



Treatment of olive mill wastewater using physico-chemical and Fenton processes

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ABSTRACT

In this study, treatability of olive mill wastewater (OMW) by acid cracking, chemical coagulation, and Fenton process was investigated. Various coagulants, such as alum, ferric chloride, ferrous sulfate, and bentonite were examined in chemical coagulation process and the chemical oxygen demand (COD), total phenols, color, and aromaticity were determined. The removal of COD, color, total phenols, and aromaticity in acid cracking were 47, 63, 30, and 57%, respectively. The pH, iron-salt, and hydrogen peroxide dosage were found to significantly affect the efficiencies of Fenton process and acidic pH conditions were the most effective. Acid cracking and Fenton process showed high efficiency of COD (83%), total phenols (98.6%), color (77%), and aromaticity (67%) removal from the OMW. As a result of this study, acid cracking and Fenton process have a significant effect in reducing the COD and total phenols from OMW.

Keywords: Acid cracking; Coagulation; Olive mill wastewater; Fenton process

1. Introduction

The production of olive and olive oil is significant agricultural activities in the Mediterranean countries [1] and approximately, 1.8×10^6 tons of olive oil are produced annually worldwide, where the majority (98%) of it is produced in the Mediterranean basin [2]. It is also approximated that around 30 million cubic meter of OMW are generated annually in this area [3]. Olive mill wastewater (OMW) generated from olive oil production is a serious environmental problem due

to its high organic content, suspended solids (SS), high concentrations of recalcitrant compounds, and resistance to biodegradation caused by its high level of polyphenol [4].

The organic fraction of OMW contains 2–15% of phenolic compounds corresponding to a concentration of 0.002–80 g/L [5,6]. The chemical oxygen demand (COD) is also high, ranging from 45 to 220 g/L, as is the biochemical oxygen demand (BOD₅), ranging from 35 to 100 g/L. The pH of OMW is acidic, approximately 4–5 [6]. In addition, OMW can contain a considerable amount of SS that can reach 1–9 g/L [7,8]. Most of the aforementioned parameters are varied

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based on source of olives; however, SS up to 190 g/L have been recorded [9].

The uncontrolled disposal of OMW constitutes serious environmental problems, such as coloring of natural waters, threat to the aquatic life, causing surface and ground water pollution, changing soil quality and plant growth, and causing odors [10]. Therefore, OMW treatment should be carried out properly, but there are some difficulties about treatability of OMW. These are mainly related to (a) high organic loading, (b) seasonal operation (typically between December and March), (c) high territorial scattering, (d) localized production low and wastewater flow rates (between 10 and 100 m³/d), and (e) presence of organic compounds which are hard to biodegrade such as long-chain fatty acids and phenolic compounds [11].

There are several processes described in the literature for the treatment of OMW. Some treatment methods practiced on a large scale have until now proved to be ineffective or very costly. Aerobic or anaerobic biological processes require long treatment times owing to the inhibition effect of phenolic compounds and do not completely remove the organic pollution load. Many physico-chemical treatment methods produce large quantities of sludge, though others have high cost and low efficiency [12]. Aktas et al. [13] have tested the lime treatment of OMW, achieving a low degree of removal (28%) of volatile phenols responsible for high COD values and moreover phytotoxic conditions. Therefore, research efforts have been directed toward the development of efficient treatment technologies that include various combinations of some physical, chemical, biological, and advanced treatment processes. Chemical + biological treatment [14], aerobic treatment + Fenton oxidation [15], electro Fenton + anaerobic treatment [16], UF + H₂O₂/UV [17], physical treatment + adsorption [18], reverse osmosis membranes [19], laboratory-scale physico-chemical methods using UV/H₂O₂ [20], and adsorption processes using different concentrations of activated carbon as adsorbent [21] have been successfully applied on OMW treatment.

Acid cracking and coagulation with various coagulants, such as chitosan, sodium dodecyl sulfate, and FeCl₃ have been used for OMW treatment and the COD has been decreased from 128 to 19.2 g/L with a removal efficiency of 85% [1]. In another study done by Kiril Mert et al. [11], acid cracking, coagulation, and Fenton and Fenton-like processes have been used and they have removed 67% of COD and 72% of total phenol by acid cracking and coagulation–flocculation. Fenton and Fenton-like processes have showed high COD (>80%) and total phenol (>85%) removal performance. Yalılı Kılıç et al. [4] have used acid cracking,

oil separation, and coagulation–flocculation processes at pilot scale and obtained high efficiency of COD (85%), oil and grease (O&G) (>97%), SS (>99%), and phenol (92%) removal from the OMW.

In recent years, new treatment technologies have been developed to reduce organic and phenolic contaminants of OMW. Among them, advanced oxidation process (AOP) which employ strong oxidant agents (ozone, hydrogen peroxide and UV, Fenton, etc.), are able to remove organic and phenolic pollutants of the OMW [22]. The Fenton process one of the AOPs is accomplished by the implementation of hydrogen peroxide (H₂O₂) and a ferrous salt (Fenton's reagent). It is an economical system characterized by its simple application and possibility of using perfectly mixed tank reactors. The system can also be adapted to different volumes and individual conditions [23].

Fenton process has been largely studied on OMW treatment and great efficiencies are reported by several authors. Dogruel et al. [24] obtained 46–63% total phenol and 40–50% COD removal, while Lucas and Peres [25,26] removed 70 and 96.8% COD, respectively. Ozdemir et al. [27] utilized two different methods of Fenton process named Conventional Fenton (CFP) and Fenton Type Processes (FTP) with zero-valent iron to remove COD and phenol from OMW. 82.4% COD and 62% phenol removals were performed under the optimum conditions by CFP, while 82% COD and 63.4% phenol were removed by FTP.

