 with acetic acid) as the mobile phase at a flow rate of 1 mL min^{-1} . Ferrous ion in the solution was analyzed by the 2,4,6-tripyridyl-s-triazine (TPTZ) method. The pH of the reaction medium was followed by means of a Crison pH meter (GLP 21). H_2O_2 was monitored either iodometrically (high concentrations) or by the *N,N*-diethyl-1,4-phenylenediamine sulfate (DPD) method (low concentrations).

Details of the analytical procedure can be found elsewhere (6).

RESULTS AND DISCUSSION

Influence of Operating Variables. Influence of Initially Added Reagents' Concentrations. Hydrogen Peroxide. After some preliminary experiments confirming the negligible effect of H_2O_2 as a single oxidant at room temperature, a series of experiments was carried out by varying the concentration of hydrogen peroxide in the presence of Fe(II) while keeping the rest of operating parameters constant. Thus, the influence of this variable was investigated in the range from 1×10^{-3} to $5 \times 10^{-3} \text{ M}$ with an initial Fe(II) concentration of 10^{-4} M (ratio, $R = H_2O_2/Fe(II)$, ranging from 10 to 50). **Figure 1** illustrates the results obtained. From this figure is observed a positive influence of this parameter in terms of the PA elimination rate when the concentration of H_2O_2 is raised from 10^{-3} M ($R = 10$, 60% conversion after 30 min) to $4 \times 10^{-3} \text{ M}$ ($R = 40$, >95% conversion after 30 min). However, a further increase to $5 \times 10^{-3} \text{ M}$ ($R = 50$) did not lead to a significant improvement of the process. The hydrogen peroxide conversion profiles strongly depended on the initial R value. As observed from **Figure 1**, H_2O_2 conversion increased as the value of R was decreased. The direct relationship between PA and H_2O_2 conversions should also be noted. Thus, the complete disappearance of H_2O_2 in the bulk water prevented the further oxidation of the target compound.

Because one of the key stages in Fenton's processes is the initiating reaction of H_2O_2 decomposition to generate the oxidizing species in the reaction medium, the results described above were expected. The role played by hydrogen peroxide in the advance of the mechanism seems to be crucial in this system; however, this is not always the case. In other systems, the

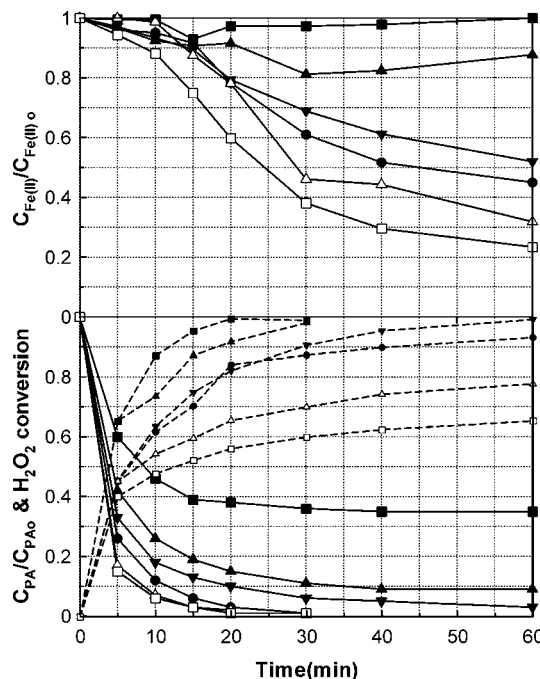


Figure 1. Degradation of protocatechuic acid in aqueous solution by Fenton's reagent. Influence of hydrogen peroxide initial concentration. Conditions: $T = 303 \text{ K}$, $pH = 3.7$, $C_{PA,0} = 6.5 \times 10^{-4} \text{ M}$, $C_{Fe(II),0} = 1 \times 10^{-4} \text{ M}$. $C_{H_2O_2,0} = (M \times 10^3)$: ■, 1.0; ▲, 2.0; ▼, 2.5; ●, 3.0; △, 4.0; □, 5.0.

