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Journal of Hazardous Materials B123 (2005) 187–195

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Application of the central composite design and response surface methodology to the advanced treatment of olive oil processing wastewater using Fenton's peroxidation

M. Ahmadi, F. Vahabzadeh*, B. Bonakdarpour, E. Mofarrah, M. Mehranian

Food Process Engineering and Biotechnology Research Center, Department of Chemical Engineering,
Amirkabir University of Technology (Tehran Polytechnic), Hafez Ave. No. 424, Tehran, Iran

Received 12 January 2005; received in revised form 26 March 2005; accepted 29 March 2005

Abstract

The central composite design (CCD) technique was used to study the effect of the Fenton's peroxidation on the removal of organic pollutants from olive oil mill wastewater (OMW). The ratio of hydrogen peroxide-to-Fe(II) (x_1) was between 1.67 and 8.33. Fe(II) concentration was constant at 0.03 M while the H_2O_2 concentration was set at three levels: 0.05, 0.15 and 0.25 M. Based on the molarity ratio, the selected ratio were in the low range of Fe(II)-to-H_2O_2 ratio ($\ll 1$). While based on the wt/wt ratio, the tested Fe(II)-to-H_2O_2 ratios were in the range of $\leq 1:5$. pH (x_2) was between 3 and 5. The concentration of OMW (x_3) was varied between 40 and 100%. The influence of these three independent variables on the four dependent variables, i.e. COD, total phenolics (TP), color and aromatocity removal was evaluated using a second-order polynomial multiple regression model. Analysis of variance (ANOVA) showed a high coefficient of determination (R^2) value of 0.902–0.998, thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data. H_2O_2-to-Fe(II) ratio had significant effect on all the four dependent variables. The positive sign for the regression coefficient of this regressor variable indicated that the level of the pollutant removal increased with the increased levels of factor x_1 from 1.67 to 8.33 and this effect was the most pronounced for TP removal. pH had also significant effect on the pollutant removal and the effect was the most noticeable for TP reduction. The negative coefficient of this variable (pH) indicated that level of the pollutant removal decreased as the pH increased from 3 to 5. The negative coefficient of the interaction between variable x_1 and x_2 indicated that a simultaneous increase in H_2O_2-to-Fe(II) ratio with decrease in the pH of the reaction led to an increase in the COD, TP and color removal. Quadratic models were predicted for the response variable, i.e. pollutant removal, and the maximum model-predicted removals were 56, 100, 33 and 32% for COD, TP, color and aromatocity, respectively. Optimum conditions for this wastewater treatment was obtained based on the performance of the Fenton's peroxidation in the experiment where the H_2O_2-to-Fe(II) ratio was at its high level (8.33) and the pH and OMW concentration were 4 and 70%, respectively.

Keywords: Advanced oxidation process; Central composite design; Empirical modeling; Fenton's peroxidation; Olive oil mill wastewater; Response surface methodology

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1. Introduction

Small olive oil mills process olives for the extraction of oil while large volumes of liquid wastewater are produced (olive oil mill wastewater, OMW 97 l/100 kg olives, when the conventional three-phase decanter is used) [1]. Phenolics present in OMW at high concentrations (1–10 g/l) are considered as the major recalcitrant compounds which possessing antimicrobial properties, and are difficult to

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Abbreviations: CCD, central composite design; OMW, olive oil mill wastewater; COD, chemical oxygen demand; TP, total phenolics; ANOVA, analysis of variance; BOD, biological oxygen demand; AOP, advanced oxidation process; AST, advanced sludge treatment; RSM, response surface methodology; $OH^\bullet$, hydroxyl radical; TSS, total suspended solids; TKN, total Kjeldahl nitrogen; CV, coefficient of variance; PRESS, predicted sum of squares

* Corresponding author. Tel.: +98 21 64543161; fax: +98 21 6405847.
E-mail address: far@aut.ac.ir (F. Vahabzadeh).

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doi:10.1016/j.jhazmat.2005.03.042

biologically degrade. Conventional biological processes for the purification of OMW are therefore inefficient. The OMW hence, constitutes a major environmental problem because of its high organic load. The chemical oxygen demand (COD) of this wastewater is in the range of 80–200 g/l while the biological oxygen demand (BOD) for OMW is in the range of 89–100 g/l [2]. These values are about 200–400 times higher than those of a typical municipal sewage [3]. Stringent environmental regulations impose increasing efforts toward the development of new technologies and methods for the reduction of the organics in wastewaters, such as OMW. Advanced oxidation processes (AOP) that utilize H_2O_2, O_3, or O_2 as the oxidant, are very promising techniques for the remediation of contaminated ground, surface, and wastewaters having non-biodegradable organic pollutants [4,5]. The AOPs involve the generation of the hydroxyl radical ($OH^{\bullet}$) that is a reactive intermediate and has a high oxidation potential [6]. One available technique in the area of AOPs is based on the Fenton's peroxidation which is considered as the iron-catalyzed H_2O_2 decomposition reaction. The Fenton's reagent is a mixture of ferrous salt and hydrogen peroxide.

