

Treatment of Olive Oil Mill Wastewater by Fenton's Reagent

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Wastewater from olive oil mills has been treated by means of the Fe(II)/H₂O₂ system (Fenton's reagent). Typical operating variables such as reagent concentration ($C_{\text{H}_2\text{O}_2} = 1.0\text{--}0.2\text{ M}$; $C_{\text{Fe(II)}} = 0.01\text{--}0.1\text{ M}$) and temperature ($T = 293\text{--}323\text{ K}$) exerted a positive influence on the chemical oxygen demand and total carbon removal. The optimum working pH was found to be in the range 2.5–3.0. The exothermic nature of the process involved a significant increase of the temperature of the reaction media. The process was well simulated by a semiempirical reaction mechanism based on the classic Fenton chemistry. From the model, the reaction between ferric iron and hydrogen peroxide [$k = 1.8 \times 10^{15} \exp((-12577 \pm 1248)/T)$] was suggested to be the controlling step of the system. Also, the simultaneous inefficient decomposition of hydrogen peroxide [$k = 6.3 \times 10^{12} \exp((-11987 \pm 2414)/T)$] into water and oxygen was believed to play an important role in the process. On the basis of stoichiometric calculations for hydrogen peroxide consumption, an estimation of the process economy has been completed.

Keywords: Fenton's reagent; olive oil mill wastewater; kinetics; iron; hydrogen peroxide; environmental remediation

INTRODUCTION

The foodstuff processing industry based on olive oil extraction and table olive preparation constitutes an important income source for many regions of the Mediterranean countries. In the first case, the oily juice of olives is extracted from the fruit through simple milling or, more recently, by means of centrifugal force. However, despite the increasing concern with regard to environmental matters, during the process relatively important amounts of wastewater are generated. Although the olive-related manufacturing industry possesses a seasonal character, the high contamination level of the wastewater generated results in serious trouble at the time for proper disposal and management. Moreover, the chelating character of some compounds present in these effluents may contribute to keeping some toxic heavy metals in solution, adding new factors of deterioration to the aquatic system. For the particular case of wastewater generated in olive oil production, a minimum dilution of 1:5000 is needed to safely dump this kind of effluent in natural aquatic streams. Because the latter action is not always possible, use of an economical and effective wastewater treatment to reduce the contaminant load of these effluents is of paramount importance.

Among the different effluent treatments reported in the literature for olive oil mill wastewater, disposal and further evaporation in artificial ponds has traditionally been the method used most widely (1). However, generation of odors due to anaerobic activity and the potential risk for the aquifers of the affected area make this method rather inadvisable. Aerobic biological treat-

ments require high residence times and previous conditioning of the wastewater to be treated (high dilution, pH adjusting, acclimation of microorganisms, etc.), the main advantage being the cheapness and simplicity of the installations needed (2). Most of the chemical oxidation processes lack effectiveness due to either the high cost of the oxidants or the low interval of chemical oxygen demand (COD) concentration for which the system is suitable (3). For example, in ozone-based processes, if oxidant wastage is to be avoided, a similar dilution to that required for the aerobic biodegradation is needed (4, 5).

In this study, olive oil mill wastewater remediation has been accomplished by means of Fenton's reagent (hydrogen peroxide plus a ferrous salt).

Fenton's reagent is a treatment suitable to process a wide variety of effluents regardless of their contaminant concentration and nature (6). It is an economical system characterized by its simple application and possibility of using perfectly mixed tank reactors; the system can be adapted to different volumes and conditions depending on the specific case (7).

Additionally, an attempt has been made to simulate the process by means of a pseudoempirical model. From the model, the apparent activation energy and pre-exponential factors of the most influential rate constants have been calculated.

MATERIALS AND METHODS

Experiments were carried out in a 500 mL glass reactor under sunlight conditions, batchwise, and in the presence of oxygen. The aqueous solution of reactants was homogenized by magnetic agitation to avoid concentration gradients. Systematically, samples were withdrawn and immediately analyzed after sampling (in <2 min). Preliminary experiments were carried out by quenching the samples with sodium thiosulfate. Results in terms of total carbon removed were compared to similar runs completed at the same conditions

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Table 1. Characteristics of Olive Oil Mill Wastewater with and without Dilution with Synthetic Urban Wastewater

| | raw wastewater | diluted wastewater (1:10) |
|--|--------------------|---------------------------|
| COD (mg L ⁻¹) | 164911 | 14650 |
| BOD ₅ (mg of O ₂ L ⁻¹) | 89000 | 10400 |
| BOD _f (mg O ₂ L ⁻¹) | 145000 | 13600 |
| TOC (mg L ⁻¹) | 66711 | 4887 |
| pH (mg L ⁻¹) | 4.85 | 5.30 |
| A ₂₅₄ (mg L ⁻¹) | 1.187 ^a | 0.673 ^b |
| N-NO ₃ ⁻ (mg L ⁻¹) | 870 | |
| N-NO ₂ ⁻ (mg L ⁻¹) | 147.6 | |
| N-NH ₄ ⁺ (mg L ⁻¹) | 1170 | |
| polyphenols ^c (mg L ⁻¹) | 5780 | 650 |
| TC (mg L ⁻¹) | 66735 | 5018 |

^a After dilution 1:200 with ultrapure water. ^b After dilution 1:20 with ultrapure water. ^c Measured as phenol.

without the addition of any quencher but immediate analysis. Because no important differences were obtained, the rest of the experiments were conducted in the absence of reducing or scavenging substances.

