



Degradation of olive mill wastewater by different methods and antioxidant activity of olive mill wastewater extraction

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Abstract

Olive wastewater (OMW) is an important environmental problem due to the high phenol level and contains organic substances such as sugars, organic acids, polyalcohols, pectins, colloids, tannins, and lipids. Removing OMW is difficult because of the high concentrations of chemical oxygen demand (COD), biochemical oxygen demand, and phenolic compounds. In this study, we concentrated on the degradation of OMW to solve this problem. The degradation of OMW at high pressure and temperature (with H_2O_2 and without H_2O_2), at room temperature and atmospheric pressure with H_2O_2 , at room temperature and atmospheric pressure with O_3 , and with ultrasound-assisted ozonation, was investigated by means of COD, phenolic compounds, and sulfur analyses. The results showed that the method of high pressure and temperature with H_2O_2 was the most successful. H_2O_2 at high pressure (O_2) and temperature removed 89.2% of COD, 91.5% of phenolic compounds, and color of OMW. With this result, we showed that the use of O_2 atmosphere instead of N_2 is important for degradation and also especially for color removing. In addition, the antioxidant property of OMW was also examined. Fourier-transform infrared spectroscopy of the extracts revealed vibration bands corresponding to acid, alcohol, and ketone groups. The results showed that high pressure and temperature treatment is very effective for removing phenolic compounds from olive oil wastewater. In addition, 2,2-diphenyl-1-picrylhydrazyl (DPPH) scavenging potential of OMW in the Çukurova area of Turkey was studied and the IC_{50} value of OMW was determined to be 118 $\mu\text{g/mL}$.

Keywords Olive mill wastewater · Subcritical water · Chemical oxygen demand · Degradation · Mersin · Antioxidant activity

1 Introduction

Olive mill wastewater occurs during the production of olive oil by olive oil factories. The olive industry is very important in Mediterranean countries, particularly Greece, Syria, Spain, Tunisia, Italy, and Turkey. OMW is a considerable source of pollution because of its high phytotoxicity. The management of OMW has been widely researched and some comprehensive and detailed reviews focusing mainly on management have been published recently [6, 9, 10, 22, 25]. Adhoum and Monser [4] studied decolorization and removal of phenolic compounds from OMW by electrocoagulation. Jarbouy et al. [15] studied OMW

evaporation pond management in five serial evaporation open-air multiponds of 50 ha located in Sfax (Tunisia). Nassar et al. [21] investigated the effectiveness of magnetic iron oxide nanoparticles for removal of large organic contaminants from OMW waters by flocculation. Beltran-Heredia et al. [7] studied the degradation of OMW by means of two chemical oxidation processes (Fenton's reagent and ozonation) with aerobic microorganisms. In addition, some filtration methods of OMW [1, 3] can be found in the literature, but these methods generally reduce the COD instead of completely exhausted. The extraction of olive oil produces waste in large quantities with environmental impact due to its high phytotoxicity. For this reason, there

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is a need for guidelines to manage these wastes with technologies that reduce the environmental impact as much as possible and lead to sustainable use of resources.

The aim of this work was to study the effect of different methods (high pressure and temperature (with H₂O₂ and without H₂O₂), at room temperature and atmospheric pressure with H₂O₂, at room temperature and atmospheric pressure with O₃, and with ultrasound-assisted ozonation) for oxidation of OMW, regarding the effect of various operating conditions (initial chemical oxygen demand (COD), pH, sulfur, phenol, and density) on the removal of color, phenolic, and organic compounds. The results of these experiments showed that the high pressure with H₂O₂ is a good choice for degradation, because subcritical water oxidation method is an environmentally friendly and effective with short treatment time that is important for cost [30] and the O₂ has an important effect for degradation and color removing. In addition, we investigated the antioxidant properties of OMW in order to evaluate it instead of degradation. The sample used in our experiments was taken from the OMW pools in Mersin (Turkey).