The aim of this study is the investigation of most appropriate treatment process combinations for OMW. For this purpose, acid cracking, chemical coagulation with various coagulants, and Fenton process have been applied and the results of these treatment processes are presented as COD, total phenol, color, and aromaticity removal efficiencies.

2. Materials and methods

2.1. Materials

Sulfuric acid, hydrochloride acid, sodium hydroxide, lime, and hydrogen peroxide were purchased from Merck. All chemicals were used without further purification. A.R. grade chemicals, H₂SO₄, NaOH, and H₂O₂ (30%) were used without any purification and were provided by Merck.

2.2. Wastewater specification

The OMW used in this study was taken from the effluents of an olive oil production plant located in Lushan Industrial, Gilan city, Iran. The factory uses a centrifugal three-phase olive oil extraction process

with maximum daily oil processing capacity of 60 tons at an average waste effluent of 430,000 L/day on the days the factory active. The pollution characteristics of this wastewater are given in Table 1.

2.3. Experimental procedure

Two types of experiments were performed: physico-chemical treatment and advanced oxidation studies using the Fenton process. An acid cracking study was performed in a 1 L cylindrical reactor, and the intermediate phase was moved to 0.5 liter beakers by the siphoning method. The pH was adjusted using sulfuric acid to obtain a pH 2.5.

In the physico-chemical treatment, experiments were performed using a jar test apparatus (Zagchimi (Iran Co.)), Ca(OH)_2 (lime), and ionic and cationic polyelectrolytes were used to investigate the coagulation–flocculation effects at various dosages.

The coagulation process was done using alum, ferric chloride, and ferrous sulfate. The pH was adjusted by NaOH before the coagulation agent. Wastewater with the coagulation agent was mixed in the jar test apparatus for 1 min at 120 rpm, and then mixed for 15 min at 30 rpm.

All the Fenton experiments were performed in a 250 ml glass batch reactor placed in a shaker. A certain amount of ferrous sulfate hepta-hydrate was added to the samples and the pH was adjusted with sulfuric acid. The aqueous solution containing the

reactants was homogenized by magnetic agitation to avoid concentration gradients. Advanced oxidation with the Fenton (Fe^{+2} -salt + H_2O_2 in acidic solution) experiments was performed using an ordinary jar test apparatus, where 0.5 liter beakers were used and pH adjustments were done manually using sulfuric acid (1 N) and sodium hydroxide (1 N). The addition of the ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) solution was done in the next step. Afterwards, hydrogen peroxide (reagent grade 30%) was added to the medium and the reaction began. The reaction was complete within 60 min (5 min rapid mixing and 55 min slow mixing). The Fenton oxidation experiments were performed under various Fe^{+2} salt, H_2O_2 , and pH values to determine the optimum conditions.

2.4. Analytical method

The COD was measured using a spectrophotometer instrument (ET108, Lovibond Co.) according to the Standard Method, Section 5220D [28,29]. Turbidity was measured using N2100 Hach (USA) after being diluted five times due to the high turbidity of the samples. Additionally, the aromaticity and color of the samples were measured after being diluted 100 times by N2100 Hach (USA) at 254 nm and 280 nm wavelengths, respectively. The last one is then called polyphenol index (A_{280}) which is a relative index of the polyphenol content [30]. The total phenol content was determined according to a modified Folin–Ciocal-

Table 1

The physico-chemical analysis of OMW before processing and after acid cracking, the Fenton test, and the coagulation test

Parameter	Raw OMW	Pretreated OMW after acid cracking at pH=2.5	Removal efficiency after acid cracking (%)	Removal efficiency after Fenton (%)	Removal efficiency after coagulation (%)	Total removal efficiency (%)
pH	5.4 ± 0.15	2.5 ± 0.15	–	–	–	–
COD (g/L)	74.4 ± 3.42	39.64 ± 2.45	47	57	27.6	83
Color (@ 280 nm) ^a	–	–	63	18	6.2	77
Turbidity (NTU)	2,665 ± 82	2,530 ± 64	97	–	–	–
Total phenols (mg/L)	1.8 ± 0.1	1.25 ± 0.05	30	97	35	98.6
Aromaticity (@ 254 nm) ^b	–	–	57.4	32	8.5	67

Notes: ^aThe absorbance value at 280 nm is measured before and after the treatment and used to calculate the color removal efficiency.

^bThe absorbance value at 254 nm is measured before and after the treatment and used to calculate the aromaticity removal efficiency.

Table 2

Removal efficiencies of wastewater pollution parameters on acid cracking at different pH values

Sample no.	pH	Removal efficiency (%)					Time (min)
		COD	Turbidity	Total phenol	Aromaticity	Color	
1	1.5	46.3	98	30.1	59.1	64.3	50
2	2.0	47.3	96	28.1	58.7	63.8	50
3	2.5	47.1	97	29.6	57.4	63.2	60
4	3.0	46.4	92	28.3	55.3	62.1	150
5	3.5	46.4	90	23.8	51.9	62.0	> 360

teu method [31]. The total phenol content was determined using 0.5 ml of Folin–Ciocalteu (fourfold diluted) phenol reagent to 10 ml of samples (20 times diluted). After 5 min, 0.5 ml of sodium carbonate solution (200 g/L) was added and the absorbance was measured at 725 nm against a blank after 30 min. The hydrogen peroxide concentration according to the standard iodometric titration method was measured by sodium thiosulfate (0.1 N) titration with a starch paste indicator.

