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Degradation, dephenolisation and dearomatisation of olive mill wastewater by subcritical water oxidation method using hydrogen peroxide: Application of multi-response central composite design

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Abstract: An environmentally friendly method to decontaminate the olive mill wastewater, which is encountered as a major environmental problem is presented in this study. The removal of both polyphenolic and aromatic content and the degradation of wastewater of olive mill supplied from Mersin/Turkey region were investigated by the subcritical water oxidation method using H_2O_2. The central composite design of response surface methodology was used to assess the effects of temperature, treatment time, and the concentration of oxidising agent. The reliability of the employed method was proved by ANOVA. The optimum experimental parameters were determined and theoretical equations were proposed in each case. The highest chemical oxygen demand removal, dephenolisation and dearomatisation values were obtained as 85.74, 96.13 and 95.94 %, respectively.

Keywords: olive mill wastewater; *COD*; degradation; total polyphenol; subcritical water medium.

INTRODUCTION

Humankind has been polluting the environment from ancient times. In recent years environmental pollution, especially water pollution, has been progressing at the fastest pace and, corresponding to that, the efforts to find a solution to this problem have increased.[1–7] The olive mill wastewater (OMWW) is seen as a major problem in many countries due to causing environmental pollution.[8] OMWW, which is a production of the olive oil factories, effects the life and the development of plants, aquatic and marine ecosystems due to its toxic effects.[9–12] When considering that 30 million t of OMWW is produced per *annum* in Mediterranean countries, it is revealed how the environment is polluted.[1,7,11]

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OMWW contains high organic content consisting of polyphenols, poly-alcohols, pectins, sugars, lipids, tannins, nitrogen compounds and fatty acids which are phytotoxic and resistant to biodegradation.[3–5,13–16] In addition, the dark color of OMWW and the oily film layer formed on the surface of the water prevents the effect of sunlight from the water surface and the transmission of oxygen into the water. Thus, the dissolved oxygen is consumed very quickly in water resources such as seas and rivers.[2] As a result, the water plants and mosses that cannot undergo photosynthesis are not able to survive and the degradation of organic content get prevented or at least decelerated. Therefore, the life of the aquatic macro and microorganisms become threatened.[17]

The high concentration of polyphenolic content from 1.0 up to 10 g L^{-1} is considered as the major reason of toxicity of OMWW.[18,19] When the high concentration of other organic compounds is involved along with polyphenolic content which accounts for a 14 % contribution to chemical oxygen demand (*COD*),[20,21] a wastewater with an extremely high *COD* value (45–130 g L^{-1}) which is several times higher than domestic waste, is encountered.[22–25] In addition, it is known that the organic content is composed of various aromatic structures such as carcinogenic and toxic aromatic amines.[17,25,26] Therefore, removal of *COD*, polyphenol and aromaticity are of great importance and the effective methods are required for degradation of OMWW.

Several chemical treatment methods (ozonation, UV irradiation, photocatalysis, hydrogen peroxide/ferrous iron oxidation, electrochemical oxidation, catalytic wet air oxidation, Fenton, supercritical wet air oxidation, subcritical wet air oxidation coupled with Fenton, wet hydrogen peroxide catalytic oxidation and sonication) and biological (anaerobic digestion, aerobic treatment, anaerobic bioremediation) as well as the combination of both of them have been used for treatment of OMWW.[1–8,17–21] Although the biological processes, namely anaerobic processes, are known as the energy and cost saving methods, they may be ineffective in the treatment of highly concentrated OMWW.[3,5] In addition, the biological treatment processes are not able to degrade the persistent compounds such as polyphenols.[3,5] Chemical processes are usually more effective comparing to biological ones, but they are also inadequate for the complete removal of COD, polyphenols and aromaticity because hazardous by-products may form during these processes.[25,27]

Subcritical water oxidation method (SWO), which offers many advantages, is a good alternative to overcome the drawbacks in the above-mentioned methods.[28,31] Moreover, when compared to traditional methods, SWO's short treatment time and high degradation yield make it irreplaceable. SWO is performed in subcritical water medium which requires water that is heated between 373 and 647 K and sufficiently pressurized to keep it in the liquid form.[32] While subcritical water medium favours the formation of hydroxyl and other active radical species, which are known for their crucial roles of attacking and destroying the target pollutants, it provides a unique medium when H_2O_2, an environmentally friendly oxidizer, is used together with them.[33–36]

In this sense, the experimental design techniques that minimize the consumption of time, reagents, the laboratory work and the industrial scale are needed. It is known that the traditional optimization method, namely one-factor-at-a-time, is far from solving this issue. According to that, this univariate method is based on the examining of only one working variables at a time, while keeping the others constant.[37–38] In addition, the univariate analysis is insufficient to reveal the relationship between variables and the response.[38] Therefore, many researchers have been widely used an optimization method called response surface method (RSM) to overcome these problems.[37–45] RSM is a chemometric technique using one of the several types of statistical design methods.[31,38] This technique provides an evaluation of the interaction between independent variables and the response, besides providing the optimization of variables at any time.[39] Among the second-order RSM models, the popularity of central composite design (CCD) is increasing due to requiring quite a few number of design points, while providing a reasonable amount of information for testing lack of fit.[46,47]

In this study, subcritical water degradation of OMWW which was supplied from the olive mill in Mersin-Turkey was performed in the presence of H_2O_2. CCD was applied to evaluate the optimum experimental conditions for the multi-response (*COD* removal, total polyphenolic content removal and total aromatic compounds removal) degradation of OMWW. Moreover, the interactions of three experimental parameters, namely the temperature, the treatment time and the concentration of oxidizing agent were evaluated and the effects of these variables on all of the three response were investigated. The theoretical models (mathematical equations) which facilitate the evaluation of system variables and which were used for predicting further response were developed.