2 Experimental section

2.1 Chemicals and reagents

Hach Cat. 2106869 PK/100 CyaniVer 3 cyanide reagent powder Pifiows for 10 mL sample, Hach Cat. 2106969 PK/100 CyaniVer 4 cyanide reagent for 10 mL sample, Hach Permachem reagents Cat. 2107069 PK/100 CyaniVer 5 cyanide reagent for 10 mL sample, Hach Cat 42449 buffer Solution Hardness 1 Solution pH 10.1 ±, Hach Permachem reagents Cat. 183699 phenol 2 reagent, Hach Permachem reagents Cat. 87299 phenol reagent, LCK 314 15-150 mg/L O₂ CSB, COD, DCO LCK 314 were the chemicals used for analytical purposes. H₂O₂ was taken from Sigma-Aldrich as a 35% solution.

2.2 OMW

OMW was obtained from the olive oil factory in Mersin (Turkey). The fresh OMW sample was initially completely cloudy and homogeneous. After 24 h, the sample was completely stationary and divided into two net layers at the macro level. For this reason, the sedimentation time was required to obtain a very clear supernatant is 24 h. The contents are shown in Table 1. The high pressure and temperature reactions were carried out in a stainless steel

Table 1 Characterization of the OMW used in the experiments

Parameter	Range
Total COD	83,000 mg/L
Total TOC	29,000 mg/L
Phenolics	4.8 g/L
Sulfur	31 mg/L
pH	4.7
Density	1.0026 mg/L
Color ^a	139 cm ⁻¹
Oil and grace	7.8 g/L

^aAbsorbance at 400 nm

reactor [17]. The experiments with O₃ and H₂O₂ were also performed at atmospheric pressure.

2.3 Experimental procedure

The experiments were carried out under seven different sets of conditions. Four experiments in high pressure and temperature were performed in the reactor. An experiment was conducted at atmospheric pressure with 3 mL of H₂O₂ at reflux temperature in a flask for 3 h. An experiment was realized at atmospheric pressure with O₃ at reflux temperature for 3 h. An experiment was effected in atmospheric pressure in the sonic-assisted reaction with O₃ at 100 °C for 3 h.

2.4 Degradation of OMW at high temperature and pressure

The reactor has 100-mL capacity with a thermostatically controlled magnetic stirrer. In condition 1, the experiment was carried out at 40 bar oxygen pressure at 150 °C for 3 h. In condition 2, the experiment was carried out at 40 bar oxygen pressure with 1 mL of H₂O₂ at 150 °C for 3 h. In condition 3, the experiment was carried out at 40 bar oxygen pressure with 3 mL of H₂O₂ at 150 °C for 3 h. In condition 4, the experiment was carried out at 40 bar nitrogen pressure with 3 mL of H₂O₂ at 150 °C for 3 h. 50 mL OMW was put into the reactor and mixed. The reactor was then shut down and turned off; gas was evacuated, and the temperature was raised to 150 °C. After the temperature reached 150 °C, the process was continued for 3 h. In addition, H₂O₂ was added to the medium in the two experiments. When the experiments were completed, analyses (COD, phenol, sulfur, density, and pH) of the OMW were performed.



2.5 With O₃ under sonochemical conditions

OMW was put into a 100-mL three-necked flask equipped with a condenser and subjected to ultrasonic irradiation at reflux temperature for the appropriate time for 3 h. After the reaction, analyses (COD, phenol, sulfur, density, and pH) of the OMW were performed. A Bandelin Soporex RK 255H model was used for ultrasonic reactions.

2.6 With O₃

A 100-mL three-necked flask was equipped with a condenser, and O₃ inlet was charged with OWM. The suspension was stirred under O₃ at room temperature for 3 h. O₃ was given continuous flow during the experiment. After the reaction, analyses (COD, phenol, sulfur, density, and pH) of the OMW were performed.

