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Degradation and Mineralization of Organic Pollutants Contained in Actual Pulp and Paper Mill Wastewaters by a UV/H₂O₂ Process

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In this work, UV/H₂O₂ treatment of actual pulp and paper mill wastewater (PPMW) was investigated. To determine optimal conditions, the effects of some experimental parameters (initial pH, initial H₂O₂ concentration, temperature, and organics load) on the UV/H₂O₂ process efficiency in terms of absorbance at 330 and 281 nm and chemical oxygen demand (COD) and total organic carbon (TOC) removals were studied. The results show that the UV/H₂O₂ system leads successfully to the almost-complete elimination of absorbance at 330 and 281 nm, COD, and TOC from an actual PPMW containing 270 mg of C L⁻¹ under natural pH (pH 11.25) using 2.1 g of H₂O₂ L⁻¹ at 28 °C. Under these optimal conditions, pseudo-first-order kinetics was determined for absorbance at 330 and 281 nm and COD decay with rate constants of 0.029, 0.02, and 0.008 min⁻¹, respectively. Furthermore, the evolution with time of the H₂O₂ concentration exhibits two parts: a linear decrease to 300 min and then exponential change until the end of the treatment. This shows that the kinetics of H₂O₂ disappearance changes during the treatment from a pseudo-zeroth-order reaction in the first steps to a pseudo-first-order reaction in the final steps. On the other hand, a continuous decrease of pH and a rapid total phenols disappearance were observed during UV/H₂O₂ treatment of PPMW. These results suggest that several steps are involved in the photochemical oxidation of organics, starting with degradation of lignin derivatives and tannins to obtain aromatic intermediates that then undergo oxidative ring opening, leading to aliphatic carboxylic acids. In the final steps, carboxylic acids are mineralized into CO₂ and H₂O.

1. Introduction

Pulp and paper manufacturing is a water-consuming industry that generates large amounts of pulp and paper mill wastewaters (PPMWs) as a result of different operations used in the production steps.[1,2] PPMWs are dark-colored effluents containing high concentrations of organics. The dark color is mainly attributed to the complex compounds derived from polymerization between lignin-degraded products and tannin during various pulping and bleaching operations.[3] The main organic compounds contained in PPMWs are resin acids, chlorinated lignin, chlorinated resin acids, phenolic compounds, fatty acids, and lignin degradation products.[4–6] These compounds are classified as environmentally hazardous because of their toxicity and very slow biodegradation.[7] The treatment of these harmful byproduct, which are released to the environment, is the most important environmental concern in the pulp and paper industries. At present, the majority of pulp and paper plants use activated sludge and aerated lagoons to treat their aqueous effluents.[8–10] The major downfall of biological treatment is that large organic compounds are not fully degraded prior to effluent discharge and they thus pose a threat to the receiving waters.[11] Therefore, a treatment that provides excellent degradation of toxic compounds is required in order to meet stringent discharge limits.

Advanced oxidation processes (AOPs) are considered one of the most attractive methods for the treatment of water and wastewater containing toxic and nonbiodegradable pollutants.[12,13] AOPs are based on the in situ production of OH• radicals, which

are powerful oxidizing agents that are able to mineralize biorecalcitrant organics in the effluents or at least convert them to easily biodegradable compounds.[14] Several research efforts aiming toward the development of efficient technologies for the destruction of the organic matter in PPMWs have been reported in the literature.[1–4,13,15–18] These studies have shown that AOPs can be successfully applied to the complete mineralization of different kinds of organics coming from pulp and paper wastes. Some studies have been conducted on the degradation of organics contained in PPMW synthetic solutions by the Fenton[19] photo-Fenton reactions,[19,20] ozone,[21] and ozone combined with UV irradiation,[13,22] showing that good efficiency in removing total organic carbon (TOC) can be obtained after the optimization of operating conditions. Most of the published literature[1–8] is focused on the treatment of synthetic solutions containing lignin derivatives under various conditions, and only a few studies have reported the treatment of actual PPMW effluents by AOPs.

A homogenous oxidation process employing hydrogen peroxide with UV light has been found to be a highly efficient AOP in the decolorization and mineralization of wastewaters containing various organic compounds.[23–25] In comparison with other AOPs such as the Fenton reaction, ozonolysis, UV/O₃ and UV/TiO₂ treatments, the photolysis of hydrogen peroxide has shown some advantages such as the complete miscibility of H₂O₂ with water, the stability and commercial availability of hydrogen peroxide, the absence of phase-transfer problems, and low investment costs. A UV/H₂O₂ process can also be carried out under ambient conditions and can lead to complete mineralization of organic carbon to CO₂ and H₂O.[26,27] Despite an extensive literature[13–27] on the application of AOPs for the removal of organics from synthetic PPMW solutions, to the best of our knowledge, there are no reports concerning the treatment of actual PPMWs with a UV/H₂O₂ process. It is also noted that

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Catalkaya and Kargi[4] studied the treatment by advanced oxidation processes of real pulp mill effluents that had already been treated by biological methods.

The objectives of this study were (1) to demonstrate the treatment efficiency of actual PPMW using a UV/H$_2$O$_2$ process; (2) to investigate the effects of several experimental parameters including pH, temperature, initial TOC, and H$_2$O$_2$ concentration on oxidation yields; and (3) to establish the related kinetic equation and rate constants based on the observed experimental results.

2. Materials and Methods

2.1. PPMW Effluent. The PPMW used in this study was obtained from a pulp and paper manufacturing factory located in Tunisia, and it was maintained in the dark at 4 °C. The main characteristics of this wastewater were a dark color and a high pH (pH 11.25). It contained 680 mg of O$_2$ L^{-1} in chemical oxygen demand (COD) and 270 mg of C L^{-1} in total organic carbon (TOC).

2.2. Chemicals. Hydrogen peroxide was a 35% (w/w) solution (AR grade, Fluka). Other chemicals including K$_2$Cr$_2$O$_7$, Na$_2$SO$_3$, H$_2$SO$_4$, NaOH, HgSO$_4$, and Ag$_2$SO$_4$ were of analytical grade and were purchased from Aldrich or Merck.

2.3. UV/H$_2$O$_2$ Treatment. Photochemical experiments were performed in a batch thermostatted Pyrex photoreactor of 2-L capacity equipped with a 40-W Heraeus Noblelight YNN 15/32 low-pressure mercury vapor lamp (Hanau, Germany) located in a quartz sleeve at the center of the reactor in an axial position and emitting at 254 nm. The pH of the solution was adjusted to the desired value by addition of sodium hydroxide or sulfuric acid. The pH was kept constant by the continuous introduction of sulfuric acid (or sodium hydroxide) into the reactor. After the light of the photoreactor had been turned on, a precise amount of hydrogen peroxide (30%) was mixed with 1000 mL of PPMW by means of a magnetic stirrer. The specific quantity H$_2$O$_2$ was determined at the beginning of the treatment, and no further H$_2$O$_2$ was added during the irradiation of PPMW. Each experiment lasted around 6 h, and 10 mL samples were periodically (every 30 min) collected; the reaction was quenched with Na$_2$SO$_3$ and then analyzed immediately to determine pH; absorbance at wavelengths of 281 and 330 nm; and removals of total phenols, TOC, and COD.