3. Results and discussion

3.1. Acid cracking test

A large amount of pollution and oil particles in OMW results in stable emulsions. De-emulsification of this stable emulsion can be done by heating or adjusting the pH using sulfuric acid or hydrochloric acid. The emulsion has a negative charge and, therefore, acidification of the solution can increase the H^+ concentration, can neutralize the negative charge and help precipitate the emulsion particles. To investigate the optimum pH of the solution, several experiments were performed at different acidic pH values using concentrated sulfuric acid. The removal efficiency of the wastewater pollution parameters was determined using the COD, turbidity, total phenol, aromaticity, and color and their relationship with pH, which is presented in Table 2. As observed from Table 2, the optimum pH was 2.5. Lower pH values just reduced the experimental time and did not show a significant difference in the removal efficiency. However, at a low pH, more NaOH is required to adjust the pH in other steps of the experiment to complete treatment, which is not an economic solution. The required sulfuric acid for the acid cracking process was measured using 1.5 ml per one liter of wastewater and the acid cracking time was approximately 1 h to complete the process. The results of this process are shown in Table 2 and indicate that acid cracking alone resulted in satisfactory treatment efficiencies.

3.2. Investigating the double effect of acid cracking

Acid cracking is an important process to decrease waste pollution parameters, such as COD, turbidity, total phenol, aromaticity, and color. Two aspects can be considered in acid cracking of OMW. One, sulfuric acid is a powerful oxidant agent that can oxidize the OMW component and reduce the COD itself. However, adding sulfuric acid results in a lower pH and improves the coagulation of OMW. To investigate the coagulation and oxidation effect of acid cracking, two separate experiments were performed at the optimum pH condition. In one of the tests, the solution was allowed to precipitate and in the other test, precipitation was avoided by being continuously stirred using a magnetic stirrer. After one hour, the COD of the solution was measured and compared. The results indicate that only 10% of the acid cracking efficiency was due to its oxidation effect, while the other 90% was related to the coagulation effect. In the case that the solution was continuously stirred and avoided to precipitate, the only process which occurred was oxidation and the COD removal at this section was low and only 10% of the whole COD removal occurred in the process which allows the solution to precipitate.

3.3. Coagulation tests

Lime ($Ca(OH)_2$) was used as the coagulation agent to precipitate the particles; however, using lime resulted in certain problems, such as a low efficiency in COD removal, an increase in water stiffness, an increase in pH up to 11–12, and the production of a large amount of slop. In this study, the use of typical coagulants, such as alum, ferric chloride, ferrous sulfate, and bentonite were examined. The ferric chloride treatment after acid cracking resulted in a 27.6% COD removal and 35% phenol removal at a dose of 6 g/L. Ferric chloride at a pH 9 showed a better efficiency to decrease the pollution parameter than the other treatments. Fig. 1. shows that the COD decrease as a result of the ferric chloride.

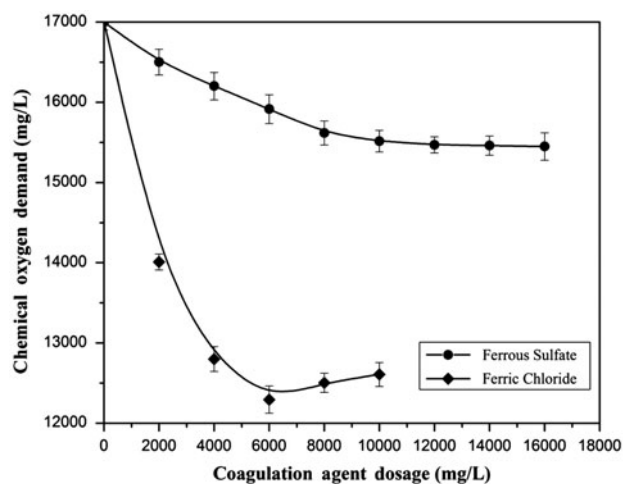


Fig. 1. COD variation by adding different dosages of ferric chloride and ferrous sulfate as coagulation agent.

Compared with the ferric chloride, the addition of ferrous sulfate up to 15 g/L did not show a significant COD removal, which indicates the effect of the cation charges on the coagulation process. Additionally, the addition of alum at the optimum pH showed a similar behavior and did not decrease the pollution parameter efficiently. However, the use of bentonite exhibited a high efficiency in color and turbidity removal; it was found that 5 g/L of bentonite can reduce the wastewater turbidity and color by 50–60% and 30–40%, respectively. Thus, bentonite can be used as an absorbent agent during the coagulation process.

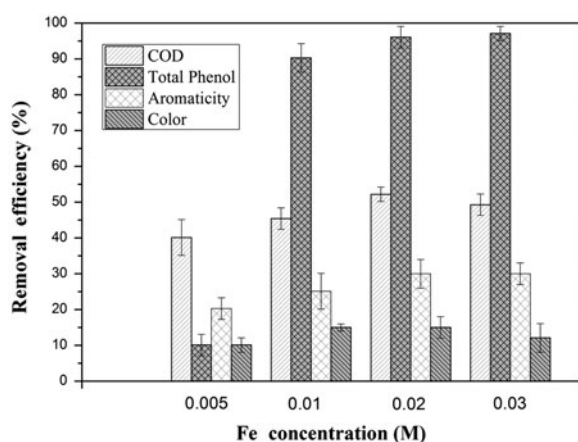


Fig. 2. Fe (II)/H₂O₂ treatment of OMW as demonstrated by the evolution of the COD removal efficiency, total phenol, aromaticity, and color with the influence of the ferrous iron initial concentration. $T_0 = 298$ K, pH = 3, H₂O₂ concentration of 0.5 M, and reaction time of 4 h at a stirring rate of 90 rpm.

