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OPTIMIZATION OF PHENOLIC COMPOUNDS ABATEMENT IN OLIVE MILL WASTEWATER BY FENTON'S LIKE TREATMENT WITH H_2O_2/Cu^{2+} UNDER MICROWAVE USING EXPERIMENTAL DESIGN

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Abstract

This work describes the application of Fenton's like system (H_2O_2/Cu^{2+}) assisted by microwaves to the removal of phenolic compounds from olive mill wastewater (OMWs). The effect of various operating conditions, namely copper ion concentrations (X_1), hydrogen peroxide (X_2), time of irradiation (X_3) and microwave power (X_4) were evaluated by factorial design of experiments. Results showed that X_1, X_2, X_3 and X_4 had significant effects on the response followed by the interactions X_1X_2, X_1X_3, X_2X_4 and $X_1X_2X_3$. The highest degradation of phenolic compounds was found for 500 mg/L copper dose, a power of 340 W, 12 M H_2O_2 and 8 min irradiation time. FTIR analysis confirmed that microwave degradation of polyphenols by means of the Fenton-like system $Cu(II)/H_2O_2$ could be an efficient solution for the treatment of olive mill wastewater.

Key words: experimental design, H_2O_2/Cu^{2+}, microwave, olive mill wastewater treatment, polyphenols

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1. Introduction

Olive mill wastewaters (OMWs) are one of the main environmental problems in the Mediterranean area, where the greatest quantities of olive oil are produced within only a few months per year (from November to February). The physico-chemical characteristics of OMW are rather variable, depending on climatic conditions, olive cultivars, degree of fruit maturation, storage time, and extraction process. The high polluting activity of OMWs is linked with their high content of organic molecules, especially polyphenol mixtures (0.5-24 g/l) (Yalili Kiliç et al., 2009) (COD) 80-200 g/L and BOD_5 (12-63 g/L) (Yalili Kiliç et al., 2009).

Therefore, OMWs must be treated to remove the phenolic content fraction, before being discharged in receiving water bodies. Various treatment methods can be used. The majority of them have been tested in laboratory scale and only some of them used on industrial scale.

Aromatic compounds are, generally, refractory to conventional chemical and biological treatments and hence other methods are being studied as alternatives. A common approach refers to the use of advanced oxidation processes (AOPs) (Badawy et al., 2006; Favier et al., 2016), which are considered as attractive methods for the treatment of wastewater containing toxic and non-biodegradable pollutants (Cheriyan et al., 2017; Santos et al., 2010). This kind of processes involves the use of one or more oxidizing agents, usually hydrogen peroxide and/or oxygen, and a catalyst for the destruction of organic contents in wastewater yielding carbon dioxide and water and/or other oxidation products.

AOPs applied to OMWs include ozonation (Beltran-Heredia et al., 2001), combination of ultrafiltration and UV/H_2O_2 (Drouiche et al., 2004),

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combination of UV/H_2O_2 and lime (Ugürlu and Kula, 2007), conductive diamond electro-oxidation (Rivas et al., 2001b) (Cañizares et al., 2007), UV/TiO_2 (El Hajjouji et al., 2008), catalytic wet air oxidation (Rivas et al., 2001a; Gomes et al., 2007), solar photocatalysis with TiO_2 and solar photo-Fenton (Gernjak et al., 2004).

The oxidation of many organic substances with H_2O_2 is improved by the addition of a catalyst (Fe (II) or Cu (II) or other transition metal ions) to activate the H_2O_2 molecule leading to the formation of hydroxyl radicals ($^\bullet OH$) (Gallard et al., 1999). Among the available catalysts, copper Cu^{2+} was successfully used in Fenton-like systems implemented for the treatment of recalcitrant compounds, like dyes (Bali and Karagozoglu, 2007), EDTA (Ghiselli et al., 2004) or phenol derivatives (Kim et al., 2007).

Fenton's reagent, which involves homogenous reaction is a system based on the generation of very reactive oxidizing free radicals, especially hydroxyl radicals, which have a strong oxidation potential, 2.8V for $^\bullet OH$ (Beltran-Heredia et al., 2001). The Fenton's reactions at acidic pH lead to the production of copper ion (Gallard et al., 1999).

