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Photo-oxidation of real olive oil mill wastewater

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ABSTRACT

Olive oil production in Turkey is quite common. A large volume of untreated olive oil mill wastewater (OMW) is being stored in evaporation rafts. Since there are high amounts of organic load, dark color, and phenolic compounds in OMW, an effective treatment process should be implemented. In this work, an advanced oxidation process (photo-Fenton) operating in a batch reactor was used to treat OMW. For this reason, the effects of some operating parameters such as the initial oxidant and catalyst concentrations and pH of water on total organic carbon (TOC) and color removals were investigated using the central composite experimental design method. The samples were analyzed at different times during the experiments to determine water quality parameters. Increasing oxidant concentrations did not imply a noticeable rise in the final removal percentages. On the contrary, the removal efficiencies for both color and TOC were decreased by increasing catalyst concentration. Optimum color and TOC removal efficiencies were achieved as 95% and 65% respectively, with the addition of 4,585 mg L^{-1} H_2O_2, 255 mg L^{-1} Fe(II), and at pH 4.7 after 90 min of oxidation under UV-C lights.

Keywords: Photo-Fenton oxidation; Central composite design; Decolorization; Olive mill wastewater

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1. Introduction

Olive oil mill wastewater (OMW) contains proteins, phenolic compounds, lipids, pectins, etc. Additionally, OMW presents low-molecular-mass phenolic compounds such as hydroxytyrosol, tyrosol, *p*-hydroxyphenylacetic acid, *p*-coumaric acid, and caffeic acid. If OMW uses for irrigation purposes without any treatment it causes toxicity effects on plants, bacteria, and aquatic organisms altering soil quality because of phenolic compounds composition [1,2].

Although olive oil wastewater is produced in small amounts (10–100 m^3), there are difficulties in the treatment of wastewater [3], which is characterized by high organic pollution, phenolic compounds, and fatty acids. Many phenolic compounds (PCs) are toxic to animal and vegetable organisms, they can be persistent and bioaccumulative, especially chlorinated forms might be dangerous to human health. Given that, PCs have a high inhibition effect on the microorganism, they interfere with the biological treatment of the OMW [4]. It is also estimated that the toxicity of OMW in terms of phenolic compounds is 1,000 times higher than that of urban sewage, as a result of this, its biodegradability is reduced [5].

The wastewater character of each olive oil operation varies greatly depending on the soil and climate characteristics of the region where the olive is grown and the chemical properties of the water used in the operation. In general, the biochemical oxygen demand (BOD_5) value ranges from 35–110 g L^{-1}, the chemical oxygen demand (COD) value is

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45–170 g L^{-1}, the total suspended solids value is 1–9 g L^{-1}, and the phenolic compound value is 0.5–24 g L^{-1} [6].

Several studies analyzed the removal of organic contaminants through the application of advanced oxidation processes (AOPs) that is able to achieve complete oxidation of organic compounds. AOPs are referred to oxidative processes where hydroxyl radical ($OH^{\bullet}$) is formed in situ from oxidant compounds such as O_3, H_2O_2 or other oxidants (sulfate radicals, permanganate, hypochlorite and chlorine dioxide), with or without catalyst and/or in the presence of energetic resources such as electrochemical, artificial ultraviolet (UV), solar light and ultrasounds [4]. The different types of AOPs are considered for wastewater pollution abatement. The hydroxyl radicals are extraordinarily reactive species, which attack the most part of organic molecules with rate constants usually in the order of 106–109 M^{-1} s^{-1} [7].

