Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2019.23758

147 (2019) 143–155
April

Mineralization of olive mill wastewater under hydrothermal conditions

Çağlar Ersanli, Asli Yüksel Özşen*

Department of Chemical Engineering, Izmir Institute of Technology, Izmir, Turkey, Tel. +902327506609; emails: asliyuksel@iyte.edu.tr (A.Y. Özşen), caglarersanli@iyte.edu.tr (Ç. Ersanli)

Received 24 July 2018; Accepted 5 January 2019

ABSTRACT

Olive mill wastewater (OMW) is highly dangerous for land and aquatic environments because of its high phenolic content, acidity, and salinity. Hence, hydrothermal degradation of OMW in subcritical water medium with and without using external oxidizer (H_2O_2) was studied to decrease its total organic carbon (TOC), total phenolic content (TPC), and color. Effects of reaction temperature (150°C–250°C), reaction time (30–120 min), and H_2O_2 content (0–100 mM) on TOC and TPC of OMW were investigated. Box-Behnken-type experimental design and statistical analysis (analysis of variance) were practiced by Design Expert 11. According to statistical analysis, effect of reaction temperature significantly affected TOC removal efficiency. The best TOC reduction (31.65%) was achieved without using H_2O_2 at 250°C for 120 min.

Keywords: Olive mill wastewater; Subcritical water; Hydrothermal reaction; Mineralization

1. Introduction

Olive oil industry has a great significance in economy of Mediterranean countries such as Spain, Italy, and Turkey. According to 2017 statistics of Food and Agriculture Organization of the United Nations, Spain is the biggest producer of olive oil and has about one million tons of annual production rate. Italy, Greece, Tunisia, Syrian Arab Republic, and Turkey follow Spain [1]. While olives are extracted with either two-phase or three-phase systems to produce olive oil, the dark red to black, liquid-phase waste, which has color value between 52 and 180 g L^{-1} Pt-Co unit is generated and named as olive mill wastewater (OMW) [2].

Characteristics of OMW depend on the many factors such as climate, quality of olives, time, place of the storage, and types of olive oil extraction (two- or three-phase extraction). OMW is a cleavable effluent due to its high amount of total organic carbon (TOC), chemical oxygen demand (COD), and biological oxygen demand (BOD) concentrations [3].TOC concentration of OMW varies between 15 and 50 g L^{-1}, COD concentration is up to 220 g $L^{-1,}$ and the ratio of COD to BOD is in the range of 2.5 and 5. Furthermore, OMW is quite acidic with a range of 3 and 5.9 [4].

OMW includes 80–85 wt.% of water, 14–18 wt.% of organic compounds, and 1–2 wt.% of organic salts. Sugars (18 wt.%), nitrogen compounds (0.524 wt.%), organic acids (0.515 wt.%), fats (0.021 wt.%), phenols, and pectins (11.5 wt.%) are examples of fractions of organic compounds in OMW [5]. High amount of phenolic compounds which are simple phenols and polyphenols are extremely dangerous for herbs and microorganisms due to the toxicity existing in OMW is in a range of 0.5–24 g L^{-1} [6]. Cinnamic acid, benzoic acid, and β-3,4-dihydrocyphenylethanol are three major types of phenolic substances present in OMW [7].

There are no legal regulations about the waste treatment of OMW in countries. Wastewater of olive oil industries is generally sent to the storage ponds and waited until all OMW evaporates. Hence, in literature, a lot of studies about OMW treatment have been proposed. Generally, the processes of OMW treatment are classified as physical, physicochemical, biological, thermochemical, hydrothermal, and membrane processes in studies.

---

* Corresponding author.

1944-3994/1944-3986

Several aerobic [8] and anaerobic [9,10] digestion processes have been performed in the field of biological OMW treatment. In these studies, inhibition effect of highly organic compounds (mainly phenolic substances) on the anaerobic digestion efficiency was observed. On the other hand, physical treatments such as dilution, evaporation, centrifugation, sedimentation, and filtration are not sufficient to reduce the total organic content of OMW itself. Thus, these processes are generally combined to get higher reduction rates of total organic content.

One of the studied treatment processes about OMW is thermochemical processes. The principle of these types of processes is to transform the biomass into the chemical compounds and energy by using the heat as energy source. Pyrolysis, gasification, and liquefaction are the three subclasses of thermochemical conversion processes [11]. The main scope of thermochemical treatment of wastewaters is to reduce the pollution and convert the biofuels to valuable energy sources. In this manner, Taralas et al. treated mixture of concentrated liquid (OMW) and solid (kernels) wastes of olive oil production industry thermochemically. In their study, particle sizes of solid wastes and moisture content were the reaction parameters. Oxygen, air, and steam were used as carrier gas, and hydrogen, carbon monoxide, and carbon dioxide were found as released main gaseous products of the pyrolysis reactions [12]. Tosti et al. catalytically reformed first filtered and then concentrated OMW via membrane reactor which was comprised of Pd-Ag permeator tubes filled with Pt/Al_2O_3 catalyst bed in order to generate hydrogen gas. In this process, they used OMW as feed of membrane reactor and almost 90% of TOC and phenolic content reduction were achieved [13]. In 2016, same group treated OMW with combined reforming of OMW and methane by using Pd membrane and Pt-based catalyst, and the similar yield of hydrogen production was obtained with reforming of OMW alone. Besides, addition of methane to the reforming process has not shown any effect on the reduction of pollution [14]. Casanovas et al. applied catalytic steam reforming process of OMW for hydrogen production by using catalytic honeycombs which were impregnated with several metals such as Pt, Ru, Rh, Pd, and Ni and functionalized with La-stabilized ceria as support. Pt- and Rh-based catalytic systems gave best results of the study, and about 90%–96% of TOC reduction was achieved [15].

Hydrothermal treatment technologies are generally categorized into two major groups. One of them is oxidative technologies which mainly consist of oxidation processes at elevated temperatures (usually higher than 200°C) and the other one is nonoxidative technologies such as thermal hydrolysis processes which occur at a lower temperature ranges (100°C–200°C) than oxidation processes.

Oxidation processes such as wet air oxidation (WAO), catalytic WAO, Fenton oxidation, and sub/supercritical fluid oxidation have been getting attendance among these types of treatment processes due to the high degree of organic content reduction of wastewaters by oxidizing agents like hydrogen peroxide and ozone. Thus, these chemicals might break up the organic compounds and lead to treatment of wastewaters.

WAO is generally defined as the oxidation of inorganic and/or organic compounds in suspension or aqueous solution in the presence of oxygen or air at high temperatures and pressures with or without catalysts [16]. For these processes, typical temperature range is between 150°C and 320°C and pressure range is between 20 and 150 bar [17]. This type of treatment process has advantage to the treatment of liquid-phase wastes, sludge, or slurries which have the higher organic content concentration when compared with water. The other advantage is that there is no generation of dioxins, fly ash, furans, and sulfur dioxides at the end of the process [18]. Besides, WAO processes are able to nearly complete conversion of toxic and harmful organic substances into the harmless end products. Main principle of these processes is the formation of free hydroxyl radicals to destroy the bigger organic substances. In one study, Rivas et al. applied supercritical WAO to OMW and achieved 79% of both TOC and COD reductions and also almost complete phenolic content reduction [19]. In other study, Rivas et al. reached 50% of COD reduction by subcritical water WAO [20]. By using solar photo-Fenton process, 90% of TOC and 99% of phenolic content removals of OMW were observed [21]. OMW degradation and the optimization of reaction parameters were studied via Fenton oxidation by using batch type and continuous stirred-tank reactor reactors. Approximately 45% of TOC reduction was observed by researchers [22]. Ozonation is also applied as an oxidative treatment for the degradation of OMW in literature. By using the combination of ultrafiltration and ozonation, 20% of COD and 93% of total phenolic content (TPC) reductions of OMW were achieved [23].

The term of hydrothermal reaction has been defined by Byrappa and Yoshimura [24]. Accordingly, in the presence of aqueous or nonaqueous solvent, any heterogeneous chemical reaction in a closed system at the reaction temperature that is higher than room temperature and under the reaction pressure, which is above 1 atm, can be called as hydrothermal reaction. Water plays a key role for hydrothermal reaction due to its high reactivity at higher temperatures. This type of characteristic of water leads to break the chemical bonds of complex organic molecules and convert these molecules to the simpler molecules which is known as hydrolysis reaction [25].