$$H_2O_2 + Cu^{2+} \rightarrow Cu^+ + H^+ + {}^\bullet OOH \qquad (1)$$

$$H_2O_2 + Cu^+ \rightarrow Cu^{2+} + OH^- + {}^\bullet OH \qquad (2)$$
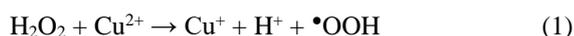
$^\bullet OOH$ is a very instable species, perhydroxyl radicals may be scavenged by reaction with another copper (Martins et al., 2010):

$$^\bullet OOH + Cu^{2+} \rightarrow Cu^+ + O_2 + H^+ \qquad (3)$$
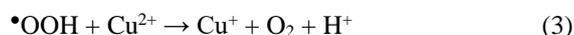
Radical chain oxidations will be then initiated by hydroxyl radicals that will react none selectively with the organic matter present in the wastewater (Catrinescu et al., 2003).

$$^\bullet OH + RH \rightarrow H_2O + {}^\bullet R \qquad (4)$$

RH organic pollutant

$$^\bullet R + Cu^{2+} \rightarrow R^+ + Cu^+ \qquad (5)$$

$$^\bullet R + H_2O \rightarrow ROH + H^+ \qquad (6)$$

$$^\bullet R + O_2 \rightarrow {}^\bullet OOR \qquad (7)$$

$$^\bullet R + H_2O_2 \rightarrow ROH + {}^\bullet OH \qquad (8)$$

$$^\bullet OOR + R'H \rightarrow ROOH + R' \qquad (9)$$

R'H organic pollutant

$$Cu^+ + {}^\bullet OH \rightarrow OH^- + Cu^{2+} \qquad (10)$$

$$^\bullet OH + H_2O_2 \rightarrow {}^\bullet OOH + H_2O \qquad (11)$$
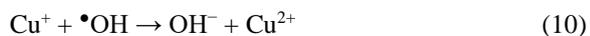
Microwaves (MW) have been widely used in organic synthesis (Yang et al., 2009) and extraction of organic compounds from plants (Amarni and Kadi, 2010; Boudissa and Kadi, 2013) due to its special heating mechanism. Microwave heating coupled with advanced oxidation processes (Karthikeyan and Gopalakrishnan, 2017; Lai et al., 2008; Zhihui et al., 2005) was found to be efficient for the treatment of persistent organic pollutants in combination with Fenton-like reagents (Liu et al., 2008), including the combination with the Cu^{2+}/H_2O_2 system (Liu et al., 2007).

The effectiveness of OMWs treatment using H_2O_2/Cu^{2+} under microwave was shown in a previous study (Iboukhoulef et al., 2013). In order to get additional information regarding this treatment, a set of factors influencing this process was studied using experimental design.

2. Experimental

An unreplicated 2^k factorial design was performed to determine the effect of four independent variables and their interactions on OMWs phenolic content degradation. Operating parameters such as MW power, radiation time, initial H_2O_2 dosage and $CuSO_4$ dosage were optimized to obtain the maximum removal of organics content. A polynomial regression model has been developed using experimental data. Comparison of spectra obtained from Fourier Transform Infrared (FTIR) spectroscopy between the original and the treated olive mill wastewater in the optimal conditions was made to characterize the structural changes of the molecules.

2.1. OMW characterization

Fresh OMWs was obtained from an olive oil continuous processing plant located in Tizi-Ouzou, 100 km from Algiers (northern Algeria). OMWs was collected in a closed plastic container and stored at 4°C. Experiments were conducted, on the decanted and diluted OMWs characterized by a pH 4.7, the COD was equal to 74 g/L and the total polyphenol was equal to 16.50 g/L. All used chemicals were of analytical grade. The amount of phenolic compounds in OMWs was in the range 0.5 to 24 g L^{-1}, namely very close to the value given by Yalili Kiliç et al. (2009). The COD value also agreed with those reported elsewhere by Chatzisymeon et al. (2013).

2.2. Treatment procedure

A household microwave oven (whirlpool) was chosen and modified in the laboratory. It maximum output was 850 W variable in 170 increments with 2450 MHz of microwave radiation frequency. The OMW (100 mL) was placed in a glass beaker and then 10 mL of copper solution (0 and 0.5 g/L) (CAS 7758-99-8) was introduced followed by 10 mL of hydrogen peroxide (4 and 12 M) (CAS 7722-84-1). The beaker was placed in the middle of the oven over a rotating dish and was exposed to microwave radiation for time spans (1 and 8 minutes) for the selected power (340

and 680 W). At the end of heating, the beaker was cooled for temperature stabilization and concentration of phenolic compounds was analyzed. In order to avoid a rapid rise in the temperature and a change of volume of the mixture during the experiment, the beaker was cooled every 0.5 min.