Olive oil mill wastewater was taken from a factory located in Navalvillar de Pela in the province of Badajoz (southwestern Spain). Experiments were carried out after dilution of the raw wastewater with synthetic urban wastewater (2) with a dilution factor of 10 (1 part olive oil mill wastewater plus 9 parts synthetic urban wastewater). The purpose of the dilution with synthetic urban wastewater was to simulate the conditions obtained if the Fenton process were integrated in a real plant for municipal wastewater treatment. Table 1 shows the main properties of the wastewater used before and after dilution.

All chemicals were provided by Aldrich and used without further purification. Analysis of COD was determined in a Dr. Lange spectrophotometer, the method based on the dichromat standard procedure. The positive interference derived from the presence of hydrogen peroxide was corrected by considering the correction factor proposed by Talinli and Anderson (8). Total carbon (TC) and organic carbon (TOC) were analyzed using a DC-190 Dohrman carbon analyzer. Biological oxygen demand (BOD) was determined by the respirometric method. In this case, 300 mL glass bottles containing known amounts of inocula were used. The content in polyphenols was measured using the reagent of Folin-Ciocalteu after liquid-liquid extraction of the sample with ethyl acetate. Results were expressed as equivalent phenol concentration. Total peroxide concentration was determined iodometrically. Ferrous ion in the solution was analyzed by the 2,4,6-tripyridyl-*s*-triazine (TPTZ) method; this analysis was carried out after hydrogen peroxide removal through decomposition with catalase. Details of the analytical procedure can be found elsewhere (4, 9). The pH of the reaction media was followed by means of a Radiometer Copenhagen pH-meter (HPM82).

RESULTS AND DISCUSSION

Influence of Operating Conditions. *Influence of Hydrogen Peroxide Initial Concentration.* A series of experiments was carried out at different hydrogen peroxide initial concentrations while the rest of the operating variables were kept constant. In these experiments COD, TC, pH, and reagent concentrations were analyzed throughout the whole reaction period. In terms of contamination level reduction, an increase of the H₂O₂ amount added to the reaction media resulted in the expected enhancement of the process (10–12). However, some other considerations could be withdrawn.

Thus, an increase of hydrogen peroxide fed to the reactor from 0.2 to 0.5 M significantly improved the conversion of COD (see Figure 1) and TC. Nevertheless, values of this reagent exceeding 0.5 M did not improve

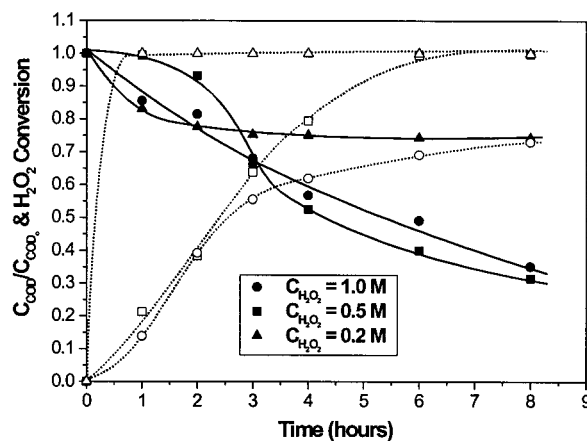


Figure 1. Fe(II)/H₂O₂ treatment of olive oil mill wastewater as demonstrated by evolution of the normalized COD concentration (solid symbols) and hydrogen peroxide conversion (open symbols) with time and the influence of H₂O₂ initial concentration. Conditions: T₀ = 293 K, pH = 2.8, C_{CO_D0} = 0.4 M (average value), C_{Fe(II)} = 0.01 M.

the process performance. Also, it should be pointed out that for the latter experiment (H₂O₂ = 0.5 M) a slight initial lag period was observed. This effect may be attributed to a different starting pH for this run (see Influence of pH). Thus, the aforementioned experiment started with a pH value of 3.11 (0.3 unit higher than the rest of experiments); however, once this parameter decreased to roughly 2.8 (within the first 1–2 h), the induction period disappeared. It is noteworthy to say that this induction period was not experienced when TC profiles were analyzed. A similar optimum value of pH has already been reported for the dechlorination of dichloroacetic acid by the Fe(III)/C₂O₄²⁻/hv/H₂O₂ system (13).

For the experiment carried out with the lowest H₂O₂ concentration (H₂O₂ = 0.2 M), COD degradation radically slowed after 1–2 h from the beginning of the reaction. This point coincided with the total hydrogen peroxide depletion from the media (see Figure 1). Therefore, this species seems to be the limiting reagent at the conditions used in this work. This is also observed after 8 h of treatment for the experiment conducted with an initial H₂O₂ concentration of 0.5 M.

Additionally, for the run completed with a large excess of hydrogen peroxide (H₂O₂ = 1 M), the maximum COD and TC conversions achieved after 24 h of reaction were roughly 70 and 55%, respectively. Values quite similar to those were found after 8 h of oxidation when H₂O₂ was still present in solution. In other words, a conversion plateau is experienced with no further reaction occurring after 8–9 h of treatment. It is evident that at these conditions, a fraction of the initial COD and/or end products generated after the oxidation (typically low molecular carboxylic acids that would explain the decrease of ~1 pH unit) are difficult to be further removed by the Fe(II)/H₂O₂ system. As discussed later, higher reductions of COD and TC can be obtained if more drastic operating conditions are used.

