



## Fenton oxidation using $\text{Fe}^{2+}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ to improve the DCO removal and to degrade the phenolic compounds in olive oil mill wastewater

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### ABSTRACT

The treatment of olive oil mill wastewater (OMWW) by Fenton oxidation using  $\text{Fe}^{3+}/\text{Fe}^{2+}$ , and hydrogen peroxide was investigated to improve the degradation of phenolic compounds and the removal of chemical oxygen demand (COD). The experimental results showed that high removal of COD ( $187.6 \text{ g L}^{-1}$ ) and polyphenols ( $4 \text{ g L}^{-1}$ ) required acidic conditions (pH 4), continuous presence of both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  (at  $50 \text{ g L}^{-1}$ ) and hydrogen peroxide. Under these conditions, the maximum COD removal (about 98.6%) was achieved after 10 h. The obtained polyphenolic compounds abatement rate was around 81%. However, after treatment with hydrogen peroxide alone, the removal rates of COD and phenolic compounds were only 69.5% and 67.5%, respectively. HPLC analysis of the extracts showed that hydroxytyrosol was the major compound detected in OMWW ( $259.10 \text{ mg L}^{-1}$ ). Tyrosol, para-hydroxyphenylacetic acid, para-coumaric acid, oleuropein, and quercetin were also identified at lower concentrations. After 10 h of OMWW Fenton oxidation treatment, the hydroxytyrosol and ferulic acid content decreased by 99% and 93%, respectively. However, when hydrogen peroxide was used alone, only 72% and 79.12%, respectively of hydroxytyrosol and ferulic acid were removed. These results showed that the removal of  $4 \text{ g L}^{-1}$  of phenol and  $187.6 \text{ g L}^{-1}$  of COD from OMWW was rapid when high amounts of  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and hydrogen peroxide were used.

**Keywords:** Olive oil mill wastewater;  $\text{Fe}^{2+}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$  system; Polyphenolic compounds; HPLC analysis; Organic pollutant abatement

### 1. Introduction

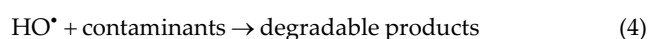
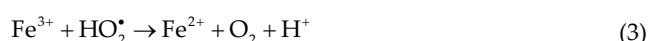
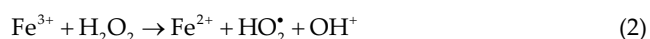
Phenols and their derivatives are common toxic pollutants in the effluents of many industries [1]. The treatment of phenol in wastewater to harmless levels is an arduous task

in the case of many biological and chemical processes due to its high solubility and stability in water [2]. The abatement of phenolic compounds in olive oil wastewater is a big challenge due to their toxicity and refractory behavior for microorganisms [3]. Because of its carcinogenic and mutagenic potential, phenol poses a risk to mammalian and aquatic life [4]. When phenol-containing water is chlorinated, toxic polychlorinated

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phenols can be formed. Due to their stability and solubility in water, their removal to a safe level (0.1–1.0 mg L<sup>-1</sup>) is not easy [5]. Several processes including biological, physical and chemical treatments have been explored for the removal of phenols from industrial wastewaters [6,7]. While, biological processes tend to be slow [8], physical methods transfer the waste compounds from one phase to another without real chemical transformations. On the other hand, chemical treatment of phenols can lead to the formation of toxic and nonbiodegradable byproducts [9]. Recently, a great interest for the development of advanced chemical processes has emerged as an important alternative for detoxification and destruction of toxic and biorefractory organic pollutants in wastewater.

A number of chemical treatments such as the oxidation of phenols with chemical reagents such as chlorine, chlorine dioxide and ozone have been developed [10]. Fenton, solar-Fenton and UV-Fenton were also examined using phenol as a model compound in simulated and industrial wastewaters [11]. Hydroxyl radicals (OH<sup>•</sup>) produced from water anodic oxidation are the main oxidizing agents for refractory chemicals [12]. Brillas et al. [13] showed that gas diffusion cathodes could also be used under acidic solutions to reduce oxygen into hydrogen peroxide at convenient rates for effluent treatment. OH<sup>•</sup> is formed from the classical Fenton's reaction between Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>. According to Walling [14] and Pignatello [15], in the conventional Fenton process, ferric or ferrous salts react with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) under acidic conditions (pH = 3–5) to generate highly reactive hydroxyl radicals (Eq. (1)), which then react with the pollutants to degrade the organic molecules in wastewater treatment [16,17].