2.4. Analytical Methods. The carbon concentration was monitored using a Shimadzu TOC-5050 analyzer. Chemical oxygen demand (COD) was determined using a Hach DR200 analyzer and measured according to colorimetric methods. Absorbance measurements were monitored by a Hach DR2500 UV−visible spectrophotometer using a quartz vat and 1-cm optic path length at two wavelengths of 280 and 400 nm. The pH was measured with a Micronal pH meter (model B474). The concentration of total phenols was determined by the Folin−Ciocalteau method[28] (the ability of phenols to reduce phosphomolybdic−phosphotungstic reagent). The total phenols content is reported in gallic acid equivalents. Hydrogen peroxide was measured according to the Eisenberg method.[29]

3. Results and Discussion

To determine optimal conditions, the treatment of PPMW by a UV/H$_2$O$_2$ process was conducted at various values of several operating parameters, including pH, initial hydrogen peroxide concentration, initial TOC (TOC$_0$), and temperature. The efficiency of the UV/H$_2$O$_2$ process was evaluated by UV−visible spectrophotometry and total phenols, COD, and
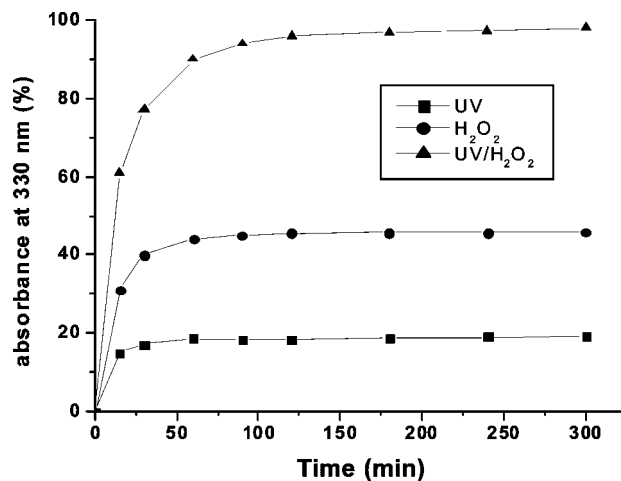
Figure 1. Evolution with time of absorbance abatement percentage at 330 nm during the treatment of PPMW by (●) UV ($\lambda = 254$ nm) irradiation alone, (◆) H$_2$O$_2$ (2.1 g L^{-1}) alone, and (▲) UV ($\lambda = 254$ nm)/H$_2$O$_2$ (2.1 g L^{-1}). Experimental conditions: TOC$_0 = 270$ mg of C L^{-1}, $T = 28$ °C, natural pH (pH 11.25).

Table 1. COD and TOC Obtained after 5-h Treatment by UV/H$_2$O$_2$,[a] H$_2$O$_2$ Oxidation,[a] and UV Irradiation[b]

treatment	COD (mg of O$_2$ L^{-1})	TOC (mg of C L^{-1})
UV/H$_2$O$_2$	56	25
H$_2$O$_2$ oxidation	612	258
UV irradiation	678	262

[a] [H$_2$O$_2$] = 2.1 g L^{-1}. [b] Experimental conditions: COD$_0 = 680$ mg of O$_2$ L^{-1}, TOC$_0 = 270$ mg of C L^{-1}, natural pH (pH 11.25), and $T = 28$ °C.

TOC analyses. The UV−visible spectrum of PPMW presents two maximum absorption bands at 281 and 330 nm attributed to aromatics and to lignin derivatives and tannins, respectively.

Preliminary experiments were conducted at room temperature and under natural pH of PPMW containing 680 mg of O$_2$ L^{-1} of COD to evaluate the viability of the UV/H$_2$O$_2$ process. Figure 1 presents the evolution with time of the absorbance abatement at 330 nm during PPMW treatment by UV irradiation ($\lambda = 254$ nm) alone, H$_2$O$_2$ (2.1 g L^{-1}) oxidation alone, and UV irradiation in the presence of H$_2$O$_2$ (2.1 g L^{-1}) for 5 h. As can be seen, UV irradiation alone and H$_2$O$_2$ oxidation alone provided removals of only 20% and 50%, respectively, of the absorbance at 330 nm. However, the combination of UV irradiation with hydrogen peroxide (UV/H$_2$O$_2$), under otherwise the same conditions, caused a 98% removal of the absorbance at 330 nm. Furthermore, COD and TOC analyses before and after PPMW treatment by UV irradiation alone, H$_2$O$_2$ (2.1 g L^{-1}) oxidation alone, and UV/H$_2$O$_2$ (2.1 g L^{-1}) treatment for 5 h are reported in Table 1. As can be observed, only the UV/H$_2$O$_2$ process achieves 92% and 90% COD and TOC removals, respectively, but no significant COD and TOC removals were monitored after 5 h of UV irradiation or H$_2$O$_2$ oxidation of PPMW.

These results show that the UV/H$_2$O$_2$ process can be applied for the treatment of the industrial effluent studied here. The efficiency of this process is due to the strong oxidation power of hydroxyl radicals (OH$^{\bullet}$) and other oxidants produced by the photodecomposition of H$_2$O$_2$ by UV irradiation.[30] The optimization of experimental conditions will allow for the achievement of greater efficiencies in the abatement of absorbance, COD, and TOC and reduce electrical energy expended to produce large quantities of OH$^{\bullet}$ radicals using minimum quantities of H$_2$O$_2$.

3.1. Influence of Experimental Parameters on UV/H$_2$O$_2$ Treatment of PPMW. UV/H$_2$O$_2$photolysis is considered to be an advanced oxidation process in which the generation of
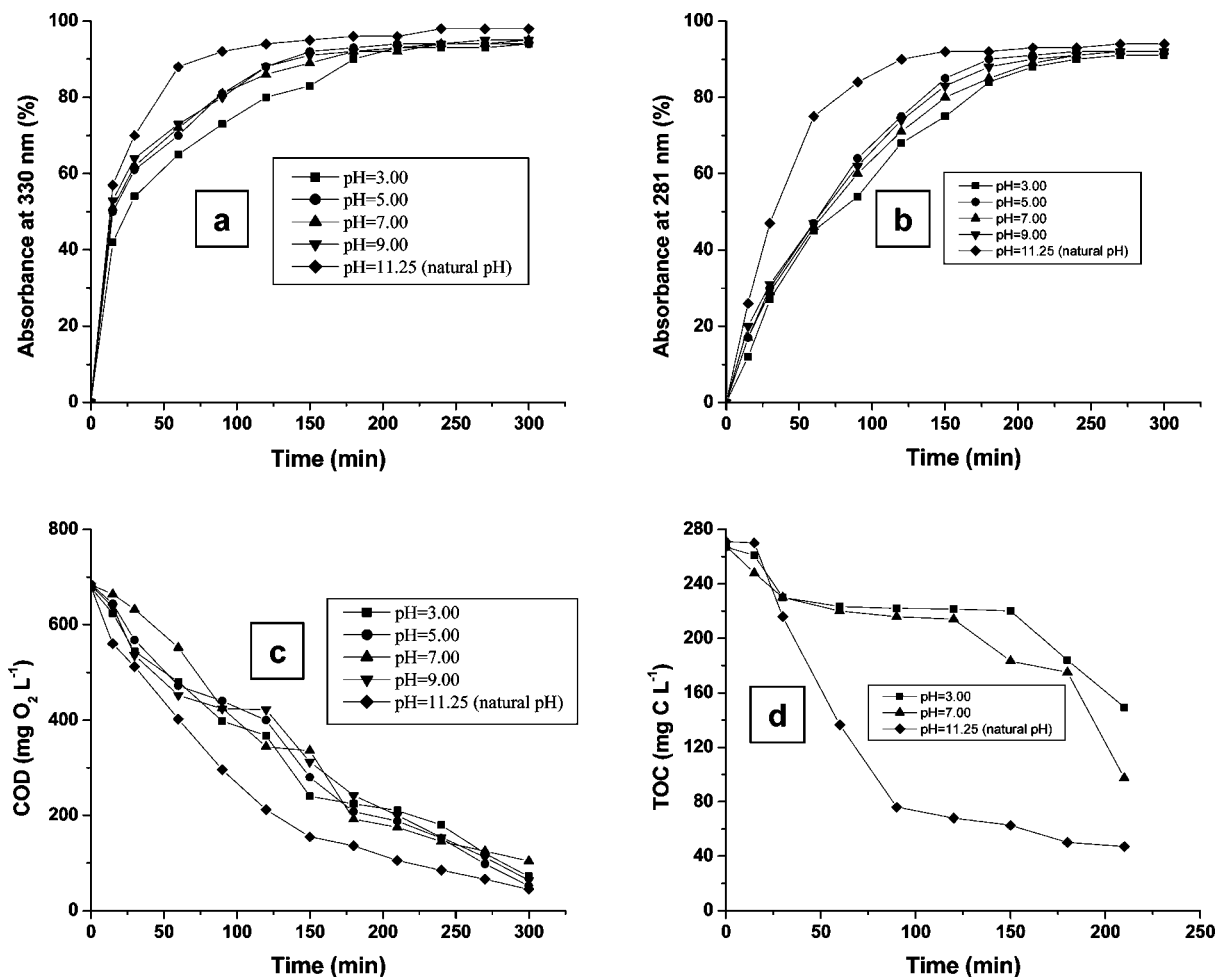
Figure 2. Influence of initial pH on the evolution with time of (a) absorbance abatement at 330 nm, (b) absorbance abatement at 281 nm, (c) COD, and (d) TOC during the treatment of PPMW by UV/H$_2$O$_2$. Experimental conditions: TOC$_0$ = 270 mg of C L^{-1}, T = 28 °C, [H$_2$O$_2$] = 2.1 g L^{-1}.