The WAO processes usually comprise a few hydrolysis and oxidation reactions in series which are capable to degrade initial complex molecules to the harmless simpler structures. In this way, there are two possibilities as complete degradation or in another word complete mineralization and partial mineralization. Generally, carbon dioxide and water vapor are the final products of complete mineralization while organic acids are the final products of the partial mineralization which can be followed by representative reaction mechanism below.

$$\text{Complex Organic Molecules} + O_2 \rightarrow CO_2 + H_2O + RCOOH^* \quad (1)$$

where RCOOH* is the organic acid which has short chains such as acetic acid and constitutes the main fraction of residual organic substances after partial mineralization.

In this study, subcritical water oxidation of OMW was applied via using water content in OMW as a reaction medium by modifying reaction temperature and pressure. As a result, created reaction environment, called ‘subcritical water’, acts as an excellent solvent for organic compounds.

The dielectric constant of subcritical water is much lower, and the number of hydrogen bonds is diminished [26]. Additionally, subcritical water has three orders of magnitude higher ion product or dissociation constant (Kw) than ambient liquid water since it approaches the critical point. Under these conditions, water can also boast a higher H^+ and OH^- ion concentrations than liquid water under certain conditions [27,28]. By using the advantages of subcritical water as a reaction medium, it was aimed to understand the effects of the reaction temperature, reaction time, and the amount of external oxidizer on the removal efficiency of TOC, color, and TPC from OMW.

2. Materials and methods

2.1. Materials

The OMW used in this study was obtained from Foça/İzmir which is the western side of Turkey. Other materials and chemicals used in this study are as follows: Folin-Ciocalteu reagent (Merck, USA), gallic acid (Merck, USA), sodium carbonate (Sigma Aldrich, Germany), and hydrogen peroxide (30% purity, Sigma Aldrich, Germany).

2.2. Experimental method

Hydrothermal reactions in the subcritical medium were carried out in a batch reactor (Parr 5500 High-Pressure Compact Reactor). The reactor was made of stainless steel (T-316) with a volume of 300 mL. The maximum temperature and pressure of the reactor are 350°C and 3,000 psi, respectively. In addition, the representative reaction temperature and pressure profile can be investigated from Fig. 1.The schematic diagram of the reactor is given in Fig. 2.

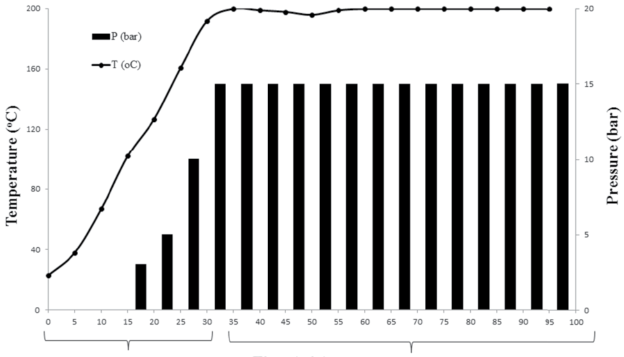

Fig. 1. Temperature-pressure profile (200°C, 15 bar, 60 min): (a) heating step and (b) reaction.

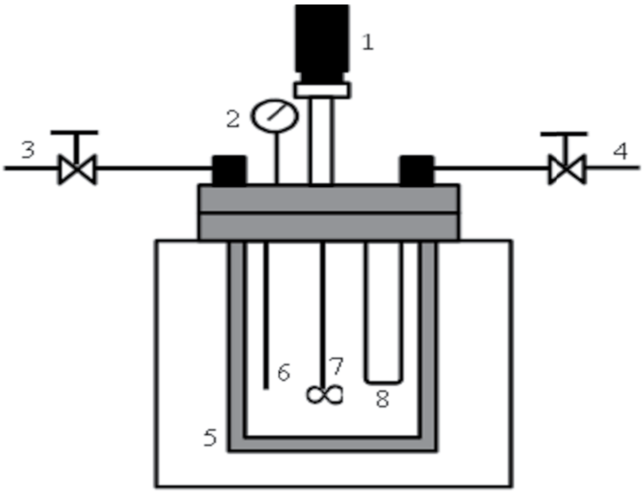

Fig. 2. Schematic diagram of high-pressure batch reactor: (1) magnetic stirrer driver, (2) pressure gage, (3) gas outlet valve, (4) gas inlet valve, (5) stainless steel beaker, (6) thermocouple, (7) stirring impeller, and (8) U-tube heat exchanger.

As a reaction solution, 100 mL of OMW was placed into the reaction vessel. For the experiments with an external oxidizer, 50 or 100 mM of hydrogen peroxide (H_2O_2) was used. Then reaction vessel was placed in the reactor, and all the pins were tightened to prevent any pressure loss. Afterward, the reactor was purged with an inert gas (nitrogen) for 5 min to remove oxygen remained in the reactor. Next, the temperature was set to desired reaction temperature (150°C, 200°C or 250°C), and the reaction mixture was continuously stirred with a magnetic stirrer. The reactions were carried out for a certain reaction time (30, 60, 90, and 120 min). When the reaction was completed, the reactor was cooled by an internal cooler until 40°C–50°C, and then the pins were opened to collect the liquid product. The liquid product solution was filtered through a filter paper to remove solid particles. Almost no solid particles were observed after experiments. After this, pH of the solution was measured, and the liquid product was analyzed by TOC and gas chromatography-mass spectrophotometer (GC-MS). TPC was determined by Folin's method. The mineralization rate of OMW was calculated in terms of TOC reduction. Since, TOC is specific to organic substances and theoretically measures all covalent bonded carbon atoms in water and also because of its detection capability in the parts-per-billion range, TOC is highly sensitive method to understand the degree of mineralization of OMW. The related equation is given below:

$$\text{TOC Reduction}(\%) = \frac{\text{TOC}(0) - \text{TOC}(t)}{\text{TOC}(0)} \times 100 \tag{2}$$

where TOC (0) is the initial TOC value and TOC (t) is the TOC value of the product solution. Initial TOC values of treated OMW were changing by the time while waiting in dark environment. Therefore, reduction percentages of each experiment were evaluated with its own initial TOC concentration, which was around 34,000 mg L^{-1} after every experiment.

2.3. Product analysis

TOC (Shimadzu, TOC-Vcph, Japan) analysis was carried out to evaluate the mineralization rate of OMW. In order to understand possible secondary pollutants, which might be formed during the hydrothermal reactions, and to identify the fractions of OMW and mineralization products, GC-MS (Agilent Technologies, 6,890–5,973 N Network, USA) analysis