With the exception of the experiment completed with an initial H₂O₂ concentration of 0.2 M, in the rest of the experiments shown in this study, Fe(II) completely reacted within the first hour of reaction. Consequently, the chemistry of the Fe(II)/H₂O₂ system would be better defined as the chemistry of the redox couple Fe(II)–Fe(III) and H₂O₂. In this sense, it was also noticed that

the Fe(II) concentration increased as the COD concentration profile was approaching the final plateau (14). Moreover, an experiment carried out by initially adding Fe(III) instead of Fe(II) resulted in >50% COD removal in less than an hour of reaction [Fe(III) = 0.03 M, H₂O₂ = 0.5 M, pH 2], confirming the above statement.

Although similar COD and TC conversion values were obtained for experiments conducted with an H₂O₂ concentration >0.2 M, a higher phenolic content removal was observed when the starting H₂O₂ concentration was 1 M (86% phenol elimination). Nevertheless, in terms of final biodegradability of the effluent, measured as the ratio BOD/COD, the optimum value for this series was obtained when an initial H₂O₂ concentration of 0.5 M was used. Thus, for this experiment the calculated ratio was 1.79, compared to 1.11 and 0.85 for the experiment with H₂O₂ = 1 M and nontreated wastewater, respectively. The, a priori, contradictory results may be explained by taking into account the fact that a significant amount of hydrogen peroxide (a well-known disinfectant) remains in solution for the experiment carried out with the highest H₂O₂ concentration, decreasing, therefore, the BOD of the effluent.

Biodegradability of the wastewater could also be assessed by determining the evolution of the average oxidation state of carbon (AOSC) and the efficiency through partial oxidation (μ_{partox}). Thus, the following expressions were used (15, 16):

$$\Delta(\text{AOSC}) = \text{AOSC} - \text{AOSC}_0 = 4 \left[\frac{\text{COD}_0}{\text{TOC}_0} - \frac{\text{COD}}{\text{TOC}} \right] \frac{M_C}{M_{\text{O}_2}} \quad (1)$$

$$\mu_{\text{partox}} = \frac{\text{COD}_{\text{partox}}}{\text{COD}_0 - \text{COD}} \quad (2)$$

where

$$\text{COD}_{\text{partox}} = \frac{\text{TOC}[\Delta(\text{AOSC})]M_{\text{O}_2}}{4M_C} \quad (3)$$

In eqs 1–3 the subindex “0” denotes conditions at time zero and M_C and M_{O_2} are the molecular weights of carbon and oxygen, respectively. Theoretically, the closer the value of μ_{partox} to 1, the higher the extension of the oxidation to generate oxygenated intermediates instead of total mineralization to carbon dioxide. Contrarily a value of $\mu_{\text{partox}} = 0$ indicates that no partial oxidation proceeds and just complete conversion to CO₂ is occurring (15). In normal circumstances, an increase of μ_{partox} should lead to a more biodegradable effluent. This was corroborated for experiments carried out with 1 and 0.5 M of initial hydrogen peroxide concentration by calculating both parameters, $\Delta(\text{AOSC})$ and μ_{partox} , after 8 h of treatment. According to biodegradability tests, the experiment showing a lower value of the ratio BOD/COD (H₂O₂ = 1 M) gave values of $\Delta(\text{AOSC}) = 0.11$ and $\mu_{\text{partox}} = 0.022$, at least 1 order of magnitude below the values calculated for the experiment with starting H₂O₂ = 0.5 M [$\Delta(\text{AOSC}) = 1.46$ and $\mu_{\text{partox}} = 0.22$].

Influence of Ferrous Iron Initial Concentration. A series of experiments was carried out to assess the influence of the initial Fe(II) concentration used while the rest of the operating conditions were kept constant. Similarly to the hydrogen peroxide effect, an increase of the initial ferrous iron amount added to the reactor

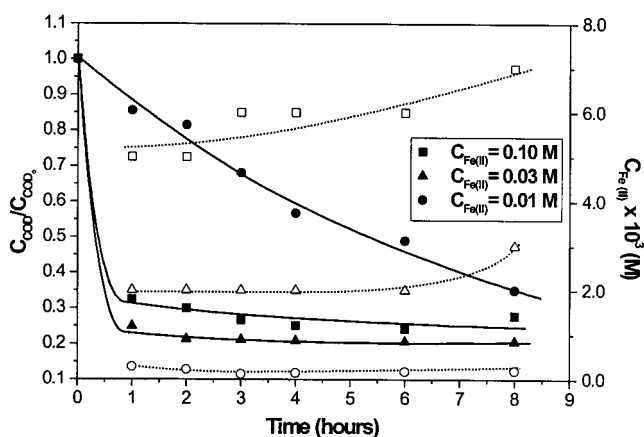


Figure 2. Fe(II)/H₂O₂ treatment of olive oil mill wastewater as demonstrated by evolution of the normalized COD (solid symbols) and Fe(II) (open symbols) concentrations with time and the influence of ferrous iron initial concentration. Conditions: $T_0 = 293$ K, pH = 2.8, $C_{\text{COD}_0} = 0.4$ M (average value), $C_{\text{H}_2\text{O}_2} = 1.0$ M.

significantly increased the COD conversion rate (see Figure 2). From this experimental series the following features were noticed.