The hydrogen peroxide and the oxygen generated facilitate the ability of microorganisms to oxidize the contaminants into biodegradable compounds [17]. In addition to the conventional Fenton reagent, which is catalyzed by Fe<sup>2+</sup>, modified Fenton reagents relying on Fe<sup>3+</sup> as the catalysts have also been investigated for their ability to degrade hazardous organic pollutants [18]. It has been found that this reagent is a powerful oxidizing agent for alcohols, ketones [19], benzene [20] and phenol [21]. Several data from literature show that the use of this process based on Fenton reagent was efficient especially in wastewater [22] or phenolic aqueous solution treatment [23]. Araujo et al. [24] applied this Fenton's reagent for the polymerization of residual lignin in black liquor. Kallel et al. [25] followed the removal of phenolic compounds from olive mill wastewater by Fenton oxidation with zero-valent iron.

The oxidation power of Fenton reagent depends widely on the operating parameters such as iron concentration,

source of iron catalysts (ferrous or ferric salts, iron powder), H<sub>2</sub>O<sub>2</sub> concentration, iron catalyst/hydrogen peroxide ratio, temperature, pH and treatment time [26]. Therefore, it is necessary to find optimal process parameters. As it has been demonstrated by Kušić et al. [26], minimal threshold concentration of ferrous ions that allows the reaction to proceed within a reasonable period of time ranges from 3 to 15 mg L<sup>-1</sup> regardless of the concentration of the organic pollutant. However, low iron levels can require excessive reaction times (10–24 h) [26].

In this study, different concentrations of ferrous and ferric iron salts (Fe<sup>2+</sup> and Fe<sup>3+</sup>) were used as Fenton's reagent under acidic conditions (pH 4) in the presence of hydrogen peroxide to increase the in situ chemical decomposition of phenolic compounds in olive oil wastewater obtained from Chichaoua City, Morocco. The main objective of the study was to determine optimal values for each Fenton type process.

## 2. Materials and methods

### 2.1. Characterization of the olive oil mill wastewater

The olive oil mill wastewater (OMWW) was obtained from an olive oil plant from Chichaoua city, Morocco. The conductivity and the pH of OMWW were measured at ambient temperature following Rodier's recommendations [27]. The dry matter (DM) was determined by evaporation of 100 mL sample in a porcelain dish at 105°C for 24 h. The total organic carbon (TOC) was determined using Anne's method based on potassium dichromate oxidation, as described by Aubert [28]. Total Kjeldahl nitrogen (TKN) was determined using the standard French procedure AFNOR T90-110. The chemical oxygen demand (COD) was determined by oxidation with potassium dichromate. After oxidation, the COD was measured using a spectrophotometer (DR/2000 direct reading spectrophotometer) according to Open Reflux Method (220-B). The characteristics of the oil raw wastewater are given in Table 1.

### 2.2. Fenton oxidation process

Hydroxyl radical was generated by the Fenton's reagent (Fe<sup>2+</sup> + Fe<sup>3+</sup> + H<sub>2</sub>O<sub>2</sub>) in different amounts (Table 2). High purity iron powder, iron (II) sulfate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O) and iron (III) chloride anhydrous (FeCl<sub>3</sub>) were used.

Table 1  
Physico-chemical parameters of raw OMWW

Parameters	Concentration
TOC (%)	106.69
TKN (g L <sup>-1</sup> )	0.16
pH	4
COD (g L <sup>-1</sup> )	187.6
DM (g L <sup>-1</sup> )	122.9
Conductivity (ms cm <sup>-1</sup> )	13.93
Polyphenol (g L <sup>-1</sup> )	4.3

TOC, total organic carbon; TKN, total Kjeldahl nitrogen; COD, chemical oxygen demand; DM, dry matter.

Table 2  
Different treatments (T) with Fenton's reagent and hydrogen peroxide

Treatments	OMWW (L)	FeSO <sub>4</sub> (g)	FeCl <sub>3</sub> (g)	H <sub>2</sub> O <sub>2</sub> (L)
T1	1	5	0	1
T2	1	10	10	1
T3	1	0	0	1
T4	1	0.2	0.2	1
T5	1	50	50	1

T: treatment.