As shown from Fig. 1, the optimum amount of ferric chloride consumption was fixed at 6 g/L. Table 1 shows that other pollution parameters decreased with the use of ferric chloride.

3.4. Fenton test

Performing Fenton followed by acid cracking to decrease the pollution parameters was also studied. Typical operating variables, such as the reagent concentration ($C_{Fe(II)}$) 0.005–0.03-M, ($C_{H_2O_2}$) 0.12–0.5 M, at a pH between 2 and 5, and reaction temperature (T) between 298 and 303 K had a positive influence on COD and total carbon removal. In this study, the optimum pH and the hydrogen peroxide and iron ion concentrations were obtained.

3.4.1. Effect of the initial amount of iron salts

Generally, the rate of degradation increases with an increase in the concentration of ferrous ions [32–34]; however, the extent of the increase is sometimes only marginal above a certain concentration, as reported by [35–37]. Additionally, an enormous increase in ferrous ions will lead to an increase in the unused quantity of iron salts, which will contribute to an increase in the TDS content of the effluent stream and is not permitted. Thus, laboratory-scale studies are required to establish the optimum loading of ferrous ions under similar conditions unless data are available in open literature [38].

The effect of the initial concentration of ferrous iron is shown in Fig. 2. As observed from the Fig. 2, the optimum load of ferrous iron is 0.02 M. An excess amount of ferrous iron does not significantly affect the removal efficiency of the total phenol, though it can reduce the COD and color removal efficiency.

3.4.2. pH effect

The performance of Fenton processes is highly affected by the reaction media pH [39,40]. Broadly speaking, low pH values between 2 and 4 favor the efficacy of the oxidation. In this study, different values of pH were investigated to ascertain the influence of this parameter on the removal of COD, color, and aromaticity.

At lower pH values (pH < 3), $Fe(OH)^{2+}$ forms, which reacts more slowly with hydrogen peroxide and therefore, produces less reactive hydroxyl radicals, which reduces the degradation efficiency [41,42]. In addition, the scavenging effect of hydroxyl radicals by H^+ becomes important at very low pH values [43]

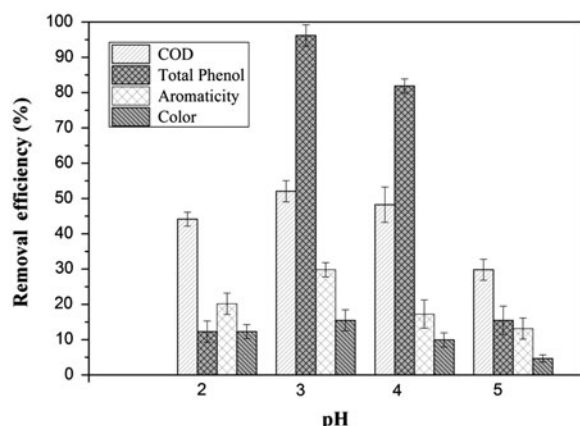


Fig. 3. Fe (II)/H₂O₂ treatment of OMW as demonstrated by the evolution of the removal efficiency of the COD, total phenol, aromaticity, and color with the influence of the pH from 2 to 5. $T_0 = 298$ K, ferrous iron initial concentration 0.02 M, H₂O₂ concentration 0.5 M, and reaction time of 4 h at a stirring rate of 90 rpm.

and the reaction of Fe³⁺ with hydrogen peroxide is also inhibited [42]. At a pH of 4, the decomposition rate decreases because of the decrease in the free iron species in the solution, likely due to the formation of Fe (II) complexes with the buffer, which inhibits the formation of free radicals and also due to the precipitation of ferric oxyhydroxides [34,44,45], which inhibits the regeneration of ferrous ions. Additionally, the oxidation potential of HO• radicals is known to decrease with an increase in pH [33]. At a higher pH and alkali pH, Fe²⁺ is converted to Fe³⁺, precipitates as Fe(OH)³⁺, and loses its catalytic effects so it is no longer active in the reaction. Furthermore, it has been

proven that the reaction potential of HO• radicals reduces with increasing pH [46]. To investigate the effect of pH, first, the hydrogen peroxide and iron ion concentrations were fixed at 0.25 and 0.02 M, respectively, and then the process was studied at different pH values (2–5). The result was an optimum pH of 3. With increasing pH, the Fe²⁺ half-life decreased and then Fe was removed from the environment as a catalyst; thus, the process efficiency decreased. The pH effect on the COD, color, and aromaticity removal is shown in Fig. 3.

3.4.3. Variation in pH during the reaction time

The pH variation during the reaction time (Fig. 4) can indicate the reaction promotion. The first decrease is due to the addition of the Fe solution with sulfuric acid and the second decrease is after adding H₂O₂ to the reaction. The decreasing pH gradually continued because of the formation of the organic acid component during the reaction.

3.4.4. Effect of the amount of hydrogen peroxide

The concentration of hydrogen peroxide plays a more crucial role in deciding the overall efficacy of the degradation process. Generally, it has been observed that the degradation percent of the pollutant increases with an increase in the peroxide dosage [33–37,47]. The presence of hydrogen peroxide is harmful to many microorganisms [48] and will affect the overall degradation efficiency significantly, where Fenton oxidation is used as a pretreatment to biological oxidation. An additional negative effect of hydrogen peroxide, if present in large quantities, is that it acts as a scavenger for the generated hydroxyl radicals. Thus, the loading of hydrogen peroxide should be adjusted in such a way that the entire amount is used, which can be determined based on laboratory-scale studies on the effluent in question.