The goal of the wastewater purification using AOP methods is the mineralization of the contaminants to carbon dioxide, water and inorganic or at least to transform into harmless products. Photolysis is a major naturally occurring degradation process that can clean up soil and water contaminated by many organic compounds. Photolysis is a chemical reaction by which some functional groups of molecules are activated by the absorption of light (irradiation) to reach an excited state, resulting in breaking down (of molecular bonds) into smaller units. Previous researches demonstrated that several organic pollutants can be partially or degraded to less toxic and more degradable substances by photolysis (only UV light) [4]. In general, organic compounds do not absorb all irradiation, which makes photolysis a slow reaction especially when degrading complex organic matter. To increase the global degradation yield of organic matter in wastewater, some combinations are applied, such as the addition of H_2O_2 or/and catalyst [8]. The photolysis of H_2O_2 generates effective oxidizing species of hydroxyl radicals, with an oxidation potential of hydroxyl radical equal to 2.8 eV. Zhang and Li [9] observed that the combined method of UV/H_2O_2 to remove PCs from wastewater was more efficient in degrading organic micropollutants than UV irradiation or H_2O_2 oxidation alone. The use of cheap, moderately reactive, and easy to handle reagents (iron and H_2O_2) makes the Fenton process cost-effective and practically viable [7]. Despite a large number of studies on dye/textile wastewaters and synthetic phenolic compounds treatment by homogeneous and/or heterogeneous Fenton-based systems, there are not enough studies about real olive mill wastewater in the literature. Instead of one organic compound, more studies on simulated and real OMWs with complex matrices, are required to be able to compare them more effectively. In addition, due to the complex nature of OMWs, a combination of Fenton/photo-Fenton or Fenton-based processes with a series of pretreatment and/or post-treatment processes will be helpful to achieve cost-effective and acceptable results.

The country standard specifies the discharge limit, monitoring, and control requirement for water pollutants of the olive oil industry. The current standard applies to the management of discharge of water pollutants from existing olive oil production facilities. In this study, color and organic matter of the olive OMW treated by using UV/H_2O_2/Fe(II) to achieve discharge standards. The degradation behavior of organic matter during the photooxidation was studied. Degradation efficiency and water quality before and after treatment were also determined.

2. Materials and methods

2.1. Characterization of the olive oil mill industry wastewater

The olive OMW samples were taken from the middle part of the depth of the wastewater retention pond of an olive oil production company treatment plant which is located in Izmir, Turkey. The wastewater contained high amounts of color. Wastewater characterizations of samples are given in Table 1.

2.2. Materials

Iron sulfate ($FeSO_4$) (analytical grade, Merck, Germany) was used as a source of Fe(II). The hydrogen peroxide (H_2O_2) solution obtained from Merck (Germany) was in a stable form (35% (w/w)). In the samples, MnO_2 was used to stop the oxidation of organics with excess H_2O_2.

2.3. Photocatalytic reactor

The experimental set up as given in Fig. 1. In the system, a 100 ml reactor with a 2 cm stirrer was used for the photooxidation reactions. For the photo-Fenton reaction, 5 Phillips UV-C lamps (UK) (each was 8 W power) were chosen, and the measured intensities of the lights are written in Table 2. During the experimental studies, pH adjusted to the desired concentrations using 0.01 M H_2SO_4 and 0.01 M NaOH. A stock solution of 10 g L^{-1} Fe(II) catalyst was prepared and kept in a dark place and added to the wastewater at necessary concentrations. After the addition of H_2O_2, the UV-C lamps were turned on. The absorbance of color was measured as soon as the samples at wavelength of 465 nm were taken by using a Varian Cary UV-VIS spectrophotometer (Australia).

2.4. Methods

The platinum-cobalt scale (Pt/Co scale or Alpha-Hazen scale) was used for color measurements at the wavelength 465 nm as given in ASTM Methods [10]. It is specific to the color yellow and is based on dilutions of a 500 mg L^{-1} platinum cobalt solution. The total organic carbon (TOC) measurements were carried out using a SHIMADZU, TOC V-CPN model TOC analyzer (Japan).