EXPERIMENTAL

Reagents and apparatus

OMWW was supplied from the effluent of olive oil mill located on the east of Mersin, Turkey. H_2O_2 was obtained from Merck (Darmstadt, Germany). Folin–Ciocalteu's phenol reagent and gallic acid (GA) were purchased from Sigma–Aldrich (St. Louis, MO). Anhydrous sodium carbonate was purchased from Fluka (USA). N_2 gas was supplied by Linde gas (Turkey). Ultra-pure water (18 MΩ cm at 25 °C) was provided using a Millipore Milli-Q Advantage A10. Chemical oxygen demand (COD) cell kits were purchased from Hach Lange (Düsseldorf, Germany). WTW Photolab 6100 Vis spectrophotometer was used to monitor the *COD* values of treated and untreated samples. UV–Vis spectrophotometer (Shimadzu UV--1601) was used to analyse total polyphenolic concentration of samples.

Degradation of OMWW

A homemade stainless steel reactor system, as shown in our previous work, was used for carrying out degradation experiments.[31] 150 mL of stock OMWW solution which had been diluted by 1:10 from original OMWW was used in each degradation experiments. Degradation runs were performed in triplicate at three levels of each independent variable, namely temperature (373, 398 and 423 K), treatment time (60, 90 and 120 min) and oxidant concentration (0.4, 0.8 and 1.2 M) as demonstrated in Table I. The pressure was fixed at 30 bar with nitrogen to supply the subcritical water medium.

COD *analysis*

The collected fractions were used for *COD* analysis by using the cell kit which can function between 0–15 g L^{-1} of value. Thus, *COD* values of treated aqueous samples and untreated samples (stock solution) were analyzed spectrometrically according to the method below at the end of the treatment time. COD removal percentages (degradation efficiency) of all treated samples were obtained by comparing *COD* values of them to that of the stock solution according to Eq. (1) where *COD* value of the stock solution was calculated to be 6.085 g L^{-1}:

$$CRE, \% = 100(c_\mathrm{i} - c_\mathrm{f})/\ c_\mathrm{i} \tag{1}$$

In this formulae, *CRE* stands for the *COD* removal efficiency; c_i and c_f represent the stock and treated sample concentration, respectively.

Total phenolic content analysis procedure

Folin–Ciocalteu's method, which is slightly modified from the previously used form that is reported by Obanda *et al.* and briefly stated as follow, was used to determine the total phenolic content of the stock solutions and the treated samples.[48,49] 1 mL of Folin–Ciocalteu's phenol reagent and 1 mL of sample solution were mixed in a test tube. The mixture tube was held in dark for 5 min. Then, 2 mL of the aqueous Na_2CO_3 solution which was prepared by dissolving 200 g of solid Na_2CO_3 in 1.0 L of distilled water was added into the mixture. This mixture was shaken and adjusted to 6 mL, by adding 2 mL of ultrapure water. The blue colour of the mixture was spectrophotometrically measured after 30 min of keeping the mixture in the dark. The concentration of total phenolic content of all samples was determined on the UV spectrophotometer at 714 nm and expressed as milligram of gallic acid equivalents (mg GAE/L) by using a standard curve ($r^2 = 0.997$). This curve is based on the absorbances of GA stock solutions (25–400 ppm) which was analyzed in the same way mentioned above for samples. The removal efficiency of total phenolic content, in other words, dephenolisation efficiency (*DPE*), was expressed in percentages using Eq. (1).

UV analysis

The efficiency of the aromatic compound removal (dearomatisation efficiency, *DAE*) of treated samples was spectrophotometrically determined and expressed as percentages of removal by comparing the absorbances that are obtained for stock solution and samples, respectively, as stated in Eq. (1). The total aromaticity of stock and treated samples was monitored at 254 nm using UV spectrophotometer.

Experimental design and optimization of degradation process using CCD

RSM is an advantageous statistical technique which has been widely used to assess the optimum experimental variables and evaluate the performance of a system.[37,45] The main goal is to optimise the response in RSM over other independent variables as well as to predict responses using theoretical equations, by carrying out a limited number of experiments. Since Box and Wilson first introduced the CCD, the use of the CCD has increased even more due to being the most efficient method among many types of RSM designs.[50-52] CCD is used to construct the full factorial or fractional factorial second-order RSM models which consist of three types of points such as cube, axial and centre that are settled in the experimental region.[38,53] Hereby, the total number of experiments can be designated by $N = 2^k + 2k + C_0$, where k stands for the number of process variables and C_0 is the run number of central points.[54] The CCD model which consists of 20 runs of degradation experiments was performed in randomized order in this work ($N = 2^k + 2k + C_0 = 2^3 + 2*3 + 6 = 20$ runs).