2.7 Analytical methods

The OMW used in this investigation was characterized by measuring pH, density, total phenols, COD, and sulfur concentration. Various parameters were measured during the experiments. The COD was determined by the reactor digestion method for COD, phenol, and sulfur range of 0–1500 mg/L using a HACH LANGEDR 5000 analyzer. pH was measured with a Mettler Toledo mp225. Infrared spectra were recorded with a Perkin Elmer Win First® Satellite and UV–Vis spectrophotometer from Shimadzu was used for antioxidant measurements. Finally, all the experiments were performed at least twice and the analytical methods were applied at least in triplicate.

2.8 COD measurement

Firstly, 1 mL of sample diluted 100 times for COD measurement. Then, 2 mL of sample from diluted solution was placed in the COD tube and it was heated at 150 °C for 2 h.

When the contents of the tube reached room temperature, the measurement was performed.

2.9 Sulfur content

Distilled water and OMW were put into the spectrophotometer cuvettes and the wavelength was adjusted to 665 nm. While the cuvettes were being shaken, 0.5 mL of sulfide 1 reagent was added. Then, during further shaking of the tubes, 0.5 mL of sulfide 2 reagent material was introduced and pink color was formed. First the distilled water and then the sample was read and the values were recorded.

2.10 Phenol content

Distilled water and OWM were placed in different separation funnels. Then, 5 mL of hardness 1 buffer was added to both separation funnels. The phenol reagent powder pillow was added to the separation funnel, which was then shaken. Next, phenol 2 reagent powder pillow was added followed by rinsing. Finally, 30 mL of chloroform was added to the two separation funnels and they were shaken thoroughly. After phase separation, the chloroform phase was read at 460 nm on the spectrophotometer. All the analyses were done in duplicate. Removal yields were assessed as phenolic loss index (PLI) [20] and sulfur loss index (SLI) using the following equations:

$$\text{PLI (\%)} = \left[\frac{(\text{Ph}_{\text{ni}} - \text{Ph}_{\text{nf}})}{(\text{Ph}_{\text{ni}})} \right] \times 100$$

(Ph_{ni} = initial phenolics concentration; (1)
Ph_{nf} = final phenolics concentration)

$$\text{SLI (\%)} = \left[\frac{(\text{S}_{\text{ni}} - \text{S}_{\text{nf}})}{(\text{S}_{\text{ni}})} \right] \times 100$$

(S_{ni} = initial sulfur concentration; S_{nf} = final sulfur concentration) (2)

2.11 Antioxidant activity of OWM extract

Antioxidant activity was measured using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging test. The antioxidant activity was performed using the DPPH radical scavenging assay. Butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) were used as reference test materials. Firstly, different concentrations (6.75–1600 µg/mL) of reference test materials and samples were prepared in EtOH. Then, 1 mL of each sample was added to 1 mL of 1 × 10⁻⁴ mM DPPH solution that prepared as newly, and they were incubated in dark for half an hour at room temperature. Then, the absorbance for each sample was measured at 517 nm. The percentage of scavenging activity in the experiment

was calculated using the formula given below. The IC_{50} (inhibitory concentration) is the concentration required to clear 50% DPPH free radicals (Eq. 3) [13].

$$\% \text{ Scavenging} = (A_o - A_s/A_o) \cdot 100$$

$$(A_o = \text{absorbance of the control; } A_s = \text{absorbance of the sample at 517 nm}) \quad (3)$$

3 Results and discussion

In our study, the degradation of OMW in subcritical water (with H_2O_2 and without H_2O_2), at room temperature and atmospheric pressure with H_2O_2 , at room temperature and atmospheric pressure with O_3 , and with ultrasound-assisted ozonation, was investigated by means of COD, phenolic compounds, and sulfur analyses. Table 2 shows the properties of the supernatant before and after oxidation. As seen, the specimen's properties after oxidation changed drastically. In particular, a large decrease in COD was observed at high pressure (O_2) and temperature in the presence of H_2O_2 . Again, the pH of the solution is slightly acidic, which may depend on the presence of high concentrations of phenolic compounds and carboxylic acids, which are classified as weak acids.