hydroxyl radicals is produced by the photodecomposition of H$_2$O$_2$ given by the equation[31,32]

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet}$$
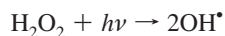
The effectiveness of this process is related to the amounts of photogenerated hydroxyl radicals. According to the literature,[33] the initial experimental conditions have a significant influence on the production of these radicals. Indeed, UV irradiation intensity, initial concentrations of H$_2$O$_2$ and organic matter, pH, and temperature are the main parameters that govern the photodecomposition of H$_2$O$_2$. It was reported[32,33] that the intensity of UV irradiation has no significant influence on the efficiency of UV/H$_2$O$_2$ process, especially for slightly polluted effluents, but its increase can result in higher electrical energy consumption. Consequently, a single UV lamp (125 W) was used.

3.1.1. Influence of Initial pH on UV/H$_2$O$_2$ Efficiency. The influence of the initial pH on the degradation and mineralization of the organics contained in PPMW by the UV/H$_2$O$_2$ process was evaluated in the pH range of 2.50−11.25. Figure 2 presents the effects of the initial pH on the evolution with time of the absorbance at 281 and 330 nm, COD, and TOC during PPMW (270 mg of C L^{-1}) treatment by UV/H$_2$O$_2$ using 2.1 g L^{-1} H$_2$O$_2$ at 28 °C. As can be seen, initial pH has no effect on the absorbance abatement at the two wavelengths investigated because the UV/H$_2$O$_2$ treatment at pH values between 2.5 and 11.25 led to 98% and 95% absorbance abatements at 281 and 330 nm, respectively. However, the initial pH has an obvious

influence on the kinetics of absorbance abatement at 281 and 330 nm. Increasing the pH from 3 to 11.25 (natural pH) increases the absorbance abatement rate for each wavelength. At the natural pH of the PPMW sample (pH 11.25), 98% and 95% absorbance abatements at 330 and 281 nm were obtained after only 2 h of treatment, but to obtain these abatements, longer treatment was needed for the other pH values. These results might be indicative of the total degradation of aromatics, lignin derivatives and tannins.

Furthermore, the initial pH influences only the COD kinetics, and it seems that COD evolution changes with increasing pH and especially becomes more rapid under alkaline conditions. In acidic media (pH 3 and 5), COD undergoes a slow decrease during the first hour to reach 30% removal, then remains constant for the second hour, and then decreases to 92% removal at the end of treatment. It seems also that, in contrast to the evolution of the absorbance and COD, the evolution of the TOC is strongly influenced by the change in the initial pH value. An increase in initial pH enhances TOC removal, but the effect of this increase is not proportional to the increase in pH, as the TOC removal is 67% for pH 3, 72% for pH 7, and 90% for pH 11.25.

The results showed that the UV/H$_2$O$_2$ treatment of PPMW achieves the almost-complete disappearance of the absorbance bands located at 330 and 281 nm regardless of the initial pH, but their evolution with time is faster at alkaline pH (natural pH). In addition, high COD removals (above 90%) were obtained at the end of PPMW UV/H$_2$O$_2$ treatment for different
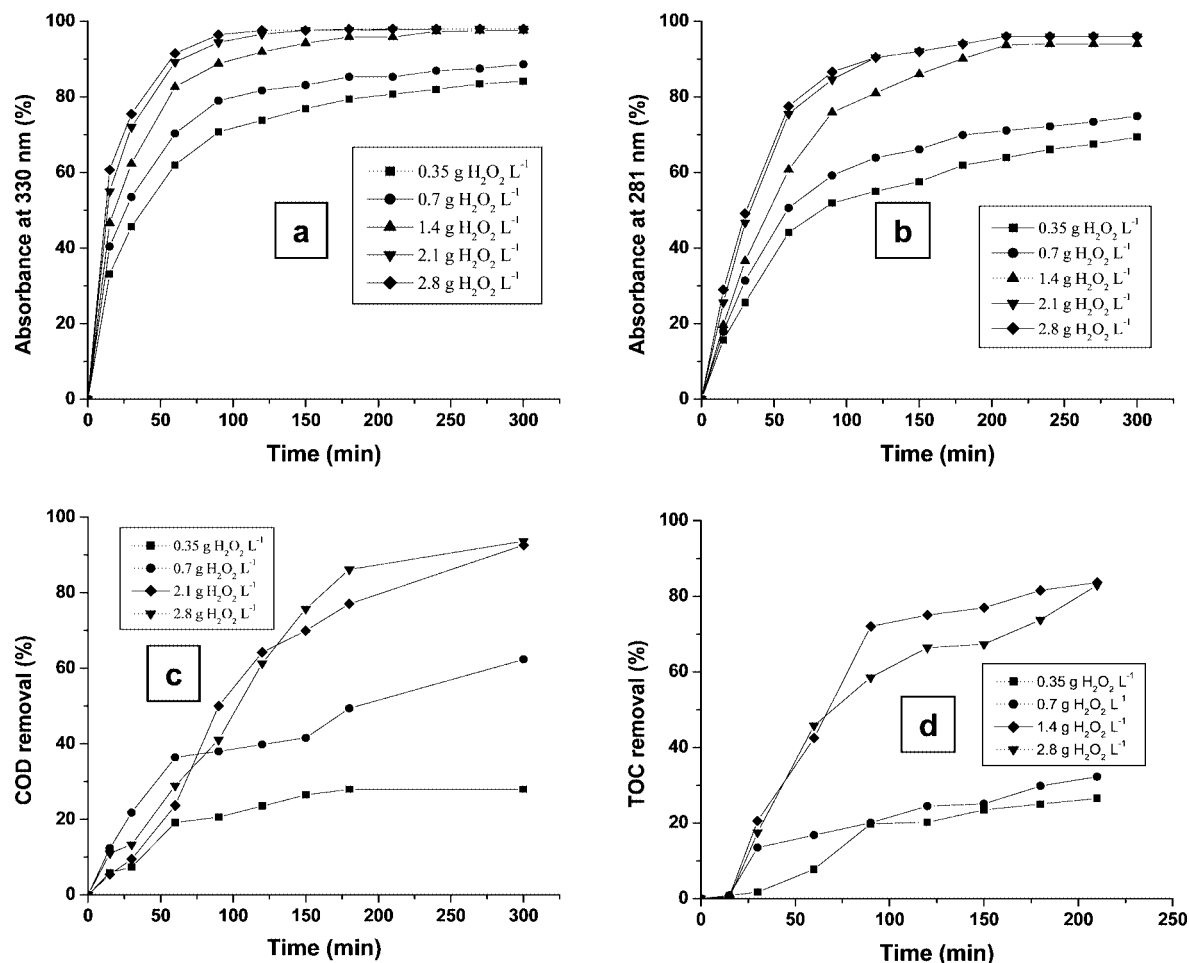
Figure 3. Influence of initial H_2O_2 concentration on the evolution with time of (a) absorbance abatement at 330 nm, (b) absorbance abatement at 281 nm, (c) COD removal, and (d) TOC removal during the treatment of PPMW by UV/H_2O_2. Experimental conditions: TOC_0 = 270 mg of C L^{-1}, T = 28 °C, natural pH (pH 11.25).