2.3. Chemical analysis

Phenolic compounds were quantified by means of the Folin–Ciocalteu colorimetric method (Gutfinger, 1981): 0.5 mL of diluted OMW with 10 mL of distilled water in glass tube. Add 0.5 mL of Folin–Ciocalteu phenol reagent was added. After 3 min, 1 mL of saturated solution of sodium carbonate was added. After 30 min in obscurity, the absorption was measured at 751 nm UV/VIS spectrophotometer (Shimadzu). Gallic acid was used for the calibration, and the results of analyses were expressed as gallic acid equivalent (GAE) with $R^2=0.997$.

COD was determined by the dichromate method. 2 ml of diluted OMW was introduced into commercially available digestion solution containing potassium dichromate, mercuric sulphate and sulphuric acid. The mixture was then incubated for 120 min at 150 °C in a COD reactor (TR320 MERCK) and the COD concentration was measured colorimetrically using a UV/V spectrophotometer (SHIMADZU) at 620 nm.

2.4. Experimental methodology

When working with experimental design techniques, it is necessary to decide the most appropriate type. Factorial designs are widely used in experiments involving several variables in order to study their effects on the response. A two level factorial design (2^k) was selected, in which each variable assumed two levels. This design is considered to be the most suitable when the study is directed towards identifying the main effects and interactions of various factors which have a significant impact on the response (Goupy, 1988). The variables considered in this study are given in Table 1. A total of 16 experiments (2^4) were carried out. The conditions applied in each experiment were modified using different combinations of the two selected levels. These levels were chosen for each variable according to bibliographic references and previous results from experiments carried out in our research group. The low (-1) and high (+1) values selected for each variable are shown in Table 1. In order to obtain the experimental variance of the response, five trials were realized in the experimental domain center.

The experimental matrix and the experimental design (in real variables) are given in Table 2. The coded values X_1, X_2, X_3 and X_4 corresponded to real variables [Cu^{2+}], [H_2O_2], exposition time and irradiation power, respectively. The selected experiments allowed the estimation of the coefficients of the model given by Eq. (12), where: Y was the response (residual phenolic content), b_0 was the medium response; b_1, b_2, b_3 and b_4 were the linear coefficients (principal effects) of variables X_1, X_2, X_3 and X_4; b_{12}, b_{13}, b_{14}, b_{24}, b_{34}, b_{123}, b_{124}, b_{134}, b_{234}, b_{1234} were the interaction terms coefficients (interaction effects).

Table 1. The coded and corresponding values of the parameters

Factors	Variables	Unit	Level		
			(-1)	0	(+1)
[Cu^{2+}]	X_1	g L^{-1}	0	0.25	0.5
[H_2O_2]	X_2	Mole L^{-1}	4	8	12
Exposition time	X_3	Minutes	1	4.5	8
Irradiation power	X_4	Watt	340	510	680

Table 2. Design matrix and results obtained for residual phenolic compounds (Y1)

Run N•	Coded values				Real values				Y (g/l)
	X_1	X_2	X_3	X_4	[Cu^{2+}]	[H_2O_2]	Time	Power	
1	-1	-1	-1	-1	0	4	1	340	15.33
2	1	-1	-1	-1	0.5	4	1	340	14.49
3	-1	1	-1	-1	0	12	1	340	11.95
4	1	1	-1	-1	0.5	12	1	340	10.27
5	-1	-1	1	-1	0	4	8	340	13.56
6	1	-1	1	-1	0.5	4	8	340	10.42
7	-1	1	1	-1	0	12	8	340	14.49
8	1	1	1	-1	0.5	12	8	340	5.68
9	-1	-1	-1	1	0	4	1	680	16.51
10	1	-1	-1	1	0.5	4	1	680	13.21
11	-1	1	-1	1	0	12	1	680	15.23
12	1	1	-1	1	0.5	12	1	680	11.65
13	-1	-1	1	1	0	4	8	680	16.50
14	1	-1	1	1	0.5	4	8	680	10.93
15	-1	1	1	1	0	12	8	680	16.50
16	1	1	1	1	0.5	12	8	680	8.48

Table 3. Estimates and statistics of coefficients for residual phenolic compounds, (IF=1, σ_{bj} = 0.136)

Name	Coefficient	$t._{exp.}$	Significance (%)
b_0	12.825	94.29	< 0.01 ***
b_1	-2.184	-16.06	< 0.01 ***
b_2	-1.044	-7.68	0.15 **
b_3	-0.755	-5.55	0.52 **
b_4	0.801	5.89	0.42 **
b_{1-2}	-0.577	-4.24	1.32 *
b_{1-3}	-1.009	-7.42	0.18 **
b_{2-3}	0.261	1.92	12.74
b_{1-4}	-0.375	-2.76	5.10
b_{2-4}	0.383	2.82	4.80*
b_{3-4}	0.231	1.70	16.46
b_{1-2-3}	-0.438	-3.22	3.23*
b_{1-2-4}	0.236	1.74	15.77
b_{1-3-4}	0.170	1.25	27.94
b_{2-3-4}	-0.213	-1.57	19.24
$b_{1-2-3-4}$	0.166	1.22	28.93