When we look at the details in this works, the reduction in COD, SLI, and PLI values fell from 43.6%, 99.7%, and 20.8%, respectively, when an ultrasonic bath was not used with ozone (Table 2/entry 2), but when using an ultrasonic bath with ozone, these values changed as 50.8%, 99.7%, and 25.0%, respectively (Table 2/entry 3). Beltran-Heredia et al. [8] studied degradation of OMW by ozonation in chemical batch reactor, and they obtained the COD reduction between 42 and 55%. It is seen that this result is approximately the same as the result we obtained in our ozonation study. These results showed that the ultrasonic bath significantly increases

the removal of OMW and can be used as an alternative method.

When only H_2O_2 was used in oxidation, the reduction in COD, SLI, and PLI values was 80.6%, 97.1%, and 14.6%, respectively (Table 2/entry 4). Several important organic reactions in subcritical water are described in the literature [17]. In particular, oxidation reactions were described using molecular oxygen as an oxidant. We also used subcritical water oxidation in the oxidation reactions. OMW was treated by molecular O_2 at high pressure and temperature water (40 bar O_2 , 150 °C). COD and the levels of sulfur and phenol are all showed decreases, which, after 3 h treatment, and reached 28%, 99.2%, and 91.0%, respectively (Table 2/entry 5). There was no significant change in pH. When the reaction (40 bar O_2 , 150 °C) was performed in the presence of 1 mL H_2O_2 , COD and the levels of sulfur and phenol decreased by 78.4%, 99.5%, and 90.2%, respectively (Table 2/entry 6). The best COD, SLI, and PLI results were observed in subcritical conditions in the presence of 3 mL of H_2O_2 at 89.2%, 99.8%, and 91.5%, respectively (Table 2/entry 7). Yabalak et al. [29] studied degradation of OMW using subcritical water conditions, and they obtained 96% COD removal in their best condition, but they did not mention color or smell removing in their best condition. Also, they have used N_2 gas for degradation process. In our works, we investigated effect of different gases (N_2 and O_2) for degradation. For this purpose, we set up the control reaction in N_2 atmosphere instead of O_2 for understanding the effect of O_2 (Table 2/entry 8). Also, we set up reactions under the low temperature in O_2 atmosphere (40 bar O_2 , 50 °C, and 40 bar O_2 , 100 °C) for understanding the effect of high temperature. According to the result of these control and optimization reactions, we could not obtain any good COD, color, and smell removing. These results showed that the subcritical water oxidation is an

Table 2 Experiments and analysis results

Rank	Conditions	COD ^a (mg/L)	COD% reduction	Sulfur (mg/L)	SLI (%)	Phenol (g/L)	PLI (%)	Density(mg/L)	pH
1	Untreated olive mill wastewater	830	–	31	–	4.8	–	1.0026	4.7
2	O_3 , 100°C, 6 h	470	43.6	0.080	99.7	3.8	20.8	1.0044	4.3
3	O_3 , 100°C, 6 h sonication	410	50.8	0.082	99.7	3.6	25.0	1.0081	2.8
4	3 mL H_2O_2 100°C, 6 h	161.5	80.6	0.89	97.1	4.1	14.6	1.0068	3
5	40 bar O_2 150°C, 3 h	600	28	0.242	99.2	0.43	91.0	1.0019	4.8
6	40 bar O_2 150°C, 3 h 1 mL H_2O_2	180	78.4	0.168	99.5	0.47	90.2	1.0018	4.7
7	40 bar O_2 150°C, 3 h 3 mL H_2O_2	90	89.2	0.072	99.8	0.41	91.5	1.0014	4.8
8	40 bar N_2 150°C, 3 h 3 mL H_2O_2	474	42.9		98.3	2.6		1.0036	4.4

^aBefore COD measurements, the samples diluted 100 times

effective method for degradation of OMW, and when, the H_2O_2 was used as co-oxidant with O_2 atmosphere, the degradation of OMW increased drastically. Also, using O_2 atmosphere instead of N_2 is very important for color and smell removing (Fig. 1).