Organic substances are oxidatively and non-selectively degraded by the generated hydroxyl radicals and although the Fenton's peroxidation mechanism of organics present in the wastewater is complex but the process has been used successfully to treat wide range of industrial wastewaters, including OMW and wastewater sludge (biosolids) [7–10]. Technical points and economic considerations of using advanced sludge treatment (AST) methods have been discussed thoroughly (biosolids) [10]. The Fenton's peroxidation mechanism of an organic compound is likely to occur in the several steps: generation of $OH^{\bullet}$ radical and its oxidative reaction with the organic compound, the direct action of H_2O_2 toward the pollutant, $OH^{\bullet}$ scavenging due to ferrous ions and H_2O_2 and reactions of Fe(III) with H_2O_2 with regenerations of ferrous ions and formation of hydroperoxyl radical ($HO_2^{\cdot}$), and reduction of Fe(III) to Fe(II) by $HO_2^{\cdot}$ [11].

Results reported by Beltran-Heredia et al. [8] showed that treating OMW by Fenton's peroxidation decreases COD by 33% while total phenolics (TP) were reduced by 93%. The H_2O_2 and ferrous ions concentration in this study were 0.78 and 0.055 M, respectively [8]. Similar findings were reported by Rivas et al. [12]. On the other hand, concentrations of ferrous ion and H_2O_2 used in the degradation of atrazine and metolachlor (two widely used herbicides) in the study conducted by Pratap and Lemley [13] were 0.0036 and 0.025 M, respectively. As pointed out by [7], the relationships between ferric, ferrous and H_2O_2 concentrations and the quantity of organic and inorganic compounds in the Fenton' peroxidation, can be quantified and this stoichiometric relationship has been used to classify the Fenton system. In this reaction mixture, at ratio of Fe(II)-to-H_2O_2 ≥ 2, when the organic compounds are absent, the reaction of $OH^{\bullet}$ is mainly with Fe(II), the rate of this reaction being ten times faster than that between $OH^{\bullet}$ and H_2O_2 [7]. The presence of organic compounds only affects the behavior of the ferrous ion in the solution and not H_2O_2, since the organic pollutant competes with Fe(II) for hydroxyl radical [7].

Conventionally, wastewater treatments, like many other industrial processes are optimized by using “one at a time” variation of treatment variables. Moreover, this method assumes that various treatment parameters do not interact and that the response variable is only function of the single varied parameter. However, the response obtained from a waste treatment method for example, results from the interactive influences of the different variables. When a combination of several independent variables and their interactions affect desired responses, response surface methodology (RSM) is an effective tool for optimizing the process [14]. RSM uses an experimental design such as the central composite design (CCD) to fit a model by least squares technique [15,16]. Adequacy of the proposed model is then revealed using the diagnostic checking tests provided by analysis of variance (ANOVA). The response surface plots can be employed to study the surfaces and locate the optimum. In several industrial processes, RSM is almost routinely used to evaluate the results and efficiency of the operations [17–21].

In the present work, a CCD in the form of a 2^3 full factorial design was used to develop mathematical equations, in terms of the pollutant removal, providing quantitative evaluation of the Fenton process used to oxidatively treat OMW. Hydrogen peroxide-to-Fe(II) ratio, pH and concentration of OMW (a real industrial wastewater) as the key parameters affecting the decomposition performance of the Fenton's reagent were studied in this evaluation.

2. Experimental

2.1. Olive oil mill wastewater and Fenton's peroxidation method

The OMW used in this study was obtained from an olive oil mill in the Roodbar region, home of the olive growing and processing sector, in the northern part of Iran. The three-phase centrifugation method has been used for the oil extraction. Fresh OMW was transported to our laboratory under refrigeration within 15 h of its production, and in order to conduct the tests with the same wastewater, appropriate amounts of OMW were distributed in 250 ml plastic bottles and stored at −20 °C until use. At the time of use, the OMW sample was thawed in a refrigerator and filtered using Whatman filterpaper #2. The OMW at different initial concentrations, i.e. different COD concentrations were used. Fenton's peroxidation experiments were carried out batchwise in a 500 ml Erlenmeyer flask with continuous stirring (130 rpm) in a shaker incubator at 25 °C. Total volume of the reaction mixture was 400 ml. The appropriate volume of the OMW was first added. Dilution of OMW when needed, was done using distilled water and in a way that sequential addition of the reagents, at the end could provide the desired concentration of the tested wastewater. This followed by dilute sulfuric acid addition (2N solution). Maintaining the acidic conditions is necessary to insure solubility of ferrous salt ($FeSO_4 \cdot 7H_2O$) which was added next. Small volume of acid or base was then added for the adjustment of pH. Hydrogen peroxide (30% solution) was added slowly at last. Slow addition of H_2O_2 is essential for proper maintenance of temperature [12]. In Fenton's peroxidation technique ambient temperature is usually used with good efficiency. This sequence for addition of reactants, as mentioned above, is considered a common practice in the Fenton's peroxidation process [5]. The reaction lasted around 4 h by that time the concentration of TP reached its lowest level. No H_2O_2 was detected after first hour, showing complete consumption of the hydrogen peroxide. Results obtained from quenching the samples using sodium hydroxide solution were compared with the results of the tests completed at the same condition but without the use of the base to raise the pH to above pH 7. There was no noticeable differences and the experiments, therefore, were conducted without the addition of NaOH solution. During time course of the reaction in each experiment, the samples were taken periodically to analyze the concentration or amount of the COD, TP, peroxides, aromatics and color according to the appropriate procedures given below. Each experiment was performed twice.