*Significant at the level of 95%, **Significant at the level of 99%, ***Significant at the level of 99.9%, IF: Inflation factor, σ_{bj}: Standard deviation of bj, $t_{exp} = (bj/\sigma_{bj})$: t of Student
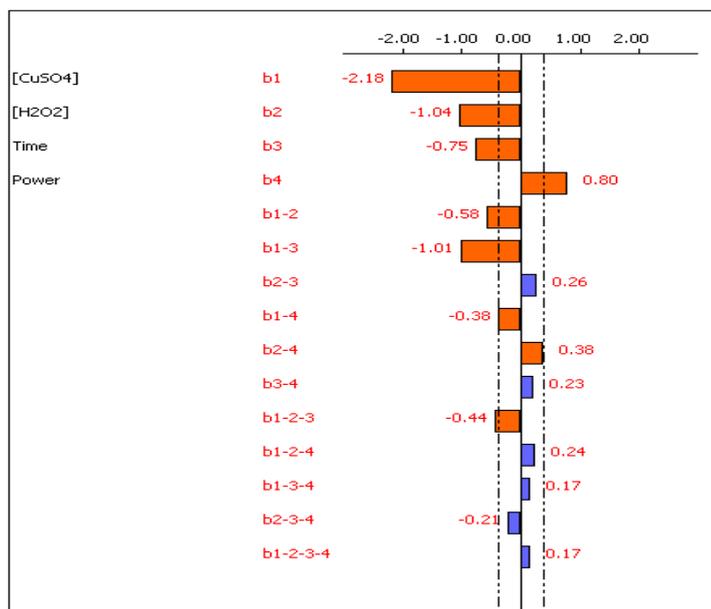
Fig. 1. Graphic study of the factor effects on the residual phenolic content

$$Y= b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 + b_{123}X_1X_2X_3 + b_{124}X_1X_2X_4 + b_{134}X_1X_3X_4 + b_{234}X_2X_3X_4 + b_{1234}X_1X_2X_3X_4 \quad (12)$$

3. Results and discussion

3.1. Statistical analysis

Experimental results given in Table 2 were processed using the Nemrodw software (Mathieu et al., 2007). It enabled to calculate the model coefficients and especially to identify the main effects of factors and the interactions between the factors that have significant influence on the response.

The standard deviation determined using the responses obtained in the domain center was 0.544 with 4 degrees of freedom. Estimated model coefficients and statistical analysis using t-test are given in Table 3. These coefficients values are represented in the effects plot shown in Fig. 1. This graphic shows both the magnitude and the importance of the effects. Statistical tools (Table 3 and Fig. 1) show that all the main effects were significant. It is found that the degradation of phenolic compounds presented a positive correlation with copper (X_1), peroxide dose (X_2) and exposition time (X_3) and negative correlation with irradiation power (X_4). The effects of the first-order interactions copper-peroxide (X_1X_2), copper-time (X_1X_3), peroxide-power (X_2X_4) and second order interaction copper-peroxide-time ($X_1X_2X_3$) were also significant. Significance levels of these effects were given in Table 3. In order to determine the experimental conditions maximizing the degradation of phenolic compounds, the influence of each interaction have to be studied (Figs. 2 and 3).

3.1.1. Interaction copper-peroxide (X_1X_2)

In order to evaluate the efficiency and the benefit of the catalytic process, degradation experiments were carried out with and without $CuSO_4$ under microwave irradiation. Fig. 2a shows the evolution of residual phenolic compounds as a function of Cu^{2+} and H_2O_2 dose. It can be observed an important improvement of the response in the presence of both compounds. In the absence of copper, H_2O_2 dose had a weak influence on the residual phenolic compounds. Contrarily, in the presence of copper, this response decreased for increasing H_2O_2 dose. The greatest diminution was found for Cu (II) = 0.5 g/L and [H_2O_2] =12 M, as reported in a previous work (Iboukhoulef et al., 2013).

The degradation of phenolic compounds was therefore clearly the result of the reaction between Cu (II) ion and hydrogen peroxide (Eqs. 1 and 2). Gallard et al. (1999) suggested that the decomposition of hydrogen peroxide in hydroxyl radical $^\bullet OH$ is catalyzed by transition metals such as iron or copper.