The process is based on the in situ OMWW decomposition with Fenton process using the reaction of ferric or ferrous salts with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) under acidic conditions (pH = 4) to generate highly reactive hydroxyl radicals. Mixture of ferrous salt (used as catalyst) and hydrogen peroxide, which is able to generate hydroxyl radicals, were tested [29]. In flask, the OMWW was treated according to different tests described in Table 2. The tests were done in July–August at ambient temperature and agitation at 250 rpm. As described by Seesuriyachan et al. [30], a mixture of Fe<sup>2+</sup> and Fe<sup>3+</sup> was added to olive mill wastewater at different concentrations, then H<sub>2</sub>O<sub>2</sub> was added to initiate the reaction. Samples were taken after 1, 2, 5 and 10 h of reaction. After the introduction of Fenton's reagent, the reactor was maintained under continuous stirring at 200 rpm. Aqueous samples were taken and the Fenton reaction was quenched instantaneously by adjusting the reaction mixture to pH 7. The reaction mixtures were filtered by Whatman filter paper to remove the precipitate before analysis.

### 2.3. Extraction and assay of phenols

For each treatment, the extraction of polyphenolic compounds was carried out in the presence of a methanol solution 80% (v/v). Total polyphenols were extracted and purified with ethyl acetate, as reported in Macheix et al. [31], and were assayed according to Folin-Ciocalteu [32]. The contents in phenolic compounds were expressed in mg L<sup>-1</sup> against a standard based on hydroxytyrosol prepared at 60 mg/100 mL in 36% methanol.

### 2.4. High performance liquid chromatography analysis

The analyses of phenol extracts were done by high performance liquid chromatography (HPLC) (column reverse-phase Interchrom C18 (4.6 × 250 mm, 5 μm). The mobile phase was made of a gradient of bi-distilled water and acetonitrile and acidified to pH 2.6 with O-phosphorous acid then filtered on Millipore (0.45 μm). The separation lasts 1 h on a gradient of 5%–80% of acetonitrile/water (V/V). The phenolic compounds were detected simultaneously at three wavelengths: 280, 320 and 350 nm and were identified after comparison with standards. Co-injections with commercial standards (hydroxytyrosol, catechol, 3,4-dihydroxyphenylethanol, caffeic acid, *p*-coumaric acid and syringic acid) were performed to confirm the presence of each compounds.

The removal rate of phenolic compounds was estimated by the following equation:

$$\text{Removal rate (\%)} = \left( \frac{A_i - A_s}{A_i} \right) \times 100 \quad (5)$$

A<sub>i</sub> is the concentration in the initial solution and A<sub>s</sub> is the concentration after each treatment.

### 2.5. Statistical analysis

The collected data were subjected to statistical analysis. The mean value was obtained from a descriptive analysis. One-way analysis of variance test was conducted to obtain *F* values and mean square errors. Tukey's test was used to determine the level of significance against the tests values in each experimental series.

## 3. Results and discussion

### 3.1. COD removal as function of reaction time, Fenton's reagent and H<sub>2</sub>O<sub>2</sub>

It has been observed that the percentage of COD removal depends on the three following parameters: (1) the reaction time, (2) the presence or absence of the Fenton's reagent and (3) the concentration of these reagents.

As shown in Fig. 1, the curve of COD removal vs. time shows an increasing trend with the increase of the concentration of both Fe<sup>2+</sup> and Fe<sup>3+</sup>. The highest COD removal (about 99%) was obtained after 10 h of treatment (T5). 85% removal of COD from textile wastewater has been reported by Lin and Peng [33] and Kang and Chang [34]. Kang et al. [35] showed that the Fenton process includes both oxidation and coagulation functions. Neyens and Baeyens [36] indicated that at low pH and in the presence of organic substrates with an excess of ferrous ions, hydroxyl radicals can add to the aromatic or heterocyclic ring and can also abstract a hydrogen atom, thereby, initiating a radical chain oxidation [14]. In their study of olive mill wastewater treatment by Fenton oxidation with zero-valent iron, Kallel et al. [25] showed that the Fenton oxidation of OMWW could not remove the organic load completely. This might be due to the generation of high concentration of intermediate compounds (mainly

