

Optimizing the removal of COD and Phenolic compounds from olive mill wastewater by Fenton oxidation using experimental design

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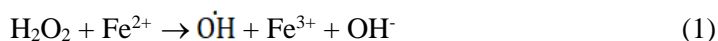
Abstract

The production of olive oil, leads to the co-production of large quantities of olive mill wastewater (OMW). This waste has a high polluting power as well as a high antibacterial activity exerted, among others, by various phenolic compounds. In this study, the Fenton process using hydrogen peroxide (H_2O_2) as oxidant and ferrous ions (Fe^{2+}) as catalyst was used to treat OMW. Box–Behnken design (BBD) based on the response surface methodology (RSM) was adopted to evaluate the effects of concentration $[H_2O_2]$, concentration $[Fe^{2+}]$ and reaction time on the chemical oxygen demand (COD) removal, phenolic compounds (PC) removal and the residual H_2O_2 level remaining in the solution. According to the Analysis of Variance (ANOVA), the three quadratic models that were developed using multiple regression analysis were reliable and successfully fit the experimental data with a high coefficient of determination R^2 ranging from 0,9969 to 0,9999. Optimal operating conditions based on the desirability function methodology were found to be $[H_2O_2] = 13,79g/l$ (0,4mol/l), $[Fe^{2+}] = 0,55g/l$ (0,01mol/l) and reaction time = 5,73h. Under the values of these variables, COD removal of 88,70% and PC removal of 84,26% with no residual H_2O_2 were predicted with a desirability value of 1.

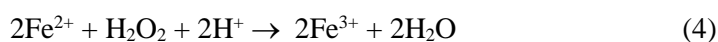
Keywords: Fenton; Olive Mill Wastewater; Response Surface Methodology; Box-Behnken Design.

1. Introduction

The industry of olive oil is one of the important agricultural activities concentrated in the edge of the Mediterranean, including Morocco who is the fourth largest exporter and producer of olive oil in the world after the European Union, Tunisia and Turkey [1]. The extraction process generates, in short periods of time, a huge quantities of Olive-mill wastewater (OMW), with the volume reaches more than 30 million m³ per year [2]. This by-product of olive oil production represents a major environmental problem due to its high and toxic organic load. OMW composition varies both qualitatively and quantitatively according to the olive variety, climate conditions, cultivation practices, the olive storage time and especially the olive oil extraction process [3]. Generally, OMW is a foul-smelling acidic wastewater composed of water (83–92%), organic matter (4–16%) and minerals (1–2%) [4]. The organic load reflected in the high biological oxygen demand (up to 100 g/L) and chemical oxygen demand (up to 200 g/L) concentrations [5,6] sugars, nitrogenous compounds, fatty acids, polyalcohol, polyphenols, pectin and fats [7,8]. The phenolic compounds that are present in olive stone and pulp tend to be more soluble in the water phase than oil. Consequently, the concentration ranges from 0,5 to 25 g/L in OMW [9]. Several studies have shown that phenolic compounds, characterized by their wide variety and complexity, are the main responsible for the toxicity and phytotoxicity of OMW rendering its bio-treatment a challenging task [10,11]. OMW also exhibit significant saline toxicity levels, including chloride, sulphate and phosphoric salts of potassium, calcium, iron, magnesium, sodium and traces of other elements [12]. In Morocco, the production of OMW is estimated to reach 250.000 m³/year [13]. This effluent does not undergo any treatment and is often poured into the town drains or stored in evaporation lagoons [14]. However, this operating method has several relevant disadvantages, such as bad odour, infiltration and insect proliferation [15]. Many studies have been published on the biological OMW treatment under aerobic [16-19] or anaerobic conditions [20-22]. However, high organic load especially phenolic compounds were found to inhibit the efficiency of anaerobic digestion and make OMW recalcitrant to biological degradation [17,23]. On the other hand, several physicochemical have been examined for the treatment of OMW, resulting in considerable organic load and toxicity abatement, such as chemical precipitation using lime [24], adsorption using different mineral substrates as adsorbents [25-27], coagulation-flocculation [28,29], Membrane filtration [30-34]. Nevertheless, these processes suffer from serious inconveniences such as high cost, low efficiency and sludge disposal problems. To overcome these difficulties, researchers have been forced in recent years to develop new technologies. Among these technologies, advanced oxidation processes (AOPs) that utilize H₂O₂, O₃, or O₂ as the oxidant, are very promising techniques for the remediation of contaminated ground, surface, and wastewaters having non-biodegradable organic pollutants [35]. AOPs produce and use highly reactive radical species, mainly hydroxyl radical ($\dot{\text{O}}\text{H}$) [36]. This very powerful oxidant, that has a high redox potential of 2,73 V/ENH, is capable to completely mineralize most organic compounds. [37,38]. A process currently used in the AOPs is based on the Fenton reagent. This method shows interesting features for full scale application, as it occurs at room temperature and pressure [6], and no sophisticated equipment is required [6,39]. In addition, it can be used as a pre-treatment stage before the biological step in order to increase the biodegradability of the recalcitrant compounds and thus lower the toxicity of the wastewaters [40]. Principally, Fenton's process relies on the production of very reactive hydroxyl radicals ($\dot{\text{O}}\text{H}$) through catalytic decomposition of hydrogen peroxide (H₂O₂), carried out by a transition metal such as ferrous iron (Fe²⁺), then to oxidize complicated organic substances (RH) and form stable ferric hydroxy complexes (Eqs.1–3) [41,42].



In overall, the net simplified reaction of chain reactions that occur in Fenton reagents is shown in Eq. 4. The more detailed mechanisms can be found in the literature [41,43].



A wide variety of Fenton's reagent applications have already been reported in scientific literature, such as cosmetic wastewater [44], dye wastewater [45], landfill leachate [46], pesticides [47], pharmaceutical wastewater [48-50], unfortunately, relatively few studies report the use of this technology to treat the OMW. Lucas and Peres [51] reported 70% COD removal after Fenton's reagent application to OMW. In a similar way, Martínez-Nieto and al. [52] studied the efficiency of Fenton's reaction for the degradation of the organic matter load present in OMW from two-phase olive-oil extraction process. It was shown that organic matter and phenolic compounds removal efficiencies above 95% were attained. Amor and al.[53] observed that the kinetics of the anaerobic treatment of OMW could be almost doubled if the effluent was pretreated with Fenton's reagents. On another study, Alver and al. [54] obtained up to 65,5% and 87,2% COD and total phenols removal efficiencies with an integrated Fenton process preceded by a coagulation pretreatment. Recently, Maamir and al. [55] studied the effect of Fenton pretreatment on anaerobic digestion of olive mill wastewater and olive mill solid waste. They found COD removal was 82%. To date, most of the studies on the optimization of wastewater treatment process have focused on the traditional one-factor-at-a time approach. However, this approach, which does not take into account the cross effects from the factors considered, is time consuming and has in poor optimization results. Response surface methodology (RSM) is an efficient way to achieve such an optimization by analysing and modelling the effects of multiple variables and their responses and finally optimizing the process [56,57]. RSM also generates a mathematical model that can be used to predict the response of a system to any new condition. In this study, olive oil mill wastewater treatment has been accomplished by means of Fenton process for removal of COD and phenolic compounds. Box–Behnken statistical experiment design and response surface methodology were used to statistically develop models and to study and evaluate main effects, interaction effects and quadratic effects of the process parameters (hydrogen peroxide concentration, ferrous salt concentration and reaction time).