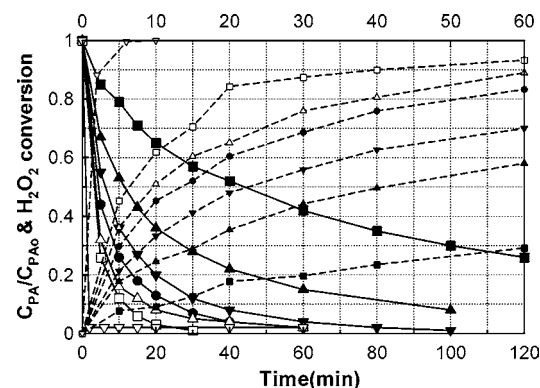


Figure 2. Degradation of protocatechuic acid in aqueous solution by Fenton's reagent. Influence of ferrous iron initial concentration. Conditions: $T = 303 \text{ K}$, $pH = 3.7$, $C_{PA,0} = 6.5 \times 10^{-4} \text{ M}$, $C_{H_2O_2,0} = 3 \times 10^{-3} \text{ M}$. $C_{Fe(II),0} = (M \times 10^5)$: ■, 1.0; ▲, 3.0; ▼, 5.0; ●, 6.5; △, 8.0; □, 10; ▽, 50.

propagation of the oxidative process proceeds through the formation of organic peroxides even in the absence of H_2O_2 (7).

Additionally, from **Figure 1**, it is inferred that the system is capable of continuously reducing Fe(III) to Fe(II) (provided that the PA conversion is not too high), i.e., it is hypothesized that some of the intermediates formed play an essential role in the reduction stage. When these intermediates are further oxidized, Fe(III) starts to accumulate because of the reaction of Fe(II) and the remaining H_2O_2 .

Fe(II). The influence of the initial ferrous iron concentration was investigated in the interval from $1 \times 10^{-5} \text{ M}$ to $5 \times 10^{-4} \text{ M}$ ($R = 300-6$). **Figure 2** depicts the evolution profiles of the normalized PA concentration and H_2O_2 conversion for the aforementioned series. As observed, this parameter exerted a significant influence in the range of values investigated, the process becoming extremely fast when the amount of Fe(II)

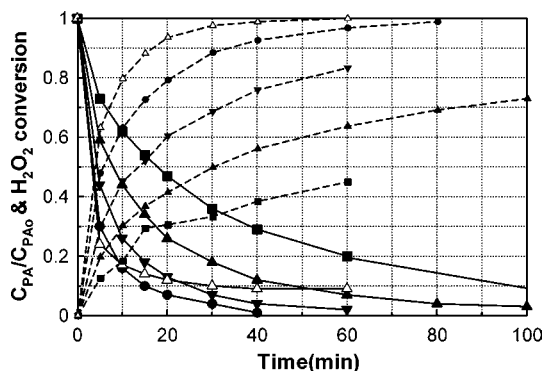


Figure 3. Degradation of protocatechuic acid in aqueous solution by Fenton's reagent. Influence of temperature. Conditions: $\text{pH} = 3.7$, $C_{\text{PA},0} = 6.5 \times 10^{-4} \text{ M}$, $C_{\text{H}_2\text{O}_2,0} = 3 \times 10^{-3} \text{ M}$, $C_{\text{Fe(III)},0} = 6.5 \times 10^{-5}$, $T = (\text{K})$: ■, 383; ▲, 393; ▼, 303; ●, 313; △, 323.

was raised to $5 \times 10^{-4} \text{ M}$ ($R = 6$). Similarly to the previous experimental series, Fe(II) did not significantly change its concentration unless the protocatechuic acid disappeared (provided that some H_2O_2 remained in solution).

Influence of Temperature. The effect of temperature was studied from 283 to 323 K. Raising this parameter always led to an increasing hydrogen peroxide removal rate (see **Figure 3**). However, H_2O_2 decomposition is not directly related to PA oxidation. Thus, on one hand, temperature likely increased the reaction rate between hydrogen peroxide and any form of ferrous/ferric iron (chelated or not), thus increasing the rate of generation of oxidizing species (hydroxyl radicals or high-valence iron species). Simultaneously, on the other hand, temperature also influences the inefficient decomposition of hydrogen peroxide into inactive species (water and oxygen). These opposite effects trigger the profiles depicted in **Figure 3**. Hence, from 283 to 313 K, the enhancement of oxidizing species formation prevails over the inefficient H_2O_2 decomposition, but a further temperature increase, to 323 K, because of the wasting of the available H_2O_2 , does not result in the expected improvement in PA degradation.

Influence of Catalyst Oxidation State. Traditionally, the efficacy of Fenton's reagent has been related to the presence of Fe(II) and the ability of the system to regenerate it. For instance, **Figure 1** shows how Fe(II) is continuously regenerated from its oxidized form when the PA conversion is below $\sim 90\%$. Consequently, a priori, the Fe(III)/ H_2O_2 system should be as effective as the Fe(II)/ H_2O_2 system once a minimum amount of Fe(II) is formed to initiate the redox cycle.