initial pH values. It should be noted that the initial pH value affects both the kinetics and the pattern of COD evolution with time. Finally, the initial pH has a significant influence on TOC removal. Only the natural pH (pH 11.25) leads to good performance in terms of TOC removal (90%).

These results can be interpreted as follows:

(1) PPMW is rich in lignin derivatives and contains small amounts of tannins. The decolorization of PPMW is the result of decomposition of polymeric derivatives into colorless compounds. Our results show that this decomposition can occur at any pH because it involves small quantities of OH[·] radicals. More rapid degradation at the natural pH of PPMW (pH 11.25) can be explained by the formation of larger quantities of hydroxyl radicals from UV irradiation of HO_2^- anions.

(2) The fact that the initial pH did not have an effect on the abatement of the absorbance at 281 nm, which is attributed to $\pi \rightarrow \pi^*$ transitions in aromatics, might be due to the presence of an excess of photogenerated hydroxyl radicals during UV/H_2O_2 treatment at different initial pH values.

(3) The influence of initial pH on the evolution of COD as a function of time can be explained by the accumulation of aromatic intermediates in acidic media following the hydrolysis and degradation of polymeric derivatives, but this accumulation does not appear under alkaline conditions because of the formation of larger quantities of hydroxyl radicals.

(4) Regarding the influence of the initial pH on TOC removal, it is clear that HO_2^- anions produced by H_2O_2 deprotonation under alkaline conditions[37] are responsible for producing larger

quantities of OH[·] radicals because HO_2^- ions absorb UV radiation better than H_2O_2 does [at λ = 254 nm, $\varepsilon_{254}(HO_2^-)$ = 240 mol^{-1} L^{-1} cm^{-1} and $\varepsilon_{254}(H_2O_2)$ = 18.6 mol^{-1} L^{-1} cm^{-1}].

It should be noted that recent studies reported in the literature have shown that the influence of pH on the efficiency of UV/H_2O_2 processes depends on the nature of the effluent studied. Bedoui et al.,[36] in our laboratory, found that the efficiency of UV/H_2O_2 treatment of olive oil mill wastewaters was independent of pH. Jiraroj et al.[37] showed that UV/H_2O_2 treatment of effluent containing ethylenediaminetetraacetic acid (EDTA) at pH 6 led to the highest percentage of TOC abatement. Catalkaya and Kargi[4] found that pH 11 gave the best performance in the UV/H_2O_2 treatment of paper and pulp effluents, which is in accordance with the results described here.

3.1.2. Influence of Initial H_2O_2 Concentration on UV/H_2O_2 Efficiency. The initial concentration of hydrogen peroxide ($[H_2O_2]_0$) plays an important role as a source of hydroxyl radicals in wastewater treatment using the UV/H_2O_2 process.[38,39] To evaluate the influence of this parameter on UV/H_2O_2 efficiency, the pH, temperature, and TOC_0 were maintained at 11.25, 28 °C, and 260 mg of C L^{-1}, and the initial H_2O_2 concentration was varied from 0.35 to 2.8 g L^{-1}.

Figure 3 shows the effects of the initial H_2O_2 concentration on the evolution with time of the absorbance abatements at 330 and 281 nm, COD, and TOC during UV/H_2O_2 treatment. As can be seen, increasing the initial H_2O_2 concentration from 0.35 to 1.4 g L^{-1} enhances the absorbance abatement at both 281

and 330 nm. Initial H_2O_2 concentrations greater than 1.4 g L^{-1} have no significant influence on the absorbance abatement percentage and result in only a slight increase in the absorbance abatement rate. Upon addition of 1.4 g of H_2O_2 L^{-1} and application of 210 min of UV/H_2O_2 treatment, the absorbance abatements at 281 and 330 nm were found to be 92% and 98%, respectively. The same percentages were obtained more rapidly (after 90 min of UV/H_2O_2 treatment) using higher initial H_2O_2 concentrations. As can also be observed, increasing the initial H_2O_2 concentration from 0.35 to 2.1 g L^{-1} influences the rates of COD and TOC evolution with time and leads to the enhancement of the COD and TOC removals. However, increasing the initial H_2O_2 concentration above 2.1 g L^{-1} gives the same COD and TOC removals.
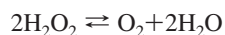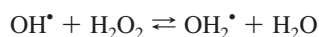
Regarding the results obtained in this part, it appears that initial H_2O_2 concentrations higher than 2.1 g L^{-1} do not markedly increase the kinetics or efficiency of UV/H_2O_2 treatment. Accordingly, 2.1 g of H_2O_2 L^{-1} seems to be the optimal initial concentration for the treatment of PPMW polluted with 270 mg of TOC L^{-1}. The influence of the initial H_2O_2 concentration can be explained by the following ideas:

(1) For low initial H_2O_2 concentrations, the amount of hydroxyl radicals generated by UV irradiation of hydrogen peroxide is not high enough to discolor, degrade, or mineralize organics contained in PPMW.

(2) As the initial H_2O_2 concentration is increased to 2.1 g L^{-1}, the amount of OH$^•$ radicals increases, and the rates of decolorization, degradation, and mineralization are also increased.

(3) For initial H_2O_2 concentrations above 2.1 g L^{-1}, although theoretically higher amounts of OH$^•$ radicals can be produced, the rates and percentages of COD and TOC removals remain constant. Indeed, when the concentration of H_2O_2 becomes sufficiently high, there is competition between three phenomena that limits the efficiency of UV/H_2O_2 process: (a) The first problem concerns the quantum yield, which becomes insufficient to produce more hydroxyl radicals because of the constant power of the lamp. (b) The second phenomenon is the competition between the reaction of hydroxyl radicals with organics and with excess H_2O_2, which does not provide an increase in the quantity of OH$^•$ radicals, so that the degradation and mineralization of organic matter cannot be accelerated. The HO$_2$$^•$ radicals formed during the reaction between H_2O_2 and OH$^•$ are less powerful oxidants than OH$^•$ radicals, but this does not affect the rates of COD and TOC removals. (c) The third phenomenon that can occur is H_2O_2 autodecomposition into O_2 and H_2O. This reaction consumes excess H_2O_2, so the quantity of OH$^•$ radicals remains invariant.