2.5. Central composite design

The Box–Wilson statistical experimental design was used to optimize the effects of experimental conditions on color and TOC removal efficiencies and to determine the interaction of parameters resulting in maximum color and TOC removal efficiencies. The Box–Wilson design is a response surface methodology which is an empirical modeling technique devoted to the evaluation of the relationship between a set of controlled experimental factors and observed results. Basically, this optimization process involves three major steps; performing the statistically

Table 1
Main characterization of OMW

Parameter (units)	Value in OMW samples
pH	7.2
Conductivity (μ cm^{-1})	1.7
COD (mg L^{-1})	11,500
TOC (mg L^{-1})	3,200
Total suspended solids (mg L^{-1})	3,400
Total volatile suspended solids (mg L^{-1})	3,150
Oil-grease (mg L^{-1})	600
NH_3–N (mg L^{-1})	<0.2
Total Kjeldahl nitrogen (mg L^{-1})	85
Total phosphorus	28
Color (Pt/Co)	1,500
Phenol (mg L^{-1})	0.3

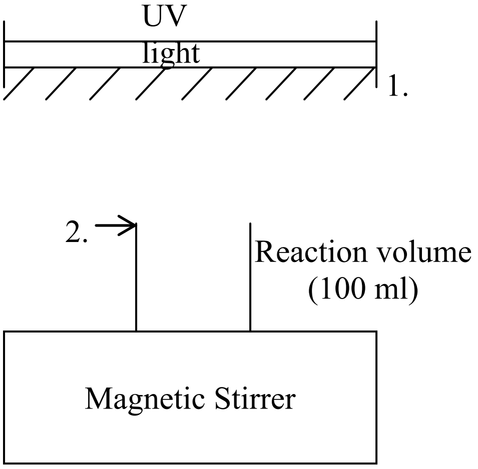


Fig. 1. Experimental set-up.

Table 2
UV intensity

Position	UV-C light intensity (W m^{-2})
1	32
2	26

designed experiments, estimating the coefficients in a mathematical model, and predicting the response, and checking the adequacy of the model. The H_2O_2 and Fe(II) amounts and pH were chosen as independent variables and titled as X_1, X_2, and X_3, respectively. Color and TOC removal efficiencies were measured as the dependent variable in the model.

The H_2O_2 concentration (X_1) was changed between 2,000 and 8,000 mg L^{-1}, the Fe(II) concentration (X_2) between 200 and 400 mg L^{-1} and pH (X_3) between 3 and 11. Experimental variables are given in Table 3. The experiments consist of six axial (A), eight factorial (F), and center points (C). The center point was repeated four times. The least-squares method was used for calculation. The color and the TOC removal efficiencies (Y) with independent parameters (X_1, X_2, X_3) were calculated according to the response function given below (Eq. (1)).

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1 2+ b_{22}X_{22} + b_{33}X_{32} \quad (1)$$

The coefficients were calculated by the Design Expert 12 computer program, in the equation; b_{11}, b_{22}, and b_{33} are quadratic coefficients, b_{12}, b_{13}, and b_{23} are cross-product coefficients, b_1, b_2, and b_3 are linear coefficients, b_0 is a constant, and finally, Y is predicted yield.

3. Results and discussions

One of the homogeneous AOPs is the Fenton reaction. It is based on electron transfer between H_2O_2 and iron ions (Fe(II)) serving as a catalyst. During the Fenton reaction, hydroxyl radicals are produced and the radicals can destroy the organic bonds. In our study, Fenton's reagent was applied to remove the olive oil production effluent, and the study aims to see the effects of initial H_2O_2, Fe(II) concentrations, and pH on color and TOC removals.

The TOC and color removal efficiencies achieved from the experimental studies were given in Table 4. The coefficients of the response functions (Eq. (1)) were calculated by the Design Expert 12 regression analysis program. After obtaining the coefficients, predicted values of color and TOC removal efficiencies were determined. The correlation coefficient (R^2) for color removal is 0.97 and for TOC removal is 0.97. These results were representing a good correlation between the observed and predicted values of color and TOC removal efficiencies.