For experiments carried out with initial Fe(II) > 10⁻² M an abrupt removal of COD and TC was observed at the beginning of the process. After this rapid conversion, the H₂O₂ concentration decreased to values of ~10⁻³ M and no further reaction was experienced. Also, after 8 h of reaction no important differences were observed in COD and TC final conversions regardless of the initial amount of Fe(II) used, confirming, therefore, the catalytic role of the couple Fe(II)/Fe(III).

A significant increase of temperature was also noticed for experiments with initial Fe(II) > 10⁻² M. Thus, for these experiments the reaction temperature rose from 20–22 to 65–67 °C in just a few minutes. Thereafter, due to heat exchange with the surrounding environment, a gradual decrease to room temperature occurred within 1.5–2 h from the start of the process.

The Fe(II) concentration also increased as the COD and TC conversions reached their final values (see Figure 2), demonstrating, therefore, the existence of reducing agents in the media.

Influence of pH. The performance of Fenton processes is highly affected by the reaction media pH (17, 18). Broadly speaking, low pH values in the interval 2–4 favor the efficacy of the oxidation. In this study different values of pH were investigated to ascertain the influence of this parameter on the removal of COD and TC.

From Figure 3 it is observed that, regardless of the starting pH of the reaction, the final COD values achieved in the process are basically the same. Similar results were obtained when the TC was measured (results not shown). Nevertheless, an induction period was experienced when the initial pH was raised from 2.8 to 7. The length of the lag period increased as the starting pH was closer to neutrality. Therefore, it is inferred that the initiating steps in the mechanism developed are markedly affected by this parameter. It should also be pointed out that the end of the induction period coincides in time to when the pH approaches a value of 3.0. The S-shaped depletion profiles observed for COD and TC suggest the development of an autocatalytic and/or radical reaction (i.e., formation of H⁺ that would accelerate the overall reaction rate). Likely, both mechanisms (autocatalytic and radical) should be

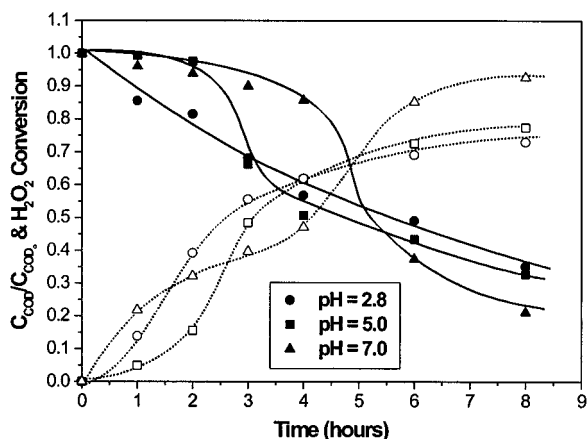


Figure 3. Fe(II)/H₂O₂ treatment of olive oil mill wastewater as demonstrated by evolution of the normalized COD concentration (solid symbols) and hydrogen peroxide conversion (open symbols) with time and the influence of pH. Conditions: $T_0 = 293$ K, $C_{\text{COD}0} = 0.4$ M (average value), $C_{\text{H}_2\text{O}_2} = 1.0$ M, $C_{\text{Fe(II)}} = 0.01$ M.

considered because it is probable that the initiating reactions are “accelerated” in acid media to generate radical species (i.e., hydroxyl radicals) or any other type of powerful oxidizing agent (i.e., high valence iron complexes) that would propagate the chain mechanism. As inferred from Figure 3, in the lag stage, the consumption of hydrogen peroxide in relation to COD removal is higher for experiments carried out at pH 5.0 and 7.0. Afterward, this overall stoichiometric factor converges for any pH once the induction phase has disappeared. Thus, by taking into account all of the experiments presented in this study, the global stoichiometric coefficient defined as the ratio of hydrogen peroxide uptake to COD removal was determined throughout the whole reaction period. An average value of 3.06 ± 0.42 mol of H₂O₂/mol of COD was obtained (calculations in the lag phase of experiments were not considered).

Influence of Temperature. A series of experiments was carried out to assess the influence of initial temperature on final COD and TC degradation extent. As stated previously, runs were completed without temperature control. Therefore, for the conditions of these experiments [$\text{Fe(II)} = 0.01$ M and $\text{H}_2\text{O}_2 = 1$ M, pH 2.8) an average increase of 14 K over the starting temperature was experienced in a few minutes after mixing of Fenton's constituent reagents. Figure 4 shows the benefits of increasing temperature on COD degradation rate. It is also observed that the extent of COD removal is raised to 85–90% in just 3–4 h for the experiment completed at initial $T = 327$ K.

Experiments carried out at $T = 317$ – 327 K showed a decrease in biodegradability properties after 8 h of treatment. Thus, by considering the ratio BOD/COD as an indicative biodegradability index, the final value for this parameter went from 0.85 for the nontreated wastewater to 0.67 and 0.63 for runs completed at initial 317 and 327 K, respectively.