Figure 4 illustrates the oxidation results obtained with the Fe(III)/ H_2O_2 system. A direct comparison to the results achieved

with the Fe(II)/ H_2O_2 system is shown in the same figure (open symbols in left figure). From **Figure 4**, it is observed that the Fenton-like system [Fe(III)/ H_2O_2] is almost analogous to the classic Fenton's reagent in terms of PA depletion profiles ($R = 30\text{--}100$). Also, from **Figure 4**, it is seen that Fe(II) is formed in stoichiometric amounts immediately after the reaction begins. This latter fact indicates a reactivity comparable to that of the Fe(II)/ H_2O_2 system. Likely, the complex formed between Fe(III) and PA (**8**) presents a higher reactivity toward H_2O_2 than the Fe(III) aquocomplexes, immediately starting the reduction to Fe(II) and the classic Fenton's mechanism. Additionally, Fe(III) might be directly reduced by PA, thereby initiating the Fe(II)/ H_2O_2 system. Both routes would eventually lead to similar results; however, reduction of Fe(III) by PA must be a slow reaction compared to the dynamics of the Fenton-like system. Thus, no traces of Fe(II) were detected after Fe(III) and PA were mixed before H_2O_2 addition (time zero), whereas stoichiometric amounts of Fe(II) were measured in less than 10 min after H_2O_2 addition (see **Figure 4**).

Perhaps, a slightly lower activity can be envisaged for the Fe(III)/ H_2O_2 reagent, likely because of the time taken to establish the aforementioned complex equilibrium and the redox cycle. Hydrogen peroxide profiles indicate a slightly higher consumption of this reagent when Fe(III) is used; the differences might be attributable to the initial H_2O_2 uptake to reduce Fe(III) to Fe(II) to set off the redox cycle. Because the H_2O_2 conversion profiles in the two sets of experiments [with Fe(II) and with Fe(III)] are quite similar, it can be suggested that, after the initial period of the reaction, reduction of Fe(III) to Fe(II) must be carried out by species other than H_2O_2 .

Influence of Protocatechuic Acid Initial Concentration. Three values of PA initial concentration (3.25 , 6.50 , and $13.0 \times 10^{-4} \text{ M}$) were tested at constant initial concentrations of H_2O_2 ($3 \times 10^{-3} \text{ M}$) and Fe(II) ($1 \times 10^{-4} \text{ M}$). **Figure 5** shows the experimental results obtained. From this figure, it is observed that, at a given time, a higher PA initial concentration results in a lower conversion. However, in terms of absolute values of the reaction rate, it is inferred that the higher the initial PA concentration, the higher the degradation rate of the parent compound. Increasing the PA concentration also involves a higher H_2O_2 uptake. As in the previous experimental series, once the PA is completely degraded, Fe(II) begins to decrease in concentration.

Influence of pH. Two experiments completed at initial pH's of 2 and 5 led to the almost total inhibition of PA degradation (results not shown). In both experiments, the H_2O_2 concentration remained practically unchanged, while Fe(II) concentration underwent a fast reduction in the initial stages of the reaction

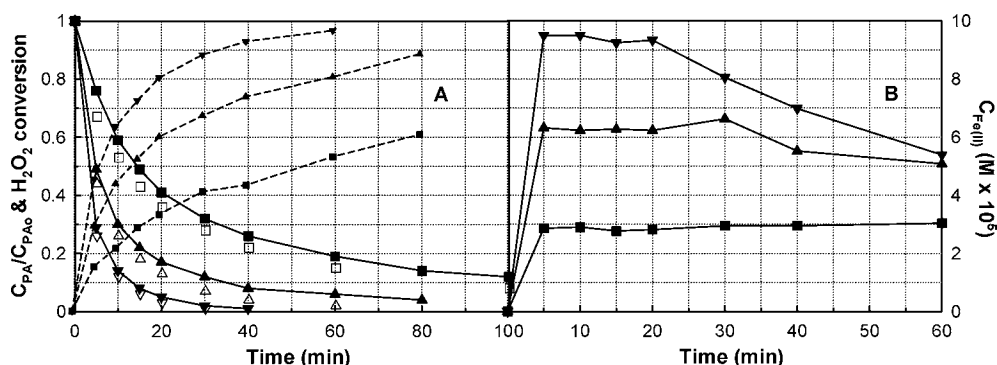


Figure 4. Degradation of protocatechuic acid in aqueous solution by Fenton-like reagent. Influence of Fe(III) initial concentration. Conditions: $T = 303 \text{ K}$, $\text{pH} = 3.7$, $C_{\text{PA},0} = 6.5 \times 10^{-4} \text{ M}$, $C_{\text{H}_2\text{O}_2,0} = 3 \times 10^{-3} \text{ M}$, $C_{\text{Fe(III)},0} = (\text{M} \times 10^{-5})$: ■, 3.0; ▲, 6.5; ▼, 10. [Open symbols in A correspond to experiments carried out with the Fe(II)/ H_2O_2 system.]