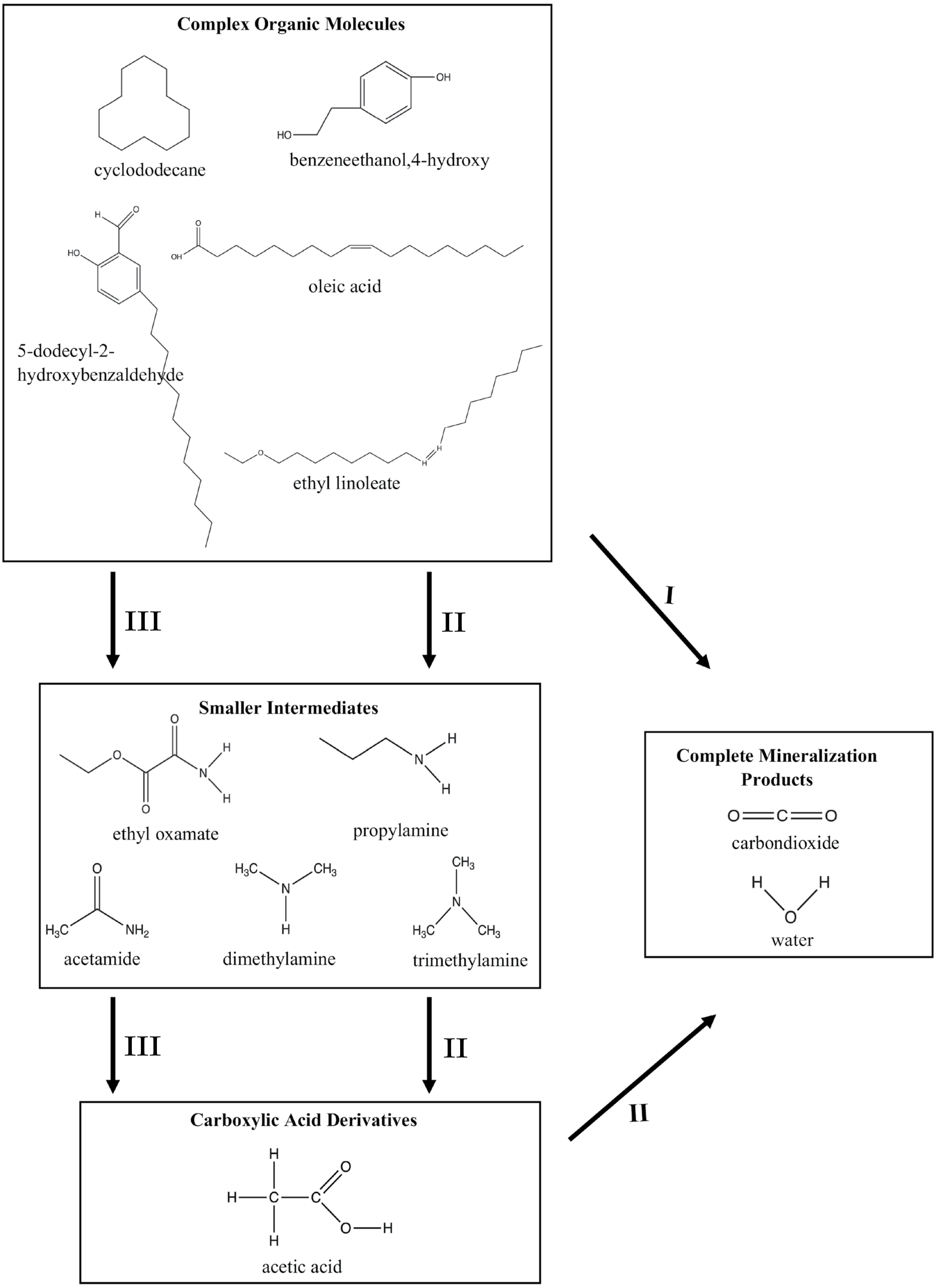

Fig. 3. Scheme of mineralization paths using molecular structure representation.

was performed. The color change was examined qualitatively by taking photographs of raw material and products. Folin-Ciocalteu method was used to evaluate the TPC of liquid products.

3. Results and discussion

OMW was mineralized at varying reaction temperatures (150°C, 200°C, and 250°C) and reaction durations (30, 60, 90, and 120 min) and with an external oxidizer (H_2O_2) with concentrations of 0, 50, and 100 mM in subcritical water medium. In order to keep water in subcritical region, the pressure of system was set as 5, 15, and 40 bars for 150°C, 200°C, and 250°C reaction temperatures, respectively.

One of the most fundamental reaction parameters affecting the reduction efficiency of OMW is reaction temperature. Hence, physicochemical properties of water in subcritical medium are influenced by increasing reaction temperature [29]. Viscosity, dielectric constant, and surface tension of water decrease with increasing temperature in subcritical region [30]. The dissociation constant of water is three orders of magnitude higher than ambient water [31]. This situation contributes to the high reactivity of subcritical water with organic compounds. Moreover, presence of the subcritical water leads to increase in mass transfer rate of reaction [29].

Lower pH values or in another words acidic media increased the degradation rate of complex molecules into the smaller intermediates [32]. Since the pH value of the OMW used in this study varies between 4 and 5, pH adjustment was not required.

Mineralization of complex molecules can be classified into three different routes [33] that are shown in Fig. 3. Complex molecules can directly be converted into complete mineralization products of CO_2 and H_2O (Path I). In another way, first, they are broken into smaller molecules, then transformed to carboxylic acid derivatives such as acetic acid, and finally converted into complete mineralization products (Path II). In the third option, these molecules are converted into stable intermediates like carboxylic acid derivatives (Path III). Paths I and II describe the total mineralization, and path III describes the partial mineralization.

3.1. Reactions without external oxidizer

In this study, both reaction temperature and reaction duration had significant effect on TOC reductions as can be seen in Fig. 4. In the view of temperature change, it can be said that TOC removal rates increased with increasing reaction temperature. For instance, after 90 min of reaction time, 10.51% and 20.26% of TOC removals were obtained with 150°C and 250°C reactions, respectively. On the other side, TOC reductions also increased with increasing reaction time. TOC reductions of 24.34% and 31.65% were obtained at 250°C after 30 and 120 min, respectively.

In literature, Daneshvar et al. revealed that TOC removal percentage of textile dye (acid orange 7) increased with increasing reaction temperature and reaction time in subcritical water medium without using any external oxidizer [34]. According to their study, the highest TOC removals were obtained with the reaction temperatures equal or higher than 120°C.

The plot of TOC reduction rates with respect to reaction time for all reaction temperatures was divided in two regions according to increment of the reduction rates. In region I, there is a sharp increase of TOC removal percentages due to the rapid decomposition of large organic substances which exist in OMW such as propanoic acid, butanoic acid, etc. and can be investigated by Fig. 5 and Table 1. Some of these substances may be converted to final mineralization products (CO_2 and H_2O), and some of them may be converted to the smaller structures like carboxylic acid derivatives.

Slight changes for TOC removals were observed in region II. The main reason is the slow removal of easily oxidized molecules and decomposition of more refractory molecules into the most refractory molecules like carboxylic acids [35]. Gomes et al. observed same situation in their catalytic WAO studies of OMW [33]. Refractory substances are more sensitive to oxidation [36]. In this study, it was analyzed that acetic acid was the final product for all experiments as can be seen in Fig. 6. Therefore, inhibition effect was determined, and up to 32% of TOC reduction rates were achieved due to the generated acetic acid which is the highly stable molecule with respect to temperature and has low molecular weight. In summary, acetic acid is made up the major fraction of organic residues in treated OMWs. The toxicity of the OMW was decreased because acetic acid has short chain and less toxic than large organic compounds. Additionally, by GC-MS analysis, control of the possible generation of secondary pollutants was examined, and it can be clearly shown that during reactions, there was no generation of secondary pollutants. Furthermore, partial mineralization occurred since acetic acid is a derivative of carboxylic acid. As explained before, complex substances are transferred into these derivatives if partial mineralization is observed (Path III in Fig. 3).

Color is another effective parameter to understand the degree of mineralization. Effect of reaction temperature and time can clearly be seen in product pictures given as Fig. 7. As reaction proceeded at high temperatures for longer reaction times, the decolorization was increased. This trend can be explained with physicochemical properties of water in subcritical region at different temperatures. The highest decolorization was observed at 250°C and 120 min of reaction time. Similarly, Wu and Yu showed that color of C.I. Reactive Red 2 dye was reduced with increasing reaction temperature by both ultraviolet (UV)/TiO_2 and ultrasound/TiO_2 systems [37]. Besides, Georgiou et al. observed that after a short reaction time of 10 min, more than 50% of color reduction of azo-reactive dye could be achieved by UV irradiation of dye in the presence of hydrogen peroxide [38].

TPC of raw OMW and products was examined with Folin-Ciocalteu method by using UV spectrophotometer at 725 nm. Results were represented in gallic acid equivalent (GAE). The change in TPC of OMW with respect to several reaction temperatures and times is shown in Fig. 8. In this study, rising reaction temperature and time have a significant effect on TPC reduction as also found in literature. The TPC removal of OMW was obtained by WAO method and increased with increasing reaction parameters such as reaction temperature, reaction time, and contact time [39]. The TPC of raw OMW used in our study was 74.73 mg GAE L^{-1}. The highest TPC reduction achieved at 250°C reaction temperature was 51.24%, while it was 31.12% for 150°C.

In addition, when reaction time was increased from 30 to 90 min, TPC removal efficiency was increased from 20.7% to 27.4%, respectively.