The pH of the medium was decreased in the 3rd and 4th experiment conditions. No significant change in OMW concentrations was observed.

3.1 FTIR spectra analysis

FTIR spectra of oxidized and non-oxidized OWM were recorded. The FTIR spectra of the seven OWM extracts show similar characteristics with some differences in band intensity (Table 3). This comment is based on the works by Tanaka et al. [28], Ouatmane et al. [23], Hafidi et al. [14], El Hajouji et al. [11], and Smidt and Meissl [27]. Absorbance bands from the IR spectra of the untreated OMW extract with hexane are given in Table 3. Absorbance bands from the IR spectra of the untreated OMW extract with ethyl acetate are given in Table 4.

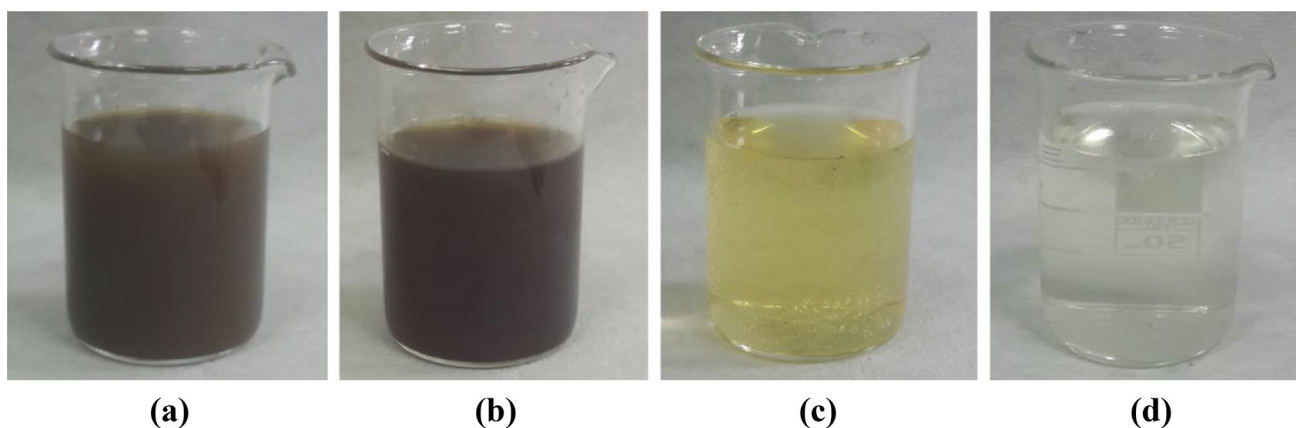


Fig. 1 Picture of the solution before and after degradation **a** OWM, **b** after degradation with condition in Table 2/entry 8, **c** after degradation with condition in Table 2/entry 6, and **d** after degradation with condition in Table 2/entry 7

Table 3 Absorbance bands from the FTIR spectra in the extract made with hexane of OMW

Wavenumber	Assignments
2954–2848 cm^{-1}	C–H stretching in aliphatic structures (fatty acids, waxes, and other long-chain structures)
1699 cm^{-1}	C=O stretching in carboxyls, acids, and ketones
1463–1431 cm^{-1}	C–H stretching in aliphatic structures
1347 cm^{-1}	C–H deformation of CH_2 and CH_3 groups, COO^- antisymmetric stretching
1347–934 cm^{-1}	C–O of ethers on an aromatic ring and the N–H of amides II
< 1000 cm^{-1}	Stretching of aromatic ethers, polysaccharides (C–H stretching)

Table 4 Absorbance bands from the FTIR spectra in the extract made with ethyl acetate of OMW