The correlation of response and independent variables can be represented by linear or quadratic models (Eq. (2)):

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

where Y symbolizes the approximation response, and x_1, x_2 and x_3 depict the coded independent variable effects, and x_1^2, x_2^2 and x_3^2 represent the square effects. x_1x_2, x_1x_3 and x_2x_3 demonstrate interaction effects. β_1, β_2 and β_3 show the linear coefficients. β_{11}, β_{22} and β_{33} represent the square coefficients. β_{12}, β_{13} and β_{23} are the interaction coefficients. β_0 and ε represent the constant and the random error, respectively.[31]

The effect of the independent process variables, namely temperature, K, x_1; treatment time, min x_2 and concentration of oxidising agent, M x_3; were investigated at three levels. The TOC removal percentage (response 1, Y_1), the total phenolic content removal percentage (response 2, Y_2) and the aromatic compound removal percentage (response 3, Y_3) were assumed to be the dependent variables. The design of the independent variables is presented in Table I. The statistical analysis was supplied using Design Expert 9.0.6.2. The interactions between the independent variables were investigated by the analysis of variance (ANOVA) and expressed by the response surface plots. In addition, the accuracies of the obtained models and the terms of the models were evaluated using ANOVA. The properties of the quadratic models were evaluated by the coefficients of determinations (R^2, R^2_{adj}), Fisher's F test, and P-value.

TABLE I. Design of the degradation experiments and the values of independent variables used in RSM

Factor	Independent variable	Coded levels				
		–1.682	–1	0	1	1.682
x_1	Temperature, K	356	373	398	423	440
x_2	Treatment time, min	40	60	90	120	141
x_3	Concentration of oxidising agent, M	0.13	0.4	0.8	1.2	1.47

RESULTS AND DISCUSSION

The effects of system variables, a relationship between these variables and the responses of the treatment process of OMWW were identified by employing CCD. The experimental and predicted values of *CRE*, *DPE* and *DAE* along with the actual/coded values of the independent variables displayed in Table II. The highest and the lowest experimental *COD* removal rates were obtained at run 18 and 14 respectively, as 85.74 and 1.84 %, respectively. Furthermore, these values were obtained as 96.13 and 46.79 % respectively, in the case of dephenolisation efficiency and 99.96 and 24.05 %, respectively, in the case of dearomatisation efficiency.

TABLE II. Experimental and predicted values of *CRE*, *DPE* and *DAE* along with actual/coded values of independent variables obtained by CCD; *CRE*: *COD* removal efficiency, *DPE*: dephenolisation efficiency, *DAE*: dearomatisation efficiency

Run	Temperature, K	Treatment time, min	Concentration of oxidizing agent, M	*CRE* / %		*DPE* / %		*DAE* / %	
				Exp.	Pre.	Exp.	Pre.	Exp.	Pre
1	373 (–1)	120 (+1)	0.4 (–1)	15.54	15.94	48.61	47.60	31.89	31.32
2	398 (0)	40 (–1.682)	0.8 (0)	26.68	28.58	87.47	88.21	76.60	76.00
3	398 (0)	90 (0)	0.8 (0)	77.51	79.17	91.68	91.94	95.88	94.53
4	398 (0)	90 (0)	1.47 (1.682)	73.62	71.41	90.65	87.36	74.76	68.05
5	398 (0)	90 (0)	0.8 (0)	79.37	79.17	91.78	91.94	93.11	94.53
6	373 (–1)	120 (+1)	1.2 (+1)	41.3	42.74	81.53	81.01	66.38	67.69
7	398 (0)	90 (0)	0.8 (0)	78.44	79.17	93.65	91.94	94.12	94.53
8	423 (+1)	60 (–1)	1.2 (+1)	67.54	67.55	86.21	87.19	76.34	77.86
9	373 (–1)	60 (–1)	1.2 (+1)	20.45	20.62	73.84	75.01	35.48	39.93
10	440 (1.682)	90 (0)	0.8 (0)	81.41	80.62	88.63	86.15	93.51	92.51
11	423 (+1)	120 (+1)	0.4 (–1)	62.46	62.70	80.43	79.23	78.30	74.80
12	398 (0)	90 (0)	0.13 (–1.682)	32.57	34.20	48.32	51.66	38.16	43.53
13	398 (0)	90 (0)	0.8 (0)	77.54	79.17	89.47	91.94	93.30	94.53
14	356 (–1.682)	90 (0)	0.8 (0)	1.63	1.84	46.79	49.31	24.39	24.05
15	398 (0)	141 (1.682)	0.8 (0)	60.26	57.78	94.86	94.17	91.47	90.72
16	373 (–1)	60 (–1)	0.4 (–1)	3.87	1.85	57.23	53.32	39.76	35.92
17	398 (0)	90 (0)	0.8 (0)	80.11	79.17	93.04	91.94	95.94	94.53
18	423 (+1)	120 (+1)	1.2 (+1)	85.74	88.17	96.13	100.00	95.18	99.96
19	398 (0)	90 (0)	0.8 (0)	81.95	79.17	92.02	91.94	94.59	94.53
20	423 (+1)	60 (–1)	0.4 (–1)	51.13	50.10	77.65	78.14	85.42	85.06

It can be seen from Table II that the high dearomatisation and dephenolisation efficiency values can be obtained in the circumstances where the *COD* removal rate is low.