3.2. Reactions with external oxidizer

Hydrogen peroxide (H_2O_2) was used as an external oxidizer in this study. H_2O_2 dissociates into H_2O and O_2 at room temperature and pressure. During this dissociation of H_2O_2, high degree of reactive hydroxyl radicals ($OH^\bullet$) are generated. Then these free radicals attack the H_2O_2 molecules rapidly. After this attack, less reactive hydroperoxide ($HO_2^\bullet$) radicals are produced as shown in reactions from (3) to (6) [40–44].

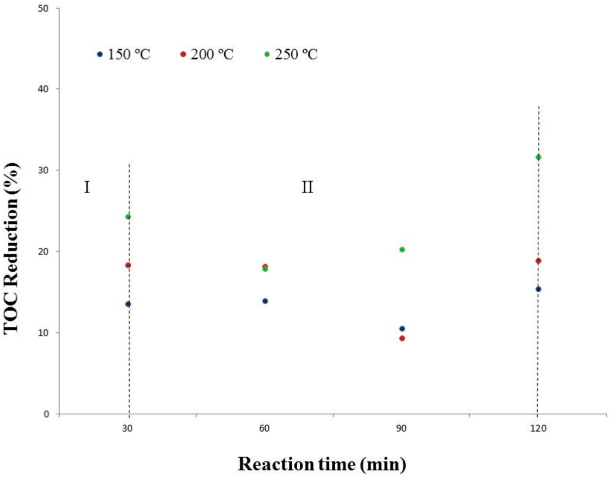

Fig. 4. The variations of TOC concentrations with respect to reaction time for reactions without using H_2O_2 at 150°C, 200°C, and 250°C with corresponding pressure values of 5, 15, and 40 bar.

$$H_2O_2 + HO^\bullet \rightarrow HO_2^\bullet + H_2O \quad (3)$$

$$H_2O_2 + HO^\bullet \rightarrow O_2^{\bullet-} + H^+ + H_2O \quad (4)$$

$$HO^\bullet + HO^\bullet \rightarrow H_2O_2 \quad (5)$$

$$HO^\bullet + HO_2^\bullet \rightarrow H_2O + O_2 \quad (6)$$

The highest TOC and color removals were observed at 250°C reaction temperature and also at 120 min reaction times that can be seen in Figs. 9 and 10.

In this study, shorter reaction times led to lowest degradation rates of OMW. At a reaction temperature of 150°C and by using 50 mM H_2O_2, the TOC reductions were 19.1% and 7.14% after 120 and 30 min, respectively. Because, highly reactive hydroxyl radicals ($OH^\bullet$) generated at 30 min reaction time was insufficient to attack to the complex organic substances exist in OMW. So, it is possible to say that shorter reaction times led to lowest degradation rates of OMW.

Rate of generation of hydroxyl free radicals ($OH^\bullet$) is proportional to H_2O_2 concentration. These radicals are highly reactive and can attack the complex compounds. Thus, degradation rate increases with higher generation rates of $OH^\bullet$ radicals. Unfortunately, hydroxyl radicals have quite limited lifetime, and they quickly reach equilibrium with H_2O_2. In this case, H_2O_2 is rather used and $OH^\bullet$ radicals react with H_2O_2 and also generation of less reactive $HO_2^\bullet$ radicals is observed, which explains the trend in TOC and color reduction of OMW in the presence of H_2O_2 [45].

On the other hand, H_2O_2 decomposes to free radicals with increasing temperature, and higher temperatures can activate $OH^\bullet$ radicals without using any activator as given below.

$$H_2O_2 \rightarrow HO^\bullet + HO^- \quad (7)$$

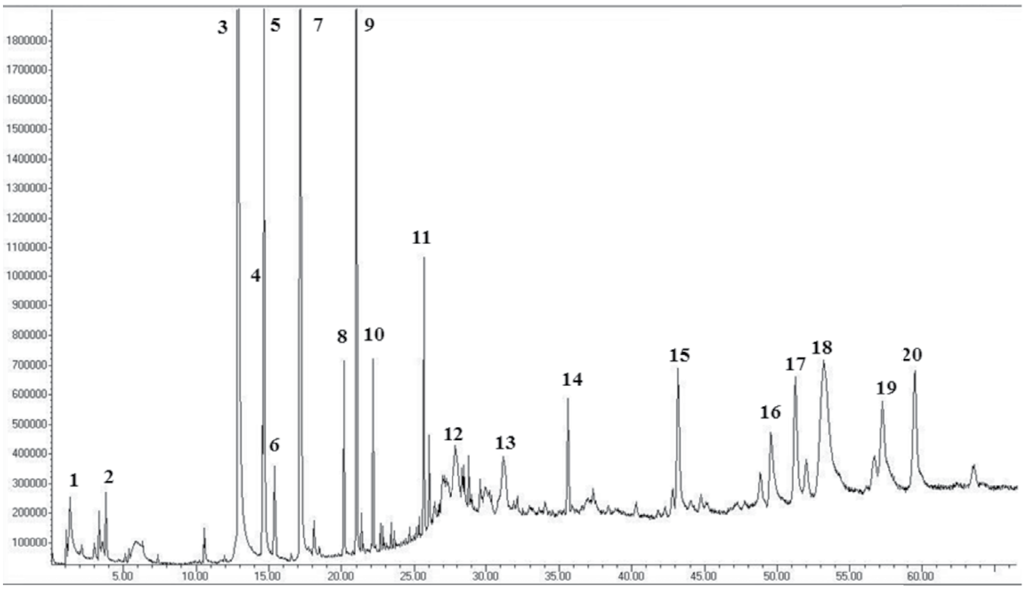

Fig. 5. GC-MS spectrum of raw OMW.

Table 1
List of main compounds in GC-MS spectrum of raw OMW

Peak number	Retention time (min)	Chemical formula	Molecular weight (g mol^{-1})	Common name
1	1.33	C_2H_4O	44.05	Ethylene oxide
2	3.80	C_2H_6O	46.07	Ethanol
3	12.85	CH_3COOH	60.05	Acetic acid
4	14.58	$C_4H_{10}O_2$	90.12	2,3-Butanediol
5	14.66	$C_3H_6O_2$	74.08	Propanoic acid
6	15.37	$C_4H_8O_2$	88.11	Isobutyric acid
7	17.15	$C_4H_8O_2$	88.11	Butanoic acid
8	20.16	$C_5H_{10}O_2$	102.13	Pentanoic acid
9	21.02	C_3H_6O	58.08	Propylene oxide
10	22.16	$C_6H_{12}O_2$	116.16	Hexanoic acid
11	25.64	$C_7H_{12}O_2$	128.17	Cyclohexanecarboxylic acid
12	27.89	$C_{20}H_{36}O_2$	308.51	Ethyl linoleate
13	31.18	$C_{12}H_{24}$	168.32	Cyclododecane
14	35.62	$C_{19}H_{30}O_2$	290.45	5-Dodecyl-2-hydroxybenzaldehyde
15	43.18	$C_7H_{10}O_2$	126.16	1,3-Cyclohexanedione, 2-methyl
16	49.59	$C_7H_{14}O_3$	146.18	Pentanoic acid, 5-methoxy-, methyl ester
17	51.26	$C_8H_{12}O_2$	140.18	Benzeneethanol
18	53.21	$C_8H_{16}NO_5P$	237.19	Dicrotophos
19	57.23	$C_{10}H_{20}O_5$	220.27	15-Crown-5
20	59.52	$C_{18}H_{34}O_2$	282.47	Oleic acid