$$Y\text{ color} = -41.21229 + 0.018840\,(H_2O_2) + 0.399827\text{ Fe(II)} + 10.97567\,(\text{pH}) - 0.000014\,(H_2O_2\text{ Fe(II)}) - 0.000177\,(H_2O_2\text{ pH}) + 0.012374\,(\text{Fe(II) pH}) - 1{,}161\text{E-06}\,(H_2O_2)^2 - 0.000696\,(\text{Fe(II)})^2 - 1.43481\,(\text{pH})^2 \quad (2)$$

$$Y_{\text{TOC}} = -45.61601 + 0.014003\,(H_2O_2) + 0.335194\text{ Fe(II)} + 7.82250\,(\text{pH}) + 1.17851\text{E-06}\,(H_2O_2\text{ Fe(II)}) - 10.000324\,(H_2O_2\text{ pH}) + 0.002652\,(\text{Fe(II) pH}) - 1.12393\text{E-6}\,(H_2O_2)^2 - 10.000562\,(\text{Fe(II)})^2 - 10.757211\,(\text{pH})^2 \quad (3)$$

The factors in front of the model terms indicate the intensity and direction of the influence of the independent variable. A positive effect of a factor means that the response is improved when the factor level increases and a negative effect of the factor reveal that the response is inhibited when the factor level increases. Based on the coefficients given in Eqs. (2) and (3), it can be stated that the percent color removal or percent mineralization increases with the concentration of H_2O_2 (X_1), Fe(II) dose (X_2), and pH (X_3). According to Eqs. (2) and (3), the variable pH exhibited the highest influence on percent TOC and color removal.

Table 3
Experimental conditions according to central composite statistical design

No.	H_2O_2 (mg L^{-1})	Fe^{2+} (mg L^{-1})	pH
A1	8,000	300	7.00
A2	2,000	300	7.00
A3	5,000	400	7.00
A4	5,000	200	7.00
A5	5,000	300	11.00
A6	5,000	300	3.00
F1	6,732	358	9.30
F2	6,732	358	4.70
F3	6,732	242	9.30
F4	6,732	242	4.70
F5	3,268	358	9.30
F6	3,268	358	4.70
F7	3,268	242	9.30
F8	3,268	242	4.70
C	5,000	300	7.00

Table 4
Observed and predicted color and TOC removal efficiencies

Analysis No.	Color removal (%)	TOC removal (%)
	Observed	Observed
A1	87	52
A2	81	49
A3	82	50
A4	88	50
A5	25	30
A6	95	60
F1	61	44
F2	93	63
F3	55	35
F4	95	64
F5	40	30
F6	95	65
F7	50	49
F8	80	55
C1	85	62
C2	86	59
C3	87	61
C4	87	60

The model acceptability is an important part of checking if the model is appropriate or not for the application. The mean squares were obtained by dividing the sum of each square of two variation sources, the model and the residual variance, by the respective degrees of freedom (DF). The main indicators of the significance and adequacy of the employed model are the model *F*-value (Fisher variation ratio), and probability value (Prob. > *F*). The model Fisher variation ratio (*F*-value) was considered by dividing the model mean square by residual mean square. Values of Prob. > *F* less than 0.0500 indicates that the model is significant, whereas the values greater than 0.1000 are usually considered as insignificant. As a result of the study, Prob. > *F* values of 0.0001 indicate the chosen models are significant for percent color removals. The correlation coefficients, R^2, adjusted R^2, and predicted R^2 are close to each other and the predicted R^2 of 0.8861 is in reasonable agreement with the adjusted R^2 of 0.9678; that is, the difference is less than 0.2.

For the TOC removal efficiency, the predicted R^2 of 0.7591 is in reasonable agreement with the adjusted R^2 of 0.9322; that is, the difference is less than 0.2.

In the second part of the study, one variable was kept constant while the others were varying within the experimental ranges to see the interactive relationships between the process variables and treatment outputs for color and TOC removals, the results were given below.

3.1. Effect of Fe(II)

H_2O_2 concentration and the Fe(II) concentration were varied between 2,000 and 8,000 mg L^{-1}, 200 and 400 mg L^{-1} in this set of experiments, respectively, while the pH was constant at 7. Variations of percent color and TOC removals from the olive oil production effluent with H_2O_2 concentrations are depicted in Fig. 2. Percent color removals were increased up to Fe(II) concentration of 300 mg L^{-1} and then were decreased with further increases. The $^{\bullet}OH$ radicals are negatively affected by the excess of hydrogen peroxide or Fe(II), as given in the following Eq. (2) [11]. Similarly high Fe(II) concentrations above 300 mg L^{-1} caused lower TOC removal efficiencies. Consequently, according to the analysis of variance (ANOVA) results, the optimum Fe(II) concentration was determined as 255 mg L^{-1} for the mineralization of the OMW by the Fe(II)/H_2O_2 process.