These phenomena can be represented by the following chemical equations

$$OH^• + R \rightleftarrows R{-}OH \ (R = \text{organic pollutant})$$

$$OH^• + H_2O_2 \rightleftarrows OH_2^• + H_2O$$

$$2H_2O_2 \rightleftarrows O_2 + 2H_2O$$

3.1.3. Influence of Temperature on UV/H_2O_2 Efficiency. The temperature plays an important role in chemical oxidation, because it represents a determinant parameter in the kinetics of homogeneous reactions.[40] The influence of this parameter on the treatment of PPMW by the UV/H_2O_2 process was investigated in the range between 20 and 35 °C. Variations in this temperature range do not cause risks for either the UV lamp or the photoreactor. Moreover, taking into account that the discharge temperature of PPMW is about 35−40 °C, working in this temperature range is suitable. Generally, in advanced

oxidation processes, high temperature favors the production of large amounts of hydroxyl radicals.[41] To investigate the effect of temperature on the rate of degradation and mineralization of organic pollutants contained in PPMW (TOC$_0$ = 270 mg L^{-1}) by UV/H_2O_2 process, several experiments were performed at 20, 28, and 35 °C using 2.1 g of H_2O_2 L^{-1} under the natural pH (pH 11.25).
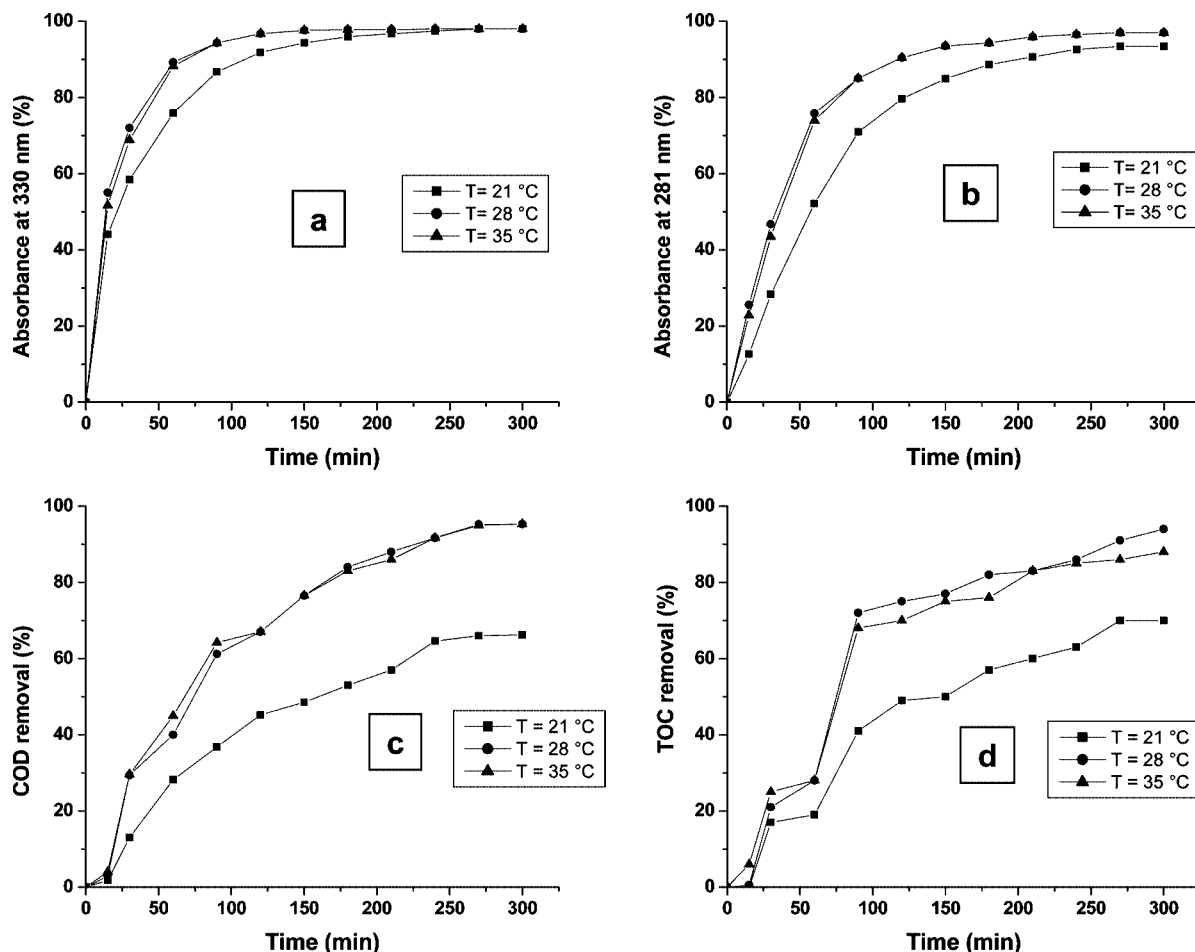
The influence of temperature on the evolution of absorbance abatement at wavelengths of 330 and 281 nm and COD and TOC removals during UV/H_2O_2 treatment of PPMW (COD$_0$ = 680 mg of O_2 L^{-1}, TOC$_0$ = 270 mg of C L^{-1}) using 2.1 g of H_2O_2 L^{-1} and natural pH (pH 11.25) is shown in Figure 4. As can be seen, in the range of temperature studied, temperature has little influence on the rate and yield of absorbance abatement at 330 nm. Absorbance at 281 nm is more sensitive to temperature variations than that at 330 nm, as shown in Figure 5b. Furthermore, the influence of temperature on the rate is more significant than that on the yield of absorbance abatement at 281 nm, especially when temperature increases from 20 to 28 °C. After 90 min, absorbance abatement at 281 nm is about 80% at 35 °C, 73% at 28 °C, and 50% at 20 °C. In addition, it is clear that raising the temperature from 20 to 28 °C increases both the kinetics and efficiency of the treatment in terms of COD and TOC removals. However, increasing the temperature beyond 28 °C has no influence on the kinetics and efficiency of the process.

These results show that treatment with temperatures above 28 °C does not improve the rate and efficiency of the UV/H_2O_2 process. Nevertheless, below 28 °C, the temperature has a slight influence on the absorbance at 330 and 281 nm and a more marked influence on the degradation and mineralization of organics (COD and TOC changes). It is remarkable that the optimum temperature for the treatment of this effluent by UV/H_2O_2 must be that of the photoreactor (close to 28 °C), to avoid any loss of energy from thermal heating of the mixture without significant gains in efficiency. The influence of temperature can be explained as follows:

(1) At temperatures above 28 °C, the quantum yield increases, which promotes the formation of larger quantities of hydroxyl radicals, but in contrast, the rate of H_2O_2 autodecomposition becomes greater. Both reactions take place at the same time, which means that the quantity of OH$^•$ radicals remains unchanged, so there is no significant influence on the kinetics and efficiency of PPMW treatment by UV/H_2O_2.

(2) At temperatures below 28 °C, it seems that the influence of temperature on H_2O_2 autodecomposition is negligible and only the quantum yield is affected by temperature. Increasing the temperature (while remaining below 28 °C) has a significant effect, especially in the final stages of the treatment, by increasing the reaction rate between OH$^•$ radicals and aliphatic intermediates generated from the degradation of aromatics (because only the COD and TOC removals are changed).