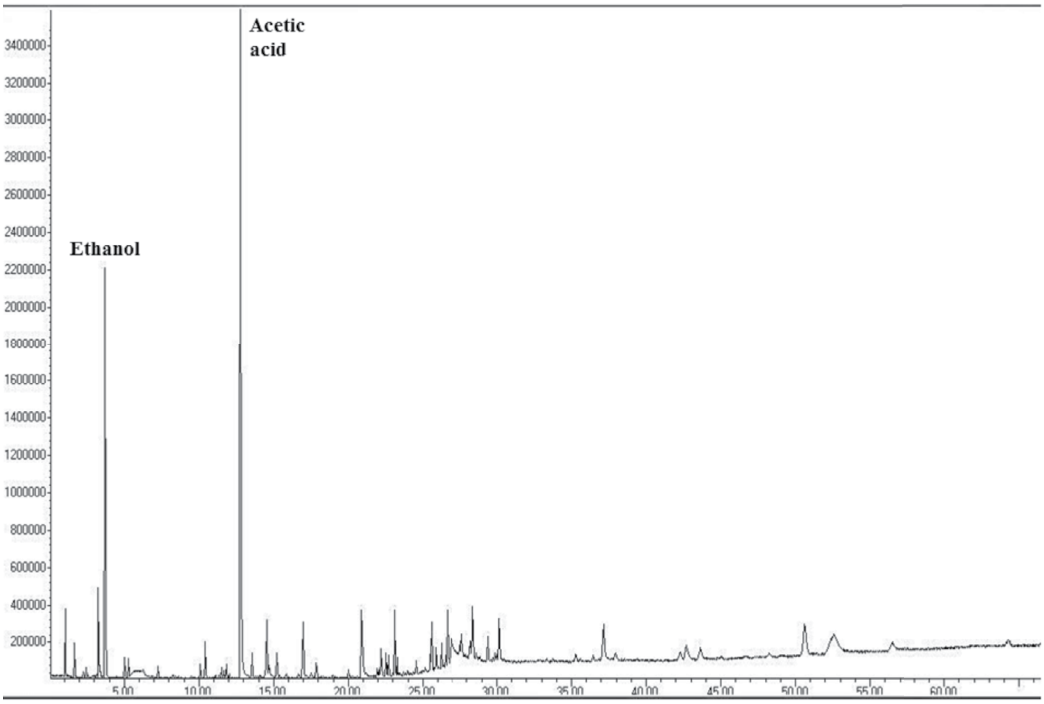

Fig. 6. GC-MS spectrum of treated OMW with 120 min reaction time at 250°C, 40 bar without using H_2O_2.

At 250°C, both TOC and color removals were higher than that at 150°C. With the addition of 100 mM H_2O_2, TOC rate was recorded as 5.6% for 30 min reaction time at 150°C. When temperature was increased to 250°C while keeping the other conditions same, the percentage of TOC removal increased to 24.25%. Similarly, Daskalaki et al. observed lowest degree of TOC removal of Reactive Red 120 in the presence of H_2O_2 due to the initially slow degradation of H_2O_2 at the lowest reaction temperatures [46]. Rezaee et al. and Laszlo revealed the competition among the hydroxyl free radicals. When high

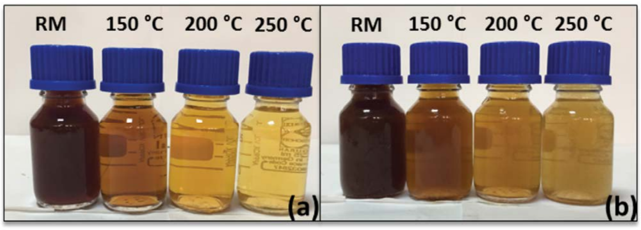

Fig. 7. Pictures of raw material (RM) and products after treatment at 150°C, 200°C, and 250°C (with no H_2O_2) with corresponding pressure values of 5, 15, and 40 bar at different reaction times of (a) 30 min and (b) 120 min.

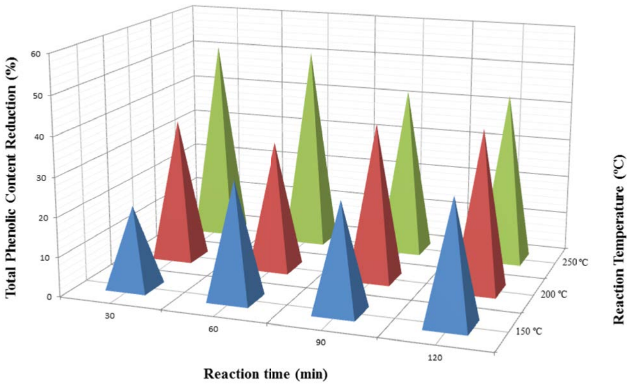

Fig. 8. Total phenolic content reduction of OMW at various reaction temperatures (150°C–250°C) with corresponding pressure values of 5–40 bar and reaction times (30–120 min) without using H_2O_2.

amount of H_2O_2 was used than optimal level, it causes lower degree of degradation rates [47].

H_2O_2 did not affect the reduction of TPC of OMW, significantly as shown in Table 2. The TPC of raw OMW was 74.73 mg GAE L^{-1}. At 250°C and 30 min, for instance, TPC removal of OMW with reactions were 42.17%, 41.71%, and 40.93% by using 0, 50, and 100 mM of H_2O_2, respectively.

There were no secondary pollutants observed during the hydrothermal reactions of OMW by using H_2O_2 as shown in Fig. 11. According to GC-MS spectrum of OMW at 150°C and 120 min, peak areas of acetic acid increased when using H_2O_2 in the reaction. The percentage of peak area of acetic acid (second peak) increased from 48% to 59% when H_2O_2 was added (100 mM) to the solution. Furthermore, hydrogen peroxide content did not significantly affect the concentration of other substances. For instance, at 150°C, the percentage of ethanol (first peak) was 5.72% and 4.43% with 50 and 100 mM H_2O_2, respectively. In addition, acetic acid is also the main organic residue in treated OMW like reactions without using H_2O_2. Therefore, inhibition effect and partial mineralization by the generation and presence of acetic acid can still be mentioned.

3.3. Statistical analysis

In this study, effects of reaction parameters which are reaction temperature, reaction time, and the concentration of

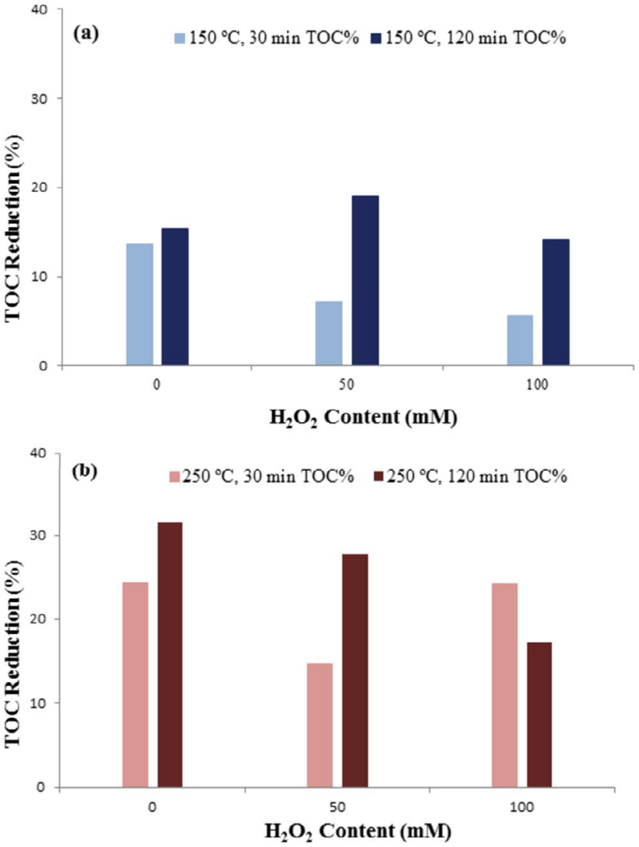

Fig. 9. Effect of H_2O_2 concentration on TOC removal rate at 30 and 120 min reaction times; (a) at 150°C, 5 bar and (b) at 250°C, 40 bar.