2. Materials and methods

Research grade reagents used during experiments: H_2O_2 (30%, w/w), TiO_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, NaOH , H_2SO_4 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were of the purest grade obtainable. The olive mill wastewater (OMW) samples were obtained from an olive oil factory located in Beni Mellal (Morocco). The raw OMW samples were collected from a homogenization tank of an olive oil semi-modern press plant. OMW was stored at low temperature and in dark after decantation to remove crude insoluble materials and oil residues. Table 1 summarizes the main physico-chemical properties of OMW that have been determined using standard methods for water and wastewater examination [58].

Table1. Characteristics of the OMW.

Characteristics	Unit	Average Value
pH		4.90 ± 0.30
Conductivity	mS/cm	18.50 ± 1.12
Chemical oxygen demand (COD)	g/L	98.21 ± 6.70
Biological oxygen demand (BOD)	g/L	37.40 ± 3.30
Total suspended solids (TSS)	g/L	5.76 ± 0.52
Phenolic compounds (PC)	g/L	6.80 ± 0.73
Total Kjeldahl nitrogen (TKN)	g/L	1.63 ± 0.05

Before performing the Fenton's oxidation tests, the OMW was filtered to minimize differences between experiments and then diluted 10 times with tap water in order to reduce the COD to 8,429 g/l. All the OMW oxidation experiments were conducted in a 250 ml batch reactor at room temperature. Based on the literature review and previous studies conducted on the same samples [55,59,60], the optimal pH for oxidation is pH 3. Thus, the initial OMW pH was adjusted to 3 with sulfuric acid. The solid $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were added to 100ml of OMW sample to achieve the targeted Fe^{2+} dosage. The Fenton reaction is triggered with the addition of a determined amount of H_2O_2 solution 30% (w/w). The reaction solutions were magnetically stirred during the reaction period. For each test, Aliquot samples in required quantity were taken from the reactors and analyzed immediately for COD and PC. The COD of the samples was analyzed by the potassium dichromate closed reflux colorimetric method using spectrophotometer at 600 nm [61]. PC were measured by spectrophotometry at 760 nm using the Folin-Ciocalteu colorimetric method [62], so PC were expressed as mg/l of tannic acid. The residual concentration of hydrogen peroxide was controlled by spectrophotometry at 410 nm using titanium (IV) ox sulfate complex [63]. It should be noted that it has been reported that residual H_2O_2 in the Fenton oxidation process interferes with the COD measurement by reacting with potassium dichromate, thus leading to high COD measurements. Hydrogen peroxide is consumed during COD analysis by the following oxidation reaction with potassium dichromate [64]:



The interference of H_2O_2 in the COD analysis was corrected by adopting the method proposed by [64]. All experiments were performed in triplicate and the average values were recorded. The removal efficiency (R in %) and the percentage of H_2O_2 residual (R' in %) was calculated using the following equations:

$$R(\%) = \frac{Y_0 - Y}{Y_0} \times 100 \quad (6)$$

$$R'(\%) = \frac{Y}{Y_0} \times 100 \quad (7)$$

Y_0 and Y represent the initial and final value of COD and PC. Fenton's oxidation process has been optimized by applying the Response Surface Methodology (RSM), Box-Behnken statistical screening design, a rotatable second order design based on three-level incomplete-factorial designs, was used to statistically develop model and to study and evaluate main effects, interaction effects and quadratic effects of the process parameters on the COD removal efficiency, PC removal efficiency and H_2O_2 residual. Controllable variables included H_2O_2 dose (X_1), Fe^{2+} dose (X_2) and processing time (X_3). Each independent variable was coded at three levels -1, 0 and +1 (Table 2) according to this equation:

$$X_i = \frac{x_i - x_0}{\Delta x_i} \quad (8)$$

Where X_i is the dimensionless value of an independent variable (-1,0,1); x_i represents the real value of the independent variable; x_0 is the real value of the independent variable in the center and Δx_i is the step change.

Table 2. Level of variables chosen for the Box–Behnken design.

Factor	Variables	Coded levels of variables		
		-1	0	+1
X_1	$[\text{H}_2\text{O}_2]$ (g/l)	3,57	8,93	14,29
X_2	$[\text{Fe}^{2+}]$ (g/l)	0,2	0,5	0,8
X_3	Réaction time (h)	2	5	8

Design-expert 11 statistical software was used for the design of experiment. The sequential model fitting test was carried out in order to choose a suitable model. A second-order polynomial model has been used to identify all possible interactions of selected factors obtained from the Box–Behnken model:

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} X_i X_j \quad (9)$$

where Y is the predicted response (COD removal, phenolic compounds removal and H₂O₂ residual, %); β_0 a constant, β_i the first-order model coefficient; β_{ii} the squared coefficient for the factor i; and β_{ij} the linear model coefficient for the interaction between factors i and j [65]. X_i and X_j are the coded independent variables. The quality of the fit of the polynomial model equation was expressed by the coefficient of determination R^2 and the values of adjusted- R^2 . The adequacy of the model was further justified through analysis of variance (ANOVA) and ANOVA tables were generated. The regression coefficients of the linear, quadratic and the interaction involved in the model and their effects were analysed by the F-test and p-value. In order to visualize the relationship between the response and experimental levels of each factor, the regression coefficients were used to make statistical calculation to generate 3D surface plots from the fitted polynomial equation. These graphs are drawn by maintaining two factors constant (at its central level) and varying the other two factors in order to understand their main and interactive effects on the dependent variables. Detailed analyses on the model have been presented in the following sections.