In this study, the iron ion and hydrogen peroxide concentrations were fixed in two ranges, (0.01, 0.02, 0.03, and 0.05 M) and (0.12, 0.24, 0.36, and 0.48 M), respectively. The results showed that the process efficiency does not increase if the amount of iron ions added to the wastewater exceeds 0.02 M. If the iron ion concentration is increased to greater than 0.02 M, the amount of iron ions will increase in the outlet wastewater, which decreases the COD removal efficiency and the process will not be as economic and environmentally friendly.

In this study, the optimum concentration was 0.36 M. If the concentration becomes greater than

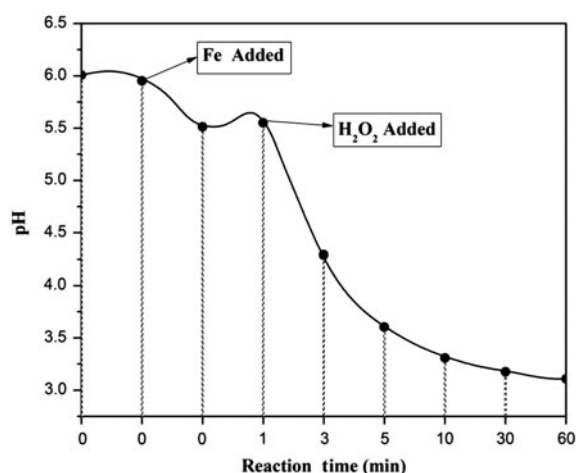


Fig. 4. Variation in pH during the reaction time and the effect of adding Fe²⁺ salt and H₂O₂.

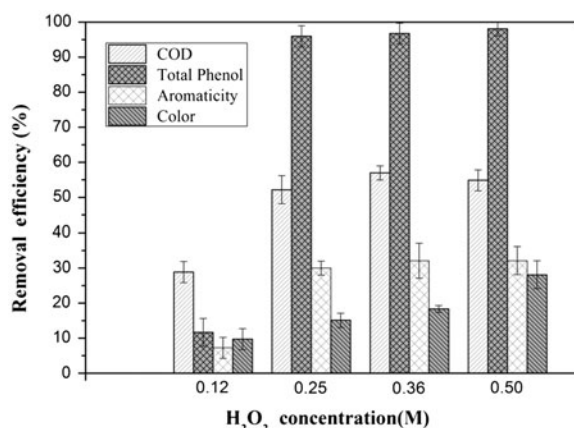


Fig. 5. Fe (II)/H₂O₂ treatment of OMW as demonstrated by the evolution of the removal efficiency of the COD, total phenol, aromaticity, and color with the influence of a H₂O₂ concentration (0.12, 0.25, 0.36, and 0.5 M), T₀ = 298 K, ferrous iron initial concentration of 0.02 M and a reaction time of 4 h at a stirring rate of 90 rpm.

0.36 M, the reaction temperature will increase and there is no way to control the solution temperature when analyzing the hydrogen peroxide; thus, the process efficiency will decrease.

Fig. 5. shows the effect of the Fenton advance oxidation in optimum iron ions and peroxide concentration (0.02 M as conc. and 0.36 M as).

3.4.5. Temperature effect

Not many studies are available depicting the effect of temperature on the degradation rates and ambient conditions can safely be used with good efficiency. Lin and Lo [30] reported an optimum temperature of 303 K, whereas Rivas et al. [33] reported that the degradation efficiency is unaffected even when the temperature is increased from 283 to 313 K. If the reaction temperature is expected to rise beyond 313 K due to exothermic reactions, cooling is recommended at temperatures greater than 313 K, which lowers the efficiency of the hydrogen peroxide due to the accelerated decomposition of hydrogen peroxide into water and oxygen [41].

A series of experiments was performed to assess the influence of temperature on the final COD, total phenol, color, and aromaticity removal extent. As stated previously, runs were completed with the temperature being controlled at 298 K. Therefore, for the conditions of these experiments [Fe(II) at 0.02 M and H₂O₂ at 0.5 M, pH at 2.5], an average increase of 10–15 K greater than the starting temperature occurred within several minutes after mixing the Fenton's

Table 3

Temperature effect on the COD, total phenol, color, and aromaticity removal efficiency; pH 2.5, Fe(II) initial concentration 0.02 M and H₂O₂ concentration 0.5 M

Parameter	Removal efficiency (%)	
	Temperature 298 K	Temperature 308 K
COD	52	51
Total phenol	96	98
Aromaticity	30	27
Color	15	18

constituent reagents. Table 3 shows the benefits of increasing the temperature on the COD degradation rate. As mentioned by Rivas et al. [33] and shown in Table 3, increasing the temperature from 298 to 308 K has no significant effect on the percentage of COD and other parameters; increasing the temperature only increases the reaction rate slightly.

3.4.6. Effect of using different amounts of hydrogen peroxide during the reaction time

The reaction time depends on several parameters, such as the initial concentration of wastewater, initial amount of hydrogen peroxide, and the amount of iron salts. Wastewater with a phenolic component less than 0.25 g/L is typically complete after approximately 30–60 min; however, it may take several hours for the high phenolic content of the OMW to be fully removed. In all experiments, the amount of iron was adjusted to 0.02 M and the removal efficiency variation of the pollution parameters, such as the COD, total phenol, aromaticity, and color, with different amounts of hydrogen peroxide during the reaction time is shown in Fig. 6(a–d). As observed from Fig. 6, after 4 h reaction is discontinued, there was no observable change in the removal efficiency. It is clear from Fig. 6(a) that the COD is rapidly removed early in the experiment and tends to become constant after 4 h. Increasing the amount of H₂O₂ from 0.12 to 0.5 M also led to an increased COD removal. Fig. 6(b) shows that the increase in H₂O₂ has less of an influence on the TP removal efficiency; however, it exhibits the intrinsic behavior of raising the amount of TP removal as H₂O₂ increases slightly. H₂O₂ has a significant effect on the aromaticity removal efficiency; a small increase in H₂O₂ from 0.12 to 0.25 M led to the aromaticity removal increasing from 5 to 30%. Similar behavior can be seen in the color removal, which can clearly be observed in Fig. 6(d). Despite all of the aforementioned points, it should be noted that in