Evaluation of ANOVA

The statistical analysis of the results was evaluated based on ANOVA. Table III shows the results of the employed quadratic models. The significance of the obtained quadratic models can be described using statistical analysis in terms of *F* values, *p* values and lack of fit values *etc.*[55] In this case, ANOVA terms verified that the quadratic models were significant for designating the effect of the variables on the responses (*CRE*, *DPE* and *DAE*). The *F* values of the models which were obtained as 372.47, 70.99 and 83.96 in the case of *COD* removal, dephenolisation and dearomatisation analysis, respectively, imply that the models are significant. The obtained 0.01 % chance values revealed that the *F*-values of this order could occur due to noise in each case.

TABLE III. ANOVA results of quadratic models obtained by CCD

Source	*COD* Removal			Dephenolisation			Dearomatisation		
	Mean square	F Value	*p*-value prob > F	Mean square	F Value	*p*-value prob > F	Mean square	F Value	*p*-value prob > F
Model	1713.31	372.47	< 0.0001	577.66	70.99	< 0.0001	1321.88	83.96	< 0.0001
x_1	7492.60	1628.87	< 0.0001	1638.23	201.32	< 0.0001	5657.99	359.39	< 0.0001
x_2	1028.65	223.62	< 0.0001	42.88	5.27	0.0446	261.48	16.61	0.0022
x_3	1671.06	363.28	< 0.0001	1539.10	189.14	< 0.0001	725.86	46.11	< 0.0001
x_1x_2	1.12	0.24	0.6327	23.22	2.85	0.1220	15.99	1.02	0.3373
x_1x_3	0.88	0.19	0.6715	79.82	9.81	0.0107	62.78	3.99	0.0738
x_2x_3	32.20	7.00	0.0245	68.74	8.45	0.0157	523.75	33.27	0.0002
x_1^2	2593.15	563.74	< 0.0001	1055.34	129.69	< 0.0001	2367.12	150.36	< 0.0001
x_2^2	2333.44	507.28	< 0.0001	1.01	0.12	0.7318	224.54	14.26	0.0036
x_3^2	1252.27	272.24	< 0.0001	906.23	111.37	< 0.0001	2703.48	171.72	< 0.0001
Residual	4.60			8.14			15.74		
Lack of Fit	6.28	2.15	0.2102	14.21	6.87	0.0272	29.99	19.99	0.0027
Pure Error	2.92			2.07			1.50		

In addition, the convenience of the model and its terms can be evaluated using *p*-values. Therefore, the *p*-values less than 0.05 are desired. Herein, x_1, x_2, x_3, x_2x_3, x_1^2, x_2^2 and x_3^2 are significant model terms in the case of *COD* removal where x_1, x_2, x_3, x_1x_3, x_2x_3, x_1^2, and x_3^2 are significant and x_1, x_2, x_3, x_2x_3, x_1^2, x_2^2 and x_3^2 are significant model terms for the dephenolisation and dearomatisation attempts, respectively. Moreover, temperature, x_1, was found to be the most favourable parameter of all cases that possessed the highest *F* values.

Evaluation of regression coefficients

The regression coefficients of the models are shown in Table IV. The standard deviation values, which are known as the square root of residual mean square values and desired to be lower, were obtained as 2.14, 2.85 and 3.97 respectively, in the case of *COD* removal, dephenolisation and dearomatisation analysis.[56] The fit of the model with each point in the design is determined using the predicted residual sum of squares values (*PRESS*) where small values are desired.[57] Thus, the *PRESS* value of *COD* removal was found to be better than that of the obtained ones in other cases. The coefficient of determination (R^2), which takes values between zero and one, represents the relationship between the variables and its value is desired to be close to 1.[57]

Herein, R^2 values were found as 0.9970, 0.9846 and 0.9869, respectively, for *COD* removal, dephenolisation and dearomatisation analysis. The amount of the variation around the mean given by the model is represented by the adjusted R^2 and the amount of variation in new data, explained by the used model, is symbolised by the predicted R^2.[56] The predicted R^2 values of 0.9832, 0.8918 and 0.9020 are in a reasonable agreement with the adjusted R^2 values of 0.9943, 0.9707 and 0.9752, respectively. The adequate precision values, which were supposed to be greater than 4 and measure the signal-to-noise ratio, were found to be 56.930, 25.981 and 27.059 for *COD* removal, dephenolisation and dearomatisation analysis, respectively. Thus, these values indicate that the models can be used to direct the design space in each case.[31]

TABLE IV. Regression Coefficients of the models obtained by CCD

Regression coeffiecient	*COD* Removal	Dephenolisation	Dearomatisation
Standard Deviation	2.14	2.85	3.97
PRESS	260.57	571.08	1181.85
R^2	0.9970	0.9846	0.9869
Adjusted R^2	0.9943	0.9707	0.9752
Predicted R^2	0.9832	0.8918	0.9020
Adequate precision	56.930	25.981	27.059

Evaluation of approximation equations

The predicted second-order polynomial equations – Eqs. (3)–(5), were obtained using the Design-Expert software.[56] These equations can be used to make the predictions about the degradation percentage for the given levels of each factor based on the evaluation of the factor coefficients (coded factors). Eqs. (3)–(5) indicated that the relative impacts of the factors for the predicted models are in the following sequence: $x_1 > x_3 > x_2 > x_2x_3 > x_1x_3 > x_1x_2 > x_3^2 > x_2^2 > x_1^2$, $x_1 > x_3 > x_2x_3 > x_2 > x_1x_2 > x_2^2 > x_1x_3 > x_3^2 > x_1^2$ and $x_1 > x_2x_3 > x_3 > x_2 > x_1x_2 > x_1x_3 > x_2^2 > x_1^2 > x_3^2$ in the case of *COD* removal, dephenolisation and dearomatisation analysis, respectively. Y_1, Y_2 and Y_3, correspond to the response of each model for the COD removal, dephenolisation and dearomatisation analysis, respectively.