3. Results and Discussions

3.1. Evaluation of fitted model and statistical analysis

15 experiments from the Box-Behnken experimental design for the three variables (X_1 - X_3) were randomly performed, and for each experiment, three responses (Y_1 - Y_3) were analyzed, including COD removal efficiency (Y_1), PC removal efficiency (Y_2) and H₂O₂ residual (Y_3). Table 3 presents the coded and uncoded variables with the experimental values and the predicted values of the responses.

Table 3. The experimental data for COD removal, PC removal and H₂O₂ residual according to Box-Behnken design.

Run	Independent variables			Response (Y, %)					
	X_1	X_2	X_3	Experimental			Predicted		
	(g/l)	(g/l)	(h)	Y_1	Y_2	Y_3	Y_1	Y_2	Y_3
1	3.57 (-1)	0.5 (0)	2 (-1)	20.44	9.66	0.00	21.81	10.02	-1.68
2	14.29 (+1)	0.8 (+1)	5 (0)	86.2	77.99	0.09	87.27	76.60	-3.42
3	14.29 (+1)	0.2 (-1)	5 (0)	58.83	61.98	78.09	59.40	64.51	79.84
4	3.57 (-1)	0.5 (0)	8 (+1)	20.53	9.75	0.00	20.80	10.52	-0.07
5	8.93 (0)	0.2 (-1)	8 (+1)	59.98	54.89	70.54	60.78	52.73	67.10
6	14.29 (+1)	0.5 (0)	8 (+1)	89.14	84.05	0.00	87.77	83.69	1.68
7	8.93 (0)	0.2 (-1)	2 (-1)	49.99	41.28	80.62	49.69	39.53	78.80
8	8.93 (0)	0.8 (+1)	2 (-1)	63.54	36.62	0.00	62.74	38.78	3.44
9	3.57 (-1)	0.8 (+1)	5 (0)	10.15	0.10	1.87	9.58	-2.43	0.12
10	8.93 (0)	0.8 (+1)	8 (+1)	65.54	44.51	0.61	65.84	46.26	2.43
11	8.93 (0)	0.5 (0)	5 (0)	74.97	64.11	0.00	75.53	64.57	-1.8E-15
12	8.93 (0)	0.5 (0)	5 (0)	75.83	65.83	0.00	75.53	64.57	-1.8E-15
13	3.57 (-1)	0.2 (-1)	5 (0)	20.43	15.49	53.38	19.36	16.88	56.89
14	8.93 (0)	0.5 (0)	5 (0)	75.79	63.77	0.00	75.53	64.57	-1.8E-15
15	14.29 (+1)	0.5 (0)	2 (-1)	72.83	64.28	15.93	72.56	63.51	15.99

Table 4. Analysis of variance (ANOVA) variables fitted to quadratic polynomial model.

Response (Y, %)	Factor	Coefficient	p-value	Remark
COD removal	X ₁	29.31	< 0.0001	Significant
	X ₂	4.52	< 0.0001	Significant
	X ₃	3.42	0.0003	Significant
	X ₁ X ₂	9.41	< 0.0001	Significant
	X ₁ X ₃	3.81	0.0011	Significant
	X ₂ X ₃	-2	0.0162	Significant
	X ₁ ²	-20.45	< 0.0001	Significant
	X ₂ ²	-11.17	< 0.0001	Significant
	X ₃ ²	-4.59	0.0005	Significant
TP removal	X ₁	31.79	< 0.0001	Significant
	X ₂	-1.93	0.0808	Not significant
	X ₃	5.17	0.0021	Significant
	X ₁ X ₂	7.60	0.0017	Significant
	X ₁ X ₃	4.92	0.0110	Significant
	X ₂ X ₃	-1.43	0.3040	Not significant
	X ₁ ²	-13.91	0.0001	Significant
	X ₂ ²	-11.52	0.0003	Significant
	X ₃ ²	-8.73	0.0011	Significant
Residual H ₂ O ₂	X ₁	5.01	< 0.0001	Significant
	X ₂	-34.21	< 0.0001	Significant
	X ₃	-3.97	< 0.0001	Significant
	X ₁ X ₂	-6.17	< 0.0001	Significant
	X ₁ X ₃	-4.22	< 0.0001	Significant
	X ₂ X ₃	4.02	< 0.0001	Significant
	X ₁ ²	1.01	0.0254	Significant
	X ₂ ²	31.06	< 0.0001	Significant
	X ₃ ²	0.8883	0.0391	Significant

The experimental values of the responses presented in Table 3 are used to compute coefficients in mathematical models where each response Y is calculated as a function of the values of the three operating variables, i. e., [H₂O₂] (X₁), [Fe²⁺] (X₂) and reaction time (X₃). Thus, the responses, COD removal efficiency (Y₁), PC removal efficiency (Y₂) and H₂O₂ residual (Y₃), was adjusted as polynomial quadratic equations 10,11 and 12 respectively, in terms of coded factors:

COD removal (%):

$$Y_1 = 75,53 + 29,31X_1 + 4,52X_2 + 3,42X_3 + 9,41X_1X_2 + 3,81X_1X_3 - 2X_2X_3 - 20,45X_1^2 - 11,17X_2^2 - 4,59X_3^2 \quad (10)$$

PC removal (%):

$$Y_2 = 64,57 + 31,79X_1 - 1,93X_2 + 5,17X_3 + 7,60X_1X_2 \quad (11)$$

$$+4,92X_1X_3 - 1,43X_2X_3 - 13,91X_1^2 - 11,52X_2^2 - 8,73X_3^2$$

Residual H₂O₂ (%):

$$Y_3 = 2,84 + 5,01X_1 - 34,21X_2 - 3,97X_3 - 6,17X_1X_2 - 4,22X_1X_3 + 4,02X_2X_3 + 1,01X_1^2 + 31,06X_2^2 + 0,8883X_3^2 \quad (12)$$

The quality of the regression model equations was evaluated by the ANOVA analysis. To determine the significance of each linear effect, quadratic effect and interaction effect of the independent variables on the two responses, the p-value was used. If the p-value of the coefficient is less than 0,05 indicates that it is important and significant. From Table 4, it can be seen that all coefficients of linear effects, quadratic effects and interaction effects of all factors [H₂O₂], [Fe²⁺] and reaction time for the two responses, the COD removal and the residual H₂O₂ in the solution are significant. Also, for the PC removal, all coefficients have a significant effect exempting the effects of the coefficients of [Fe²⁺] and the interaction between [Fe²⁺] and the reaction time. The statistical analysis for approximate mathematical models (Y₁ and Y₂) obtained from ANOVA is given in Table 5.

Table 5. ANOVA for the response surface quadratic polynomial model.

