Pre-treatment studies on olive oil mill effluent using physicochemical, Fenton and Fenton-like oxidations processes

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ABSTRACT

In this paper, the results of olive oil mill wastewater (OOMW) using physicochemical pre-treatment and Fenton and Fenton-like processes are presented. On the other hand, acute toxicities of raw, physicochemical pre-treated, and Fenton and Fenton-like oxidations applied samples of OOMW on activated sludge microorganisms using respiration inhibition test (ISO 8192) are presented. Chemical pre-treatment (acid cracking and coagulation–flocculation) positively affected the biodegradability and inhibition on activated sludge was considerably removed (>67% COD and >72% total-phenol removal). Fenton and Fenton-like processes showed high COD (>80%) and total-phenol (>85%) removal performance on evaluated effluents. Inhibitory effect of Fenton-like reagents applied samples on activated sludge mixture was considerably removed. In addition to the toxicity, total-phenol and COD removal efficiencies of applied processes, their associated operating costs were also determined in this paper.

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1. Introduction

Olive oil processing poses a serious environmental pollution especially in the Mediterranean, Aegean and Marmara regions that account for approximately 95% of worldwide olive oil production. Current oil extraction techniques require high quantity of water, about 40–120 L per tones of olive mill and, consequently, high volumes of olive mill wastewater (OOMW) are produced [1–4].

OOMW composition varies and depends on climatic, cultivation parameters and on the milling method applied for the olive oil production [5]. Several traditional and modern processes are used for olive oil production, such as traditional pressing process, three-phase decanting and two-phase decanting processes. The traditional methods of extraction based on presses and the continuous three-phase decanting processes generate one stream of olive oil and two streams of wastes which is containing aqueous and solid wastes. During the two-phase decanting process two streams of wastes are also generated. But, aqueous wastes of two-phase decanting process has low organic load than that of three-phase decanting process. Three-phase decanting process is generally used for olive oil production in Turkey [6].

Olive oil mill wastewaters can be characterized by high concentrations of several organic compounds, such as organic acids, sugars, tannins, production cycle or as raw material for other processes [7]. The main characteristics of OOMW respect to its pollutant capacity are; in general, 50–100 g/L biochemical oxygen demand (BOD) and chemical oxygen demand (COD) 80–200 g/L, total solids 24–120 g/L, total-phenolics 2–15 g/L, fats 0.5–1 g/L, pH 4.5–5.2 g/L [8–12]. The biochemical oxygen demand (BOD) and COD values are 200–400 times more comparing with the domestic wastewaters [2,13].

Olive oil is a typical Mediterranean product, the treatment of olive oil milling wastewater (OOMW) is of crucial importance and a common problem in several European and Mediterranean countries [14]. The difficulties of treatment of olive mill effluents 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 m^3/d) and (e) presence of organic compounds which are hard to biodegrade such as long-chain fatty acids and phenolic compounds [15,16].

When disposed into the environment, OOMW create serious deteriorations such as colouring of natural waters, a serious threat to the aquatic life, pollution in surface and ground waters, alterations in soil quality, phytotoxicity and odour nuisance [3].

Many different processes have been proposed to treat the OOMW: lagooning or direct watering on fields [17], co-composting [18], physicochemical methods (flocculation, coagulation [19,20], filtration [21,22], open evaporating ponds [23,24], electrocoagulation [25] and ultra filtration/reverse osmosis [26,27]). However, the reported results identified significant drawbacks and indicated that no single technology could be applied to OOMW as a stand-alone

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treatment option [28]. On the other hand, most of these treatment methods are also not cost effective. Advanced oxidation processes (AOPs) have specific advantages against to conventional treatment methods. AOPs can be applied to wide range of organics and waste streams. Among AOPs, Fenton process is cost effective, easy to apply and effective method containing organic compounds [29]. One of the advantages of the Fenton's reagent is that no energy input is necessary to activate hydrogen peroxide. Therefore, this method offers a cost effective source of hydroxyl radicals, using easy-to-handle reagents. Furthermore, it commonly requires a relatively short reaction time compared with other AOPs. Thus, Fenton's reagent is frequently used when a high reduction of COD is required [30].

The Fenton oxidation process, in which Fe^{2+} reacts with H_2O_2 to generate $\cdot OH$, was employed to degrade organic pollutants [31]. The mixture of $FeSO_4$ or any other ferrous complex and H_2O_2 (Fenton's reagent) at low enough pH (2–4), results in Fe^{2+} catalytic decomposition of H_2O_2 and proceeds via a free radical chain process that produces hydroxyl radicals which have extremely high oxidizing ability and can oxidize hard-to-decompose organic compounds in a short time [32,33]. The following redox reactions will occur [34]:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^\bullet \qquad (1)$$

$$HO^\bullet + RH \rightarrow H_2O + R^\bullet \qquad (2)$$
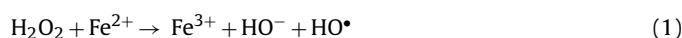
This advanced oxidation process (AOP) has been largely studied and great efficiencies are reported for the treatment of wastewaters polluted with different organics. The results show that only 60–80% COD removal percentages are obtained [35]. As regards the Fenton's process, literature data give an average OOMW polyphenol removal up to 99% and a COD removal efficiency of about 70% [33–37]. In the studies which are similar like this study seen that lower removal efficiencies achieved. As an example, the study by Beltran-Heredia et al. [38] and by Rivas et al. [39], in the treatment of OOMW with Fenton process reported efficiency is in COD 33% and in total-phenol 93%.