Kinetic Modeling of the Process. *Mechanism Proposal.* Given the complexity of the mechanism involved in Fenton chemistry and the multicomponent nature of the wastewater treated, the establishment of a rigorous reaction sequence to model this process is a rather difficult task. However, a semiempirical model can be proposed on the basis of the following:

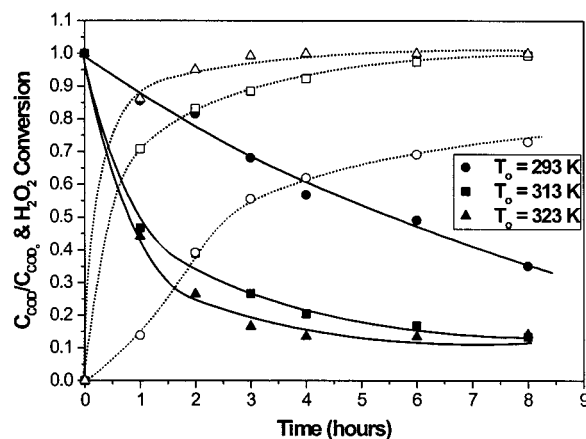
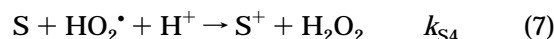
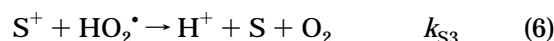


Figure 4. Fe(II)/H₂O₂ treatment of olive oil mill wastewater as demonstrated by evolution of the normalized COD concentration (solid symbols) and hydrogen peroxide conversion (open symbols) with time and influence of initial temperature. Conditions: pH 2.8, $C_{\text{COD}0} = 0.4$ M (average value), $C_{\text{H}_2\text{O}_2} = 1.0$ M, $C_{\text{Fe(II)}} = 0.01$ M.

• The classic Fenton reaction mechanism (19) may be the base to initiate the modeling process. For simplicity purposes, the hydroxyl radical is assumed to be the only oxidizing agent generated in the system able to reduce COD. Nevertheless, the existence of similar reactive species in the media (high valence iron complexes, organic radicals, etc.) should be kept in mind and not be ruled out (20).

• Given the low reactivity of peroxy (O_2^-) and hydroperoxy (HO_2^*) radicals with most organic substances, these species may be considered not to participate in COD removal. • Hydrogen peroxide decomposition has been shown to be highly sensitive to the presence of dissolved substances and/or solid surfaces. Thus, homogeneous decomposition of hydrogen peroxide proceeds through formation of a free radical species (i.e., eqs 9 and 10), which may contribute to oxidize organic substances or, contrarily, may terminate the chain reaction through eqs 23–25. In a parallel way, it has been well documented that H₂O₂ heterogeneously decomposes to a higher or lesser extent by direct interaction with the solid surfaces in contact with this reagent (21–23). In this case, potential oxidizing radical species formed on the surface may be immediately deactivated with the subsequent wastage of hydrogen peroxide. Thus, a mechanism similar to that proposed by Miller and co-workers (22) may occur at the reactor wall surface:



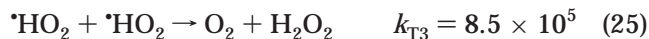
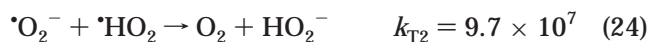
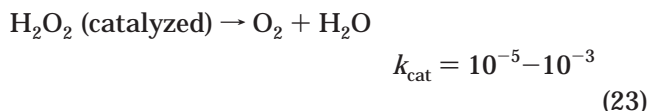
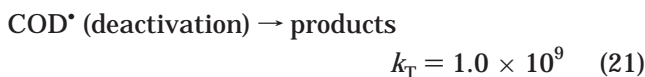
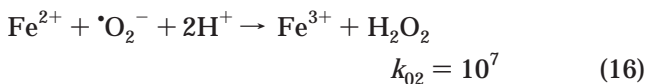
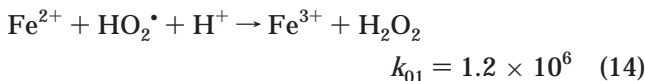
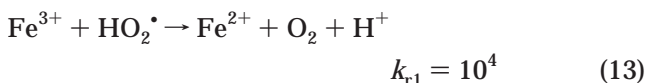
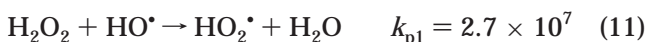
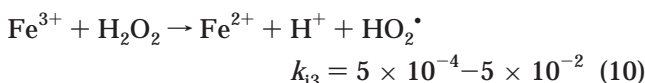
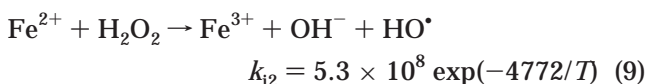
Consequently, depending on the nature of S, the surface will behave as a catalyst for the oxidation or as an inhibitor of the process by trapping the generated radicals. In any case, by assuming the steady-state hypothesis to radical species, it is easily deducible that hydrogen peroxide decomposition does follow a first-order kinetics ($k_{\text{S}4} \gg k_{\text{S}3}$).

Therefore, by considering all of the above statements, a step has been included in the mechanism to account for the ineffective disproportionation of H_2O_2 in either a homogeneous or heterogeneous manner. For simplicity purposes, this step has been assumed to follow a first-order kinetics. A similar strategy was also adopted to model the wet air oxidation of phenol in the presence of hydrogen peroxide (24).

• Reactions involving radical species have been considered not to depend on temperature because low activation energies are reported for this type of reaction (24).