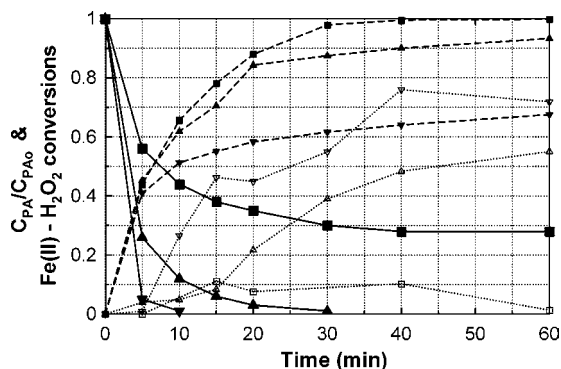


Figure 5. Degradation of protocatechuic acid in aqueous solution by Fenton's reagent. Influence of protocatechuic acid initial concentration. Conditions: $T = 303\text{ K}$, $\text{pH} = 3.7$, $C_{\text{H}_2\text{O}_2,0} = 3 \times 10^{-3}\text{ M}$, $C_{\text{Fe(II),0}} = 1 \times 10^{-4}\text{ M}$, $C_{\text{PA},0} = (\text{M} \times 10^4)$: ■, 13.0; ▲, 6.5; ▼, 3.25. [Open symbols: Fe(II) conversion.]

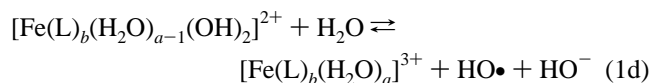
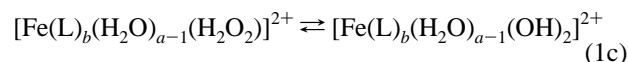
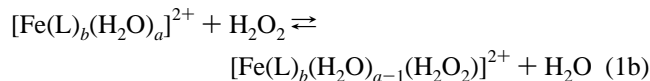
(i.e., roughly 80% conversion in less than 5 min). The decrease of Fe(II) at pH 5 can be attributed to autoxidation with dissolved oxygen (and/or H_2O_2) and further precipitation of Fe(III) oxohydroxides, which would eventually stop the oxidation. The inactivation of the system at pH 2 seems to be the consequence of the inhibition of Fe(III) reduction reactions. Thus, Fe(II) is immediately oxidized by hydrogen peroxide, but the further regeneration of the catalyst does not proceed at acceptable rates (see reaction 2 in the mechanism), and the process comes to a halt.

Kinetic Analysis. Fenton's chemistry is characterized by the complexity of the mechanism involved. In addition to the redox reactions implicated in the process, factors such as the presence

of chelating agents, formation of active organic peroxides, presence of Fe(III) reducing agents, etc., strongly influence the performance of this system. Even the nature of the oxidizing species is a matter of controversy (9).

The following features have been contemplated in the establishment of the mechanism:

(i) The initiating reaction of H_2O_2 decomposition depends on the species involved (see reactions 1a–1d). In this sense, several equilibrium reactions might take place, leading to different H_2O_2 decomposition rates depending on the operating conditions used.



Thus, the nature of L (an organic or inorganic chelating agent), the ratio a/b , and other factors actually influence the generation of hydroxyl radicals. (To simplify the mechanism, the ferryl ion in reaction 1c is not considered to be involved in the oxidation process.) Because the equilibrium constants for reactions 1a–1d cannot be known (i.e., L might be a high number of species), the initiating mechanism was reduced to a