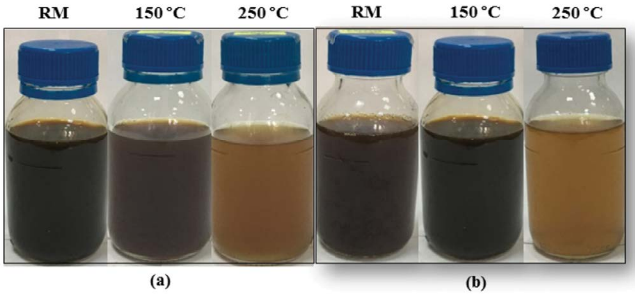

Fig. 10. Qualitative analysis of raw material and products of 120 min reactions at 150°C, 5 bar and 250°C, 40 bar with (a) 50 mM H_2O_2 and (b) 100 mM H_2O_2.

external oxidizer (H_2O_2) on the TOC reduction rate were evaluated and validated via three levels and three-factorial Box-Behnken-type response surface method. TOC was preferred to understand the effects of reaction parameters due to its specificity and detection capability for covalent bonded carbon atoms. In this manner, Box-Behnken design and other response surface design types such as three-level factorial and central composite designs were compared, and Box-Behnken design was found more effective than the other types. The results of the experimental design were evaluated by using Design

Table 2
Concentration of phenolic compounds in OMW at 150°C, 5 bar, and 250°C, 40 bar reaction temperatures, 30 and 120 min reaction times, and using various amount of H_2O_2 (0, 50, and 100 mM)

Reaction temperature (°C)	Reaction time (min)	H_2O_2 concentration (mM)	Total phenolic content (mg GAE L^{-1})
150	30	0	46.36
		50	53.18
		100	40.00
	120	0	51.47
		50	41.55
		100	39.38
250	30	0	36.43
		50	39.53
		100	41.40
	120	0	42.17
		50	41.71
		100	40.93

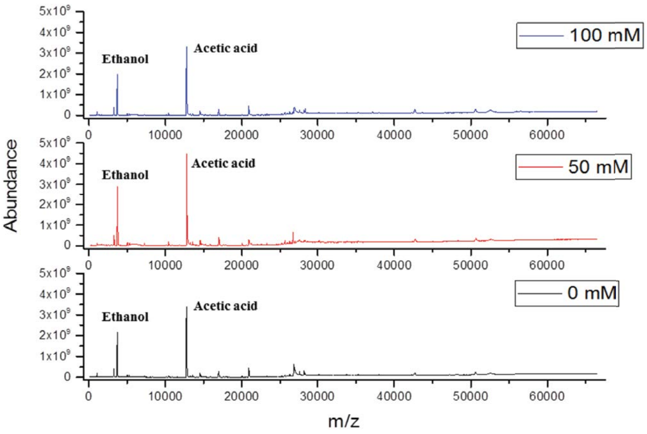

Fig. 11. GC-MS spectrum of treated OMW at 150°C, 5 bar, and 120 min with 0, 50, and 100 mM H_2O_2.

Table 3
Box-Behnken experimental design

Std	Run	Factor 1 A: temperature	Factor 2 B: Time	Factor 3 C: H_2O_2	Response TOC%
10	1	200	120	0	18.88
6	2	250	75	0	18.68
9	3	200	30	0	18.35
12	4	250	120	100	18.23
16	5	200	75	50	15.71
14	6	200	75	50	13.8
4	7	250	120	50	27.84
13	8	200	75	50	15.85
1	9	150	30	50	7.14
3	10	150	120	50	19.1
7	11	150	30	100	5.6
2	12	250	30	50	14.65
8	13	250	30	100	24.25
17	14	200	75	50	15.6
5	15	150	75	0	13.92
15	16	200	75	50	15.4
11	17	250	30	100	24.1

Expert version 11 (trial version). The experimental design of the study was given in Table 3 below.

Independent variables of the experimental design are reaction temperature (A), reaction time (B), and H_2O_2 concentration (C) while response or dependent variable is TOC reduction percentage (R).

Cubic model which also consists of both linear and quadratic models was selected for the optimization of experimental design of the study because this model was best fit to the responses rather than the other model of equations. The representation and obtained cubic model equations are given in Eqs. (8) and (9), respectively.

$$\begin{aligned} R = {} & C_0 + C_A A + C_B B + C_C C + C_{AB} AB + C_{AC} AC + C_{BC} BC + C_{AA} A^2 + \\ & C_{BB} B^2 + C_{CC} C^2 + C_{ABC} ABC + C_{AAB} A^2 B + C_{AAC} A^2 C + \\ & C_{ABB} AB^2 + C_{ACC} AC^2 + C_{BBC} B^2 C + C_{BCC} BC^2 + C_{AAA} A^3 + \\ & C_{BBB} B^3 + C_{CCC} C^3 \end{aligned} \tag{8}$$

where R is the response, A, B, and C are the independent variable's effects, A^2, B^2, and C^2 are the square and A^3, B^3, and C^3 are triple effects of independent variables. Hence, ABC, A^2B, A^2C, AB^2, AC^2, B^2C, and BC^2 are the interaction effects. Besides, C_0 is the intercept of the model equation.

$$\begin{aligned} \text{TOC\%} = {} & 15.27 + 4.06A - 7.32B - 2.88C + 0.3075AB + \\ & 3.55AC - 7.58BC + 0.7295A^2 + 1.18B^2 - \\ & 0.7132C^2 - 1.99ABC + 13.60A^2B \end{aligned} \tag{9}$$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

In the next step, sufficiency of the recommended model equation, in other words, the degree of correlation of experimental and theoretical values of TOC%, was checked by the analysis of variance (ANOVA), and ANOVA results for this study are shown in Table 4. The convenience of the proposed model was checked by the determination coefficient (R^2), and according to the results, 99.43% R^2 value was obtained which is really high. On the other hand, adjusted R^2 value is 98.17%, which is also high, and investigation of this value is required for checking the sufficiency of the model equation. Since the determined values of R^2 and adjusted R^2 are relatively close to 1, the model equation has high possibility for correlation. Furthermore, the perfect correlation between experimental and predicted responses (TOC%) was shown in Fig. 12.

The adequate precision is the measure of the signal to noise ratio. A ratio greater than 4 is required for the processes. The adequate precision ratio for this process is 35.198, which indicates an adequate signal. Hence, it can be said that this model can be used to navigate the design space.

Acceptable p value was 0.05. The p values of individual effects of reaction temperature, reaction time, and H_2O_2 concentration were 0.0001, 0.0093, and 0.0285, respectively. According to the results, it is obvious that reaction temperature was the most significant reaction parameter for this study. All considerations about the individual and two-way interaction effects of reaction parameters were shown in Fig. 13. Surface plots can also check the conclusions of the experimental results in the sections 3.1, 3.2, and 3.3.

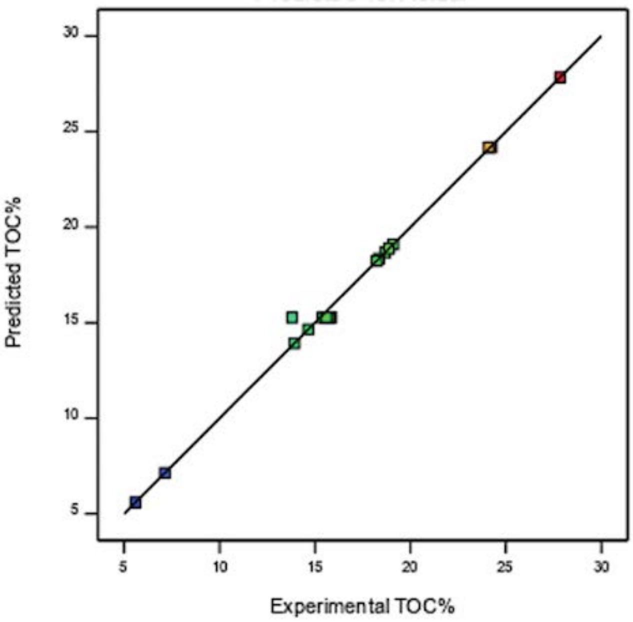

Fig. 12. Diagnostic plot of the study.