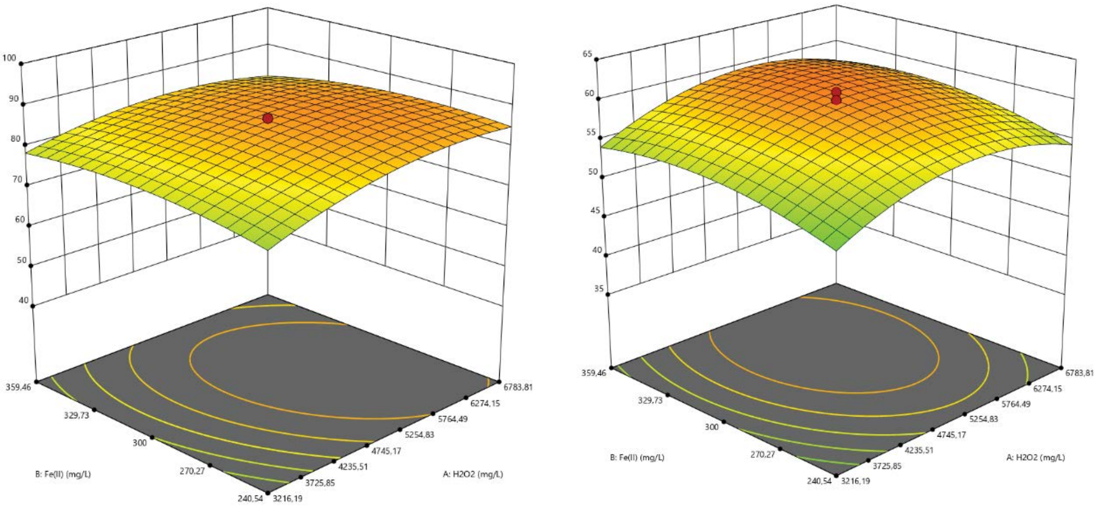
$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \quad (4)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow OH^{-} + Fe^{3+} \quad (5)$$

The optimum molar ratio in the Fenton process is 32 according to our results and this ratio is comparable with the literature. Casero et al. [12] and Solozhenko et al. [13] found the optimum molar ratio in Fenton oxidation as 20 and 40, respectively.