3.1.4. Influence of Initial TOC Content on UV/H_2O_2 Efficiency. According to the literature,[42] the initial concentration of organics contained in industrial effluents plays a crucial role in UV/H_2O_2 treatment. The higher the concentration of organics, the greater the amount of hydroxyl radicals needed for total mineralization. This suggests that the ratio of H_2O_2 concentration to TOC must be fixed to observe the influence of the concentration of organics on the kinetics and efficiency of treatment with UV/H_2O_2. In the previous parts of this work, a concentration of 2.1 g of H_2O_2 L^{-1} and a temperature of around 28 °C were found to be the optimal conditions giving the highest efficiency for the UV/H_2O_2 process during the treatment of aqueous

Figure 4. Influence of temperature on the evolution with time of (a) absorbance abatement at 330 nm, (b) absorbance abatement at 281 nm, (c) COD removal, and (d) TOC removal during the treatment of PPMW by UV/H_2O_2. Experimental conditions: $TOC_0 = 270$ mg of C L^{-1}, $[H_2O_2] = 2.1$ g L^{-1}, natural pH (pH 11.25).

effluents containing 270 mg of C L^{-1} in terms of TOC. These experimental conditions correspond to a ratio of $[H_2O_2$ (mg $L^{-1})]/[TOC$ (mg of C $L^{-1})] = 8$. For the experiments reported in this section, this ratio is maintained constant and equal to 8.
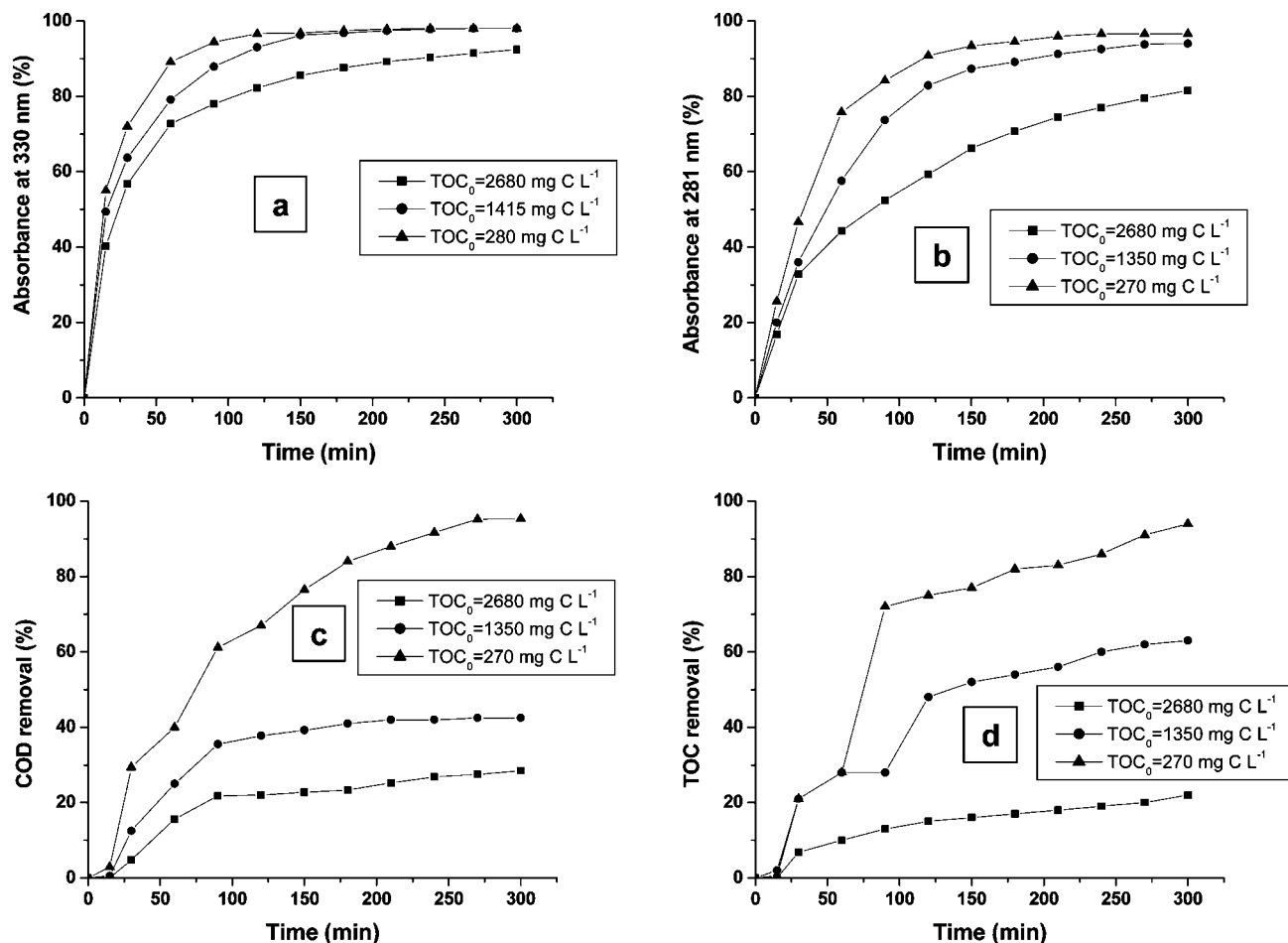
Figure 5 shows the evolution with time of the absorbance abatements at 330 and 281 nm and the COD and TOC removals, during treatment of PPMW at pH 11.25 for different initial TOC concentrations. As can be seen, the influence of the initial TOC concentration on the COD and TOC removals is much higher than that on the absorbance abatements at the two wavelengths studied. Indeed, the total disappearance of absorbance at 330 nm was obtained independent of the initial TOC concentration, but it is clear that high concentrations of TOC affect the rate of absorbance abatement at 281 nm. The curves of Figure 5 show that increasing the initial TOC concentration decreases COD and TOC removals. These removals do not exceed 25% for initial TOC concentration of 2680 mg of C L^{-1} after 5 h of UV/H_2O_2 treatment. The curves show that, after 120 min, the COD and TOC removals remain unchanged, especially for highly concentrated PPMW.

In conclusion, UV/H_2O_2 treatment of effluents with high TOC concentrations leads to almost total absorbance abatements at 330 and 281 nm, but it cannot sufficiently mineralize the organic matter contained in these effluents. To explain these results, it should be taken into account that the higher the TOC concentration, the greater the extent to which the quantum yield for the production of hydroxyl radicals is too low. This is mainly due

to the absorption of significant amounts of UV radiation by organic molecules.

Some authors have reported that this problem can be surmounted by increasing the lamp power, a parameter that was maintained constant in our work. Moreover, H_2O_2 concentration becomes very important when high initial TOC concentrations are contained in PPMW, which promotes the consumption of excess H_2O_2 by side reactions (autodecomposition, scavenging of hydroxyl radicals, etc.), and as a result, the efficiency of the process decreases. On the other hand, high concentrations of TOC and H_2O_2 lead to the accumulation of short-chain carboxylic acids, which are very difficult to mineralize with OH$^•$ radicals, so that the COD and TOC removals are unchanged.