$$\begin{gathered} Y_1 = 79.17 + 23.42x_1 + 8.68x_2 + 11.06x_3 - 0.37x_1x_2 - 0.33x_1x_3 + \\ +2.01x_2x_3 - 13.41x_1^2 - 12.72x_2^2 - 9.32x_3^2 \end{gathered} \tag{3}$$

$$\begin{gathered} Y_2 = 91.94 + 10.95x_1 + 1.77x_2 + 10.62x_3 + \\ +1.70x_1x_2 - 3.16x_1x_3 + 2.93x_2x_3 - 8.56x_1^2 - 0.26x_2^2 - 7.93x_3^2 \end{gathered} \tag{4}$$

$$\begin{gathered} Y_3 = 94.53 + 20.35x_1 + 4.38x_2 + 7.29x_3 - \\ -1.41x_1x_2 - 2.80x_1x_3 + 8.09x_2x_3 - 12.82x_1^2 - 3.95x_2^2 - 13.70x_3^2 \end{gathered} \tag{5}$$

Effects of temperature and treatment time on the COD *removal, dephenolisation and dearomatisation efficiency*

Fig. 1a–c demonstrates the 3D plots displaying the effect and the interaction of the temperature and the treatment time, at a fixed H_2O_2 concentration of 1 M, on the response as independent variables. Responses represent the percentages of *COD* removal, dephenolisation and dearomatisation efficiency in Fig. 1a–c, respectively. Considering the Fig. 1, one can notice that while higher temperature and longer treatment time are more effective on the *COD* removal, milder conditions are sufficient for obtaining the high yield in the dephenolisation and dearomatisation processes. This can be attributed to the fact that, though the structures of phenolic and aromatic compounds can be degenerated even under the lower values of temperature and treatment time, more harsh conditions are required for the oxidation of mentioned structures, consequently for the high *COD* removal. Also, the removal efficiencies of the aromatic compounds may vary with the structure type of them.[58]

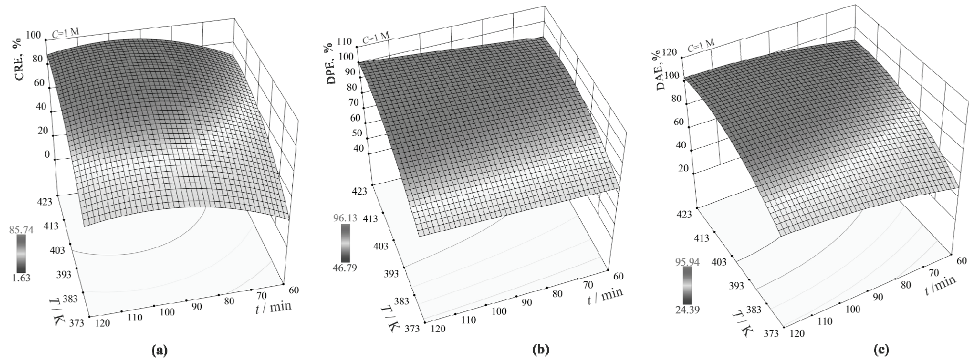


Fig. 1. Effects of temperature (*T*) and treatment time (*t*) on: a) the COD removal, b) dephenolisation and c) dearomatisation efficiency of OMWW using H_2O_2 at fixed $c = 1$ M.

In addition, a certain time is required for the generation of the adequate free $^\bullet$OH.[31] On the basis of this necessity, it is obvious that effect of the treatment time is essential especially in the higher temperature values for obtaining a high yield. Thus, the increasing treatment time has a significant effect on the each case. For instance, the increasing treatment time from 60 up to 100 min raised *COD* removal, dephenolisation and dearomatisation percentages, respectively, from 59.96 to 84.18, from 91.76 to 96.31 and from 82.38 to 97.11 under fixed temperature of 398 K and H_2O_2 concentration of 1 M. Increasing the temperature from 373 K up to 423 K raised the *COD* removal, dephenolisation and dearomatisation percentages respectively from 47.64 to 93.90, from 77.82 to 97.70 and from 65.82 to 100 under fixed H_2O_2 concentration of 1 M and the treatment time of 100 min.

Effects of treatment time and concentration of oxidizing agent on the COD *removal, dephenolisation and dearomatisation efficiency*

The combined effect of treatment time and H_2O_2 concentration on the response is shown in Fig. 2a–c at fixed temperature of 398 K. It is clearly shown from Fig. 2a that the darker area, which demonstrates the high yield, is smaller than that of Fig. 2b and c. This situation suggests that *COD* removal requires more severe conditions when comparing dephenolisation and dearomatisation processes. Nevertheless, while concentration of H_2O_2 is essential in the generation of free radicals, an adequate amount of free radicals might be formed beyond a certain time. Thus, the medium and high levels of H_2O_2 concentration raised the yield of *COD* removal above the medium levels of the treatment time. Also, high dephenolisation yields were obtained above medium levels of H_2O_2 concentration in all treatment time and high dearomatisation yields were obtained at lower levels of concentration of H_2O_2 and the treatment time. For instance, increasing treatment time from 60 up to 100 min raised *COD* removal, dephenolisation and dearomatisation percentages respectively from 57.77 to 80.65, from 89.90 to 92.49 and from 86.21 to 95.55 under fixed temperature of 398 K and H_2O_2 concentration of 1.0 M. Increasing H_2O_2 concentration from 0.4 up to 1.0 M raised *COD* removal, dephenolisation and dearomatisation percentages, respectively, from 59.60 to 84.18, from 72.98 to 96.31 and from 71.86 to 97.12 under the fixed temperature of 398 K and the treatment time of 100 min.