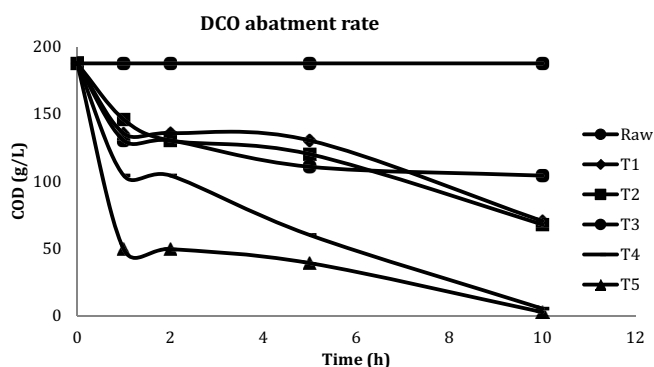


Fig. 1. DCO abatement rate with different treatment (T) by Fe<sup>2+</sup>, Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub>.

carboxylic acids) that cannot be further oxidized by hydroxyl radicals and consequently are accumulated in the system. The concentration of refractory carbon seems to be a feature of the effectiveness of the Fenton oxidation [37] whereas higher concentrations of both  $\text{H}_2\text{O}_2$  and Fenton's reagent ( $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ) at pH 4 are necessary to obtain the highest level of COD removal ( $187.6 \text{ g L}^{-1}$ ). This indicates that the mechanism for the removal of COD from olive oil wastewater by the Fenton process is different from that of other wastewater sources. Catrinescu et al. [38] showed that the COD removal depends on the PILC-catalyst concentration (up to  $0.5 \text{ g L}^{-1}$ ). Kang et al. [35] showed that to remove simultaneously color and COD, relatively high concentrations of ferrous ions and  $\text{H}_2\text{O}_2$  were necessary. Since ferric coagulation favors COD removal, it is important to prevent the reduction of ferric ions into ferrous ions in the reaction system.

When only  $\text{H}_2\text{O}_2$  was applied (treatment T3), the COD removal was about 69.5% and it remained constant after 5 h of treatment. At high level of  $\text{H}_2\text{O}_2$ , the COD removal decreased which is similar to the results obtained by Kang et al. [35]. They explained that at high  $\text{H}_2\text{O}_2$  concentration, the low COD removal is due to residual  $\text{H}_2\text{O}_2$ . Kallel et al. [25] reported that when the reactants  $\text{H}_2\text{O}_2$  or  $\text{Fe}^{2+}$  were overdosed, they could react with the hydroxyl radicals and, therefore, inhibit the oxidation reaction [39,40]. They found that 0.06 M of  $\text{H}_2\text{O}_2$  was needed for the removal of 1 g of COD and the use of higher concentrations did not increase the COD removal. It is well known that the decomposition of organic compound can be reduced in the presence of high concentration of hydroxyl radicals. This is due to the reaction of these radicals with hydrogen peroxide to produce less reactive radicals according to Eq. (6) [14].



### 3.2. Phenol decomposition with Fenton/ $\text{H}_2\text{O}_2$ reaction

The experiments were designed to investigate the interaction of the mixtures of the three catalysts. The amounts of Fenton's reagents were varied to give the best iron catalyst/ $\text{H}_2\text{O}_2$  system. Fig. 2 shows the evolution of the abatement rate after phenol degradation by  $\text{Fe}^{2+}/\text{Fe}^{3+}$  salts and hydrogen peroxide at pH 4.

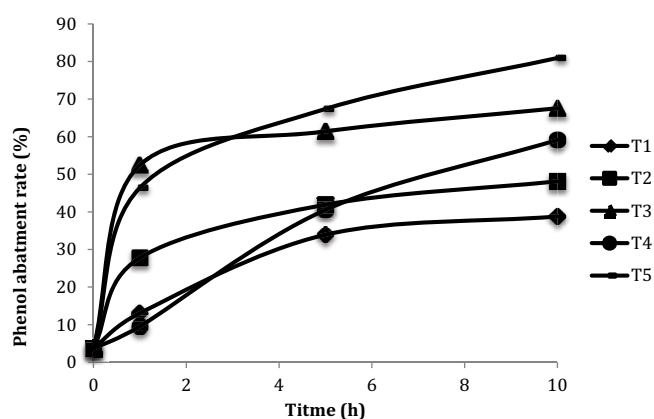


Fig. 2. Phenol abatement rate with different treatment (T) by  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$ .