3.2. Kinetic Analysis and Main Steps Involved during the UV/H_2O_2 Process. 3.2.1. Kinetic Analysis. The complex nature of PPMW makes a kinetic analysis of UV/H_2O_2 treatment based on the evolution of individual compounds quite difficult. Rather, an approach based on the evolution with time of the absorbance at 330 and 281 nm and the COD was applied to carry out a kinetic analysis of the treatment of PPMW ($TOC_0 = 270$ mg of C L^{-1}) by the UV/H_2O_2 process under optimal conditions (pH 11.25, $T = 28$ °C, and $[H_2O_2]_0 = 2.1$ g of H_2O_2 L^{-1}). It is remarkable that the rates of the absorbance abatements at 330 and 281 nm are higher than those of COD and TOC removals. This result can be explained by a succession of several steps starting with the degradation of lignin derivatives and tannins to obtain aromatic intermediates. These intermediates then undergo oxidative ring opening, leading to aliphatic

Figure 5. Influence of initial total organic carbon (TOC_0) on the evolution with time of (a) absorbance abatement at 330 nm, (b) absorbance abatement at 281 nm, (c) COD removal, and (d) TOC removal during the treatment of PPMW by UV/H_2O_2. Experimental conditions: $T = 28$ °C, $[H_2O_2] = 2.1$ g L^{-1}, natural pH (pH 11.25).

carboxylic acids. In the final steps, the carboxylic acids are mineralized into CO_2 and H_2O. To better understand what happens during UV/H_2O_2 treatment of PPMW, the evolutions with time of the absorbance, total phenols (TP), COD, and TOC were studied.

The evolution with time of the absorbance at 330 and 281 nm during UV/H_2O_2 treatment of paper industry effluent (COD_0 = 680 mg of O_2 L^{-1}, TOC_0 = 270 mg of C L^{-1}) under natural pH (pH 11.25) at 28 °C using 2.1 g of H_2O_2 L^{-1} is shown in Figure 6. The absorbance at both wavelengths undergoes a rapid decrease to become negligible after 120 min of treatment. It is remarkable that the rate of reduction of the intensity of the band at 330 nm is higher than that of the band at 281 nm. On the other hand, the inset in Figure 6 shows that plots of $\ln(Abs_0/Abs_t) = f(t)$, where Abs_0 is the initial absorbance and Abs_t is the absorbance at time t, are linear. This is in accordance with pseudo-first-order kinetics. The rate constants deduced from the two plots are 0.029 and 0.02 min^{-1} for absorbance at 330 and 281 nm, respectively. These values confirm that the reduction of the absorbance at 330 nm is faster than that at 281 nm, as mentioned above.

Figure 7 shows the variations of COD and TOC as functions of time during the UV/H_2O_2 treatment of PPMW under the same conditions. At the beginning of the treatment, COD and TOC remain constant during the first 15 min, after which they undergo a rapid decrease to 120 min, but this decrease becomes slower during the final 3 h. It is clear that the two parameters exhibit similar profiles. The decrease in TOC during the treatment
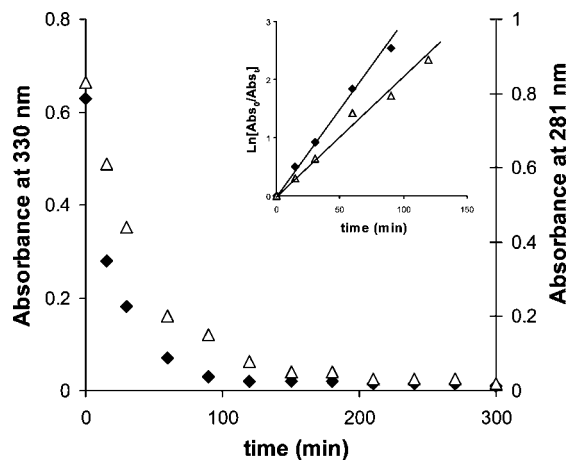

Figure 6. Evolution with time of absorbance at (◆) 330 and (△) 281 nm during the treatment of PPMW by UV/H_2O_2. Inset: Pseudo-first-order kinetics assimilation for absorbance decay. Experimental conditions: TOC_0 = 270 mg of C L^{-1}, $T = 28$ °C, $[H_2O_2] = 2.1$ g L^{-1}, natural pH (pH 11.25).

means the transformation of organic carbon into CO_2 and, as a result, the mineralization of organic matter. The evolution of COD with time also follows pseudo-first-order kinetics confirmed by the linearity of a plot of $\ln(COD_0/COD_t) = f(t)$ (see Figure 7 inset). The rate constant of COD removal deduced from Figure 7 is equal to 0.008 min^{-1}. This rate constant is lower than the rate constants of absorbance at 330 and 281 nm,
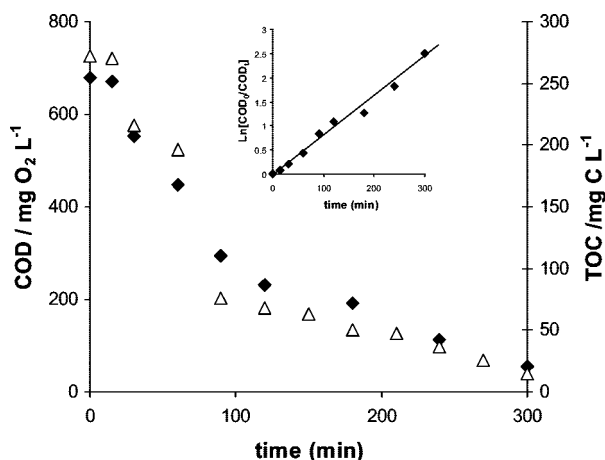
Figure 7. Evolution with time of (◆) COD and (Δ) TOC during the treatment of PPMW by UV/H₂O₂. Inset: Pseudo-first-order kinetics assimilation for COD decay. Experimental conditions: $TOC_0 = 270$ mg of C L^{-1}, $T = 28$ °C, $[H_2O_2] = 2.1$ g L^{-1}, natural pH (pH 11.25).
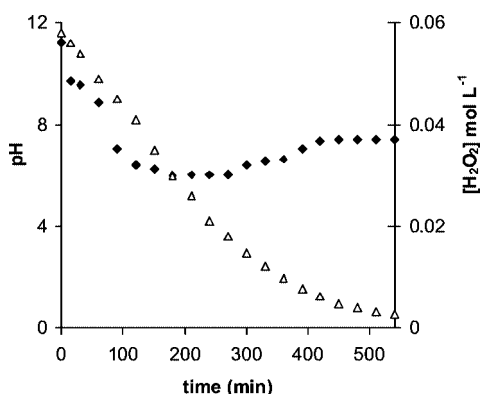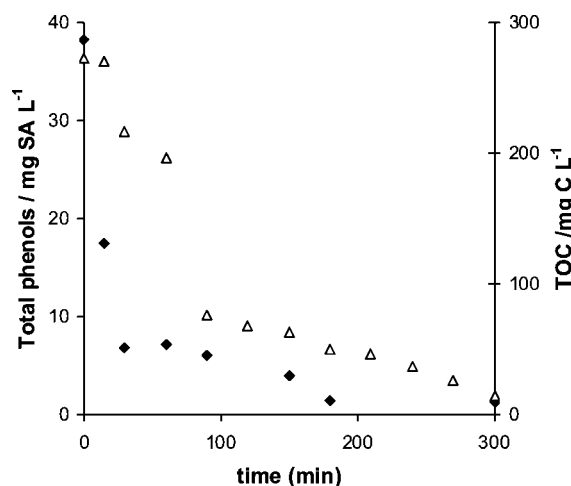

Figure 8. Evolution with time of (◆) pH and (Δ) H₂O₂ concentration during the treatment of PPMW by UV/H₂O₂. Experimental conditions: $TOC_0 = 270$ mg of C L^{-1}, $T = 28$ °C, $[H_2O_2] = 2.1$ g L^{-1}, natural pH (pH 11.25).

indicating that decolorization is more rapid than aromatic ring opening, which is faster than mineralization.