Some characteristics of the OMW used in the present study are listed in Table 1.

2.2. Analyses of OMW samples

COD, total suspended solids and turbidity, were determined according to standard methods for the examination of water and wastewater [22]. The TP concentration was determined using the Folin–Ciocalteau reagent after prior extraction of the OMW sample with ethyl acetate according to the protocol described by Garcia et al. [23]. The result of the reaction was a blue polymer in an alkaline medium, and the absorbance was measured at 725 nm [24]. The polyphenol content was expressed as mg/l of caffeic acid. The aromatic content of the OMW was determined spectrophotometrically and the optical density (OD) was measured at 254 nm: at this wavelength, the aromatic and unsaturated compounds present in the sample exhibit an absorption maximum [25]. Color removal in the treated OMW was also determined spectrophotometrically by measuring the absorbance of the sample at 288 nm [26]. Hydrogen peroxide was analyzed iodometrically [27].

Table 1
Characteristics of the OMW used in the present study

pH	COD (g/l)	TSS[a] (g/l)	TKN[b] (%)	Turbidity (NTU[c])	TP[d] (g/l)
5.38	167–181	36–39	0.08	14.6–14.8	5.2

[a] Total suspended solids.
[b] Total Kjeldahl nitrogen.
[c] Nephelometric turbidity units.
[d] Total polyphenols.

Table 2
Independent variables and their levels for the central composite design used in the present study

Variable	Symbol	Coded variable levels[a]		
		−1	0	1
H_2O_2-to-Fe(II) ratio	x_1	1.67	5	8.33
pH	x_2	3	4	5
OMW concentration (%)	x_3	40	70	100

[a] For passage from coded variable level to natural variable level, the following equations were used: $x_1 = (\text{ratio} - 5)/3.33$; $x_2 = \text{pH} - 4$; $x_3 = (\text{OMW}(\%) - 70)/30$.

2.3. Experimental design and data analysis

As shown in Table 2, a CCD in the form of 2^3 full factorial design was used, in which three independent variables were converted to dimensionless ones (x_1, x_2, x_3,), with the coded values at 3 levels: −1, 0, +1. The selection of variable levels was based on the results obtained through our previous work (see below). The arrangement of CCD as shown in Table 3 was in such a way that allows the development of the appropriate empirical equations (second order polynomial multiple regression equations) [14–16]:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \quad (1)$$

The predicted response (y) was therefore correlated to the set of regression coefficients (β): the intercept (β_0), linear (β_1, β_2, β_3), interaction (β_{12}, β_{13}, β_{23}) and quadratic coefficients (β_{11}, β_{22}, β_{33}). The "Design expert" (version 5) and "Statistica" (version 5) softwares were used for regression and graphical analyses of the obtained data.

Table 3
Arrangement of the CCD for the three independent variables used in the present study

Experiment no.	Variable levels/coded values		
	H_2O_2-to-Fe(II) ratio (x_1)	pH (x_2)	OMW concentration (x_3)
1	−1	−1	−1
2	+1	−1	−1
3	−1	+1	−1
4	+1	+1	−1
5	−1	−1	+1
6	+1	−1	+1
7	−1	+1	+1
8	+1	+1	+1
9	−1	0	0
10	+1	0	0
11	0	−1	0
12	0	+1	0
13	0	0	−1
14	0	0	+1
15	0	0	0