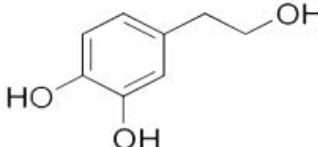
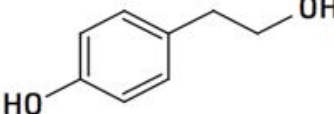
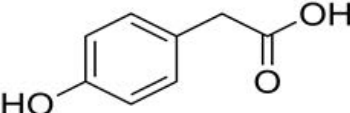
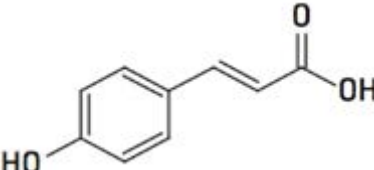
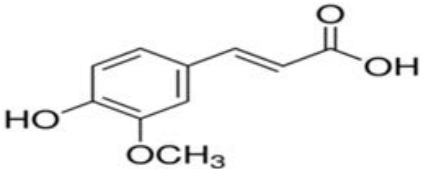
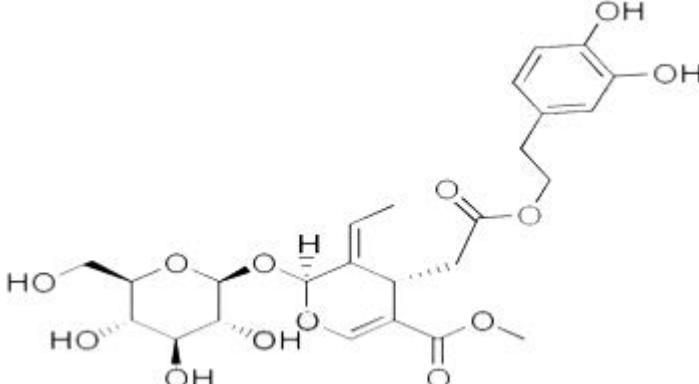
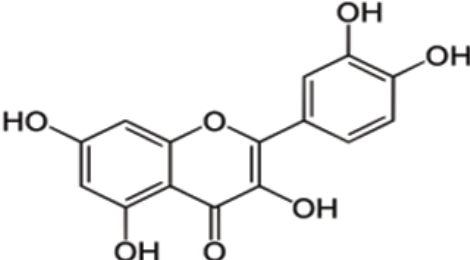
High rate of phenol degradation was observed after 10 h reaction time (about 81%, [T5]). This long reaction time was due to high load of polyphenols ( $4 \text{ g L}^{-1}$ ) and their recalcitrant character. Oxidation by  $\text{H}_2\text{O}_2$  alone was not very effective since only an abatement rate (phenol degradation) of about 67.5% was obtained (T3). When the  $\text{Fe}^{2+}$  was added at low concentration, the phenol degradation was very low (about 39%, [T1]). However, the results showed that in parallel with the  $\text{Fe}^{2+}$  rise, the phenol removal increased up to 60% (T2). The highest mineralization extent of phenol solution was obtained by using  $\text{H}_2\text{O}_2$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  at high concentrations. In this study,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  concentration levels interacted because the ability of  $\text{Fe}^{2+}$  to be regenerated by the reaction of  $\text{Fe}^{3+}$  with  $\text{H}_2\text{O}_2$  was inhibited at acidic pH [15]. As described by Tantiwa et al. [41], the synergistic effects for the phenol degradation enhanced chemical reactions between the two catalysts and  $\text{H}_2\text{O}_2$ . They showed that synergistic catalytic reaction with  $\text{Fe}^0$ ,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  generated higher levels of OH radicals than the reactions with either  $\text{Fe}^0$ ,  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  alone. The same authors showed that by mixing high concentrations of  $\text{Fe}^0$ ,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$ , the decolorization rate increased. In fact,  $\text{H}_2\text{O}_2$  acts as an important co-chemical reagent in Fenton and Fenton-like reactions. It needs to react with either  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  to get high degradation efficiency. Catrinescu et al. [38] showed that by further increasing the amount of the catalyst (up to  $1 \text{ g L}^{-1}$  with an initial concentration of  $250 \text{ mg L}^{-1}$ ), only a slight increase in phenol removal was observed after 1 h, while after 3 h reaction time, a COD removal efficiency can be depicted. They reported that typical  $\text{Fe}:\text{H}_2\text{O}_2$  ratios were 1:5–10 wt./wt. However, iron concentrations of less than 25–50  $\text{mg L}^{-1}$  can require excessive reaction times (10–24 h). This is particularly true when the oxidation products (organic acids) block the iron with the formation of complexes, thereby, removing it from the catalytic cycle [14]. Araujo et al. [24] showed that the degradation of phenolic groups reached its maximum after increasing the concentration of oxygen hydroxide species in the Fenton's reagent. Nevertheless,  $\text{H}_2\text{O}_2$  alone caused only a partial degradation of phenolic compounds inducing the fragmentation of lignin molecule. Lucas et al. [42] showed that Fenton and Fenton-like reactions using synergistic catalytic actions were more efficient than using one catalyst alone. Chu et al. [43] showed that in the absence of  $\text{Fe}^0$ , phenol degradation was decreased by 12% after 2.5 h reaction time at both low and high concentrations of  $\text{Fe}^0$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$ . The oxidation efficiency of the Fenton process on the removal of lignin, aromatics and COD was very low or suppressed. The use of only one catalyst in the reaction could mitigate the removal of lignin, aromatic compounds, and COD. Kallel et al. [25] demonstrated that the zero-valent  $\text{Fe}/\text{H}_2\text{O}_2$  system is efficient to enhance the biodegradability of this toxic effluent. However, efficiency was still low and the effluent needed more time for a better treatment.