• Among the variety of substances found in olive oil mill wastewater, the presence of phenolic type compounds is of particular interest. On the one hand, they show a significant inhibitory or toxic effect toward microorganisms. Consequently, phenol removal is of paramount importance if a further biological treatment is to be carried out. On the other hand, it has been reported previously that this type of chemical structure may play an important role in the reduction of Fe(III) to Fe(II) in the Fenton mechanism (9, 14). Therefore, in the proposed model, the existence of phenol-like compounds as a part of the total COD has been considered and their role in the Fe(II)/Fe(III) redox cycle accounted for. For that purpose the parameter α is defined as the fraction of phenol-type substances (measured as phenol) in relation to the total COD. The value of this parameter was always in the range of 0.015–0.020.

Reaction Mechanism



[Units in moles, liters, and seconds; rate constant k_{i2} taken from Hardwick (25); and, unless specified, the rest of the kinetic constants are from Chen and Pignatello (14).]

From the mechanism and rate constants shown above, some assumptions must be considered. Thus, the rates of initiating reactions 9 and 10 depend on the presence of chelating agents able to significantly increase/decrease the value of k_{i2} and/or k_{i3} . The actual magnitude of k_{i2} does not constitute a serious handicap because for the normal range of values taken by this rate constant, reaction 9 is not a controlling step in the proposed mechanism (see Sensitivity Analysis). Therefore, its value has been considered to be similar to that found in organic-free water (25). However, reaction 10 has been found to play a significant role in the overall COD removal process. Consequently, k_{i3} was numerically calculated for each experiment. Values for the reaction between the hydroxyl radical and COD (k_{hi}) were taken in the range $10^8 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ as reported for most organic molecules in the literature (26). Although k_{hi} probably decreases as the reaction proceeds to give low oxygenated species (up to values of $\sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$), the value of k_{hi} may vary with time in the interval $10^7 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ without affecting the simulated results obtained; that is, it is not a controlling step. Organic radicals generated after the reaction of the COD phenolic fraction with the hydroxyl radical have also been considered to be capable of reducing Fe(III) to Fe(II). The rate constant value used has been supposed to be of the same order of magnitude as the value reported for the reduction of Fe(III) by the semiquinone radical (14) and similar organic radicals (9). In addition, COD^{\bullet} may terminate the radical mechanism either by undergoing deactivation processes (dimerization, disproportionation to nonradical products, etc.) or because Fe(III) reduction does not occur. In this case a value of $k_T = 10^8 \text{ s}^{-1}$ typical of radical-radical reactions or deactivation processes (24) has been taken.

The set of first-order differential equations for a batch reactor system derived from the mechanism of reactions 9–26 was solved by means of a kinetic simulator software package based on the evolutionary programming (EP) method (27). This method is a computational technique that mimics evolution and is based on reproduction and selection (28).

A sensitivity analysis of the proposed model showed that the kinetic constants in reactions 10 and 23 were the most influential parameters affecting COD and H_2O_2 depletion profiles. Consequently, to achieve the best fit of theoretical and experimental results, these two parameters were numerically calculated by the computer program. Figures 5 and 6 present the influence of both rate constants in the COD evolution with

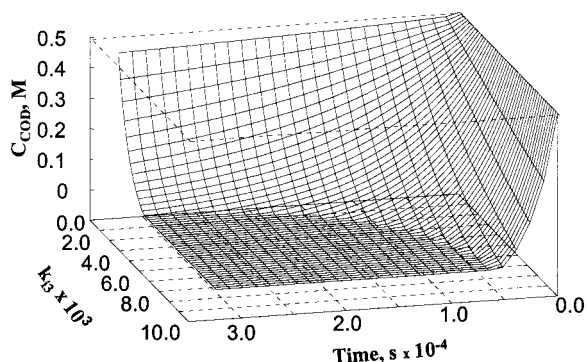


Figure 5. Modeling of the Fe(II)/H₂O₂ treatment of olive oil mill wastewater as demonstrated by evolution of the COD concentration with time and influence of k_{13} . Conditions: pH = 2.8, C_{COD_0} = 0.5 M, $C_{\text{H}_2\text{O}_2}$ = 1.0 M, $C_{\text{Fe(II)}}$ = 0.01 M.

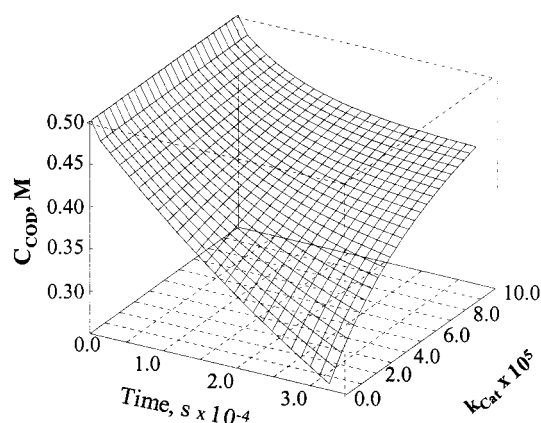


Figure 6. Modeling of the Fe(II)/H₂O₂ treatment of olive oil mill wastewater as demonstrated by evolution of the COD concentration with time and influence of k_{cat} . Conditions: pH = 2.8, C_{COD_0} = 0.5 M, $C_{\text{H}_2\text{O}_2}$ = 1.0 M, $C_{\text{Fe(II)}}$ = 0.01 M.

time. As observed, the value of k_{13} significantly influences the decontamination level achieved by the system. The value of k_{13} is affected by a number of factors such as temperature, presence of chelating agents, and pH (9, 20). Therefore, it should be calculated for each individual type of wastewater and system. Similarly, k_{cat} depends on different chemical and physical operating variables and should also be calculated and defined according to the wastewater nature and conditions.