Response (Y, %)	Source	SS	DF	MS	F-value	p-value
COD removal	Model	9463.95	9	1051.55	836.55	< 0.0001
	Residual	6.29	5	1.26		
	Lack of fit	5.81	3	1.94	8.23	0.1103
	Pure error	0.4712	2	0.2356		
	R ² = 0.9993					
	R ² adj = 0.9981					
	R ² pred = 0.9901					
PC removal	Model	9961.93	9	1106.88	177.23	< 0.0001
	Residual	31.23	5	6.25		
	Lack of fit	28.79	3	9.60	7.87	0.1149
	Pure error	2.44	2	1.22		
	R ² = 0.9969					
	R ² adj = 0.9913					
	R ² pred = 0.9534					
Residual H ₂ O ₂	Model	13551.76	9	1505.75	3983.65	< 0.0001
	Residual	1.89	5	0.3780		
	Lack of fit	1.72	3	0.5728	6.68	0.1330
	Pure error	0.1715	2	0.0857		
	R ² = 0.9999					
	R ² adj = 0.9996					
	R ² pred = 0.9979					

All three models had sufficiently high F-values of 836,55, 177,23 and 3983,65 with very low p-values (p<0,0001) indicating the significance of the regressions. The statistical parameter F is an important parameter for evaluating statistical significance, so that a large value of F indicates that most of the variation in response can be explained by the regression equation and the corresponding p-value is given to estimate whether the value F is large enough to indicate

statistical significance [66]. As can be seen, the lack of fit is not significant for responses Y_1 to Y_3 because it has p-values ($> 0,05$), which shows that the models were adequate. In addition, the ANOVA for the three responses (Y_1 to Y_3) indicates that the quadratic models successfully fit the experimental data with high values of the regression coefficient R^2 (0,9993, 0,9969 and 0,9999 for COD removal, PC removal and residual H_2O_2 , respectively). Furthermore, the adjusted R^2_{adj} values of 0,9981, 0,9913 and 0,9996, respectively, for the three models Y_1 , Y_2 and Y_3 showed that there was no inflation effect on R^2 due to the introduction of insignificant variables [67]. Predicted R^2 is a measured parameter to indicate how the model predicts a response value in the design range. The adjusted R^2_{adj} and the predicted R^2_{pred} must be about 0,20 from each other to be in reasonable agreement. In our case, the predicted R^2_{pred} values of 0,9534 to 0,9979 were in good agreement with the adjusted R^2_{adj} of 0,9913 to 0,9996 indicating that response models can be used to navigate in the design space. Finally, the actual and predicted values obtained from the mathematical models Y_1 , Y_2 and Y_3 prove again that they are reliable to describe COD removal, PC removal and residual H_2O_2 in the Fenton process because the data obtained from the figures 1(a) and 1(b) were very close to the linearity.

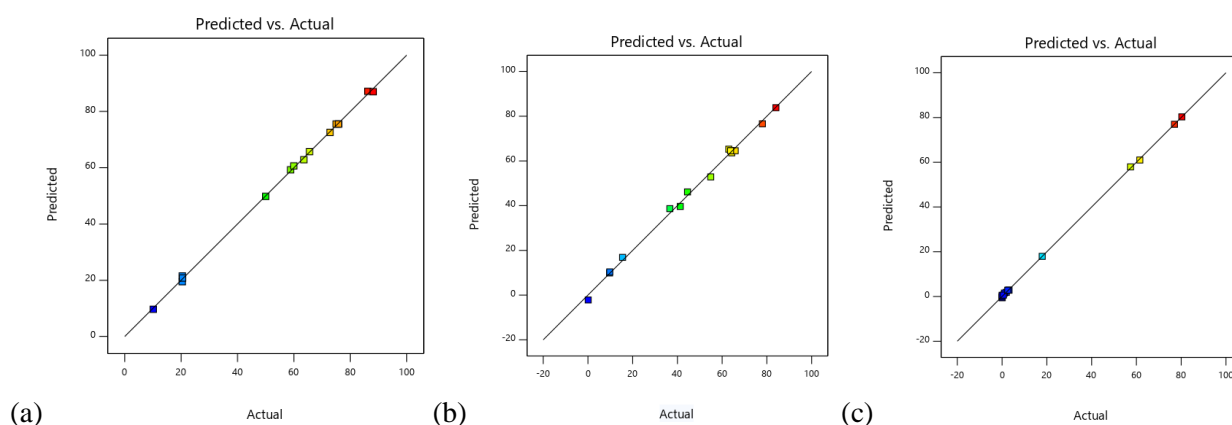
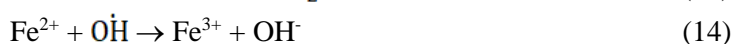


Figure 1. Actual vs. predicted values for the responses (a) COD removal, (b) PC removal and (c) Residual H_2O_2 .

In order to better understand the results, a detailed analysis to show the relationship between the response and the experimental variables was performed and was based on the three-dimensional response surface graphs and their contour curves.

3.2. COD removal efficiency

The graphs for the measured response were constructed from the regression equation. These representations were developed according to two factors by keeping the other factors at their coded level 0. Figures 2(a), 2(b) and 2(c) show the combined effects of $[Fe^{2+}]$ and $[H_2O_2]$, $[H_2O_2]$ and reaction time, and $[Fe^{2+}]$ and reaction time, respectively, on COD removal efficiency. As shown in Fig. 2(a), the combined effect of $[Fe^{2+}]$ and $[H_2O_2]$ clearly had a positive effect on COD removal and the best results could be obtained under conditions of $[H_2O_2]$ concentration greater than 12g/l and $[Fe^{2+}]$ greater than 0,6g/l, where the response achieved a consistent trend without further significant change. This phenomenon could be explained by critical concentrations of Fenton reagents. Beyond the critical dosages, the secondary scavenging reactions (13) and (14) that occur due to overdoses of Fe^{2+} and H_2O_2 [68], induce a decrease in the quantity of hydroxyl radicals available in solution and subsequently inhibition of the pollutant degradation process. This phenomenon is very well documented in the literature by several authors [69-71].