Table 4
Results of regression model of ANOVA

Source	Sum of squares	Degrees of freedom	Mean square	F value	p value
Model	491.48	11	44.68	79.00	<0.0001
A	66.02	1	66.02	116.72	0.0001
B	9.54	1	9.54	16.87	0.0093
C	5.26	1	5.26	9.29	0.0285
AB	0.3782	1	0.3782	0.6687	0.4507
AC	5.17	1	5.17	9.13	0.0293
BC	11.25	1	11.25	19.89	0.0066
A^2	0.9953	1	0.9953	1.76	0.2420
B^2	2.52	1	2.52	4.45	0.0887
C^2	0.5403	1	0.5403	0.9553	0.3733
ABC	0.8024	1	0.8024	1.42	0.2871
A^2B	27.96	1	27.96	49.43	0.0009
A^2C	0.0000	0			
AB^2	0.0000	0			
AC^2	0.0000	0			
B^2C	0.0000	0			
BC^2	0.0000	0			
A^3	0.0000	0			
B^3	0.0000	0			
C^3	0.0000	0			
Pure error	2.83	5	0.5656		
Cor total	494.30	16			

Fit statistics
R^2: 0.9943, Adjusted R^2: 0.9817, Adequate precision: 35.1981, Coefficient of Variation (%): 4.45; Totals corrected for the mean (Cor total)

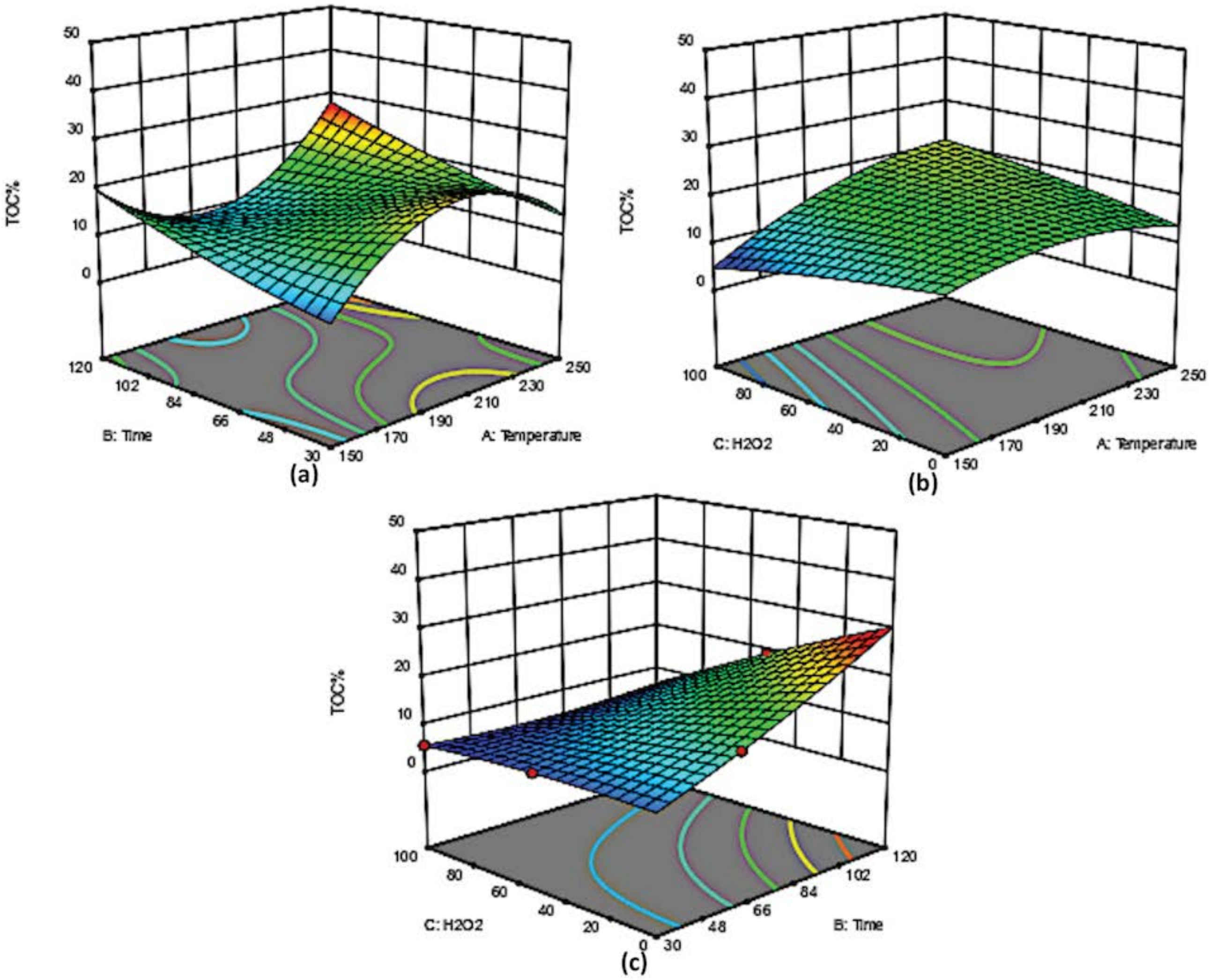

Fig. 13. Surface plots of two-way interactions of (a) temperature and time at constant H_2O_2 concentration (50 mM), (b) temperature and H_2O_2 concentration at constant time (60 min), and (c) time and H_2O_2 concentration at constant temperature (150°C).

4. Conclusion

Partial mineralization of OMW was successfully performed in subcritical water medium under hydrothermal conditions by using high-temperature high-pressure batch reactor. Various effects such as reaction temperature (150°C, 200°C, and 250°C), reaction time (30, 60, 90, and 120 min), and H_2O_2 concentrations (0, 50, and 100 mM) on TOC removal and TPC were revealed. Corresponding pressure values were 5, 15, and 40 bar at 150°C, 200°C, and 250°C, respectively. According to the statistical analysis obtained from the study, TPC, TOC, and color removals were directly proportional to increment in reaction temperature and reaction time as expected. On the other hand, increase in concentration of H_2O_2 did not affect removal efficiencies proportionally due to the competition among the hydroxyl ($OH^\bullet$) and hydroperoxide ($HO_2^\bullet$) free radicals. The best reduction rate of TOC was achieved with a reaction at 250°C and 120 min without using H_2O_2. Acetic acid was the main organic residue for reactions with and without H_2O_2. The presence of acetic acid, which is a short-chain carboxylic acid, caused the inhibition effect on TOC removal rate due to its refractory characteristics. Additionally, the treated OMW is less toxic than untreated OMW because acetic acid is a short-chain compound with no toxic effects when compared with large organic compounds. Furthermore, the presence of acetic acid in the treated OMW signaled to the partial mineralization.

This study has several advantages such as there is no need of pH adjustment because of high acidity of OMW, easy setup and performance, and no requirement of any activator like ozone and metal ions because of the excellent solvent properties of water in subcritical region. Besides, water is green solvent and has no toxicity, and also because of the 80–85 wt.% water content of OMW, additional water for reaction medium was not used. In this study, partial mineralization of OMW was observed; so to achieve complete mineralization, any alternative catalyst or higher reaction temperatures (up to 374°C) might be preferred to high degree of reduction of TOC concentration.

Acknowledgement

We would like to thank to Dr. Meral Dükkancı (Chemical Engineering Department, Ege University) for her support on COD analysis. TOC and GC–MS analyses were conducted at ''Environmental Research and Development Center'' at Izmir Institute of Technology.