Wavelength	Assignments
3300 cm^{-1}	OH (phenols, alcohols, and carboxylic groups)
3065 cm^{-1}	C–H stretching in aromatic structures
2938 cm^{-1}	C–H stretching in aliphatic structures (fatty acids, waxes, and other long-chain structures)
1709 cm^{-1}	C=O stretching in carboxyls, acids, and ketones
1374 cm^{-1}	OH deformation and C–O stretching in phenolic OH, C–H deformation of CH_2 and CH_3 groups, COO^- antisymmetric stretching
1239 cm^{-1}	C–H stretching and OH deformation in carboxyls, C–O of ethers on an aromatic ring, and the N–H of amides II
1045 cm^{-1}	Stretching of aromatic ethers, polysaccharides (C–H stretching)

Fig. 2 DPPH scavenging activities of OMW extract and standard antioxidant BHT and BHA

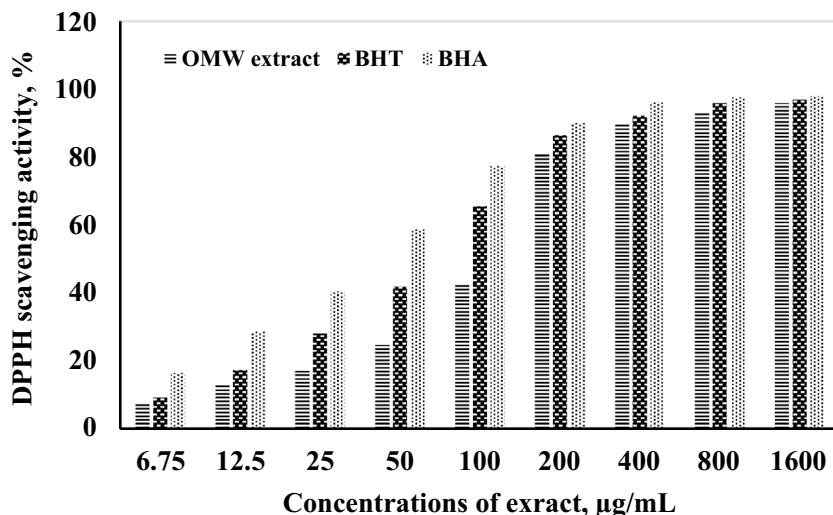
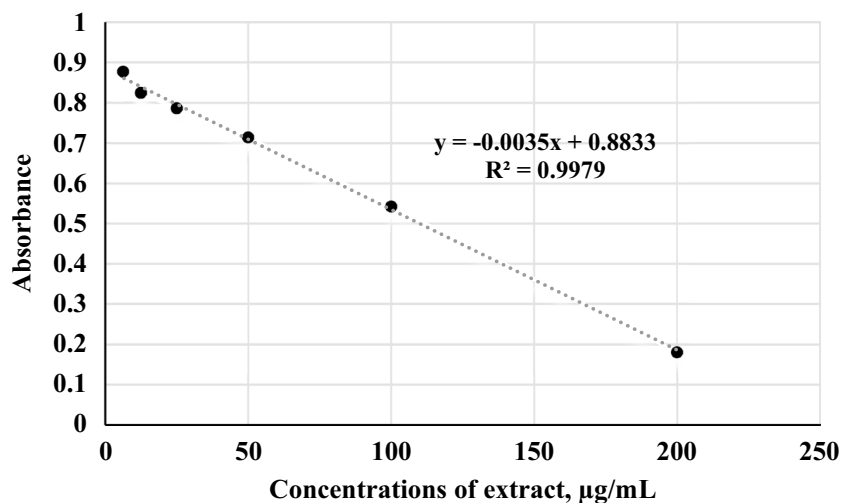


Fig. 3 Calculation of IC₅₀ value for OMW extract



Advanced oxidation processes (AOP) involve the formation and activation of hydroxyl radicals, which are unstable and reactive species formed by an oxygen source and an energy source.