Hence, olive oil mill process wastewaters contain high concentrations of organics, which lead to the complete inhibition of activated sludge processes. These wastewaters cannot be discharged to central canal systems without any pre-treatment operation [3]. As well known, many centralized wastewater treatment plants are generally designed to treat domestic wastewater, which should not have an effect on the microorganisms involved in the biological treatment processes. For this purpose, the activated sludge respiration inhibition test is an appropriate tool for the determination of toxicity towards heterotrophic biomass. For the determination of toxicity of waste streams on activated sludge or aquatic organisms, various toxicity evaluation methods have been described in the literature. OECD [40] and ISO [41] have established a standard activated sludge inhibition test for evaluating the toxicity of chemicals, or wastewater to activated sludge bacteria [42]. But, the effectiveness of chemical pre-treatment and advanced oxidation processes employing powerful oxidants in eliminating toxicity from industrial wastewater or toxic chemicals has not yet been widely studied in literature.

The main objective of this study is the determination of most appropriate pre-treatment process combinations for OOMW, according to changes in acute toxicities of applied treatment processes. In parallel to this aim, acid cracking + chemical treatment ($FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$), Fenton and Fenton-like processes were studied and acute toxicities of each process on activated sludge [41] were determined.

Table 1
Environmental characterization of wastewater samples.

Parameter	Unit	Value
Total COD	g/L	115 ± 11
Filtered COD	g/L	34 ± 6
Total-phenol	g/L	5.58 ± 0.11
Oil and grease	g/L	23 ± 2.1
Suspended solids (SS)	g/L	32 ± 3.0
Total-N	g/L	0.42 ± 0.05
Total-P	g/L	0.12 ± 0.01
pH	–	5.2

2. Materials and methods

2.1. Industrial wastewater samples

Composite wastewater samples used in this study were collected from the homogenization tanks of an olive mill plant with a daily olive processing capacity of 30 tones in Bursa City, Turkey. Environmental characterization of olive oil mill wastewater is given in Table 1.

According to Turkish Water Pollution Control regulation, only COD, oil and grease and pH parameters are stipulated [43]. Final discharge concentrations of COD and oil and grease parameters must below 230 and 40 mg/L, respectively. Discharge limit of pH in this regulation is 6–9. Existing levels of these parameters are higher than the discharge limits. On the other hand other conventional and important environmental parameters such as total-phenol, suspended solids (SS), total nitrogen (total-N) and total phosphorus (total-P) levels are not included in this regulation. Therefore, olive oil mill wastewater cannot be treated by means of classical biological processes.

2.2. Acid cracking and coagulation experiments

Acid cracking was first applied to all samples by adjusting pH manually to less than 2 using sulphuric acid. The reaction time for this operation was 3 h. Samples used in all other experiments such as chemical coagulation, Fenton and Fenton-like tests were carried out using these acid cracked samples. In chemical treatment experiments using Jar test apparatus (Velp Scientifica FC6S model, Italy), $Al_2(SO_4)_3 \cdot 18H_2O$, $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ (supplied from Merck, Germany) reagents were used at varying dosages between 500 and 6000 mg/L. Optimum pH and reagent doses that provide best COD removal were determined for each chemical at room temperature (20 °C). One liter of a wastewater sample given in Table 1 was dosed with each chemical at varying dosages separately. One hour sedimentation was applied following coagulation time of 30 min (20 rpm) after flash mixing for a minute (120 rpm). Supernatants at the end of sedimentation period were analyzed as described in Section 2.5.

2.3. Fenton and Fenton-like experiments

Fenton and Fenton-like experiments were conducted at room temperature using varying $FeSO_4 \cdot 7H_2O$–H_2O_2 (for Fenton experiments) and $FeCl_3 \cdot 6H_2O$–H_2O_2 (for Fenton-like experiments) dosages at varying pH values in order to determine optimum dosages give better results in COD removal. The pH was manually adjusted to desired range (pH 2–7) using 1N sulphuric acid and/or sodium hydroxide before starting the experiments. During the determination of optimum pH value, doses of $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$ (supplied from Merck) and H_2O_2 (supplied from Merck, 35%, w/w) were fixed at 500 mg/L. H_2O_2, $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ dosages, change between 500 and 3500 mg/L were used

Table 2
Acid cracking and coagulation results of coagulants on olive oil mill wastewater samples.