### 3.3. Chromatogram analysis

The identified phenolic compounds with their retention times and chemical structures are shown in Table 3.

The HPLC chromatograms of the raw material and two treated (T3 and T5) extracts obtained from OMWW are shown in Fig. 3.

Table 3  
Chemical structures and retention time of HPLC identified phenolic compound

Pic	RT (mn)	Name	Molecular structure
1	11.76	Hydroxytyrosol	
2	15.99	Tyrosol	
3	18.72	<i>p</i> -Hydroxyphenyl acetic acid	
4	24.16	<i>p</i> -Coumaric acid	
5	29.66	Ferulic acid	
6	32.8	Oleuropein	
7	46.15	Quercetin	

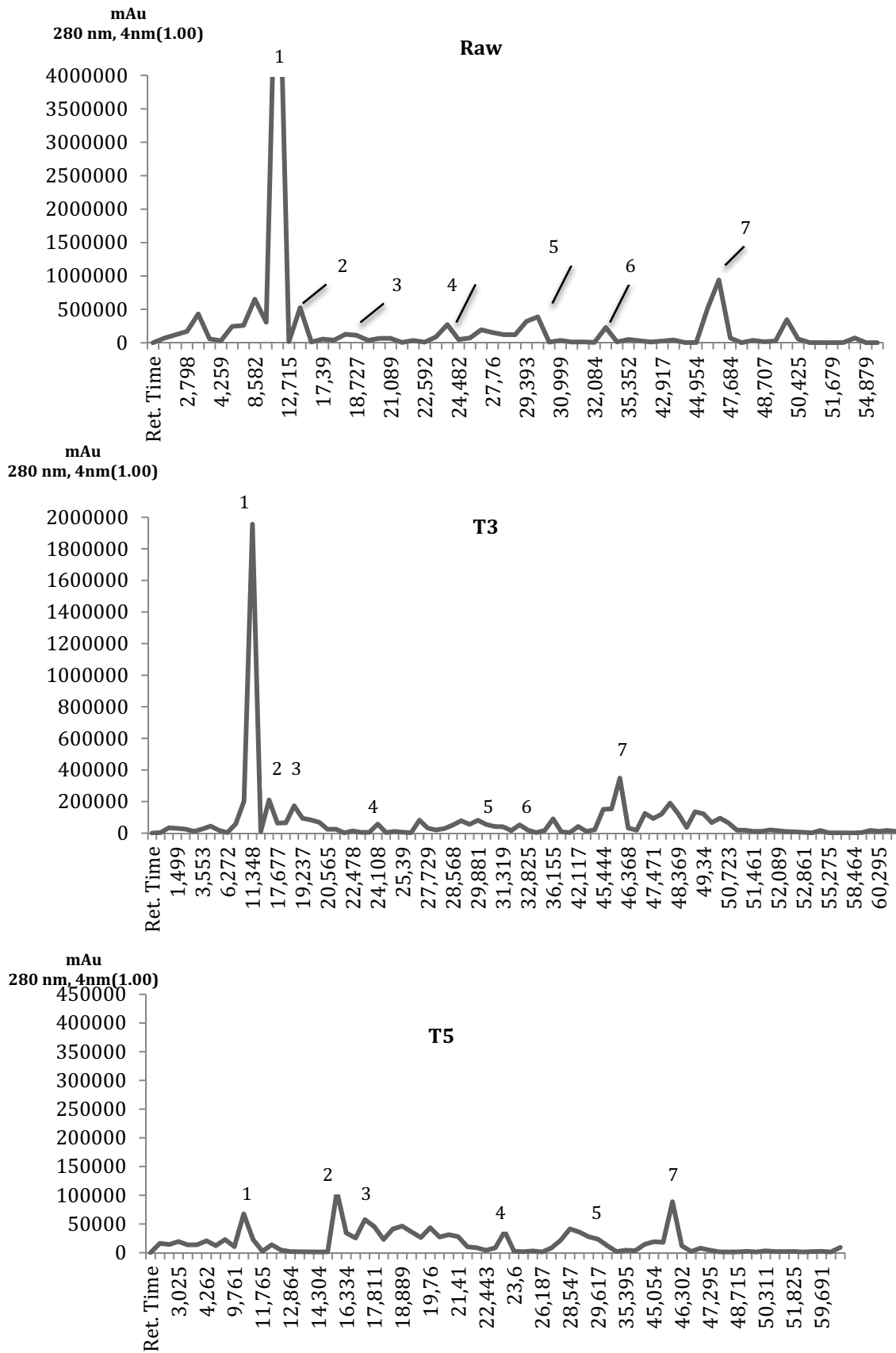


Fig. 3. HPLC chromatogram for OMWW raw matter, treatment T3 and T5 after 10 h.

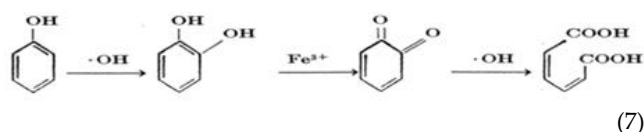
Hydroxytyrosol was the major component detected in this study at 259.1 mg L<sup>-1</sup>. Tyrosol, para-hydroxyphenylacetic acid, para-coumaric acid, oleuropein and quercetin, were present at lower concentrations (Table 4). Several authors have shown that the phenolic compounds identified in olive oil mill wastewater have never been identical. They vary from one study to one another due to variability of the source and the kind of the samples. However, in almost all studied fractions, hydroxytyrosol is the compound identified most frequently [3,25,44]. Fki et al. [45] found that the concentration of hydroxytyrosol in OMWW was 100 to 500 fold higher than that in olive oil. Most of the published research has dealt with hydroxytyrosol as the most interesting ortho-diphenol that is present in olives and their derivatives, due to its antioxidation, antibacterial and beneficial effects on human health [46,47].