According to Figure 2(b), for the lowest doses of H_2O_2 , the degradation of COD is almost complete in 2h and the time between 2h-8h hours is insignificant. In addition, for the highest doses of H_2O_2 , the elimination of the maximum COD

obtained after 6h and the change that became insignificant between 6h-8h. The same observation is reported by Rivas and al. [59], the higher the initial concentration of H_2O_2 the longer the treatment time. With the same trend in Figure 2(c), the interactive effect between $[\text{Fe}^{2+}]$ and reaction time caused a distinguished peak around a concentration of Fe^{2+} of 0,55g/l and a reaction time of 6h. A separate optimization of the response was performed. This analysis gave a predicted efficacy of 89,17% of COD removal with $[\text{H}_2\text{O}_2]$ 12,4g/l (0,36mol/l), $[\text{Fe}^{2+}]$ 0,68g/l (0,012mol/l) and treatment time 7,29h. According to these results, the $\text{H}_2\text{O}_2/\text{DCO}$ ratio that gives the best degradation results has been calculated and its value $R = \text{H}_2\text{O}_2/\text{DCO} = 1,47$, this ratio is consistent with the ratio 1,75 found by Lucas and Peres [51], also the optimal molar ratio $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}] = 30$ (18,23 by weight) found in this study is twice as large as the ratio recommended by Lucas and Peres [51]. The high value of the ratio $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ is due to the choice of using a low dose of Fe^{2+} , because the higher the iron concentration, the higher the amount of $\text{Fe}(\text{OH})_3$ sludge, which means correspondingly high conditioning and disposal costs [44]. The optimal reaction time required for the degradation of the maximum COD in this case studied is close to that of the Rivas's work [59] of 8h to treat.

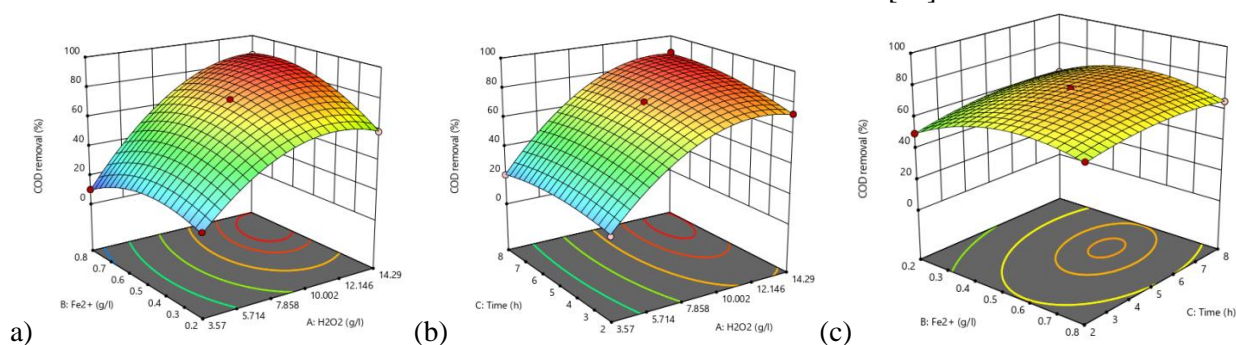


Figure 2. Effects of (a) $[\text{H}_2\text{O}_2]$ and $[\text{Fe}^{2+}]$, (b) $[\text{H}_2\text{O}_2]$ and reaction time, (c) $[\text{Fe}^{2+}]$ and reaction time, on COD removal efficiency.

3.3. PC removal efficiency

The surface response curves of the quadratic model that describe the removal efficiency of PC as a function of $[\text{H}_2\text{O}_2]$ and $[\text{Fe}^{2+}]$, $[\text{H}_2\text{O}_2]$ and reaction time, and $[\text{Fe}^{2+}]$ and reaction time, are shown in Figures. 3(a), 3(b) and 3(c), respectively. Fig. 3(a) shows that the efficiency of PC removal increases with increasing H_2O_2 and Fe^{2+} doses to an optimal region, and if one of them is not present in its optimal dose [72], a decrease in PC removal is observed, and this is due as explained in the case of COD removal to the scavenging effect of H_2O_2 and Fe^{2+} on hydroxyl radicals according to eqs. 13 and 14. As can be seen from Fig. 3(b) that the time to complete the reaction is dependent on the initial concentration of H_2O_2 , then this species appears to be the reagent limiting the operating conditions used in this study [59]. In addition, Fig. 3(C) shows a clear peak, suggesting that the optimal condition for maximum removal of PC is well within the design limit. The results of the individual optimization of the PC elimination response indicate that the combined levels of a concentration of 13,96 g/l (0,41 mol/l) H_2O_2 , 0,49 g/l (0,0088 mol/l) Fe^{2+} and 6,94 h reaction time were estimated to lead to a very high elimination of PC reaching 84,68%. The optimal ratio $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}] = 28,49$ w/w (47 mol/mol) found in this study is slightly lower than the ratio recommended by El-Gohary and al.[73], which gives a ratio of 50 mol/mol which leads to an 84% removal efficiency of phenolic compounds.

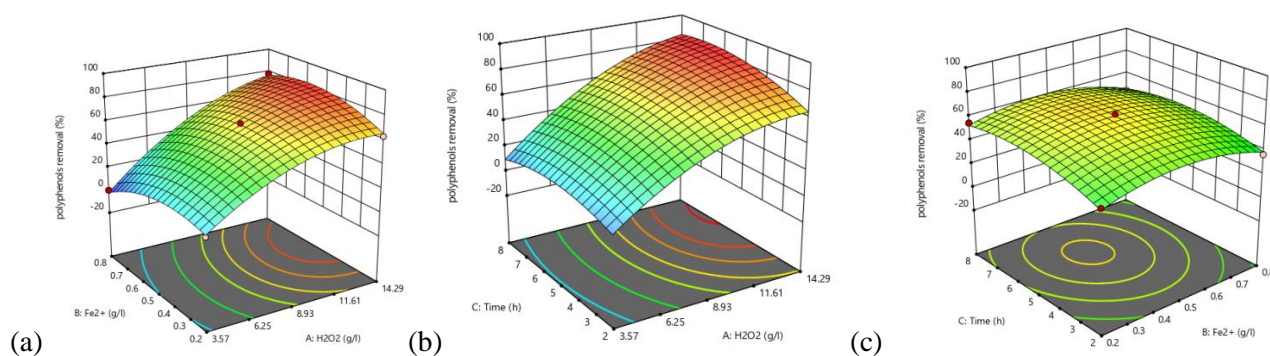


Figure 3. Effects of (a) $[\text{H}_2\text{O}_2]$ and $[\text{Fe}^{2+}]$, (b) $[\text{H}_2\text{O}_2]$ and reaction time, (c) $[\text{Fe}^{2+}]$ and reaction time, on TP removal efficiency.