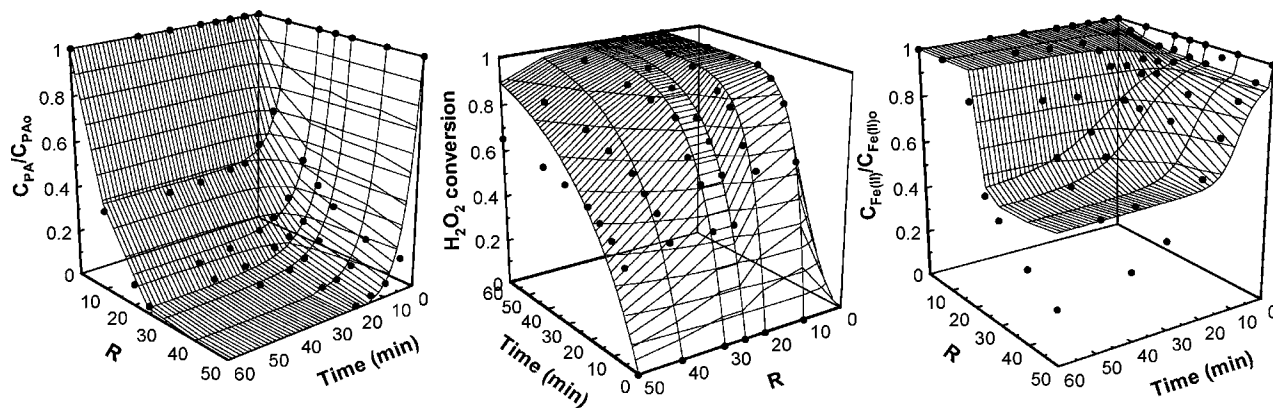


Figure 6. Degradation of protocatechuic acid in aqueous solution by Fenton's reagent. Influence of hydrogen peroxide initial concentration. Conditions as in Figure 1. (Symbols, experimental data; surface, model calculations.)

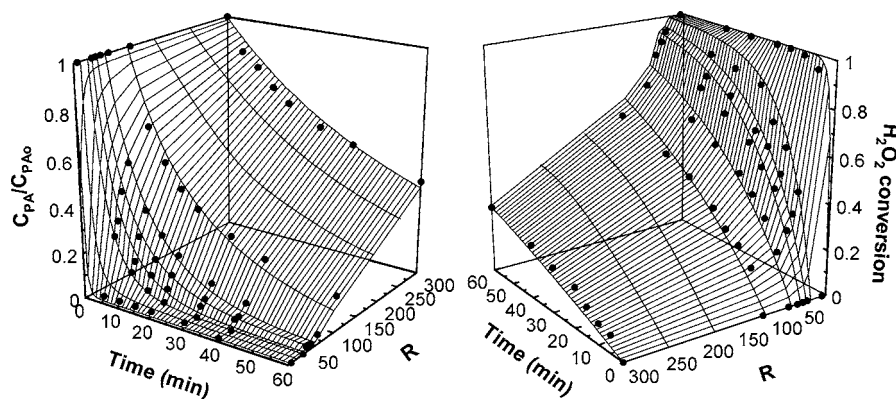
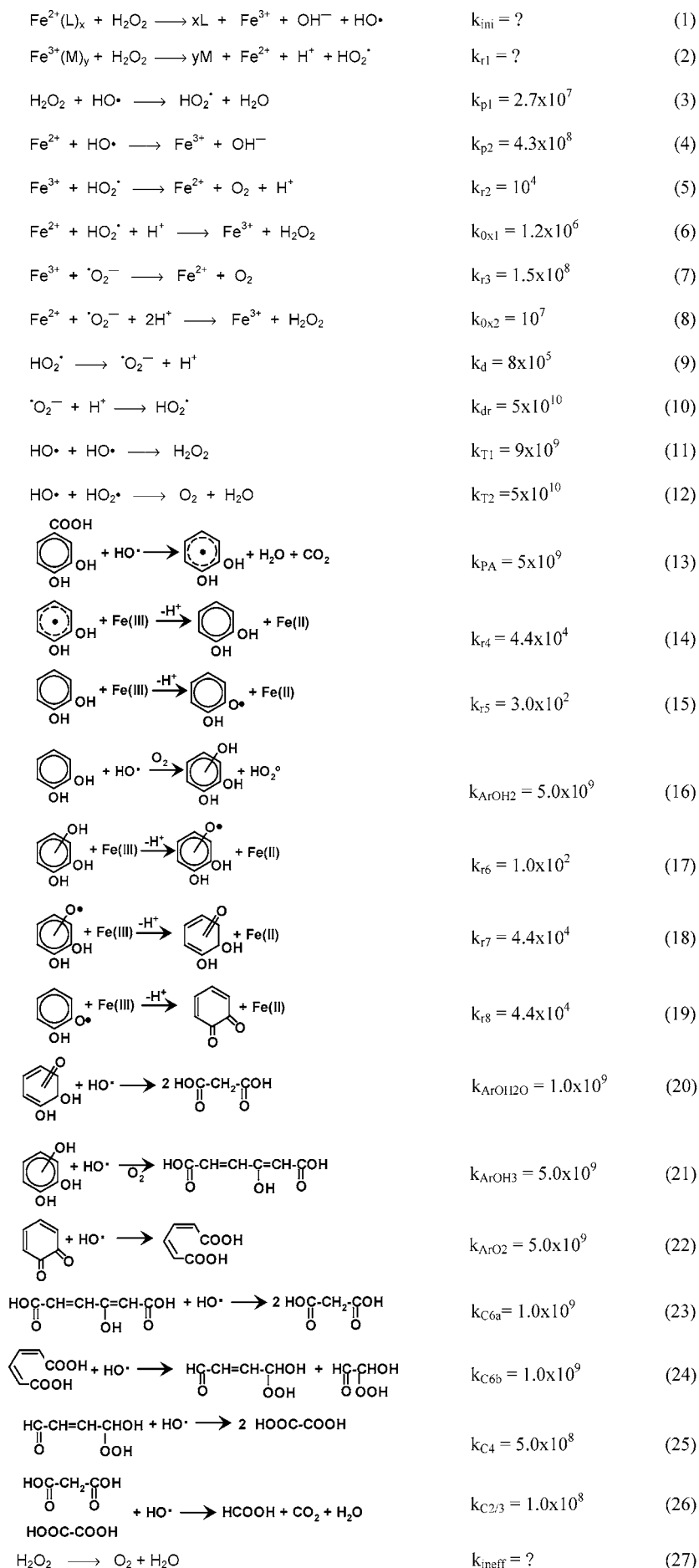