In addition, k_{13} and k_{cat} are assumed to follow Arrhenius law. Consequently, experiments conducted to check the proposed model should be carried out isothermally. For that purpose, and having in mind the increase in reaction temperature experienced at the beginning of the oxidation, some experiments were completed by using a thermostatic bath to control the temperature of the reaction media.

Figure 7 shows the computed and experimental COD and H₂O₂ concentrations for a series of experiments carried out at different temperatures while the rest of the operating variables were kept constant. As observed from this figure, the model does a good job in fitting both the COD and H₂O₂ depletion profiles with time. These experiments were carried out in duplicate, so error bars indicating a 95% confidence interval have been added by considering the standard deviation obtained for each couple of experimental points.

Although the proposed mechanism gives a good fit between experimental and calculated concentrations, it should be pointed out that the model presents some

limitations inherent to the complex nature of the system treated. Thus, the following drawbacks may be noted:

- The rate constants k_{13} and k_{cat} are specific for each system and have to be experimentally calculated. Because these two kinetic constants are determined simultaneously, other values may numerically be obtained, which could make the model work properly. As a consequence, k_{13} and k_{cat} have to be considered with caution.

- The model does not consider the influence of pH on reagent stability and solubility. As a result, it cannot predict the negative influence of this parameter on the effectiveness of the process. Apparently, in a Fenton treatment plant this should not be a problem because special care is taken to keep the pH value in the suitable operating range.

- The mechanism was theoretically tested at different conditions of initial COD, H₂O₂, and Fe(II) concentrations. Calculated results were acceptable and followed a logical trend; however, no isothermal runs have been conducted to validate the model at these conditions. In this sense, the kinetic model is being tested with a similar effluent (wastewater from table olive preparation) by applying a wider range of conditions. Results will be shown in a forthcoming paper.

As stated previously, k_{13} and k_{cat} depend on temperature. Therefore, considering the different values of these rate constants obtained from the model, they were adjusted to an Arrhenius expression (see Figure 8) as follows:

$$k_{13} = 1.8 \times 10^{15} \exp\left(\frac{-12577 \pm 1248}{T}\right) \quad (27)$$

$$k_{\text{cat}} = 6.3 \times 10^{12} \exp\left(\frac{-19987 \pm 2414}{T}\right) \quad (28)$$

As inferred from reaction 9 and eq 27, the H₂O₂ decomposition by Fe(III) does depend on temperature to a greater extent than the decomposition in the presence of Fe(II). In this sense, the degradation of *p*-hydroxybenzoic acid by Fe(II)/H₂O₂ was reported not to be significantly influenced by temperature (9). Thus, at the conditions described by these authors, the controlling step in that case was the reaction between Fe(II) and H₂O₂ with an activation energy 3 times lower than the activation energy found in the presence of ferric iron. In this study, it is therefore reasonable to admit a higher influence of temperature because the limiting reaction rate (k_{13}) presents a higher activation energy.

Operability and Economics of the Process. General Considerations. Although this was not the purpose of this work, some general conclusions can be considered for the operability of this system to treat highly contaminated wastewater.

Olive oil manufacturing industries are in most cases small factories with a low wastewater flow, typically between 10 and 100 m³ day⁻¹ (29). Therefore, a small Fenton plant would be enough to cope with the effluents produced. Given the simplicity of these installations, capital costs are normally low, but increase if the system is equipped with automatic controllers (7). Typically, a basic 4 m³ unit equipped with simple on-off valves, pH and redox potential sensors, stirrer, and pumps would cost U.S. \$40000 USA \$ (7).

In general, operating costs associated with hydrogen peroxide based oxidation systems are higher than those calculated for conventional biological treatments. How-