3. Results and discussion

3.1. Selecting the ratio for Fenton's reagent

The overall efficiency of the Fenton's peroxidation process as pointed out by Neyens and Baeyens, depends on the key parameters of the Fenton reaction and the their relationships in terms of formation and utilization of hydroxyl radicals [7]. Ferrous and ferric ions, H_2O_2, pH, temperature and amount of the pollutant (organic and/or inorganic), all contribute to the proper performance of the Fenton's peroxidation process [5]. In the present study, when working with undiluted OMW and using 0.25 M H_2O_2 solution, the lowest concentration of Fe(II) which was responsive to the Fenton process and made the reaction proceed, was 0.03 M. Decomposition of the H_2O_2 at the concentration of 0.25 M did not occur at any Fe(II) level less than 0.03 M. It is shown elsewhere that degradation of the phenolic compounds did not occur using only H_2O_2 and in the absence of Fe(II) [11]. In the present work and at constant Fe(II) concentration, two other H_2O_2 concentrations namely 0.05 and 0.15 M were also selected. Three H_2O_2-to-Fe(II) ratios were corresponded to low ratio of Fe(II)-to-H_2O_2 [7]. Excess amount of H_2O_2 is not recommended since unutilized hydrogen peroxide contributes to COD (l mg/l of H_2O_2 contributes 0.25–0.27 mg/l to the COD concentration) [28,9]. Also, H_2O_2 in large quantity acts as $OH^\bullet$ radical scavenger [5,7] point out that reaction of hydroxyl radical with H_2O_2 proceeds to a greater extent when Fe(II)-to-H_2O_2 is at a low level ($\ll 1$) and when pollutants are present. The optimum Fe(II)-to-H_2O_2 ratio is usually 1:5 (w/w) [5] which corresponds to H_2O_2-to-Fe(II) ratio of about 10. The high ratio of H_2O_2-to-Fe(II) used in the present study was about 1:5 (w/w) ratio. While the other two ratios of H_2O_2-to-Fe(II) selected in the present study, were about 1:3 and 1:1 (w/w) ratio. Moreover, the concentrations and ratios used in the present study were in the range reported by others when the Fenton system has been applied to the treatment of OMW wastewater [8,12].

3.2. Variation of the pollutant concentration with the reaction time

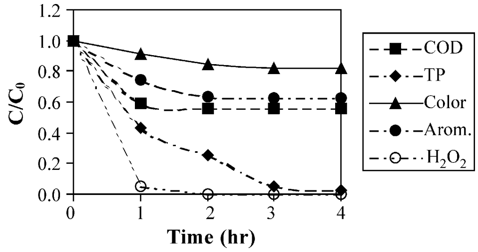

Fig. 1. Fenton's peroxidation treatment of OMW as shown by evolution of COD, TP, color, aromatocity and H_2O_2 with reaction time (data is taken from experiment no. 6). C_0 is the initial amount of the dependent variable.

Fig. 1 shows the trend of the changes of the pollutants with the reaction time for experiment no. 6 (see Table 3). As can be seen, H_2O_2 was almost completely consumed by 1 h, whereas the TP content, which showed a much higher rate of decrease compared to the rate of removal of color, COD and aromatocity, was not totally removed until the fourth hour of reaction. COD, color and aromatocity reached a nearly constant level after around 2 h of reaction time which corresponds to complete depletion of H_2O_2. Maximum percentage removal of COD and aromatocity was 40% whereas only 20% of color has been removed. Similar observations have been reported by others [8,12]. It has been reported also elsewhere that H_2O_2 at concentration of 0.2 M when Fe(II)-to-H_2O_2 ratio was $\ll 1$ (i.e., 0.05) the complete H_2O_2 depletion from the OMW media occurred after 1–2 h. However, when higher concentrations of H_2O_2 were used (i.e., 0.5 M) the total consumption of H_2O_2 occurred after 8 h of the treatment [12]. Kang et al. [29] have pointed out that the decomposition performance of the Fenton's peroxidation is mainly determined by the availability of ferrous ions, which have a major role in the formation of hydroxyl radicals. A set of redox reactions which are operative at an early stage of the reaction are involved in the formation of organic radicals and intermediates while ring-opened products formed at a later stage of the reaction have decisive role in trapping iron species [29]. In fact, generation of Fe(II) continues even after H_2O_2 depletes, which indicates that some of the ring-opened products and/or some organic acids or acid radicals, may have roles in this regeneration process [29]. The overall decomposition kinetics of the Fenton system, as pointed out by Kang et al. [29], is determined by the reactions directly involved in governing the levels of hydroxyl radicals and ferrous ions.

3.3. Central composite design and fitted regression models as related to the pollutant removal

In the present work, the relationship between four criteria of the pollutant removal (namely COD, TP, color, and aromatocity) and three controllable factors (namely H_2O_2-to-Fe(II) ratio, pH and OMW concentration) was studied. A CCD shown in Table 3 allows the development of mathematical equations where each response variable y is assessed as a function of H_2O_2-to-Fe(II) ratio (x_1), pH (x_2) and OMW concentration (x_3) and calculated as the sum of a constant, three first-order effects (terms in x_1, x_2 and x_3), three interaction effects (terms in x_1x_2, x_1x_3 and x_2x_3) and three second-order effects (x_1^2,x_2^2 and x_3^2) according to the Eq. (1). The results obtained were then analyzed by ANOVA to assess the "goodness of fit". Only terms found statistically significant were included in the model. β_3 coefficient for the COD, TP and color removal and β_{11} for the TP removal and β_{13} for the COD and color removal and β_{23} for all the four responses were non-significant. Therefore, these coefficients were dropped from the model and then a new ANOVA was performed for the reduced model. The models for COD, TP, color and aromatocity removal (y_1 to y_4) were significant by the F-test at the 5% confindence level ($\text{Prob} > F < 0.05$). The following fitted regression models (equations in terms of coded values for the regressors) were used to quantitatively investigate the effects of H_2O_2-to-Fe(II) ratio, pH and OMW concentration on the characterization of the Fenton process for the pollutants removal:

COD removal:

$$y_1 = 36.58 + 13.15x_1 - 6.32x_2 + 6.92x_1^2 - 18.44x_2^2 \\ -7.19x_3^2 - 4.74x_1x_2$$

TP removal:

$$y_2 = 70.94 + 29.09x_1 - 14.23x_2 - 29.66x_2^2 \\ -10.79x_1x_2 - 4.38x_1x_3$$

Color removal:

$$y_3 = 19.51 + 6.5x_1 - 2.37x_2 + 7.14x_1^2 \\ -10.63x_2^2 - 8.88x_3^2 - 1.94x_1x_2$$

Aromatocity removal:

$$y_4 = 16.51 + 6.70x_1 - 3.77x_2 + 5.34x_3 + 8.98x_1^2 \\ -8.66x_2^2 - 6.73x_3^2 + 3.81x_1x_3$$

Statistical parameters obtained from the ANOVA for the reduced models of the pollutant removal are given in Table 4. Since R^2 always decreases when a regressor variable is dropped from a regression model, in statistical modeling the adjusted R^2 which takes the number of regressor variables into account, is usually selected [17]. The R^2 coefficient gives the proportion of the total variation in the response variable explained or accounted for by the predictors (x's) included in the model. In the present study, the adjusted R^2 ranged from 0.804 (for aromatocity removal) to 0.982 (for color removal). The R^2 coefficient in this study ensured a satisfactory adjustment of the quadratic model to the experimental data. High R^2 values do not necessarily mean that decrease of these pollutants, all follow the same trend and are strongly correlated (see Fig. 1). The removal patterns of the different pollutants do not coincide to each other and some intermediate molecules formed during the reaction may exert considerable influence on the pattern of removal of the other pollutants. For example, it has been shown that the solubilization of ferric ions at pH 6 by organic acids such as gallic acid facilitates the degradation of the certain organic pollutant by Fenton's peroxidation [30]. In the Fenton's peroxidation, rate of generation and consumption of hydroxyl, hydroperoxyl radicals and ferrous ions all, are under strong influence of pH [11,5]. A range of iron complexes are formed at either low or higher pH ($pH < 2.5$ and $pH > 4$). In the Fenton's peroxidation and at a particular Fe(II)-to-H_2O_2 ratio, as is pointed out by Neyens and Baeyen [7], decomposition mechanisms and rate-limiting steps may be differed.

As it is given in Table 4, the coefficient of variance (CV) for the COD, TP, color and aromatocity removal has been found to be (%) 9.68, 10.54, 10.84 and 38.75, respectively. The CV as the ratio of the standard error of estimate to the mean value of the observed response (as a percentage) is a measure of reproducibility of the model and as a general rule a model can be considered reasonably reproducible if its CV is not greater than 10% [19]. The model fitted for aromatocity removal had a relatively high CV which may be related to some difficulties in obtaining a representative sample for the aromatocity measurement. This model had high R^2 value and showed no lack of fit. By applying diagnostic plots such as normal probability plot of residual, plot of residuals versus predicted values for the aromatocity removal, the assumptions of normality, independence and randomness of the residuals were satisfied. The fitted model for the aromatocity removal was accepted. The adequate precision value, is a measure of the "signal to noise ratio" and was found to be in the range of 9–39, which indicates an adequate signal (see Table 4). A ratio >4 is desirable [19]. The predicted models can be used to navigate the space defined by the CCD.

The relative contribution of each factor to each dependent variable (y_1 to y_4: COD, TP, color and aromatocity removal) was directly measured by the respective coefficient in the fitted model. A positive sign for the coefficients (β_1s) in the fitted models for y_1 to y_4 indicated that the level of pollutant removal increased with increased levels of factor x_1 (H_2O_2-to-Fe(II) ratio). The greatest coefficient ($\beta_1 = 29.09$) in the fitted model was obtained for TP removal, which revealed the high sensitivity of the total phenolics to removal by the Fenton's peroxidation. On the other hand, the lowest β_1s were obtained for color and aromatocity removal which indicates that the removal of these pollutants is less affected by H_2O_2-to-Fe(II) ratio. Moreover, a negative sign for the regression coefficient of β_2s, indicates that the ability of the system to remove the pollutant decreases with increase in the pH value (x_2).

In order to gain a better understanding of the results, the predicted models are presented in Figs. 2–5 as the three-dimensional response surface plots. The predicted values for the COD, TP, color and aromatocity removal of OMW treatment in the present study are given in Table 5 (the regression coefficients of the reduced models). The same table includes the measured data for these response variables.