3.1.2. Interaction copper-time (X_1X_3)

The positive effect of copper was also proved in the interaction copper-time shown in Fig. 2b. Residual phenolic compounds did not vary with time in the absence of copper, while in the presence of copper, the response decreased when the time varied from 1 min to 8 min. From this interaction, the best reduction of phenolic compounds in OMW was found to be Cu (II) = 0.5 g/L and time= 8 min (Iboukhoulef et al., 2013).

3.1.3. Interaction peroxide-power (X_2X_4)

Fig. 2c shows that whatever the radiation power used, the phenolic content remaining in OMW decreased when the dose of hydrogen peroxide increased. Increasing the dosage of hydrogen peroxide would result in more production of hydroxyl radicals, which could enhance the oxidation capacity of the system, so that more organic compounds were eliminated. This augmentation was similar to the findings presented by Gulkaya et al. (2006), stating that increasing the dosage of H_2O_2 improved both the overall removal efficiency and the oxidation efficiency.

In addition, Fig. 2c indicated that, at low power, residual phenolic compounds were lower for 12 M dose of hydrogen peroxide. At high power, hydrogen peroxide decomposition into oxygen and water became very significant (Zhihui et al., 2005). This rapid decomposition at a high temperature is a common behavior in the Fenton Process leading to a decline in the overall efficiency. So the best reduction was found for [H_2O_2] = 12 M and power equal to 340W.

3.1.4. Interaction copper-peroxide-time ($X_1X_2X_3$)

The effects of the second-order interactions are usually negligible. However, when they are significant, two diagrams must be drawn for their interpretation. To analyze the interaction copper-peroxide-time, the first order interaction copper-peroxide for two different time periods (1 min and 8 min) must be therefore examined.

(a)

(b)

(c)
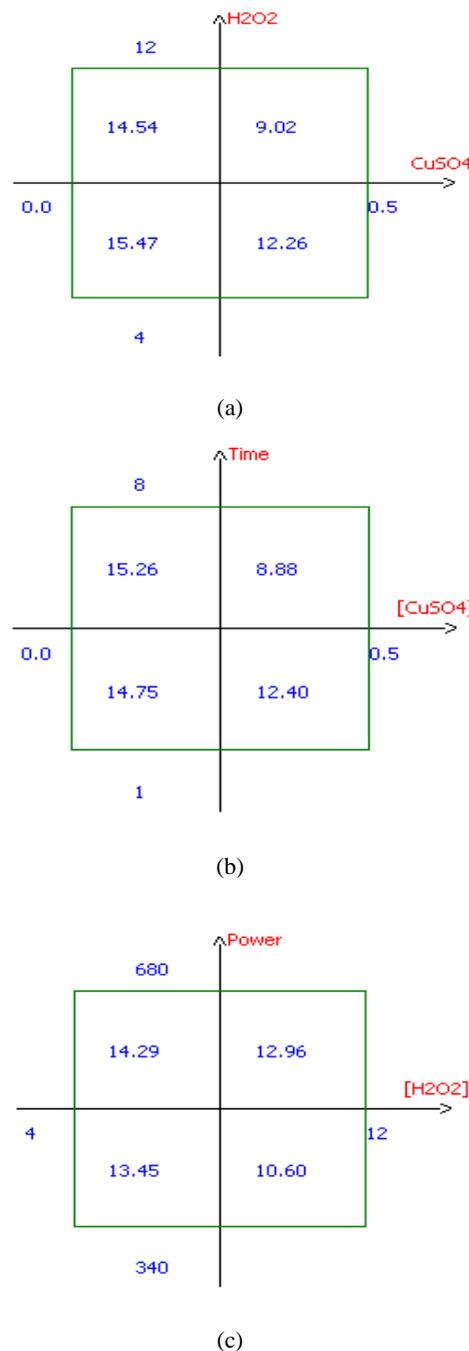
Fig. 2. Interactions copper-peroxide ($X_1 X_2$) (a), copper-time ($X_1 X_3$) (b) and power-peroxide ($X_2 X_4$) (c)

Figs. 3a and 3b show that the treatment was more effective in the presence of copper and when the dose level of hydrogen peroxide was at the high level. The hydroxyl radical is highly reactive to aromatic compounds (Bali and Karagozoglu, 2007). High doses of hydrogen peroxide mean a high production of hydroxyl radicals, which attack the unsaturated bonds of phenolic compounds and cause the ring opening; of course the presence of copper as catalyst is needed. In addition, increasing the Cu and the H_2O_2

concentrations, as well as the reaction time, improve the degree of degradation.