3.2 Antioxidant activity of phenolic extracts and NMR results of extracts

The release of OMW in large quantities creates the idea of evaluation instead of removing [2]. Therefore, the antioxidant activity of OMW was investigated. For this purpose, 50 mL of OWM was extracted with 3 × 50 mL ethyl acetate. After the solvent was evaporated, 2.1 g of extract was obtained. OMW extracts were tested for antioxidant activity using a stable free radical DPPH as test [13, 16]. The result of DPPH scavenging activity for each sample concentration was given as percentage (Fig. 2). Then, the IC₅₀ values were calculated for OMW extract (Fig. 3) and

Table 5 Scavenging effects (IC₅₀ µg/mL) of OMW extracts on DPPH free radicals

	OMW extract	BHT	BHA
IC ₅₀ (µg/mL)	118	69	38

references. According to all of these results, the extract of OMW showed good DPPH scavenging activity (Table 5).

Antiradical activity IC₅₀ (µg/mL) was defined as the concentration of extracts necessary to decrease the initial DPPH radical concentration by 50%. With this result, we showed that the OMW can be used as antioxidant instead of degradation. Lafka et al. [18] and Abbasi-El et al. [2] investigated antioxidant activity of OMW with different extraction methods, and they showed that the activity of extracts changed according to extraction solvent. While Abbasi-El et al. [2] obtained IC₅₀ values between 123 and

263 $\mu\text{g/mL}$, Azaizeh et al. [5] obtained values between 20 and 34 $\mu\text{g/mL}$, and we obtained the value as 118 $\mu\text{g/mL}$. These results showed that the IC_{50} values can be changed according to extraction methods of OMW or region where take the OMW.

Also, DPPH scavenging activity of OWM after degradation with condition in entry 7 (Table 2) was investigated. For this purpose, the OWM was extracted with 3×50 mL ethyl acetate after degradation proses, and 0.08 g extract was obtained that showed only 7% antioxidant activity for 1600 $\mu\text{g/mL}$ concentration. This result supported the successful degradation of the phenolic compounds in OWM with condition in entry 7 (Table 2). Besides the COD measurement, these results showed that we can support antioxidant activity measurement whether the OMW degradation achieved or not. In addition, we investigated the NMR spectrum of extracts before and after degradation. When these NMR spectra were compared, it was observed that all the phenolic compounds and the majority of other compounds in OWM were removed (Fig. 4).

4 Conclusion

Olive oil wastewater is a big environmental problem worldwide. Every year, millions of tons of toxic wastes are produced, and most of them cause serious damage to the environment. It is known that different olive wastes contain phenolic compounds at high concentrations [12, 19, 24, 26]. The presence of organic pollutants was determined by FTIR measurements of the extract obtained from hexane and ethylacetate extraction of OMW. Therefore, it is necessary to either reduce the damage by oxidizing the OMW or make it usable. In this study, oxidation methods are presented for the disposal of OMW. Eight different studies were performed. High-pressure tests were limited to 3 h, and atmospheric pressure tests were limited to 3 h. As a result, although the time was short, the reaction with H_2O_2 at high temperature and high pressure was observed to be successful. This also shows that high-pressure and high-temperature reactions were successfully used for dephenolysis, desulfurization, and COD removal from