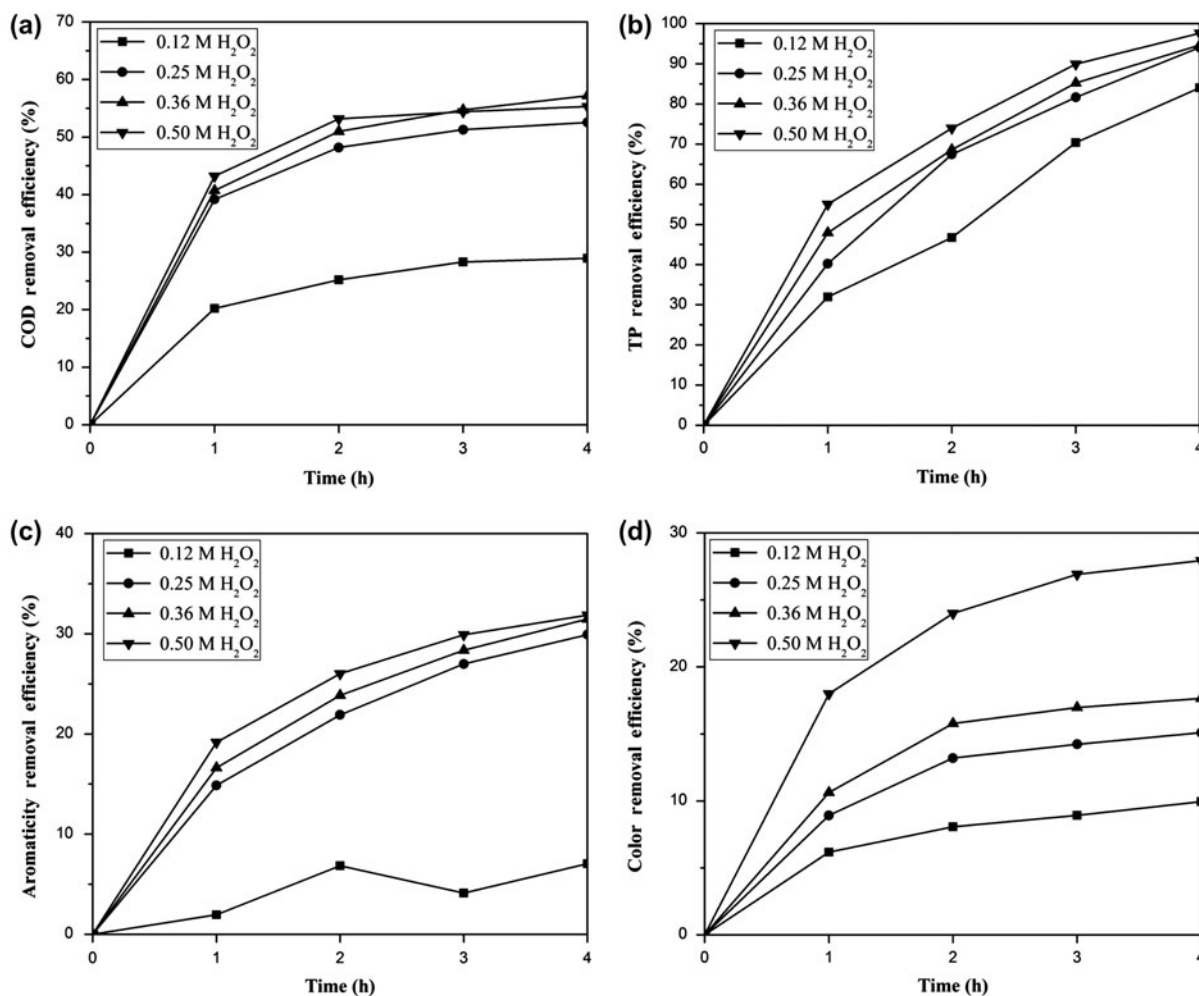


Fig. 6. Effect of using different amounts of hydrogen peroxide during the reaction time on the removal efficiency of the COD, total phenol, aromaticity, and color; $T_0 = 298$ K, ferrous iron initial concentration 0.02 M, H_2O_2 concentration of 0.12, 0.25, 0.36, and 0.5 M.

Fig. 6(a–d), additional amounts of hydrogen peroxide improved the removal efficiency of the pollution parameters.

Conclusion

In this study, acid cracking, chemical coagulation, and Fenton processes were applied on OMW. The conclusions can be drawn from this study.

- (1) The acid cracking at pH 2.5 removed 97, 47, 30, 63, and 57% of the turbidity, COD, total phenol, color, and aromaticity, respectively.
- (2) The results of the experiments showed that the temperature increase from 298 to 308 K does not have a considerable effect on the efficiency process and only slightly increases the rate of the reactions.

- (3) It is obtained more than 83, 98.6, 77, and 67% removal of COD, total phenol, color, and aromaticity by the combination of acid cracking, chemical coagulation, and Fenton processes.

Consequently, it can be concluded that a combination of acid cracking, chemical coagulation, and Fenton processes can be used as a suitable treatment processes for OMW treatment.

Conflict of interest

The authors have declared no conflict of interest.