(a)

(b)
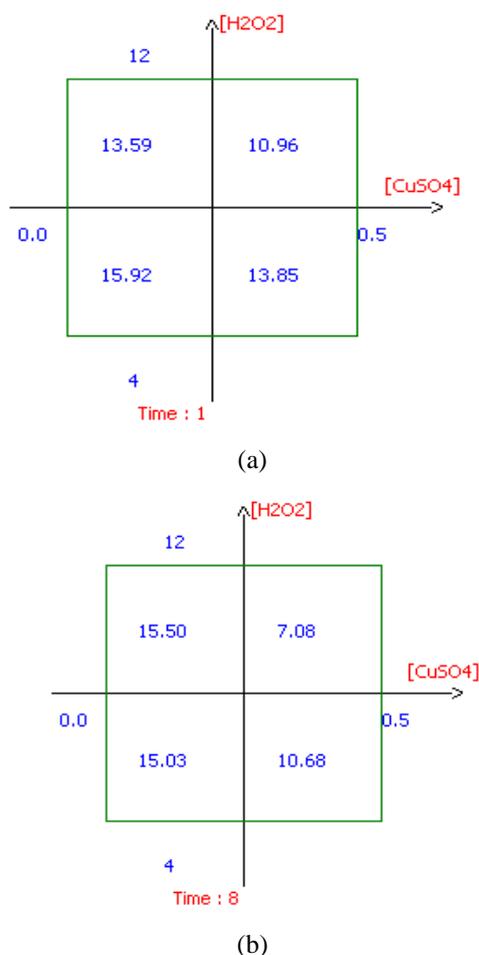
Fig. 3. Second-order interaction copper-peroxide-time: (a) time= 1 min; (b) time= 8 min

The highest removal of polyphenols was achieved for an H_2O_2 concentration of 12M, 8 min radiation time, in the presence of copper. In addition, taking the significant coefficients into consideration, the model explained the degradation of the phenols content:

$$Y= 12.825 - 2.184 \ X_1 - 1.044X_2 - 0.755X_3 + 0.801 \ X_4 - 0.577X_1X_2 - 1.009X_1X_3 - 0.375 \ X_1X_4 + 0.383 \ X_2X_4 - 0.438 \ X_1X_2X_3 \qquad (12)$$

One can also find the significant effects by using the normal half plot (Fig. 4). This figure gives the probability of the main effects and interaction effects of the model (Eq. 12). It clearly shows that the points ranging from 0.166 to 0.261 tended to form a straight line, suggesting that effects corresponding to these points were not significant. The remaining factors, showing estimated effects out of this straight line were consequently significant with different degrees of importance. This method, less powerful than the preceding one, gave an additional significant effect (b_{14}) which corresponded to the interaction between copper and power.
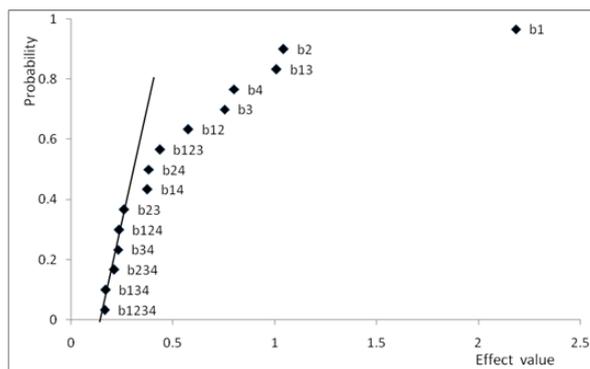
Fig. 4. Diagram of effects probability (normal half plot)

3.2. FTIR spectra of original and treated OMW

The FTIR spectra of original and treated OMW show a great similarity in some absorption bands, but with different intensities (Fig. 5).
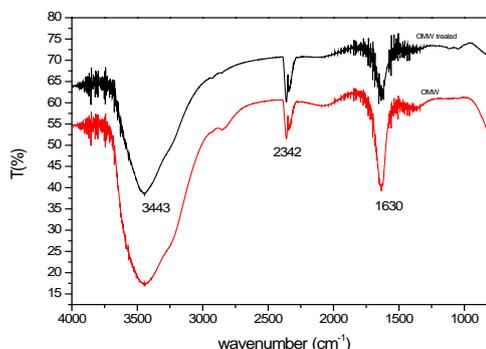
Fig. 5. FTIR spectrum for original and treated OMW

The principal absorption bands in the FTIR spectra were an intense broad band centred between 3450 and 3300cm^{-1} usually attributed to O–H stretching in carboxylic functions, and –H bonded O–H groups of phenols and N–H stretching in amide functions. These specified functions and compounds were abundant in OMW. A band at 2342 cm^{-1} corresponded to C-H stretching of methyl and methylene group of aliphatic chains. A peak near 1630 cm^{-1} reflects the absorption of several groups including aromatics C=C, C=O stretching of amide groups, ketones and/or quinones; and aliphatics (Hachicha et al., 2009).