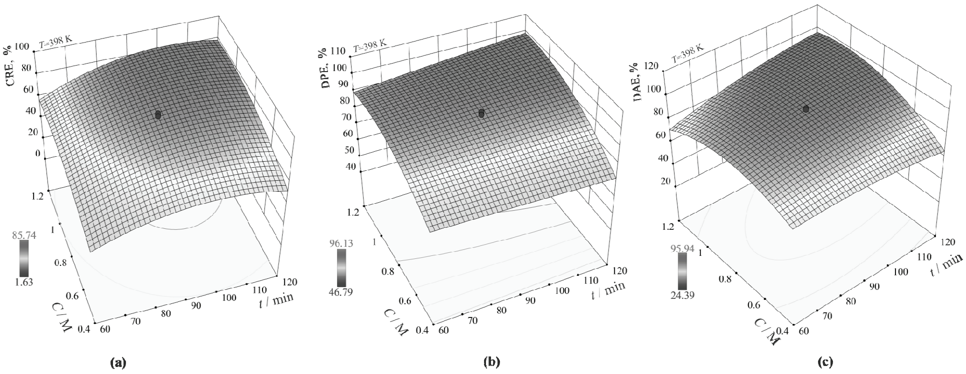
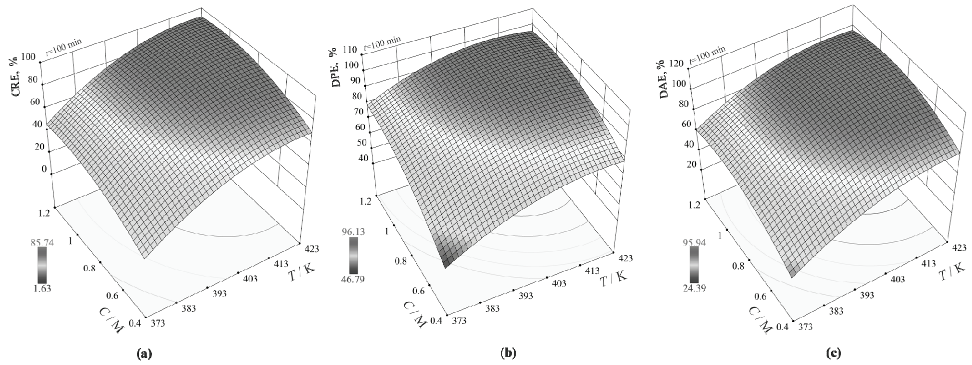


Fig. 2. Effects of treatment time (*t*) and concentration of oxidizing agent (*C*) on: a) the COD removal, b) dephenolisation and c) dearomatisation efficiency of OMWW using H_2O_2 at fixed $T = 398$ K.

Effects of concentration of oxidizing agent and temperature on the COD removal, dephenolisation and dearomatisation efficiency

The combined effect of temperature and H_2O_2 concentration significantly increased the yield in each case shown in Fig. 3a–c. For instance, increasing the temperature from 373 up to 423 K raised *COD* removal, dephenolisation and dearomatisation percentages respectively from 43.90 to 90.52, from 72.43 to 95.34 and from 62.73 to 100 under the fixed treatment time of 100 min and H_2O_2 concentration of 0.8 M. Increasing the H_2O_2 concentration from 0.4 M up to 1.2 M raised *COD* removal, dephenolisation and dearomatisation percentages respectively from 22.59 to 46.57, from 49.85 to 79.14 and from 36.34 to 61.53 under the fixed treatment time of 100 min and even temperature of 373 K.

Increasing H_2O_2 concentration might affirmatively effect the efficiencies due to the possible increase in the amount of $^{\bullet}OH$ that can easily attack the target compound and therefore enhance the degradation rates.[30,59] In addition, the temperature might favour the mentioned generation of free radicals. However, the temperature can reduce the yields above the certain point due to the possible degradation of H_2O_2, or an undesirable reaction might occur between the matrix and H_2O_2.[60] Thus, temperatures adversely affect the efficiency above 420 K. For instance, increasing the temperature from 418 to 423 K only, caused the decrease in the *COD* removal, dephenolisation and dearomatisation percentages respectively from 67.69 to 67.55, from 89.05 to 87.19 and from 78.68 to 77.85 under the fixed H_2O_2 concentration of 1.2 M and the treatment time of 60 min.



(a) (b) (c)

Fig. 3. Effects of concentration of oxidizing agent (*C*) and temperature (*T*) on: a) the *COD* removal, b) dephenolisation and c) dearomatisation efficiency of OMWW using H_2O_2 at fixed t = 100 min.