No important effect was observed during the treatment with only hydrogen peroxide (treatment T3). Under these conditions, para-hydroxyphenyl acetic acid showed a slight decrease (about 16.42%) (Table 4). However, a high abatement rate of phenol was observed during the treatment T5 after 10 h. The rates were 99%, 67.43%, 59%, 86.37%, 93% and 90.6% for hydroxytyrosol, tyrosol, para-hydroxyphenyl acetic acid, para-coumaric acid, ferulic acid, and quercetin, respectively. Oleuropein completely disappeared during treatment T5 after 10 h (Table 4 and Fig. 3). In the presence of metallic iron, acid medium and concentrated H<sub>2</sub>O<sub>2</sub> (9.5 M), Bremner et al. [48] showed that the degradation of phenol started slowly. After 1.25 h, 91.5% of phenol was still present in the solution, but its concentration decreased after 3 h. Their results showed a complete phenol degradation after 48 h. In the same study, the concentration of phenol dropped to only 40% of the original concentration and this value did not further decrease when the H<sub>2</sub>O<sub>2</sub> was diluted (0.34 M) [48]. However, when dilute hydrogen peroxide was added sequentially, the recorded time for total phenol removal was about 150 h. Santos et al. [49] have shown that the degradation of phenol involving hydroxyl radicals proceeds via aromatic hydroxylation followed by further hydroxylation/oxidations to yield CO<sub>2</sub> and H<sub>2</sub>O.