3.4. *Response surface plotting and optimization of the treatment based on the pollutant removal*

For the graphical interpretation of the interactions, the use of three-dimensional plots of the regression model is highly recommended [14–16]. Variables giving quadratic and interaction terms with the largest absolute coefficients in the fitted models, were chosen for the axes of the response surface plots to account for curvature of the surfaces. Hydrogen peroxide-to-Fe(II) ratio and pH were selected for the RSM plots of COD, TP and color removals, while OMW concentration was

Table 4
Statistical parameters obtained from the analysis of variance for the reduced models

Variable	COD removal	Polypohenol removal	Color removal	Aromatocity removal
R^2	0.988	0.982	0.992	0.902
R^2 adjusted	0.979	0.972	0.982	0.804
F_{exp}[a]	111.66	99.76	134.11	9.21
Prob > F	<0.0001	<0.0001	<0.0001	0.0045
Std. Dev.	2.33	5.39	1.22	4.74
Coefficient of variance	9.68	10.54	10.84	38.75
PRESS	142.66	623.1	49.71	766.11
Adequate precision	33.94	28.05	39.53	9.85

[a] F_{exp} defined as the ratio of the mean square of the model to mean square of the error.

kept at the central level (i.e., 70%) (Figs. 2–4). The interaction implies that the effect produced by changing the H_2O_2-to-Fe(II) ratio, as the one regressor variable depends on the level of pH as the other regressor variable. In the models for the COD and TP removal, x_1 was the major regressor variable affecting the responses (greatest coefficients, β_1s) while this variable had a significant interaction with x_2. The regression coefficient (β_{12}) was −4.74 and −10.79 for the removal of COD and TP, respectively. Fig. 2 shows the dependence of the COD removal (variable y_1) on x_1 and x_2 for the OMW concentration set at its central level (70%). The plot shows a strong degree of curvature of three-dimensional surfaces. The COD removal increased as the H_2O_2-to-Fe(II) ratio increased to its high level (8.33). The COD removal also increases with pH to its central level (pH 4). Thereafter, COD decreases as the pH increases toward its high level, i.e. pH 5 and the stronger

Table 5
Experimental and theoretically predicted values for COD, polyphenols, color and aromatocity removal of olive oil mill wastewater treatment in the present study

Experiment no.	For COD removal (%)		For polyphenol removal (%)		For color removal (%)		For aromatocity removal (%)	
	Actual value	Predicted value	Actual value	Predicted value	Actual value	Predicted value	Actual value	Predicted value
1	3.2	6.31	7.8	11.24	1.33	1.05	2.15	5.36
2	41.08	42.08	99.9	99.77	17.16	17.96	9.64	11.42
3	1.85	3.15	4.5	4.37	0.69	0.19	0.91	−1.91
4	21.26	19.97	51.80	49.73	8.88	9.35	4.08	3.88
5	9.89	6.31	21.2	20.01	1.38	1.05	8.33	8.69
6	43.94	42.08	94.13	91.00	17.72	17.96	37.44	29.72
7	4.10	3.15	8.70	13.14	0.72	0.19	3.44	1.15
8	18.72	19.97	40.10	40.96	9.2	9.35	15.45	22.18
9	30.23	30.35	52.35	41.85	18.50	20.13	17.52	18.78
10	55.76	56.65	99.50	100.00	34.80	33.16	32.78	32.19
11	23.14	24.47	54.50	55.51	11.67	11.25	9.52	11.62
12	12.15	11.83	30.14	27.05	6.10	6.51	5.50	4.08
13	30.24	29.40	70.42	70.94	12.15	10.63	6.69	4.44
14	27.55	29.40	61.32	70.94	9.12	10.63	12.20	15.12
15	38.60	36.58	71.10	70.94	19.48	19.51	17.86	16.51

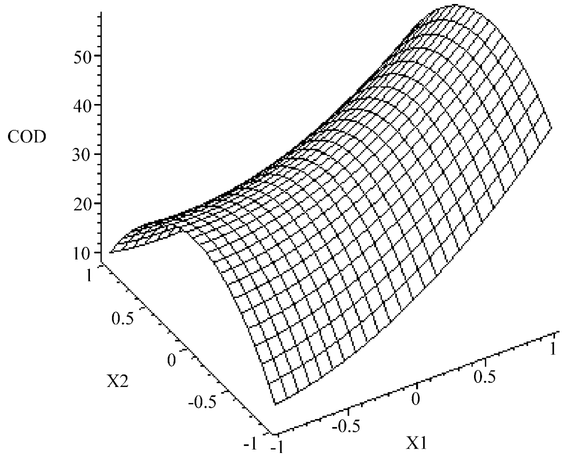

Fig. 2. Second-order response surface plot in the COD removal (y_1) for the OMW treatment by Fenton's peroxidation. Dependence of y_1 on the H_2O_2-to-Fe(II) ratio (x_1) and pH (x_2) is shown (OMW concentration, $x_3 = 0$).