Figure 8 shows the evolution with time of the pH and H₂O₂ concentration during the UV/H₂O₂ treatment of PPMW (270 mg of C L^{-1}) at the natural pH (pH 11.25) and 28 °C using 2.1 g of H₂O₂ L^{-1}. As can be seen, pH decreases rapidly with time to reach a value of approximately 6 after 180 min, then it remains constant for 2 h, and it undergoes a slight increase to become constant and close to 7.4 at the end of the treatment. The decrease of the pH can be explained by the accumulation of carboxylic acids during the first steps of PPMW treatment. Carboxylic acids, which are difficult to oxidize, persist in the medium but at the end of the treatment, these compounds disappear, which is why the pH becomes neutral.

On the other hand, the H₂O₂ concentration undergoes a gradual disappearance. The curve $[H_2O_2] = f(t)$ presents two parts: a linear decrease up to 300 min and then and exponential change until the end of the treatment. This shows that the kinetics of H₂O₂ disappearance change during the treatment, which indicates that H₂O₂ photodecomposition by UV irradiation depends largely on the H₂O₂ concentration in the medium.

3.2.2. Main Steps Involved during UV/H₂O₂ Process. The evolution with time of the pH and the absorbance at 330 and 281 nm showed that, in the early stages of the treatment, lignin derivatives and tannins degrade to form numerous aromatic intermediates, leading to the total decolorization of PPMW. The

Figure 9. Evolution with time of (◆) total phenols and (Δ) H₂O₂ concentration during the treatment of PPMW by UV/H₂O₂. Experimental conditions: $TOC_0 = 270$ mg of C L^{-1}, $T = 28$ °C, $[H_2O_2] = 2.1$ g L^{-1}, natural pH (pH 11.25).
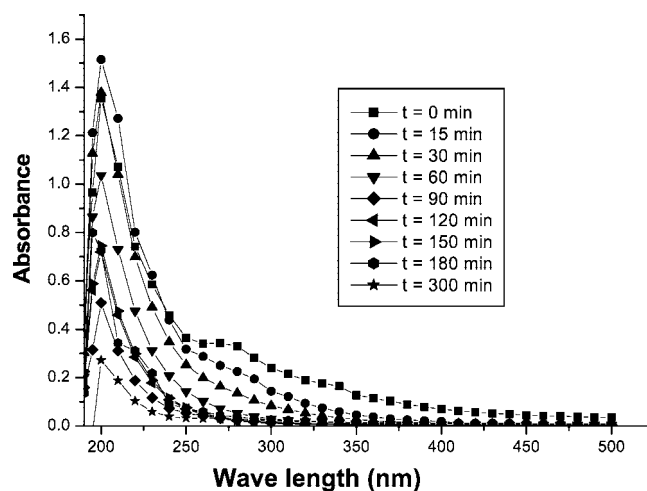

Figure 10. UV–visible spectra recorded at different times during the treatment of PPMW by UV/H₂O₂: (◇) 0, (■) 15, (▲) 30, (×) 60, (*) 90, (●) 120, (○) 150, (+) 180, (Δ) 300 min. Experimental conditions: $TOC_0 = 270$ mg of C L^{-1}, $T = 28$ °C, $[H_2O_2] = 2.1$ g L^{-1}, natural pH (pH 11.25).

aromatic compounds undergo oxidative opening of benzene rings to form aliphatic carboxylic acids, in accordance with the decrease in pH from 11 to 6. These carboxylic acids accumulate and consume large quantities of hydroxyl radicals to be transformed into CO₂ and H₂O.

The total phenols (TPs) concentration (in mg of gallic acid L^{-1}) was monitored during UV/H₂O₂ photochemical treatment of PPMW. Figure 9 shows that the concentration of total phenols disappeared much more rapidly than that of TOC. The total disappearance of TPs was obtained after 120 min of treatment, and at this time, the TOC removal did not exceed 50%. This confirms that the degradation of aromatic compounds and particularly phenols takes place in the earlier stages of PPMW treatment by photochemical oxidation.

Moreover, the evolution of UV–visible spectra during the UV/H₂O₂ treatment of PPMW is illustrated in Figure 10. As can be seen, a continuous decrease in the intensity of the bands at 281 and 330 nm was observed. In contrast, a slight increase in the intensity of the band at 200 nm was monitored at the beginning of the treatment, after which it decreased continuously, but it could not be totally eliminated at the end of the
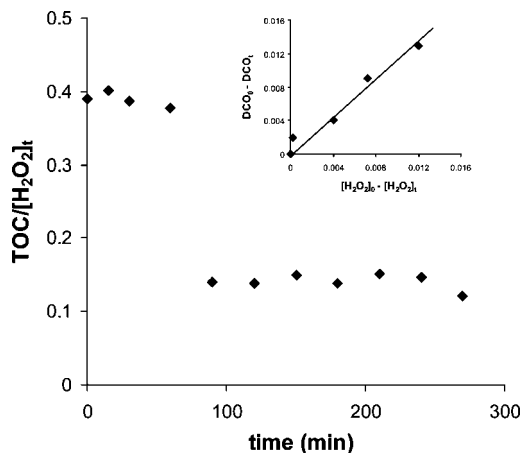
Figure 11. Evolution with time of $TOC/[H_2O_2]_t$ molar ratio during the treatment of PPMW by UV/H_2O_2. Inset: Evolution of COD consumed (mol of O_2 L^{-1}) vs amount of H_2O_2 consumed (mol L^{-1}). Experimental conditions: $TOC_0 = 270$ mg of C L^{-1}, $T = 28$ °C, $[H_2O_2] = 2.1$ g L^{-1}, natural pH (pH 11.25).

treatment. These observations confirm that rapid degradation of aromatics takes place in the first steps of photochemical treatment of organics, leading to the formation of aliphatic compounds, mainly carboxylic acids that are difficult to oxidize, and small amounts of them remain in the solution as refractory organic carbon at the end of the treatment.

Furthermore, changes with time of the molar ratio between the TOC and H_2O_2 concentrations (both in mol L^{-1}), shown in Figure 11, shows that this molar ratio remains almost constant at the beginning of treatment, after which it undergoes a rapid decrease to reach a value of 0.15 at the end of treatment. This result shows that the degradation of lignin derivatives, tannins, and aromatic compounds consumed much lower quantity of H_2O_2 than was required for the oxidation of carboxylic acids into CO_2. During the first 2 h of treatment, as shown in the inset of Figure 11, similar amounts of H_2O_2 and COD were consumed. However, the proportionality factor between the two concentrations increased for the remaining treatment time. These results show that, at the beginning of UV/H_2O_2 treatment, the hydroxyl radicals generated from H_2O_2 photodecomposition are completely consumed for removing chemical oxygen demand. When carboxylic acids accumulate in the system, only some of the hydroxyl radicals are consumed to reduce COD.

4. Conclusion

The main conclusions of this work can be summarized as follows:

(1) UV/H_2O_2 treatment of an actual industrial effluent leads to high yields of absorbance decay, degradation, and mineralization.

(2) The influence of experimental conditions on the efficiency of the UV/H_2O_2 process permits a determination of the following optimal conditions for the treatment of actual pulp and pulp mill wastewaters containing 680 mg L^{-1} of COD and 260 mg L^{-1} of TOC: natural pH (pH 11.25), $[H_2O_2] = 2.1$ g L^{-1}, and $T = 28$ °C.

(3) Using these optimal conditions, the degradation kinetics are pseudo-first-order. The rate constants of absorbance abatement at 330 and 281 nm and COD removal are 0.029, 0.02, and 0.008 min^{-1}, respectively. This suggests that the degradation of lignin derivatives and tannins is faster than aromatic ring opening, which is also faster than COD removal.

(4) The pH decrease and the rapid TP disappearance indicate the total conversion of aromatics to aliphatic carboxylic acids.

These compounds are harmless organic compounds that could be treated in conventional wastewater plants.

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