4. Conclusions

The obtained results showed that the use of microwave radiation is a promising alternative to conventional treatment of OMWs. Indeed, a reduction of 73.3 % in phenolic compounds required about 5 min instead of 15 min for the traditional method. This new process consumed less energy and rejected in nature 218 g CO_2 /L of OMWs. This value was 238 times lower than that previously found using the conventional system.

References

Amarni F., Kadi H., (2010), Kinetics study of microwave-assisted solvent extraction of oil from olive cake using hexane Comparison with the conventional extraction, *Innovative Food Science and Emerging Technology*, **11**, 322-327.

Badawy M.I., Montaser Y., Ghaly T.A., Gad-Allah A., (2006), Advanced oxidation processes for the removal of organophosphorus.pesticides from wastewater, *Desalination*, **194**, 166-175.

Bali U., Karagozoglu B., (2007), Performance comparison of fenton process, ferric coagulation and $Cu(II)/pyridine/H_2O_2$ system for decolorization of Remazol-Turquoise Blue G-133, *Dyes and Pigments*, **74**, 73-80.

Beltran-Heredia J., Torregrosa J., Garcia J., (2001), Degradation of olive mill wastewater by the combination of Fenton's reagent and ozonation processes with an aerobic biological treatment, *Water Science and Technology*, **44**, 103-108.

Boudissa F., Kadi H., (2013), Transfer of phenolic compounds from olive mill wastewater to olive cake oil, *Journal of the American Oil Chemists' Society*, **90**, 717-723.

Cañizares P., Lobato J., Paz R., Rodrigo M.A., Sáez C., (2007), Advanced oxidation processes for the treatment of olive oil mills wastewater, *Chemosphere*, **67**, 832-838.

Catrinescu C., Teodosiu C., Macoveanu M., Miehe-Brendle J., Le Dred R., (2003), Catalytic wet peroxide oxidation of phenol over Fe-exchanged pillared beidellite, *Water Research*, **37**, 1154-1160.

Chatzisymeon E., Foteinis S., Mantzavinos D., Tsoutsos T., (2013), Life cycle assessment of advanced oxidation processes for olive mill Wastewater treatment, *Journal of Cleaner Production*, **54**, 229-234.

Cheriyan A.J., S. Feroz, Baawain M.S.A., Sarkar J.P., (2017), A study on the removal of contaminants from secondary treated municipal wastewater by solar photocatalysis, *Environmental Engineering and Management Journal*, **16**, 1451-1456.

Drouiche M., Mignot V.L., Lounici H., Belhocine D., Grib H., Pauss A., Mameri N.A., (2004), A compact process for the treatment of olive mill wastewater by combining UF and UV/H_2O_2 techniques, *Desalination*, **169**, 81-88.

El Hajjouji H., Barje F., Pinelli E., Bailly J.-R., Richard C., Winterton P., Revel J.-C., Hafidi M., (2008), Photochemical UV/TiO_2 treatment of olive mill wastewater (OMW), *Bioresource Technology*, **99**, 7264-7269.

Favier L., Simion A.I., Matei E., Grigoras C.-G., Kadmi Y., Bouzaza A., (2016), Photocatalytic oxidation of a hazardous phenolic compound over TiO_2 in a batch system, *Environmental Engineering and Management Journal*, **16**, 1059-1068.

Gallard H., de Laat J., Legube B., (1999), Comparative study of the rate of decomposition of H_2O_2 and of atrazine by $Fe(III)/H_2O_2$, $Cu(II)/H_2O_2$ and $Fe(III)/Cu(II)/H_2O_2$, *Revue des Sciences de l'Eau*, **12**, 713-728.

Gernjak W., Maldonado M.I., Malato S., Caceres J., Krutzler T., Glaser A., (2004), Pilot plant treatment of olive mill wastewater (OMW) by solar TiO_2 photocatalysis and solar photo-Fenton, *Solar Energy*, **77**, 567-572.