3.4. Residual H_2O_2

One of the unfavourable points in the Fenton process is the concentration of H_2O_2 remaining in the solution (residual H_2O_2) after the reaction time, because the residual H_2O_2 contributes to the measurement of COD and it is able to hinder biological treatment of waste water [74]. Then monitoring the change in H_2O_2 during the oxidation period is obligatory. The surface curves for the residual H_2O_2 level in Figs. 4(a), 4(b) and 4(c) show the effects of $[\text{H}_2\text{O}_2]$ and $[\text{Fe}^{2+}]$, $[\text{H}_2\text{O}_2]$ and reaction time, and $[\text{Fe}^{2+}]$ and reaction time, respectively. Fig. 4(a) shows that no residual H_2O_2 concentration was measured when the Fe^{2+} concentration is between 0,5 and 0,8 g/l with the increase in H_2O_2 concentration from 3,57 to 14,29 g/l, but a high residual H_2O_2 level is recorded in high H_2O_2 concentrations with low Fe^{2+} concentrations. This is mainly due to the fact that the decomposition of H_2O_2 by forming hydroxyl radicals is favourable with the presence of a sufficient amount of Fe^{2+} ions. This is consistent with previous reviews [75,76]. According to Fig. 4(b), the high level of residual H_2O_2 was noted in a very short time with the highest concentration of H_2O_2 . The same remark was reported by [77]. It is also shown in Fig. 4(C) that with the low levels of $[\text{Fe}^{2+}]$ and reaction time, the residual H_2O_2 level is high and is explained in the same way as in Fig. 4(a).

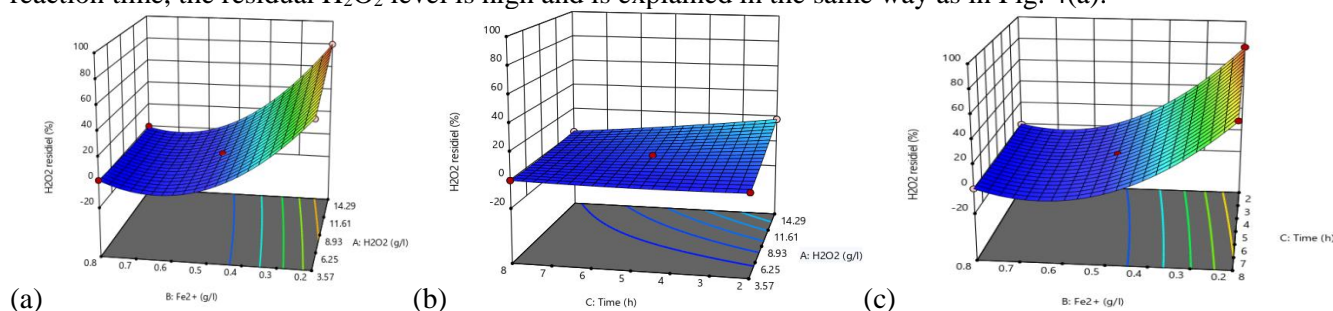
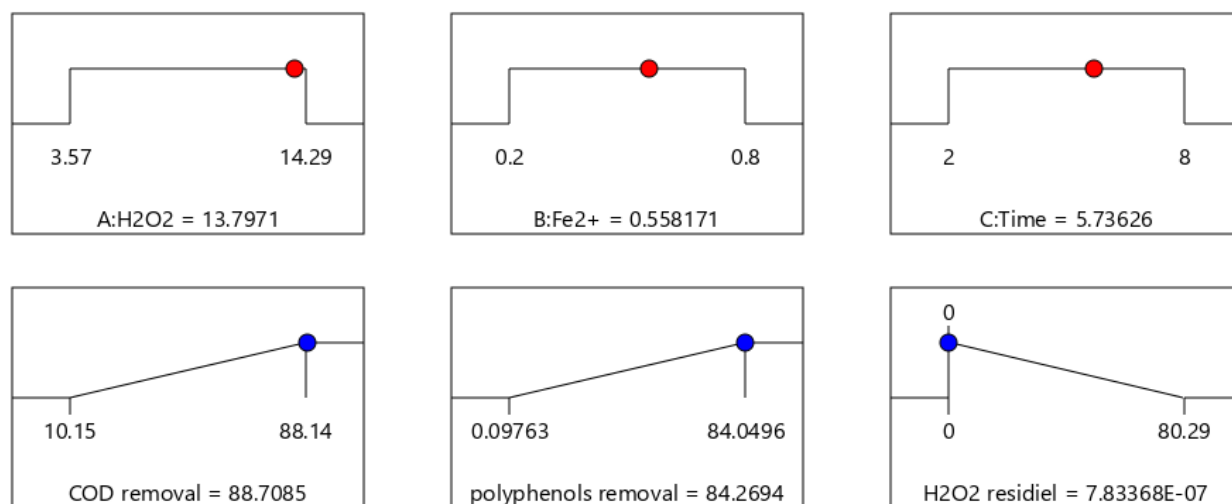


Figure 4. Effects of (a) $[\text{H}_2\text{O}_2]$ and $[\text{Fe}^{2+}]$, (b) $[\text{H}_2\text{O}_2]$ and reaction time, (c) $[\text{Fe}^{2+}]$ and reaction time, on Residual H_2O_2 .

3.4. Simultaneous optimization of responses and optimal conditions

The objective of a response optimization study is to determine the combination of optimal values of the variables that satisfy the objectives defined for the response. With multiple responses, it is necessary to find the optimal condition where all parameters simultaneously respond to the criteria placed on each of the responses and factors. Thus, to achieve the best compromise between several responses, the Desirability function of Derringer [78] is adopted. This function varies between 0 and 1 and the optimal solution occurs when the desirability function gets its maximum. Using the numerical optimization of the Design Expert software, the optimal condition that maximizes the desirability function was found. To optimize all two responses at the same time, three criteria were applied: maximizing COD and PC removals with no residual H_2O_2 . According to numerical optimization, the best maximum that satisfies our

objectives was found to be at H_2O_2 concentration of 13,79 g/l, Fe^{2+} concentration of 0,55 g/l and reaction time of 5,73 h. Under these operating conditions, a COD removal of 88,70% and PC removal of 84,26% with no residual H_2O_2 were predicted with a desirability value of 1 (figure 5).



Desirability = 1.000

Figure 5. Desirability ramp for numerical optimization of the two responses.

finally, to confirm the optimization process, duplicate validation experiments were performed using the optimal parameters and the experimental results was compared to the results achieved from models. In the optimization verification experiments, the responses obtained from the experiments and the models were in close agreement (errors $\leq 7\%$ and standard deviations $\leq 5\%$) [79]. As shown in table 6, experimental results for the three responses (the maximum value of 6.53% and 4.23% for error and standard deviation, respectively) were in close agreement with the model prediction.

Table 6. Verification experiments at optimum conditions.