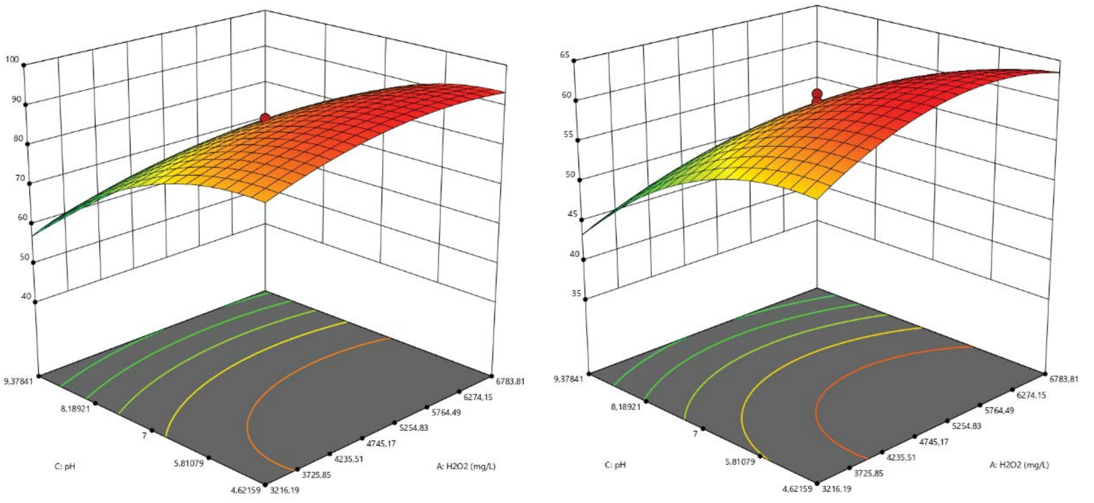
3.2. Effect of H_2O_2

To see the effect of H_2O_2 concentration on the oxidation of OMW, data were analyzed at different pH and with variable H_2O_2 concentration at a constant Fe(II) concentration (300 mg L^{-1}). The variation of percent color and TOC removals with the H_2O_2 concentration at constant initial Fe(II), the reaction time of 90 min are given in Fig. 3. The increasing amount of H_2O_2 to the UV system improved color and TOC removals. Both percent color and TOC removals slightly increased by increasing H_2O_2 concentration up to 6,732 mg L^{-1} and then decreased with excess H_2O_2 addition. The high amount of hydrogen peroxide undoubtedly caused as a free-radical scavenger, therefore, decreased in



(a) (b)

Fig. 2. Variation of decolorization (a) and TOC removal (b) efficiencies as a function of Fe(II) concentrations at different H_2O_2 concentrations (pH = 7).



(a) (b)

Fig. 3. Variation of decolorization (a) and TOC removal (b) efficiencies as a function of H_2O_2 concentrations at different pH (Fe(II) = 300 mg L^{-1}).

the hydroxyl radical concentration [14,15]. According to ANOVA results, the optimum concentration for H_2O_2 was obtained as 4,585 mg L^{-1}. Therefore, instead of the experimental results, it could be seen that less hydrogen peroxide is enough for the oxidation.

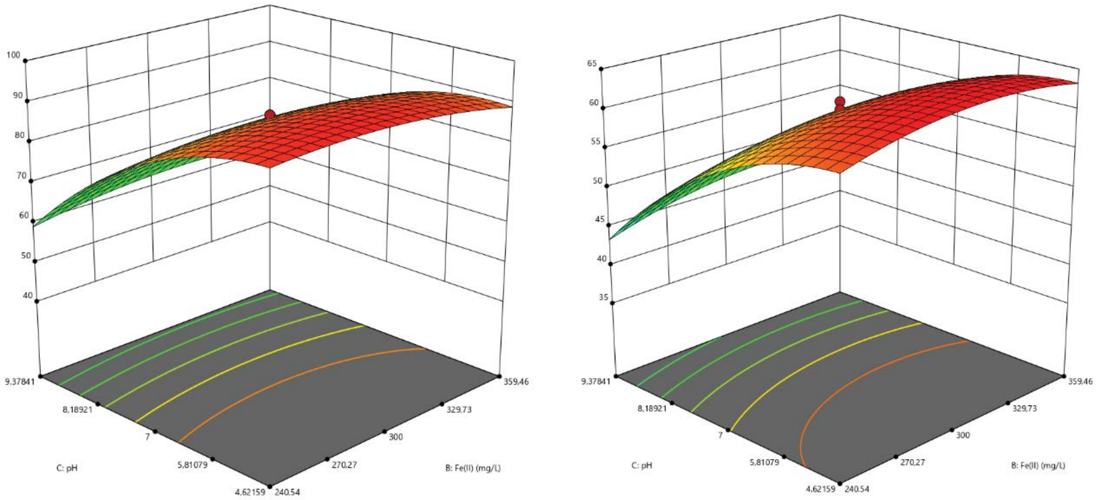
$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + HO_2^\bullet \quad (6)$$