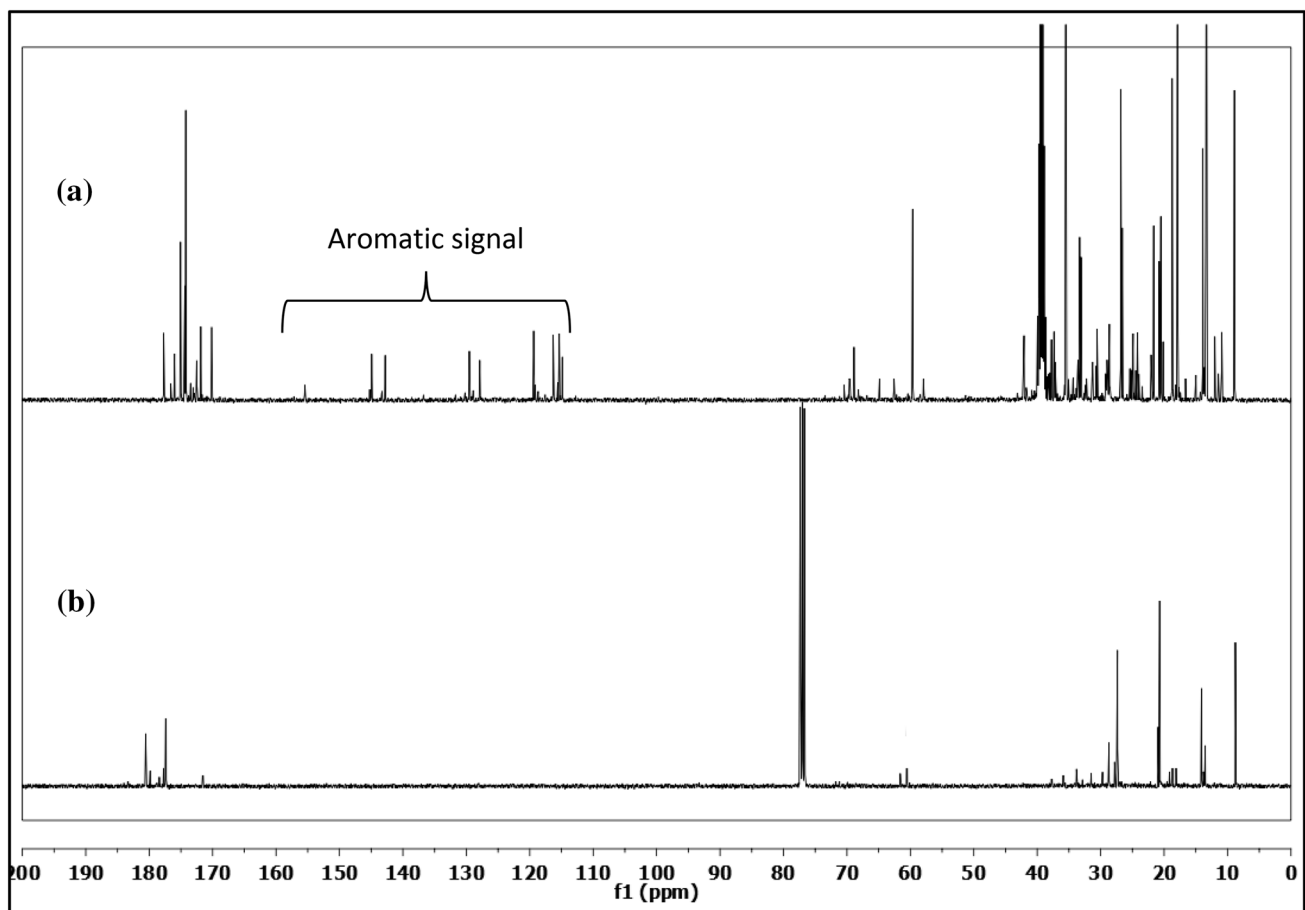


Fig. 4 ^{13}C NMR spectrum **a** extracts of OWM with EtOAc and **b** extracts of OWM with EtOAc after degradation process with condition in Table 2/entry 7

real OMW. Oxidation reactions of OMW were carried out in seven separate systems. The high pressure and temperature oxidation with 3 mL of H₂O₂ was very effective for the removal of many organic pollutants from OMW. Treatment with O₂ and 3 mL of H₂O₂ for 3 h caused disappearance of the majority of the phenolic compounds (91.5%). In addition, 89.2% reduction in compounds responsible for COD was achieved. Antioxidant measurements were also performed to make OMW available. It was seen that OMW's phenolic extracts have high antioxidant potential. The results of our study show that these extracts could be used as an antioxidant source. In further studies can be investigated the content of OMW extracts in detail, and molecules responsible from antioxidant activity.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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