Response (Y, %)	Model value (%)	Experimental value (%)	Error (%)	Standard deviation (%)
COD removal	88.70	82.72	6.53	4.23
PC removal	84.26	84.13	0.15	0.09
Residual H_2O_2	0.00	5.11	5.11	3.61

4. Conclusion

The Fenton process is a very useful method for achieving high removal efficiencies of COD organic matter and recalcitrant PC compounds existing in oil mill wastewater. The response surface methodology has proven to be a robust tool for modelling and optimizing operating conditions. The results confirmed that the three variables, $[\text{H}_2\text{O}_2]$, $[\text{Fe}^{2+}]$ and reaction time, had a significant influence on the two responses, COD and PC removals. Simultaneous optimization of the two responses by adopting the Derringer desirability function indicated an optimal point in the experimental region where maximum COD removal of 88,70% and maximum PC removal of 84,26% with no residual

H₂O₂ can be achieved under the optimal conditions: H₂O₂ dosage of 13,79 g/l, Fe²⁺ dosage of 0,55 g/l and reaction time of 5,73h.

References

- [1] F. Mansouri, A. Ben moumen, K. Belhaj, G. Richard, M. Fauconnier, M. Sindic, H. Serghini Caid, A. Elamrani, Emirates Journal of Food and Agriculture, 30 (2018) 549-562.
- [2] A. El-Abbassi, H. Kiai, A. Hafidi, Food Chemistry, 132 (2012) 406-412.
- [3] A. Fiorentino, A. Gentili, M. Isidori, P. Monaco, A. Nardelli, A. Parrella, F. Temussi, Journal of agricultural and food chemistry, 51 (2003) 1005-1009.
- [4] G. Greco Jr, G. Toscano, M. Cioffi, L. Gianfreda, F. Sannino, Water Research, 33 (1999) 3046-3050.
- [5] D. Bouknana, B. Hammouti, R. Salghi, S. Jodehe, A. Zarrouk, I. Warad, A. Aouniti, M. Sbaa, J. Mater. Environ. Sci., 5 (2014) 1039-1058.
- [6] J.M. Ochando-Pulido, S. Oimentel-Mora, V. Verardo, A. Martinez-Ferez, Separation and Purification Technology, 179 (2017) 161-174.
- [7] M. Hamdi, Environmental Technology, 14 (1993) 495-500.
- [8] M. Aggoun, R. Arhab, A. Cornu, J. Portelli, M. Barkat, B. Graulet, Food Chemistry, 209 (2016) 72-80.
- [9] C.J. McNamara, C.C. Anastasiou, V. O'Flaherty, R. Mitchell, International Biodeterioration & Biodegradation, 61 (2008) 127-134.
- [10] S.M. Paixao, E. Mendonc, A.M. Anselmo, Environmental Toxicology, 14 (1999) 263-269.
- [11] D.P. Komilis, E. Karatzas, C.P. Halvadakis, Journal of Environmental Management, 74 (2005) 339-348.
- [12] P. Paraskeva, E. Diamadopoulos, Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology, 81 (2006) 1475-1485.
- [13] N. Haouache, A. Bouchaleta, J. Mater. Environ. Sci., 7 (2016) 2288-2294.
- [14] R. Borja, E. Sánchez, F. Raposo, B. Rincón, A.M. Jiménez, A. Martín, Waste Management, 26 (2006) 477-486.
- [15] A. Roig, M.L. Cayuela, M.A. Sánchez-Monedero, Waste Management, 26 (2006) 960-969.
- [16] R. Borja, J. Ala, A. Mancha, A. Martin, V. Alonso, E. Sanchez, Bioprocess Engineering, 18 (1998) 127-134.
- [17] H. Rizki, M. Mouhib, A. Nabloussi, F. kzaiber, H. Latrache, h. Hanine, Mor. J. Chem. 7 N°3 (2019) 538-547
- [18] S.G. Velioglu, K. Curi, S.R. Camlilar, Water research 26 (1992) 1415-1420.
- [19] K. Fadil, A. Chahlaoui, A. Ouahbi, A. Zaid, R. Borja, International Biodeterioration & Biodegradation, 51 (2003) 37-41.
- [20] M. Hamdi, Anaerobic digestion of olive mill wastewaters, Process Biochemistry, 31 (1996) 105-110.
- [21] I.P. Marques, Desalination, 137 (2001) 233-239.
- [22] N. Assas, L. Ayed, L. Marouani, M. Hamdi, Process Biochemistry, 38 (2002) 361-365.
- [23] M. Beddiar, W. Benchalel, S. Boucetta, Z. Bouslama, H. Elmsellem, Mor. J. Chem. 8 N°2 (2020) 486-496
- [24] E.S. Aktas, S. Imre, L. Ersoy, Water Research, 35 (2001) 2336-2340.
- [25] C.A. Santi, S. Cortes, L.P. D'Acqui, E. Sparvoli, B. Pushparaj, Bioresource Technology, 99 (2008) 1945-1951.
- [26] P. Galiatsatou, M. Metaxas, D. Arapoglou, V. Kasselouri-Rigopoulou, Waste Management, 22 (2002) 803-812.
- [27] K. Al-Malah, M.O.J. Azzam, N.I. Abu-Lail, Separation and Purification Technology, 20 (2000) 225-234.
- [28] M. Achak, N. Ouazzani, A. Yaacoubi, L. Mandi, Revue des sciences de l'eau/Journal of Water Science, 21(2008) 53-67.
- [29] S. Khoufi, F. Feki, S. Sayadi, Journal of Hazardous Materials, 142 (2007) 58-67.
- [30] A. Cassano, C. Conidi, E. Drioli, Water Research, 45 (2011) 3197-3204.