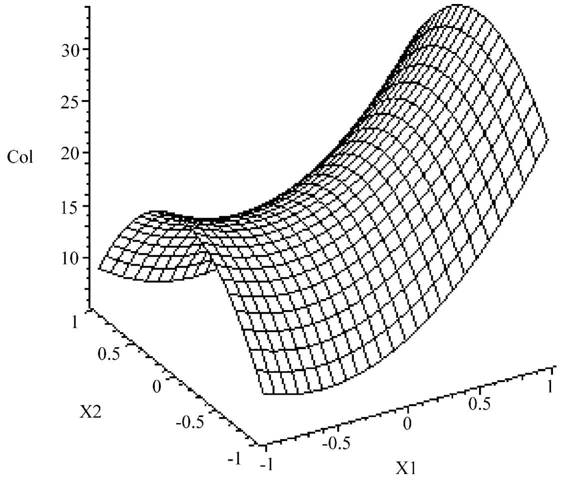

Fig. 4. Second-order response surface plot in the color removal (y_3) for the OMW treatment by Fenton's peroxidation. Dependence of y_3 on the H_2O_2-to-Fe(II) ratio (x_1) and pH (x_2) is shown (OMW concentration, $x_3 = 0$).

influence of pH occurs when the pH was at its high level. The efficiency of the Fenton process in terms of increased COD removal is influenced by the pH and besides the initial pH adjustment, controlling pH during the reactions is important. pH affects the formation of different iron complexes [5]. Availability of free iron species (Fe(II), Fe(III)) is as important as hydroxyl radical generation and its utilization. Almost the same interpretation can be given for the TP removal except that the applicable range of TP removal is wider as compared to that of the COD removal (30–90% versus 35–55%). The dependence of the TP removal on H_2O_2-to-Fe(II) ratio and pH is shown in Fig. 3 and TP removal increases almost linearly as H_2O_2-to-Fe(II) ratio increases to its high level (8.33) while the curvature type relationship exists between the TP removal and pH. At pHs above 4 the TP removal decreases with increasing pH toward its high level (i.e., pH 5). The strong decreasing effect of pH on the TP removal occurred at pH 5. The pH control and adjustment is less restricted for the TP removal as compared to that for the COD removal (see Figs. 2 and 3). Degradation of phenolic compounds yields phenolic acids which may have a considerable effect in keeping the pH, in the appropriate acidic range for a longer period of time.

Fig. 4 shows the second-order response surface plot for the color removal process. Squared terms in the relevant equations for the fitted models represent the curvature of the surface. The degree of curvature of the surface for the color removal in this wastewater treatment is higher than that of the COD removal. In studies on the textile wastewater treatment, it is suggested that Fenton could be better used as a

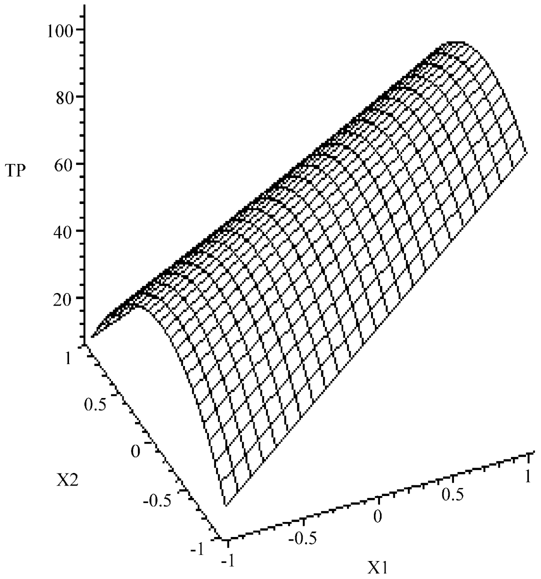

Fig. 3. Second-order response surface plot in the TP removal (y_2) for the OMW treatment by Fenton's peroxidation. Dependence of y_2 on the H_2O_2-to-Fe(II) ratio (x_1) and pH (x_2) is shown (OMW concentration, $x_3 = 0$).

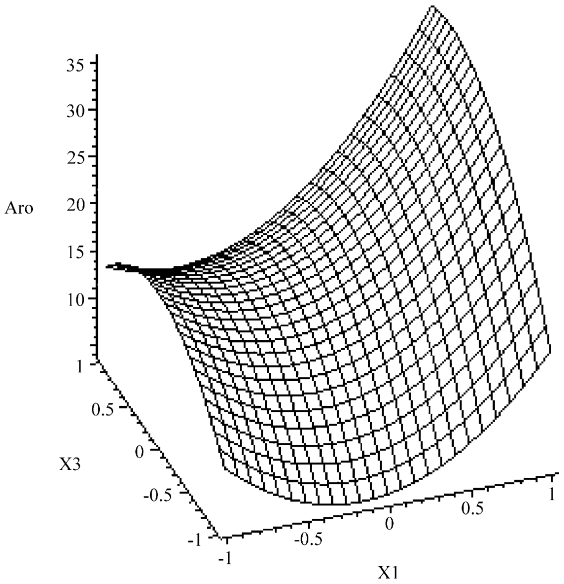

Fig. 5. Second-order response surface plot in the aromatocity removal (y_4) for the OMW treatment by Fenton's peroxidation. Dependence of y_4 on the H_2O_2-to-Fe(II) ratio (x_1) and OMW concentration (x_3) is shown (pH, $x_2 = 0$).