Figure 7. Degradation of protocatechuic acid in aqueous solution by Fenton's reagent. Influence of ferrous iron initial concentration. Conditions as in Figure 2. (Symbols, experimental data; surface, model calculations.)

Scheme 1



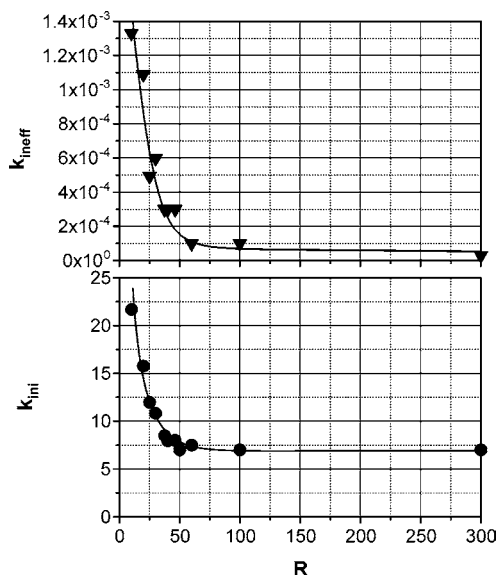


Figure 8. Optimization of k_{ini} and k_{ineff} under different values of R . Conditions: $T = 303$ K, $pH = 3.7$, $C_{PA,0} = 6.5 \times 10^{-4}$ M.

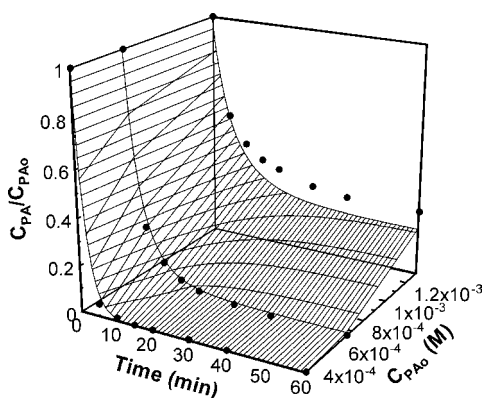


Figure 9. Degradation of protocatechuic acid in aqueous solution by Fenton's reagent. Influence of protocatechuic acid initial concentration. Conditions as in Figure 4. (Symbols, experimental data; surface, model calculations.)

simple reaction between Fe(II) and H_2O_2 (reaction 1), whose constant was taken as an adjustable parameter in the mechanism. Similarly to the catalytic effect of Fe(II), and for analogous reasons, the reaction of Fe(III) with H_2O_2 was also taken as an adjustable parameter.