- [31] J.M. Ochando-Pulido, G. Hodaifa, M.D. Victor-Ortega, S. Rodriguez-Vives, A. Martinez-Ferez, *Journal of hazardous materials*, 263 (2013) 168-176.
- [32] J.M. Ochando-Pulido, A. Martinez-Ferez, *Science of the Total Environment*, 2017, 587 (2017) 414-422.
- [33] J.M. Ochando-Pulido, M.D. Víctor-Ortega, A. Martínez-Ferez, *Separation and Purification Technology*, 168 (2016) 177-187.
- [34] T. Coskun, E. Debik, N.M. Demir, *Desalination*, 259 (2010) 65-70.
- [35] P. Gogate, A. Pandit, *Advances in Environmental Research*. 8 (2004) 504-551.
- [36] O. Legrini, E. Oliveros, A.M. Braun, *Chemical reviews*, 93 (1993) 671-698.
- [37] H. Zhang, H.J. Choi, C.P. Huang, *Journal of hazardous materials*, 136 (2006) 618-623.
- [38] M. Kallel, C. Belaid, R. Boussahel, M. Ksibi, A. Montiel, B. Elleuch, *Journal of Hazardous Materials*, 163 (2009) 550-554.
- [39] P. Bautista, A.F. Mohedano, J.A. Casas, J.A. Zazo, J.J. Rodriguez, *Journal of Chemical Technology & Biotechnology*, 83 (2008) 1323-1338.
- [40] B. Bianco, I. De Michelis, F. Vegliò, *Journal of hazardous materials*, 186 (2011) 1733-1738.
- [41] E. Neyens, J. Baeyens, *Journal of hazardous materials*. 98 (2003) 33-50.
- [42] M. Umar, H.A. Aziz, M.S. Yusoff, *Waste Management*, 30 (2010) 2113-2121.
- [43] J.J. Pignatello, E. Oliveros, A. MacKay, *Critical reviews in environmental science and technology*, 36 (2006) 1-84.
- [44] P. Bautista, A.F. Mohedano, M.A. Gilarranz, J.A. Casas, J.J. Rodriguez, *Journal of hazardous materials*, 143 (2007) 128-134.
- [45] J.H. Ramirez, C.A. Costa, L.M. Madeira, *Catalysis Today*, 107 (2005) 68-76.
- [46] H. Zhang, H.J. Choi, C.P. Huang, *Journal of hazardous materials*, 125 (2005) 166-174.
- [47] K.H. Chan, W. Chu, *Chemosphere*, 51 (2003) 305-311.
- [48] H. Tekin, O. Bilkay, S.S. Ataberk, T.H. Balta, I.H. Ceribasi, F.D. Sanin, F.B. Dilek, U. Yetis, *Journal of hazardous materials*, 136 (2006) 258-265.
- [49] I. Arslan-Alaton, S. Dogruel, *Journal of hazardous materials*, 112 (2004) 105-113.
- [50] H. Shemer, Y. Kacar-Kunukcu, K.G. Linden, *Chemosphere*, 63 (2006) 269-276.
- [51] M.S. Lucas, J.A. Peres, *Journal of hazardous materials*, 168 (2009) 1253-1259.
- [52] L. Martínez Nieto, G. Hodaifa, S. Rodríguez Vives, J.A. Giménez Casares, J. Ochando, *Chemical Engineering Journal*, 173 (2011) 503-510.
- [53] C. Amor, M.S. Lucas, J. García, J.R. Dominguez, J.B. De Heredia, J.A. Peres, *Journal of Environmental Science and Health*, 50 (2015) 161-168.
- [54] A. Alver, E. Bastürk, A. Kılıc, M. Karatas, *Process Safety and Environmental Protection*, 98 (2015) 319-324.
- [55] W. Maamir, Y. Ouahabi, S. Poncin, H.Z. Li, K. Bensadok, *International Journal of Green Energy*, 14 (2017) 555-560.
- [56] R.H. Myers, D.C. Montgomery, (2002), 2nd Edition, John Wiley & Sons, New York.
- [57] J.P. Wang, Y.Z. Chen, Y. Wang, S.J. Yuan, H.Q. Yu, *Water research*, 45 (2011) 5633-5640.
- [58] APHA (1998) *Standard Methods for the Examination of Water and Wastewater*, 18th ed., American Public Health Association, Washington, DC, USA.
- [59] F.J. Rivas, F.J. Beltrán, O. Gimeno, J. Frades, *Journal of agricultural and food chemistry*, 49(2001) 1873-1880.
- [60] B.K. Mert, T. Yonar, M.Y. Kiliç, K. Kestioğlu, *Journal of hazardous materials*, 174 (2010) 122- 128.

- [61] Centre d'expertise en analyse environnement du Québec (2014), Détermination de la demande chimique en oxygène : méthode de reflux en système fermé suivi d'un dosage par colorimétrie avec le bichromate de potassium, MA. 315- DCO 1.1, Rév. 3, Ministère du Développement durable, de l'Environnement, de la Faune et des Parcs du Québec, 11 p.
- [62] V.L. Singleton, J.A. Rossi, American journal of Enology and Viticulture, 16(1965) 144-158.
- [63] G. Eisenberg, Industrial & Engineering Chemistry Analytical Edition, 15(1943) 327-328.
- [64] E. Lee, H. Lee, Y.K. Kim, K. Sohn, K. Lee, International Journal of Environmental Science & Technology, 8(2011) 381-388.
- [65] J. Prakash Maran, S. Manikandan, Dyes and Pigments, 95 (2012) 465-472.
- [66] M. Galehdar, H. Younesi, M. Hadavifar, A.A. Zinatizadeh, CLEAN–Soil, Air, Water, 37(2009) 629-637.
- [67] S.S. Kumar, S.K. Malyan, A. Kumar, N.R. Bishnoi, J. Mater. Environ. Sci, 7 (2016) 4456-4466.
- [68] Y. Deng, Journal of Hazardous Materials, 146(2007) 334-340.
- [69] Y. Wu, S. Zhou, F. Qin, X. Ye, K. Zheng, Journal of hazardous materials, 180(2010) 456-465.
- [70] A. Talebi, N. Ismail, T.T. Teng, A.F. Alkarkhi, Desalination and Water Treatment, 52 (2014) 1524-1530.
- [71] A. Amiri, M.R. Sabour, Waste management, 34(2014) 2528-2536.
- [72] C.T. Benatti, C.R.G. Tavares, T.A. Guedes, Journal of environmental management, 80(2006) 66-74.
- [73] F.A. El-Gohary, M.I. Badawy, M.A. El-Khateeb, A.S. El-Kalliny, Journal of hazardous materials, 162(2009) 1536-1541.
- [74] A. Chavoshani, A. Rostami, F. Golzari, A. Gholinia, Iranian Journal of Health, Safety and Environment, 3 (2016) 565-569.
- [75] M. Ahmadi, F. Vahabzadeh, B. Bonakdarpour, E. Mofarrah, M. Mehranian, Journal of Hazardous Materials, 123(2005) 187-195.
- [76] N. Kang, D. S. Lee, J. Yoon, Chemosphere, 47(2002) 915-924.
- [77] S. A. R. Mousavi, A. H. Mahvi, S. Nasseri, S. Ghafari, Iranian Journal of Environmental Health, Science and Engineering, 8(2011) 129-138.
- [78] G. Derringer, R. Suich, Journal of quality technology, 12(1980) 214-219.
- [79] H. Li, S. Zhou, Y. Sun, J. Lv, Waste Management, 30(2010) 2122-2129.