The $HO_2^\bullet$ (per hydroxyl radicals) generated as in Eq. (2) possibly decreased the available active hydroxyl radicals by further scavenging ${}^\bullet OH$, as shown in Eq. (4):

$$HO_2^\bullet + {}^\bullet OH \rightarrow H_2O + O_2 \quad (7)$$

3.3. Effect of pH

The effect of pH on color and TOC removal efficiency was good concerning the literature data in our study. Because acidic pH ranges are suggested especially for photo-Fenton oxidation. The pH effect was particularly studied in other experimental studies, which showed the COD reduction of olive mill wastewater [16]. As a result of that study, for the response factor, pH 3–4 was found to be optimum. Many organic molecules can undergo a series of autoxidation reactions in the basic to neutral conditions. Such reactions result in the production of some species which, consequently, have poor interaction with the cationic surfactant. Thus, to



(a) (b)

Fig. 4. Variation of decolorization (a) and TOC removal (b) efficiencies as a function of pH at different Fe(II) concentrations (H_2O_2 = 5,000 mg L^{-1}).

prevent autoxidation reactions, lower pH is preferred to near-neutral and basic conditions [16].

In this study, the maximum color removal efficiency was obtained as 95% in 90 min at a Fe(II) concentration of 248 and 358 mg L^{-1} and at pH 4.70. Fig. 4 depicts variations of percent color and TOC removals with the different Fe(II) concentration and different pH at a constant initial H_2O_2 of 5,000 mg L^{-1} for the reaction time of 90 min.

In the literature, the degradation grade of the OMW organic matter slightly improved with TiO_2 as a catalyst on the H_2O_2/UV/TiO_2 oxidation [17]. The highest TOC degradation was obtained at 53.5% with the addition of 1 g L^{-1} of TiO_2. Most probably, at this concentration TiO_2 particles create a barrier effect avoiding light penetration, and thus reducing the illuminated surface area of semiconductor catalysts as suggested by Sauer et al. [17] and Cuomo et al. [18].

Finally, it is interesting to indicate that in previous work, Martínez-Nieto et al. [19] have designed and implanted an industrial plant for OMW (from the two-phase process) treatment by chemical oxidation with treated water flow at the exit of plant equal to 3–5 m^3 h^{-1}. In this process, the COD removal by the Fenton reaction (chemical oxidation reactor) during 3 h was only 56.1% and the whole purification yield obtained by the industrial plant was 86.2%. In this sense, the integration of the new chemical oxidation based in photo-Fenton instead of Fenton reaction would imply a substantial improvement of the final water quality.

There is no internationally accepted wastewater treatment method for olive oil production wastewater. In this regard, each country has set its national standard. The photocatalytic oxidation method is considered as a method that can be applied to olive oil wastewater in terms of both color and organic matter removal. However, this method does not seem to be able to purify the organic material sufficiently to meet discharge standards. On the other hand, it is considered appropriate to use oxidation processes as pre-treatment to adjust the quality of the final water to the parameters set by the legislation. Finally, given the limited degradation capacity of the UV and photo-Fenton oxidation methods, they can be used before biological treatment to reduce the inhibitory effect of the wastewater.

4. Conclusions

As a result of the experimental studies, it is possible to say that Fe(II) and H_2O_2 concentrations are important parameters for color and TOC removals. The UV irradiation accelerates the formation of OH radicals as Fe(II) does. However, increasing Fe concentrations (>300 mg L^{-1}) in the reactor reduced the removal efficiency in the oxidation process because the turbidity occurred by the excess Fe concentration, therefore UV radiation efficiency was decreasing. But the pH is much more affected than the others to obtain higher removal efficiencies both color and TOC elimination.

According to the results, the required amount of H_2O_2 per g COD corresponds to about 2.125 g H_2O_2/g COD. This result is consistent with the data in the literature (1 gO_2/g COD corresponding to 2.125 g H_2O_2/g COD). Likewise, an excessive concentration of H_2O_2 caused a decrease in the efficiency of the decolorization of olive oil production wastewater. No excess H_2O_2 is required for the decolorization of the olive oil production wastewater.

The optimal conditions over 95% color removal of the olive oil production were determined as 4,585 mg L^{-1} H_2O_2 and 255 mg L^{-1} Fe(II) concentration at pH 4,70.

With Fe(II)/H_2O_2/UV-C process, very high yields were obtained in TOC removal in olive oil wastewater. This process provides 65% TOC removal.

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