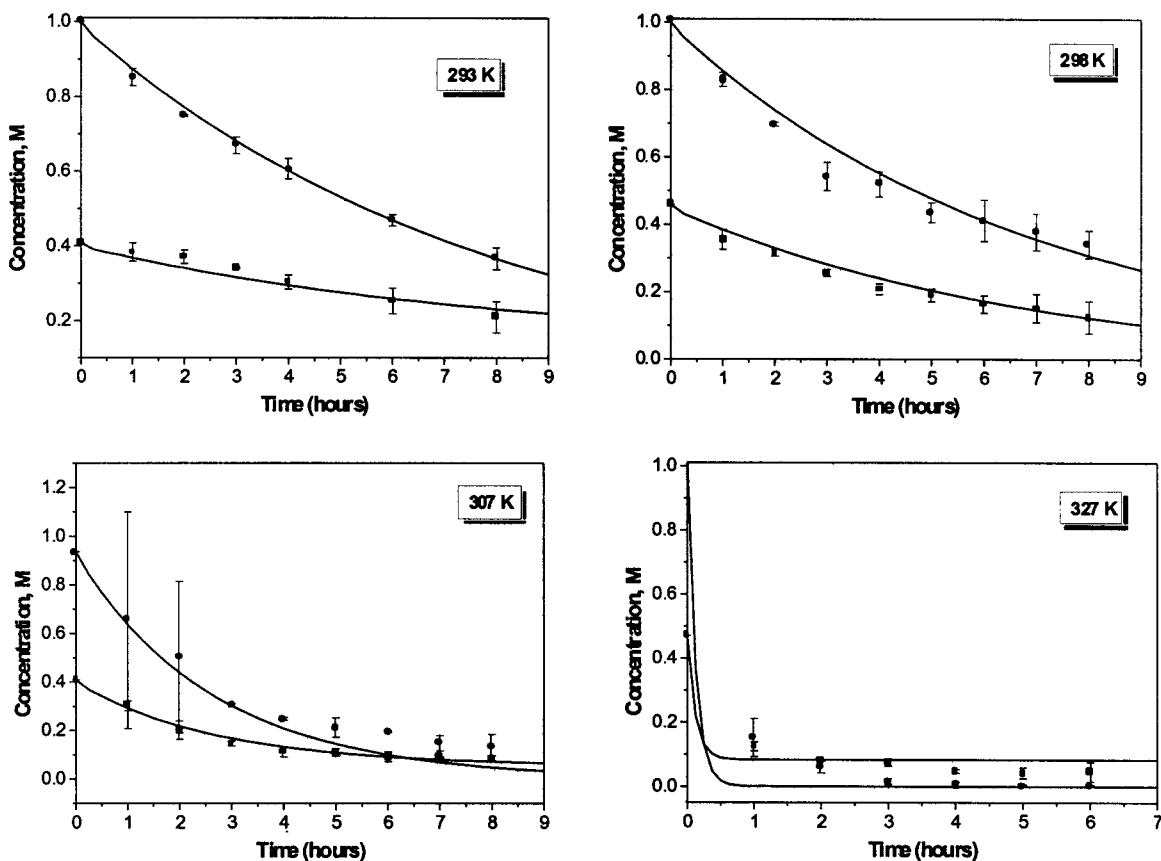


Figure 7. Modeling of the Fe(II)/H₂O₂ treatment of olive oil mill wastewater as demonstrated by evolution of the COD (squares) concentration and hydrogen peroxide conversion (circles) with time and influence of temperature. Conditions: pH 2.8, $C_{\text{COD}_0} = 0.42$ M (average value), $C_{\text{H}_2\text{O}_2} = 1.0$ M, $C_{\text{Fe(II)}} = 0.01$ M. Symbols indicate experimental results and dotted lines, model calculations.

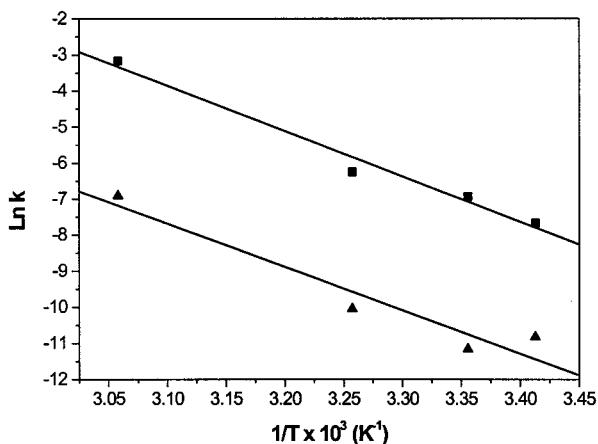


Figure 8. Modeling of the Fe(II)/H₂O₂ treatment of olive oil mill wastewater as shown by an Arrhenius plot of k_{33} (squares) and k_{cat} (triangles). Conditions: pH 2.8, $C_{\text{COD}_0} = 0.42$ M (average value), $C_{\text{H}_2\text{O}_2} = 1.0$ M, $C_{\text{Fe(II)}} = 0.01$ M.

ever, these costs approximate each other as the biological system becomes more sophisticated (30). Moreover, chemical oxidation emerges as a suitable alternative when biological degradation is not applicable. Thus, to properly process olive oil mill wastewater, a dilution factor of 100 would be needed in conjunction with the use of acclimated seeds.

For the operating conditions used in this work some preliminary operating costs can be calculated and compared with similar systems. Thus, by considering the average stoichiometric factor found in this study (3 mol of H₂O₂/mol of COD degraded), the price of H₂O₂

(~U.S. \$300/ USA \$ per ton of a 50% solution), and the reduction of COD obtained, the cost associated with hydrogen peroxide consumption can be estimated. This value would be ≈U.S. 2.4×10^{-3} USA \$ per m³ of wastewater treated and ppm of COD removed. If the aforementioned value is assumed to represent 75% of the total operating costs, for a system like this (3) the final cost would be ≈U.S. 3.2×10^{-3} USA \$ per m³ of wastewater treated and ppm of COD removed. Similar calculations have been reported for oxidation systems treating pure substances and real effluents (7, 30, 31). Thus, Bidga (7) showed an estimation of ≈U.S. 4.0×10^{-3} USA \$ per m³ of wastewater treated and ppm of COD removed when considering the oxidation of phenol from an inlet concentration of 1000–5000 ppm to an outlet concentration of 1 ppm. Also, Oliver (30) reported a value of ≈U.S. 1.0×10^{-2} USA \$ per m³ of wastewater treated and ppm of COD removed for an effluent coming from an organic synthesis plant in Spain.

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Received for review October 10, 2000. Revised manuscript received January 30, 2001. Accepted February 6, 2001. This work has been supported by the Junta de Extremadura and Fondo Social Europeo (Project IPR99C002).

JF001223B