decolorizing agent due to the presence of the color forming substances in this wastewater [31]. Chromophoric compounds are more sensitive to degradation by strong oxidants such as hydroxyl radicals, when compared to a non-colored saturated compound [31]. Fig. 1 shows profiles for color changes versus reaction time and extent of this removal is less than that of the other three pollutants. A linear relationship between TP removal and H_2O_2-to-Fe(II) ratio and nonlinear effect of this ratio on the COD and color removal (see Figs. 2–4) is an indication of differences that exist in the degradative capacity of the Fenton's reagent to reduce TP, nonphenolic organic compounds and phenolics/nonphenolics and their interactions products in developing the colored substances. During course of the pollutant removal, i.e. decolorization, some degraded species may appear which act as the iron scavenger(s) [29]. Critical role of available ferrous ions in the formation of $OH^{\bullet}$ has been emphasized [10,7]. In the present study, the decomposition efficiency of the Fenton's peroxidation was less for the color removal as compared to that of removal of other tested pollutants. The ease or difficulty of the pollutant removal in the present study was in the following decreasing order: TP > COD > color. There are more interests in use of combined forms of chemical and biological oxidation in wastewater treatments and to study the mechanisms involved in the reduction of hazardous materials would therefore increase the efficiency of the particular wastewater treatment [4,32].

Fig. 5 shows the dependency of the aromatocity removal on the H_2O_2-to-Fe(II) ratio and OMW concentration when pH was kept at its central level (pH 4). The aromatocity removal increases as OMW concentration increases to 70% and thereafter aromatocity removal decreases as the concentration of OMW increases. The greatest decreasing effect of OMW concentration on the aromatocity removal occurred when the concentration was at the low level (40%). Polyphenolic compounds are however the major aromatic compounds of OMW and known as the most common refractory COD compounds in this wastewater, although other organic substances including nitrogenous compounds, sugars are and pectins are also linked with the polluting activity of this wastewater [33]. The degradation of individual *p*-hydroxybenzoic acid, tyrosol and *p*-coumaric acid in aqueous solutions by the Fenton's reagent has elsewhere been shown, to be different as compared to that when these phenolics were oxidized simultaneously (same initial concentration) [34]. The explanation was based on the presence of oxidizing agents other than hydroxyl radical that have different selectively toward the phenolics studied [34]. At the initial stages of the Fenton reaction, hydroxyl radicals are the major oxidizing agent having a non-selective role in degrading aromatics. The Folin–Ciocalteau method which was used in the present study to measure the TP content, does not provide the measure and extent of nonphenol aromatics present in OMW, such as polymerin [33]. Carbohydrates, melanin, proteins, phenols and amino acids are the major components of the polymerin of OMW while metal cations naturally present in OMW have been bound to the polymerin [33]. In AOPs, sensitivity of organic compounds to Fenton's peroxidation is different and some are more vulnerable than others [7]. Moreover, certain organic molecules are partially degraded by a particular oxidant and a stronger oxidizing system is required to achieve higher degree of the degradation [6]. In the present work, aromatocity decreased in a similar manner as the COD removal and extent of the color reduction was lowest among the tested pollutants (see Fig. 1). The non-selective behavior of the hydroxyl radicals puts a limitation on the oxidizing capacity of the system such as Fenton process. By use of a biological treatment, especially when peroxidases are involved, in addition to Fenton's peroxidation, chances of pollutant degradation may increase considerably.

4. Conclusions

Fenton's peroxidation for the OMW treatment was studied using CCD and RSM. Optimum conditions for this form of an advanced oxidation process could be achieved by setting the experiment with OMW at 70% concentration (central level of the regressor x_3) while the other two regressors (H_2O_2-to-Fe(II) ratio and pH) were at the high (8.33) and the midrange level studied (pH 4), respectively (i.e., experiment no. 10). Adjustment of the quadratic model with the experimental data was satisfactory. Analysis of variance showed a high coefficient of determination value in the range of 0.902–0.992. It was possible therefore, to develop the empirical equations describing and predicting the removal of the major pollutants. The adjustment and control of the pH was found to be more important for COD removal as compared to that of the TP removal. The decolorization capacity of the Fenton's reagent was less pronounced in the studied range in the present work.

Acknowledgments

The authors sincerely thank the Industrial Development and Renovation Organization of Iran for financial support of this project. A continuous and valuable computer assistance of Alireza Monazzami, Director of the Computer Center of the Chemical Engineering Department is highly appreciated.

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