Ghiselli G., Jardim W.F., Litter M.I., Mansilla H.D., (2004), Destruction of EDTA using Fenton and photo-Fenton-like reactions under UV-A irradiation, *Journal of Photochemistry and Photobiology A: Chemistry*, **167**, 59-67.

Gomes H.T., Figueiredo J.L., Faria J.L., (2007), Catalytic wet air oxidation of olive mill wastewater, *Catalysis Today*, **124**, 254-259.

Goupy J., (1988), *Statistical Experimental Design* (in French), Dunod, Paris, France.

Gulkaya I., Surucu G.A., Dilek F.B., (2006), Importance of H_2O_2/Fe^{2+} ratio in Fenton's treatment of a carpet dyeing wastewater, *Journal of Hazardous Materials*, **B136**, 763-769.

Gutfinger T., (1981), Polyphenols in olive oils, *Journal of the American Oil Chemists' Society*, **58**, 966-968.

Hachicha S., Sellami F., Cegarra J., Hachicha R., Drira N., Medhioub K., Ammar E., (2009), Biological activity during co-composting of sludge issued from the OMW evaporation ponds with poultry manure. Physico-chemical characterization of the processed organic matter, *Journal of Hazardous Materials*, **162**, 402-409.

Iboukhoulef H., Amrane A., Kadi H., (2013), Microwave-enhanced Fenton-like system, $Cu(II)/H_2O_2$, for olive mill wastewater treatment, *Environmental Technology*, **34**, 853-860.

Karthikeyan S., Gopalakrishnan A.N., (2017), Effect of microwaves on photocatalytic degradation of phenol and cresols in a microwave-ultraviolet reactor, *Environmental Engineering and Management Journal*, **16**, 285-292.

Kim J.K., Martinez F., Metcalfe I.S., (2007), The beneficial role of use of ultrasound in heterogeneous Fenton-like system over supported copper catalysts for degradation of p-chlorophenol, *Catalysis Today*, **124**, 224-231.

Lai T.-L., Lee C.-C., Huang G.-L., Shu Y.-Y., Wang C.-B., (2008), Microwave-enhanced catalytic degradation of 4-chlorophenol over nickel oxides, *Applied Catalysis B: Environmental*, **78**, 151-157.

Liu Z.H., Du J., Tang J.-J., Li Z.-Q., Tao C.-Y., (2007), Microwave assisted $Cu2+-H_2O_2$ system for COD removal in landfill leachate, *Journal of Central South University of Technology*, **14**, 396-398.

Liu Z.H., Tao C.Y., Du J., Sun D.G., Li B.Z., (2008), Microwave-assisted Fenton-like decolorization of methyl orange solution using chromium compounds, *Journal of Chongqing University (English Edition)*, **7**, 165-170.

Martins R.C., Rossi A.F., Quinta-Ferreira R.M., (2010), Fenton's oxidation process for phenolic wastewater remediation and biodegradability enhancement, *Journal of Hazardous Materials*, **180**, 716-721.

Mathieu D., Nony J., Phan Tan- Luu R., (2007), *NemrodW Software*, LPRAI, Marseille, France.

Rivas F.J., Beltrán F.J., Gimeno O., Acedo B., (2001a), Wet air oxidation of wastewater from olive oil mills, *Chemical Engineering and Technology*, **24**, 415-421.

Rivas F.J., Gimeno O., Portela J.R., de la Ossa E.M., Beltrán F.J., (2001b), Super critical water oxidation of olive oil mill wastewater, *Industrial & Engineering Chemistry Research*, **40**, 3670-3674.

Santos A., Yustos P., Rodríguez S., Romero A., (2010), Mineralization lumping kinetic model for abatement of organic pollutants using Fenton's reagent, *Catalysis Today*, **151**, 89-93.

Ugürlu M., Kula I., (2007), Decolourization and removal of some organic compounds from olive mill wastewater by advanced oxidation processes and lime treatment, *Environmental Science and Pollution Research*, **14**, 319-325.

Yalili Kiliç M., Kiril Mert B., Kestioğlu K., (2009), Investigation of treatability of olive mill wastewater using Fenton process, *Uludağ Üniversitesi Mühendislik-Mimarlık Fakültesi Dergisi*, **14**, 23-29.

Yang Y., Wang P., Shi S., Liu Y., (2009), Microwave enhanced Fenton- like process for the treatment of high Concentration pharmaceutical wastewater, *Journal of Hazardous Materials*, **168**, 238-245.

Zhihui A., Peng Y., Xiaohua L., (2005), Degradation of 4-Chlorophenol by microwave irradiation enhanced advanced oxidation processes, *Chemosphere*, **60**, 824-827.