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Abbreviations

OMW	—	olive mill wastewater
BOD ₅	—	biological oxygen demand
COD	—	chemical oxygen demand
SS	—	suspended solids
AOP	—	advanced oxidation process
H ₂ O ₂	—	hydrogen peroxide

References

- [1] M. Yalılı Kılıç, K. Kestioğlu, G. Kaya, Physico-chemical treatability of olive mill wastewater (OMW), *J. Nat. Sci. Appl. Sci.* 13 (2009) 271–276.
- [2] J. Benitez, J. Beltran-Heredia, J. Torregrosa, J.L. Acero, V. Cercas, Aerobic degradation of olive mill wastewaters, *Appl. Microbiol. Biotechnol.* 47 (1997) 185–188.
- [3] R. Casa, A. D'Annibale, F. Pieruccetti, S.R. Stazi, G. Giovannozzi Sermanni, B. Lo Cascio, Reduction of the phenolic components in olive-mill wastewater by an enzymatic treatment and its impact on durum wheat (*triticum durum* desf) germinability, *Chemosphere* 50 (2003) 959–966.
- [4] M. Yalılı Kılıç, T. Yonar, K. Kestioğlu, Pilot-scale treatment of olive oil mill wastewater by physicochemical and advanced oxidation processes, *Environ. Technol.* 34(12) (2013) 1521–1531.
- [5] A. Ben Sassi, A. Boularbah, A. Jaouad, G. Walker, A. Boussaid, A comparison of olive oil mill wastewaters (OMW) from three different processes in Morocco, *Process Biochem.* 41 (2006) 74–78.
- [6] N. Azbar, A. Bayram, A. Filibeli, A. Muezzinoglu, F. Sengul, A. Ozer, A review of waste management options in olive oil production, *Crit. Rev. Env. Sci. Technol.* 34 (2004) 209–247.
- [7] D. Mantzavinos, N. Kalogerakis, Treatment of olive mill effluents: Part I. Organic matter degradation by chemical and biological processes—An overview, *Environ. Int.* 31 (2005) 289–295.
- [8] N. Zouari, Decolorization of olive oil mill effluent by physical and chemical treatment prior to anaerobic digestion, *J. Chem. Technol. Biotechnol.* 73 (1998) 297–303.
- [9] P. Cañizares, J. Lobato, R. Paz, M.A. Rodrigo, C. Sáez, Advanced oxidation processes for the treatment of olive-oil mills wastewater, *Chemosphere* 67 (2007) 832–838.
- [10] Ü. Tezcan Ün, S. Uğur, A.S. Koparal, Ü. Bakır Ögütveren, Electrocoagulation of olive mill wastewaters, *Sep. Purif. Technol.* 52 (2006) 136–141.
- [11] B. Kiril Mert, T. Yonar, M. Yalılı Kılıç, K. Kestioğlu, Pre-treatment studies on olive oil mill effluent using physicochemical, Fenton and Fenton-like oxidations processes, *J. Hazard. Mater.* 174 (2010) 122–128.
- [12] A. Giannis, M. Kalaitzakis, E. Diamadopoulos, Electrochemical treatment of olive mill wastewater, *J. Chem. Technol. Biotechnol.* 82 (2007) 663–671.
- [13] E.S. Aktas, S. Imre, L. Ersoy, Characterization and lime treatment of olive mill wastewater, *Water Res.* 35 (2001) 2336–2340.
- [14] A. Chiavola, G. Farabegoli, E. Rolle, Combined biological and chemical-physical process for olive mill wastewater treatment, *Desalin. Water Treat.* 23(1–3) (2010) 135–140.
- [15] M. Kotsou, A. Kyriacou, K. Lasaridi, G. Pilidis, Integrated aerobic biological treatment and chemical oxidation with Fenton's reagent for the processing of green table olive wastewater, *Process Biochem.* 39 (2004) 1653–1660.
- [16] S. Khoufi, F. Aloui, S. Sayadi, Treatment of olive oil mill wastewater by combined process electro-Fenton reaction and anaerobic digestion, *Water Res.* 40 (2006) 2007–2016.
- [17] M. Drouiche, V. Le Mignot, H. Lounici, D. Belhocine, H. Grib, A. Pauss, N. Mameri, A compact process for the treatment of olive mill wastewater by combining of and UV/H₂O₂ techniques, *Desalination* 169 (2004) 81–88.
- [18] M.O. Azzam, K.I. Al-Malah, N.I. Abu-Lail, Dynamic post-treatment response of olive mill effluent wastewater using activated carbon, *J. Environ. Sci. Health A Toxic/Hazard. Subst. Environ. Eng.* 39 (2004) 269–280.
- [19] T. Coskun, A. Yildirim, C. Balcik, N. Manav Demir, E. Debik, Performances of reverse osmosis membranes for treatment of olive mill wastewater, *Clean – Soil, Air, Water* 41(5) (2013) 463–468.
- [20] A. Bedoui, K. Sindi, N. Bensalah, Treatment of refractory organics contained in actual agro-industrial wastewaters by UV/H₂O₂, *Clean – Soil, Air, Water* 36 (4) (2008) 373–379.
- [21] M.-O.J. Azzam, K. Al-Malah, Z. Al-Gazzawi, S.A. Al-Omari, Dynamic treatment response of olive mills wastewater using series of adsorption steps, *Clean – Soil, Air, Water* 38(9) (2010) 822–830.
- [22] R. Andreozzi, M. Canterino, I. Di Somma, R. Lo Giudice, R. Marotta, G. Pinto, A. Pollio, Effect of combined physico-chemical processes on the phytotoxicity of olive mill wastewaters, *Water Res.* 42 (2008) 1684–1692.
- [23] A.G. Vlyssides, H.N. Loukakis, P.K. Karlis, E.M.P. Barampouti, S.T. Mai, Olive mill wastewater detoxification by applying pH related Fenton oxidation process, *Fresenius Environ. Bull.* 13 (2004) 501–504.
- [24] S. Dogruel, T. Olmez-Hanci, Z. Kartal, I. Arslan-Alaton, D. Orhon, Effect of Fenton's oxidation on the particle size distribution of organic carbon in olive mill wastewater, *Water Res.* 43 (2009) 3974–3983.
- [25] M.S. Lucas, J.A. Peres, Removal of COD from olive mill wastewater by Fenton's reagent: Kinetic study, *J. Hazard. Mater.* 168 (2009) 1253–1259.
- [26] M.S. Lucas, J.A. Peres, Treatment of olive mill wastewater by a combined process: Fenton's reagent and chemical coagulation, *J. Environ. Sci. Health A Toxic/Hazard. Subst. Environ. Eng.* 44 (2009) 198–205.
- [27] C. Özdemir, H. Tezcan, S. Sahinkaya, E. Kalipci, Pre-treatment of olive oil mill wastewater by two different applications of Fenton oxidation processes, *Clean – Soil, Air, Water* 38(12) (2010) 1152–1158.
- [28] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 21st ed., American Public Health Association, Washington, DC, 2005.