(ii) The oxidation of PA involves the generation of reducing species capable of transforming Fe(III) into Fe(II). Similarly to

reaction 1, the effect of PA addition on Fe(III) reduction in the presence of H_2O_2 is considered by adjusting the k_{r1} value in reaction 2. Scheme 1 comprising reactions 1–27 was therefore adopted. These reactions considered the classic Fenton's steps (reactions 1–12) plus the oxidation of PA and some of the potential intermediates formed. Reactions 14–26 represent the reactivity of species of similar nature, i.e., acetic acid is likely formed after ring cleavage, although it does not specifically appear in the mechanism proposed, so it can be assumed to be represented by oxalic acid (the same applies for other potential intermediates).

The route for protocatechuic acid oxidation was built on the basis of the works of Rivas et al. (6), Chen and Pignatello (10), and Bailey (11). The rate constants corresponding to $HO\bullet$ attack were taken from literature values or assigned a generic value in the range of $(5 \times 10^9) - (1 \times 10^8)$ depending on the analogies between the compounds considered and other species whose kinetic constants are known. A similar strategy was followed in the case of the rest of reactions [i.e., Fe(III) reduction reactions].

(iii) Finally, H_2O_2 is considered to partially decompose into inert molecules (oxygen and water), the extent of this inefficient reaction depending on the operating conditions used, the nature and geometry of the reactor, the presence of trace elements, etc. This stage is represented by reaction 27.

The set of first-order differential equations derived from reactions 1–27 occurring in a batch reactor were solved with Mathematica5. The adjustable parameters k_{ini} , k_{r1} , and k_{ineff} were optimized to fit experimental and model results.

Figure 6 shows the evolution profiles of PA, Fe(II), and H_2O_2 corresponding to the experimental series shown in **Figure 1** as a function of R [$R = C_{H_2O_2,0}/C_{Fe(II),0}$]. As observed from this figure, the PA concentration profiles were adequately modeled by the proposed mechanism. Also, the hydrogen peroxide conversion curves were acceptably simulated, with a slight overestimation of this parameter for the highest R values used in this work. A similar trend was observed for the Fe(II) concentration profiles, i.e., a good fitting was obtained for low values of R , and some discrepancies at high reaction times were experienced for values of R above 40.

Figure 7 depicts the performance of the model when simulating the experimental series shown in **Figure 2**. In contrast to the previous series, even for high R values, the mechanism is capable of simulating the process with minor differences between theoretical and calculated profiles.

As stated previously, the values of k_{ini} and k_{ineff} depend on the operating conditions used. As a consequence, the optimization procedure gave a range of values for these constants, which

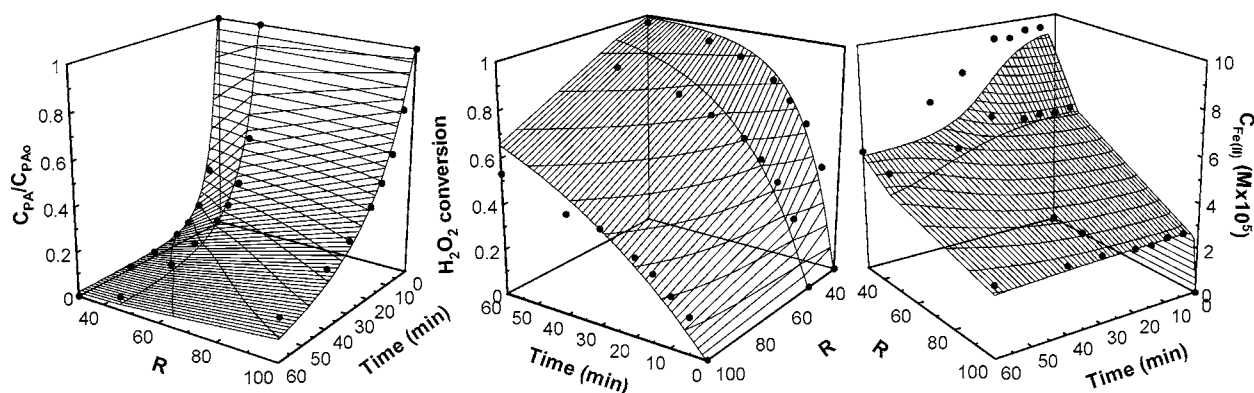


Figure 10. Degradation of protocatechuic acid in aqueous solution by Fenton's such as reagent. Influence of Fe(III) initial concentration. Conditions as in Figure 5. (Symbols, experimental data; surface, model calculations.)