CONCLUSION

Based on the use of simple but impressive experimental set-up, this study has been proposed as an important and advantageous alternative to the inefficient and inapplicable conventional processes for the treatment of OMWW. Moreover, it should be noted that H_2O_2, which leaves no residues after treatment, was used as the oxidising agent. Results show that the co-effect of a subcritical medium and H_2O_2 have a remarkable effect on responses. The high yields obtained in terms of *COD* removal, dephenolisation and dearomatisation indicate that the OMWW is effectively cleansed and can be safely discharged using the eco-friendly subcritical water oxidation method. CCD was performed to fully evaluate the effect of each temperature, concentration and treatment time on the *COD* removal, dephenolisation and dearomatisation rates. The ANOVA results were considered to reveal the convenience of the models and model terms. Besides determining these experimental parameters and the interactions between them, the approximation equations were proposed in each case. The temperature was found to be the most effective variable in all cases, especially in *COD* removal.

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ИЗВОД

ДЕГРАДАЦИЈА, ДЕФЕНОЛИЗАЦИЈА И ДЕАРОМАТИЗАЦИЈА ОТПАДНЕ ВОДЕ ОД МЛИНА ЗА ЦЕЂЕЊЕ МАСЛИНА МЕТОДОМ ОКСИДАЦИЈЕ ПОТКРИТИЧНЕ ВОДЕ КОРИШЋЕЊЕМ ВОДОНИК-ПЕРОКСИДА: ПРОЈЕКТОВАЊЕ ЦЕНТРАЛНОГ КОМПОЗИТА МЕТОДОМ ОДГОВОРА АНАЛИЗЕ ПОВРШИНЕ

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У овој студији је представљена метода прихватљива за животну средину, којом се деконтаминира отпадна вода млина за цеђење маслина, што се испоставило као значајан проблем у заштити животне средине. Испитано је уклањање полифенолних и ароматичних остатака и разлагање отпадне воде из млина у региону Mersin у Турској – помоћу оксидације поткритичне воде коришћењем водоник-пероксида. За процену утицаја температуре, дужине трајања третмана и концентрације оксидационог агенса коришћено је пројектовање централног композита методом одговора анализе површине. Поузданост употребљене методе је доказана ANOVA анализом. Одређени су оптимални експериментални параметри и у сваком од случајева предложене су теоријске једначине. Најефикасније уклањање *COD*, дефенолизација и деароматизација остварене су у износима од 85,74, 96,13 и 95,94 %, редом.

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REFERENCES

1. M. Hamdi, *Appl. Biochem. Biotechnol*. **37** (1992) 155
2. C. McNamara, C. Anastasiou, V. Oflaherty, R. Mitchell, *Int. Biodeter. Biodegr.* **61** (2008) 127
3. D. Mantzavinos, N. Kalogerakis, *Environ. Int.* **31** (2005) 289
4. A. Ginos, T. Manios, D. Mantzavinos, *J. Hazard. Mater.* **133** (2006) 135
5. F. J. Benitez, J. Beltran-Heredia, J. Torregrosa, J. L. Acero, *Bioprocess Eng.* **17** (1997) 169
6. P. Paraskeva, E. Diamadopoulos, *J. Chem. Technol. Biotechnol*. **81** (2006) 1475
7. D. P. Minh, P. Gallezot, S. Azabou, S. Sayadi, M. Besson, *Appl. Catal., B* **84** (2008) 749
8. E. Moreno, J. Perez, A. Ramos-Cormenzana, J. Martinez, *Microbios*. **51** (1987) 169
9. M. Rinaldi, G. Rana, M. Introna, *Field Crops Res.* **84** (2003) 319
10. A. Pavlidou, E. Anastasopoulou, M. Dassenakis, I. Hatzianestis, V. Paraskevopoulou, N. Simboura, E. Rousselaki, P. Drakopoulou, *Sci. Total Environ.* **497** (2014) 38
11. A. Mekki, A. Dhouib, S. Sayadi, *Int. J. Recycl. Org. Waste Agric.* **2** (2013) 15
12. I. Karaouzas, E. Cotou, T. Albanis, A. Kamarianos, N. Skoulikidis, U. Giannakou, *Environ. Toxicol.* **26** (2011) 669
13. D. P. Komilis, E. Karatzas, C. P. Halvadakis, *J. Environ. Manage.* **74** (2005) 339
14. S. M. Paixao, E. Mendonca, A. Picado, A.M. Anselmo, *Environ. Toxicol*. **14** (1999) 263
15. V. Balice, C. Carrieri, O. Cera, *Riv. Ital. Sostanze Grasse.* **67** (1990) 9