- [29] ASTM, Standard Test Methods for Chemical Oxygen Demand of Water Annual Book of ASTM Standards. Report d 1252-06, Philadelphia, USA, 1996.
- [30] J. González-Rodríguez, P. Pérez-Juan, M.D. Luque de Castro, Method for the simultaneous determination of total polyphenol and anthocyan indexes in red wines using a flow injection approach, *Talanta* 56 (2002) 53–59.
- [31] J.D. Box, Investigation of the folin-ciocalteau phenol reagent for the determination of polyphenolic substances in natural waters, *Water Res.* 17 (1983) 511–525.
- [32] F.J. Benitez, J.L. Acero, F.J. Real, F.J. Rubio, A.I. Leal, The role of hydroxyl radicals for the decomposition of p-hydroxy phenylacetic acid in aqueous solutions, *Water Res.* 35 (2001) 1338–1343.
- [33] B.G. Kwon, D.S. Lee, N. Kang, J. Yoon, Characteristics of p-chlorophenol oxidation by Fenton's reagent, *Water Res.* 33 (1999) 2110–2118.
- [34] S.H. Lin, C.C. Lo, Fenton process for treatment of desizing wastewater, *Water Res.* 31 (1997) 2050–2056.
- [35] Y.W. Kang, K.-Y. Hwang, Effects of reaction conditions on the oxidation efficiency in the Fenton process, *Water Res.* 34 (2000) 2786–2790.
- [36] S.H. Lin, C.M. Lin, H.G. Leu, Operating characteristics and kinetic studies of surfactant wastewater treatment by Fenton oxidation, *Water Res.* 33 (1999) 1735–1741.
- [37] F.J. Rivas, F.J. Beltrán, O. Gimeno, J. Frades, Treatment of olive oil mill wastewater by Fenton's reagent, *J. Agric. Food Chem.* 49 (2001) 1873–1880.
- [38] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions, *Adv. Environ. Res.* 8 (2004) 501–551.
- [39] H.K. Obied, D. Bedgood, R. Mailer, P.D. Prenzler, K. Robards, Impact of cultivar, harvesting time, and seasonal variation on the content of biophenols in olive mill waste, *J. Agric. Food Chem.* 56 (2008) 8851–8858.
- [40] G. Ranalli, C. Belli, G. Lustrato, L. Pizzella, L. Liberatore, M. Bressan, Effects of combined chemical and biological treatments on the degradability of vulcanization accelerators, *Water Air Soil Pollut.* 192 (2008) 199–209.
- [41] H. Gallard, J. De Laat, B. Legube, Influence du pH Sur la Vitesse D'oxydation de Composes Organiques par Fe(II)/H₂O₂. Mecanismes reactionnels et modelisation [Influence of pH on the H₂O₂ oxidation of organic compounds by speed Fe(II)/H₂O₂. Reaction mechanisms and modeling], CNRS, Paris, France, 1998.
- [42] J.J. Pignatello, Dark and photoassisted Fe³⁺-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, *Environ. Sci. Technol.* 26 (1996) 944–951.
- [43] W.Z. Tang, C.P. Huang, 2,4-dichlorophenol oxidation kinetics by Fenton's reagent, *Environ. Technol.* 17 (1996) 1371–1378.
- [44] R.J. Bigda, Consider Fenton's chemistry for wastewater treatment, *Chem. Eng. Prog.* 91 (1995) 62–66.
- [45] F.K. Nesheiwat, A.G. Swanson, Clean contaminated sites using Fenton's reagent, *Chem. Eng. Prog.* 96 (2000) 61–66.
- [46] S. Parsons, *Advanced Oxidation Processes for Water and Wastewater Treatment*, 1st ed., IWA Publishing, London, 2004.
- [47] S.H. Lin, C.F. Peng, Treatment of textile wastewater by Fenton's reagent, *J. Environ. Sci. Health A Toxic/Hazard. Subst. Environ. Eng.* 30 (1995) 89–98.
- [48] K. Ito, W. Jian, W. Nishijima, A.U. Baes, E. Shoto, M. Okada, Comparison of ozonation and AOPs combined with biodegradation for removal of THM precursors in treated sewage effluents, *Water Sci. Technol.* 38 (1998) 179–186.