References

[1] C. Faith, Olive Oil Production by Country, WorldAtlas.com.
[2] M. Niaounakis, C.P. Halvadakis, Olive Processing Waste Management Literature Review and Patent Survey, Elsevier, Netherlands, 2006.
[3] E. Tsagaraki, H.N. Lazarides, K.B. Petrotos, Olive Mill Wastewater Treatment, V. Oreopoulou, W. Russ, Eds., Utilization of By-Products and Treatment of Waste in the Food Industry, Springer, Boston, MA, 2004, 133–157.
[4] Ü. Tezcan Ün, S. Uğur, A.S. Koparal, Ü. Bakir Öğütveren, Electrocoagulation of olive mill wastewaters, Sep. Purif. Technol., 52 (2006) 136–141.
[5] F. Hanafi, O. Assobhei, M. Mountadar, Detoxification and discoloration of Moroccan olive mill wastewater by electrocoagulation, J. Hazard. Mater., 174 (2010) 807–812.
[6] P. Paraskeva, E. Diamadopoulos, Technologies for olive mill wastewater (OMW) treatment: a review, J. Chem. Technol. Biotechnol., 81 (2006) 1475–1485.
[7] L. Lesage-Meessen, D. Navarro, S. Maunier, J.C. Sigoillot, J. Lorquin, M. Delattre, J.L. Simon, M. Asther, M. Labat, Simple phenolic content in olive oil residues as a function of extraction systems, Food Chem., 75 (2001) 501–507.
[8] N. Assas, L. Ayed, L. Marouani, M. Hamdi, Decolorization of fresh and stored-black olive mill wastewaters by *Geotrichum candidum*, Process Biochem., 38 (2002) 361–365.
[9] M. Hamdi, Toxicity and biodegradability of olive mill wastewaters in batch anaerobic digestion, Appl. Biochem. Biotechnol., 37 (1992) 155–163.
[10] I.P. Marques, Anaerobic digestion treatment of olive mill wastewater for effluent re-use in irrigation, Desalination, 137 (2001) 233–239.
[11] A. Demirbas, Biohydrogen, in: Green Energy Technologies, Springer, London, 2009, pp. 163–219.
[12] G. Taralas, M.G. Kontominas, Thermochemical treatment of solid and wastewater effluents originating from the olive oil food industry, Energy Fuels, 19 (2005) 1179–1185.
[13] S. Tosti, C. Cavezza, M. Fabbricino, L. Pontoni, V. Palma, C. Ruocco, Production of hydrogen in a Pd-membrane reactor via catalytic reforming of olive mill wastewater, Chem. Eng. J., 275 (2015) 366–373.
[14] S. Tosti, M. Fabbricino, L. Pontoni, V. Palma, C. Ruocco, Catalytic reforming of olive mill wastewater and methane in a Pd-membrane reactor, Int. J. Hydrogen Energy, 41 (2016) 5465–5474.
[15] A. Casanovas, A. Galvis, J. Llorca, Catalytic steam reforming of olive mill wastewater for hydrogen production, Int. J. Hydrogen Energy, 40 (2015) 7539–7545.
[16] L.Y. Zou, Y. Li, Y.-T. Hung, Wet Air Oxidation for Waste Treatment, in: Advanced Physicochemical Treatment Technologies, Humana Press, Totowa, N.J., 2007, pp. 575–610.
[17] H. Debellefontaine, J.N. Foussard, Wet air oxidation for the treatment of industrial wastes Chemical aspects, reactor design and industrial applications in Europe, Waste Manage., 20 (2000) 15–25.
[18] S. Baroutian, M. Robinson, A.M. Smit, S. Wijeyekoon, D. Gapes, Transformation and removal of wood extractives from pulp mill sludge using wet oxidation and thermal hydrolysis, Bioresour. Technol., 146 (2013) 294–300.
[19] F.J. Rivas, O. Gimeno, J.R. Portela, E.M. de la Ossa, F.J. Beltrán, Supercritical water oxidation of olive oil mill wastewater, Ind. Eng. Chem. Res., 40 (2001) 3670–3674.
[20] F.J. Rivas, F.J. Beltrán, O. Gimeno, B. Acedo, Wet air oxidation of wastewater from olive oil mills, Chem. Eng. Technol., 24 (2001) 415–421.
[21] W. Gernjak, M.L. Maldonado, S. Malato, J. Cáceres, T. Krutzler, A. Glaser, R. Bauer, Pilot-plant treatment of olive mill wastewater (OMW) by solar TiO_2 photocatalysis and solar photo-Fenton, Sol. Energy, 77 (2004) 567–572.
[22] B.M. Esteves, C.S.D. Rodrigues, L.M. Madeira, Synthetic olive mill wastewater treatment by Fenton's process in batch and continuous reactors operation, Environ. Sci. Pollut. Res., 25 (2018) 34826–34838.
[23] R.C. Martins, A.M. Ferreira, L.M. Gando-Ferreira, R.M. Quinta-Ferreira, Ozonation and ultrafiltration for the treatment of olive mill wastewaters: effect of key operating conditions and integration schemes, Environ. Sci. Pollut. Res., 22 (2015) 15587–15597.
[24] K. Byrappa, M. Yoshimura, Hydrothermal Technology-Principles and Applications, in: Handbook of Hydrothermal Technology, Elsevier, Oxford, 2013, pp. 1–41.
[25] G. Brunner, Near critical and supercritical water Part I hydrolytic and hydrothermal processes, J. Supercrit. Fluids, 47 (2009) 373–381.
[26] D.J. Miller, S.B. Hawthorne, Method for determining the solubilities of hydrophobic organics in subcritical water, Anal. Chem., 70 (1998) 1618–1621.
[27] P.E. Savage, Organic chemical reactions in supercritical water, Chem. Rev., 99 (1999) 603–622.
[28] A. Kruse, E. Dinjus, Hot compressed water as reaction medium and reactant 2 degradation reactions, J. Supercrit. Fluids, 41 (2007) 361–379.
[29] J. Wiboonsirikul, S. Adachi, Extraction of functional substances from agricultural products or by-products by subcritical water treatment, Food Sci. Technol. Res., 14 (2008) 319–328.
[30] Y. Yang, M. Belghazi, A. Lagadec, D.J. Miller, S.B. Hawthorne, Elution of organic solutes from different polarity sorbents using subcritical water, J. Chromatogr. A, 810 (1998) 149–159.
[31] Y. Yang, F. Hildebrand, Phenanthrene degradation in subcritical water, Anal. Chim. Acta, 555 (2006) 364–369.
[32] J. Fernández, J. Kiwi, J. Baeza, J. Freer, C. Lizama, H.D. Mansilla, Orange II photocatalysis on immobilised TiO_2: effect of the pH and H_2O_2, Appl. Catal., B, 48 (2004) 205–211.
[33] H.T. Gomes, J.L. Figueiredo, J.L. Faria, Catalytic wet air oxidation of olive mill wastewater, Catal. Today, 124 (2007) 254–259.
[34] S. Daneshvar, N. Hidemi, F. Salak, N. Mahinpey, Degradation of textile dyes under subcritical water conditions in the presence of hydrogen peroxide, Can. J. Chem. Eng., 92 (2014) 615–622.
[35] M.A. Imteaz, A. Shanableh, Kinetic model for the water oxidation method for treating wastewater sludges, Asia-Pac. J. Chem. Eng., 12 (2004) 515–530.
[36] F. Luck, Wet air oxidation: past, present and future, Catal. Today, 53 (1999) 81–91.
[37] C.H. Wu, C.H. Yu, Effects of TiO_2 dosage, pH and temperature on decolorization of CI Reactive Red 2 in a UV/US/TiO_2 system, J. Hazard. Mater., 169 (2009) 1179–1183.
[38] D. Georgiou, P. Melidis, A. Aivasidis, K. Gimouhopoulos, Degradation of azo-reactive dyes by ultraviolet radiation in the presence of hydrogen peroxide, Dyes Pigm., 52 (2002) 69–78.
[39] A. Katsoni, Z. Frontistis, N.P. Xekoukoulotakis, E. Diamadopoulos, D. Mantzavinos, Wet air oxidation of table olive processing wastewater: determination of key operating parameters by factorial design, Water Res., 42 (2008) 3591–3600.
[40] J.A. Onwudili, P.T. Williams, Reaction mechanisms for the decomposition of phenanthrene and naphthalene under hydrothermal conditions, J. Supercrit. Fluids, 39 (2007) 399–408.
[41] M.B. Kasiri, A.R. Khataee, Photooxidative decolorization of two organic dyes with different chemical structures by UV/H_2O_2 process: Experimental design, Desalination, 270 (2011) 151–159.

[42] M.A. Behnajady, N. Modirshahla, H. Fathi, Kinetics of decolorization of an azo dye in UV alone and UV/H_2O_2 processes, J. Hazard. Mater., 136 (2006) 816–821.

[43] A.H. Gemeay, I.A. Mansour, R.G. El-Sharkawy, A.B. Zaki, Kinetics and mechanism of the heterogeneous catalyzed oxidative degradation of indigo carmine, J. Mol. Catal. A: Chem., 193 (2003) 109–120.

[44] A. Aleboyeh, H. Aleboyeh, Y. Moussa, Decolorisation of Acid Blue 74 by ultraviolet/H_2O_2, Environ. Chem. Lett., 1 (2003) 161–164.

[45] B. Kayan, B. Gözmen, Degradation of Acid Red 274 using H_2O_2 in subcritical water: application of response surface methodology, J. Hazard. Mater., 201–202 (2012) 100–106.

[46] V.M. Daskalaki, E.S. Timotheatou, A. Katsaounis, D. Kalderis, Degradation of Reactive Red 120 using hydrogen peroxide in subcritical water, Desalination, 274 (2011) 200–205.

[47] A. Rezaee, M.T. Ghaneian, S.J. Hashemian, G. Moussavi, A. Khavanin, G. Ghanizadeh, Decolorization of reactive blue 19 dye from textile wastewater by the UV/H_2O_2 process, J. Appl. Sci., 8 (2008) 1108–1112.