16. M. Della Greca, P. Monaco, G. Pinto, A. Pollio, L. Previtera, F. Temussi, *Bull. Environ. Contam. Toxicol.* **67** (2001) 352
17. R. Öztekin, D. Teresa Sponza, *J. Chem. Technol. Biotechnol.* **88** (2013) 212
18. F. D. Demian, D. P. Makris, *J. Waste Manage.* 2013 (**2013**), Article ID 630209, doi: 10.1155/2013/630209
19. S. Azabou, W. Najjar, M. Bouaziz, A. Ghorbel, S. Sayadi, *J. Hazard. Mater.* **183** (2010) 62
20. J. Pérez, T. de la Rubia, J. Moreno J. Martinez, *Environ. Toxic. Chem.* **11** (1992) 489
21. G. Greco J.R., G. Toscanoa, M. Cioffi, L. Gianfreda, F. Sannino, *Wat. Res.* **33** (1999) 3046
22. M. Niaounakis, C. P. Halvadakis, *Olive Processing Waste Management*, Elsevier, Mytilene, 2006
23. I. Saadi, Y. Laor, M. Raviv, S. Medina, *Chemosphere* **66** (2007) 75
24. R. Cossu, N. Blakey, P. Cannas, *Water Sci. Technol.* **27** (1993) 261
25. D. T. Sponza, R. Öztekin, *Ultrason. Sonochem.* **21** (2014) 1244
26. L. Bertin, M. Majone, D. Di Gioia, F. Fava, *J. Biotechnol.* **87** (2001) 161
27. D. Di Gioia, F. Fava, L. Bertin, L. Marchetti, *Appl. Microbiol. Biotechnol.* **55** (2001) 619
28. Z. Emire, E. Yabalak, Ö. Görmez, A. Gizir, *J. Serb. Chem. Soc.* **82** (2017) 99
29. R. M. Liou, S. H. Chen, *J. Hazard. Mater.* **172** (2009) 498
30. V. M. Daskalaki, E. S. Timotheatou, A. Katsaounis, D. Kalderis, *Desalination* **274** (2011) 200
31. E. Yabalak, H. A. Döndaş, A. M. Gizir, *J. Environ. Sci. Heal., A* **52** (2017) 210
32. E. Yabalak, A. M. GİZİR, *J. Serb. Chem. Soc.* **78** (2013) 1013
33. V. G. Molina, M.L. Arias, M. Florczyk, E. Chamarro, S. Esplugas, *Water Res.* **39** (2005) 795
34. R. S. Ribeiro, M.T. A.J. L. Silva, J. L. Figueiredo, J. L. Faria, H. T. Gomes, *Appl. Catal., B* **187** (2016) 428
35. P. R. Gogate, A. B. Pandit, *Adv. Environ. Res.* **8** (2004) 501
36. S. Daneshvar, N. Hidemi, F. Salak, N. Mahinpey, *Can. J. Chem. Eng.* **92** (2014) 615
37. P. Izadiyan, B. Hemmateenejad, *Food Chem.* **190** (2016) 864
38. V. A. Sakkas, Md. A. Islam, C. Stalikas, T.A. Albanis, *J. Hazard. Mater.* **175** (2010) 33
39. D. O Aksoy, E. Sagol, *Fuel* **183** (2016) 609
40. S. Das, S. Mishra, *J. Environ. Chem. Eng.* **5** (2017) 588
41. V. Vatanpour, A. Karami, M. Sheydaei, *Chem. Eng. Process.* **116** (2017) 68
42. K. Vivek, K. V. Subbarao, B. Srivastava, *Ultrason. Sonochem.* **32** (2016) 328
43. T. Belwal, P. Dhyani, I. D. Bhatt, R. S. Rawal, V. Pande, *Food Chem.* **207** (2016) 115
44. C. Stalikas, Y. Fiamegos, V. Sakkas, T. Albanis, *J. Chromatogr., A* **1216** (2009) 175
45. E. Yabalak, Ö. Görmez, B. Gözmen, A. M. Gizir, *Int. J. Ind. Chem.* **6** (2015) 23
46. A. Rai, B. Mohanty, R. Bhargava, *Food Chem.* **192** (2016) 647
47. A. Somayajula, P. Asaithambi, M. Susree, M. Matheswaran, *Ultrason. Sonochem.* **19** (2012) 803
48. E. Yabalak, A. Gizir, *J. Turkish Chem. Soc., Sect. Chem.* **4** (2017) 691
49. M. Obanda, P. O. Owuor, *J. Sci. Food Agric.* **74** (1997) 209
50. D. S. Correia, C. V.Gonçalves, S. S. da Cunha Jr., V. A. Ferraresi, *J. Mater. Process. Technol.* **160** (2005) 70
51. G. Box, W. Hunter, J. Hunter, *Statistics for Experimenters*, John Willey, New York, 1978

52. R. H. Myers, D. C. Montgomery, C. M. Anderson-Cook, *Response Surface Methodology: Process and Product Optimization Using Designed Experiments*, John Willey, New York, 2009
53. C. R. T. Tarley, G. Silveira, W. N. L. dos Santos, G. D. Matos, E. G. P. da Silva, M. A. Bezerra, M. Miró, S. L. C. Ferreira, *Microchem. J.* **92** (2009) 58
54. M. A. Bezerra, R. E. Santelli, E. P. Oliveira, L. S. Villar, L. A. Escaleira, *Talanta* **76** (2008) 965
55. E. Yabalak, S. Könen adigüzel, A. Adigüzel, R. S. Ergene, M. Tunçer, A. Gizir, *Desalin. Water Treat.* **81** (2017) 186
56. *Design-Expert Software*, ver. 9.0.6.2, Stat-Ease, Minneapolis, MN, 55413
57. M. J. Anderson, P. J Whitcomb, *RSM simplified: optimizing processes using response surface methods for design of experiments*, CRC Press, New York, 2005
58. S. Amir, M. Hafidi, G. Merlina, H. Hamdi, J. C. Revel, *Agronomie* **24** (2004) 13
59. D. Kalderis, S. B. Hawthorne, A. A. Clifford, E. Gidarakos, *J. Hazard. Mater.* **159** (2008) 329
60. S. Wang, Y. Guo, C. Chen, J. Zhang, Y. Gong, Y. Wang, *Waste Manage.* **31** (2011) 2027.