Kušić et al. [26] showed that by further increasing hydrogen peroxide concentration, phenol degradation efficiency was decreased due to the scavenging nature of hydrogen peroxide towards OH radicals when they are present in high concentration. It has been demonstrated by other investigators [50,51] that hydroxyl radical and singlet oxygen are

able to react with lignin, causing its chemical degradation. Araujo et al. [24] showed that H<sub>2</sub>O<sub>2</sub> alone caused only a partial degradation of phenolic compounds. At the highest concentration of H<sub>2</sub>O<sub>2</sub>, Fenton's reagent could readily degrade phenolic molecules [52]. Xiang and Lee [53] reported that the cationoid species formed by the protonation of H<sub>2</sub>O<sub>2</sub> under acidic conditions are able to react with the electrons of the benzene ring resulting in ring cleavage reactions.

The efficiency of Fenton-type processes is influenced by the concentration of Fe<sup>2+</sup> ions which catalyze hydrogen peroxide decomposition resulting in OH radical production and consequently the degradation of organic molecules [26]. Kang et al. [35] indicated that the availability of Fe<sup>2+</sup> and its interaction with organic intermediates present a crucial importance to improve the decomposition performance of phenolic compounds. The same authors showed that the Fenton oxidation with zero-valent iron is effective to transform the organic compounds present in the OMWW into more readily biodegradable and less toxic byproducts. In addition, they showed that Fe<sup>2+</sup>/HO system is a promising process for the degradation of polyphenols. As reported by Eisenhauer [54], a number of substituted phenols can be oxidized by Fenton's reagent in the same manner as for phenol. In general, the greater the degree of substitution of the aromatic ring, the slower was the rate of reaction, particularly when the substituents were in the ortho and para positions. When all available positions were blocked (e.g., pentachlorophenol), no reaction occurred. Methyl-substituted phenols were more resistant to oxidation than phenol. However, most halophenols were rapidly oxidized. This could be attributed to the electronegativity of the halogen group. Phenols containing meta-directing groups, such as carboxyl and nitrochemical groups, were very rapidly oxidized by Fenton's reagent. On the other hand, Pospisil et al. [55] demonstrated that catechol could be oxidized in high yield to muconic acid by hydrogen peroxide and a ferrous salt, thereby, suggesting that the phenol oxidation proceeds according to Eq. (7).



Eisenhauer [54] explained that when hydrogen peroxide and a ferrous salt are reacting, the ferrous ion is oxidized

Table 4  
Concentrations and the abatement rates of identified phenolic compound during OMWW treatment after 10 h

Pic	Compounds	Concentration (mg L <sup>-1</sup> )			Abatement rate (%)		
		Raw	T3	T5	Raw	T3	T5
1	Hydroxytyrosol	259.10	73.01	2.52	–	72	99
2	Tyrosol	19.47	7.83	6.34	–	60	67.43
3	<i>p</i> -Hydroxyphenyl acetic acid	4.20	3.51	1.73	–	16.42	59
4	<i>p</i> -Coumaric acid	10.13	2.13	1.38	–	79	86.37
5	Ferulic acid	14.47	3.02	1.03	–	79.12	93
6	Oleuropein	8.51	1.97	0.00	–	76.85	0.00
7	Quercetin	35.13	12.99	3.31	–	63.02	90.6

into the ferric state. In the absence of phenol, the ferric ion is rapidly hydrolyzed to deposit ferric hydroxide at pH 3 and above. However, in the presence of phenol, ferric hydroxide does not precipitate during the reaction. This could be explained by Eq. (7) in which the ferric ion is reduced into the ferrous state by catechol with the formation of *o*-quinone. Even after completion of the reaction, the mixture remains homogeneous possibly due to a ferric ion complexing phenomenon associated with the formation of muconic acid.

#### 4. Conclusion

The combination of hydrogen peroxide and a ferrous salt is considered as a potent oxidizing agent for polyphenols and COD in acidic OMWW. It requires 50 g L<sup>-1</sup> of Fe<sup>3+</sup>, 50 g L<sup>-1</sup> Fe<sup>2+</sup>, 1 L of H<sub>2</sub>O<sub>2</sub> and 10 h reaction time to achieve 98.6% and 81% of COD and polyphenol removal, respectively. This reaction affects significantly the hydroxytyrosol with 99% of abatement rate. HPLC analysis showed a high degradation rate of identified phenolic compounds and an increasing biodegradability of the treated OMWW. This study shows that Fenton reagent Fe<sup>3+</sup>, Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> can be considered as an effective alternative solution for the OMWW treatment.

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