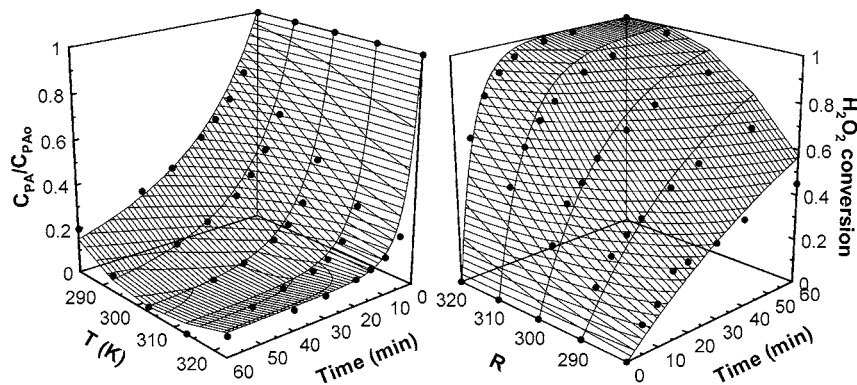


Figure 11. Degradation of protocatechuic acid in aqueous solution by Fenton's reagent. Influence of temperature. Conditions as in Figure 3. (Symbols, experimental data; surface, model calculations.)

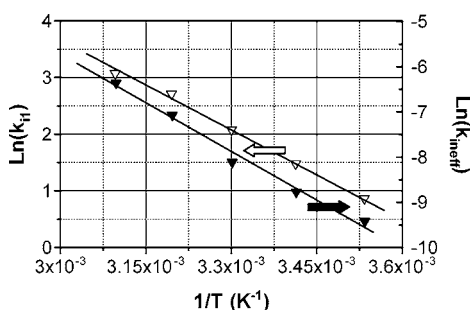


Figure 12. Degradation of protocatechuic acid in aqueous solution by Fenton's reagent. Arrhenius plots of k_{ini} and k_{ineff} . Conditions as in Figure 3.

are presented in **Figure 8**. From this figure, some points should be highlighted. First, the two rate constants follow similar patterns with minor changes when R is raised above 50. The highest values of k_{ini} and k_{ineff} were found when the lowest R values were utilized, i.e., both the effective and the inefficient H_2O_2 decomposition rates increased as the amount of Fe(II) was raised regarding to the amount of hydrogen peroxide. Additionally, the low value of k_{ini} , below the available value of $76 \text{ M}^{-1} \text{ s}^{-1}$ reported in organic free water, is noted. The reason for this remains unclear. In this sense, this type of compound (phenols) has been reported to enhance the H_2O_2 decomposition rate (6) in the presence of Fe(II)/Fe(III). In contrast, other authors have reported the antioxidant effect of PA by inactivating the Fe(II) molecule after the formation of a complex (12).

Once k_{ini} and k_{ineff} had been calculated for a range of R values, the validity of the model was tested for the experiments carried out at different initial PA concentrations. **Figure 9** corroborates the suitability of the mechanism by adequately modeling the experimental data obtained, in this case without optimization of any kinetic parameter.

The value of k_{r1} was obtained by using the experiments shown in **Figure 4**. [This rate constant played a minor role in the Fe(II)/ H_2O_2 system]. The values of k_{ini} and k_{ineff} used were taken from the previous analysis, so the only adjustable parameter was k_{r1} . A value of $k_{r1} = 5 \text{ M}^{-1} \text{ s}^{-1}$ was obtained after minimization of the accumulated errors. **Figure 10** displays the evolution profiles corresponding to PA degradation, H_2O_2 conversion, and Fe(II) generation.

As inferred from **Figure 10**, the mechanism does a good job even when dealing with the Fenton-like system instead of Fenton's reagent. The model qualitatively simulates the fast Fe(II) formation followed by a slight decrease as the parent compound disappears.

Finally, the series of experiments conducted at different temperatures were modeled. For this purpose, k_{ini} and k_{ineff} were

again considered as adjustable parameters. Likely, other reactions included in the mechanism are also affected by a change in temperature. However, a sensitivity analysis of the mechanism indicates that these two stages are the most important reactions taking place. Additionally, reactions involving radicals normally show a low activation energy, so their rate constants do not appreciably vary with temperature. **Figure 11** shows the experimental and calculated results for this series. Additionally, **Figure 12** depicts the Arrhenius plots corresponding to k_{ini} and k_{ineff} . From this representation, the following expressions were obtained:

$$\ln(k_{ini}) = -5168T^{-1} + 19.1 \quad (R^2 = 0.996) \quad (28)$$

$$\ln(k_{ineff}) = -7120T^{-1} + 15.6 \quad (R^2 = 0.986) \quad (29)$$

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