Process/coagulants	Optimum pH	Optimum chemical dosage (mg/L)	COD removal efficiency (%)	Phenol removal efficiency (%)	Oil and grease removal efficiency (%)	Suspended solids removal efficiency (%)	Sludge volume (mL/L)
Acid cracking (H_2SO_4)	2	9583	46	37	94	92	150
Acid craking + $FeCl_3 \cdot 6H_2O$	9	4000	67	72	>99	>99	450
Acid craking + $FeSO_4 \cdot 7H_2O$	10	4000	66	69	>99	>99	450
Acid craking + $Al_2(SO_4)_3 \cdot 18H_2O$	8	5000	64	63	>99	>99	500

to decide chemical dosages after the optimum pH was determined. Four hour sedimentation was applied following the pH adjustment (7.5–8) after 2 min of rapid mixing at 120 rpm and 20 min of slow mixing were applied at Jar Test setup. COD and phenol analyses were carried out on 50 mL of supernatant which was taken after 4 h precipitation.

2.4. Activated sludge inhibition tests

Activated sludge inhibition tests of raw, physicochemical pre-treated and Fenton and Fenton-like oxidations applied wastewater samples were conducted in accordance with a test procedure described in International Organization for Standardization (ISO 8192) [41]. Experiments were carried out under constant temperature (20 ± 2 °C). Activated sludge used in all tests was withdrawn directly from the aeration tank of domestic wastewater treatment plant in Bursa, Turkey. Sludge was settled for the removal of impurities and then washed with chlorine-free tap water. The sludge was aerated continuously using aeration pumps. The heterotrophic biomass used in inhibition tests was fed with synthetic municipal wastewater as described in ISO 8192. This synthetic domestic wastewater (SDW) was diluted (COD_{SDW} = 320 mg/L) prior to use. Total suspended solids (TSS), volatile suspended solids (VSS) and sludge volume index (SVI) values of domestic sludge were determined as 3230, 2860 and 230 mL/g, respectively. The F/M ratio was fixed as approximately 0.1 mg COD/mg MLVSS for the measurement of microbial responses at reasonable aeration time (t = 30 and 180 min). According to ISO 8192 procedure, 3-5-di-chlorophenol was used as a reference toxic chemical for controlling the sensitivity of activated sludge culture. During these tests, activated sludge culture was mixed in a 500-mL test flask with distilled water, synthetic municipal wastewater and several raw and pre-treated concentrations of industrial wastewater (5–100% volumetric dilutions). pH of the test mixture was adjusted to 7.5 ± 0.2. The test mixtures were aerated for 30 and 180 min test periods. Different diluted test mixtures for industrial wastewater samples (5–100%) were prepared for activated sludge inhibition test procedure. Approximately, 300 mL of test mixture was transferred to the respiration vessel and the respiration rate was determined using an oxygen electrode (WTW OXI 340i). The respiration tests were conducted at selected time intervals (5–10 s). Oxygen meter connects with the computer through a RS-232 interface. Multi Lab Pilot software was used for this application. The oxygen consumption rate (mg O_2/(L h)) and the percent inhibition (I_{OUR}, %) were calculated at each test condition. The concentration of inhibiting oxygen consumption by 50% (EC_{50}) is calculated by interpolation (Eq. (3)).

$$I_{OUR}(\%) = \frac{R_B - (R_T - R_{PC})}{R_B}, \tag{3}$$

where R_T is the oxygen consumption rate by the test mixture, R_B is the oxygen consumption rate by the blank control and R_{PC} is the oxygen consumption rate by the physicochemical control [41]. Further details are described in ISO 8192 protocol.

2.5. Analytical procedure

Due to interferences of ferrous ion and H_2O_2 with the analytical measurements, pH of supernatant increased with the addition of NaOH around >11 [44] for the precipitation of ferrous iron as $Fe(OH)_3$ and MnO_2 powder was added to destroy residual H_2O_2 in the treated solution [45–47]. The concentration of residual H_2O_2 in the test solution was controlled by use of test strips (Merck Merckoquant Peroxide Test). Before each analysis, samples were filtered on 0.45 μm Millipore membranes to remove $Fe(OH)_3$ and MnO_2. On the other hand, for the elimination of oil interference from samples for phenol determination, pH of supernatant increased with the addition of NaOH around >12,5 and oil was extracted from aqueous solution with 50 mL chloroform. Oil containing chloroform layer discarded and excess chloroform evaporated before phenol analysis. "5530B. Cleanup Procedure" was applied to all phenol including samples for the removal of nonvolatile impurities from samples [47]. COD (using closed reflux method), suspended solids (SS), BOD, oil and grease, total-phenol, total nitrogen and phosphorus were measured in accordance with Standard Methods [47].

3. Results and discussion

3.1. Acid cracking and coagulation experiments

As mentioned in materials and methods, COD and total-phenol removal experiments consisted of two stages being chemical coagulation and Fenton and Fenton-like oxidation processes after acid cracking in order to compare the results. Characteristics of OOMW after acid cracking are given in Table 2. Acid cracking resulted in 46% COD, 37% total-phenol removal and significant amount of oil and grease removal (94%) (Table 2). $Al_2(SO_4)_3 \cdot 18 H_2O$, $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ coagulant were used during the chemical treatment experiments with varying dosages under varying pH conditions. Optimum pH values, optimum coagulant dosages, COD, phenol, suspended solids and oil and grease removal efficiencies of applied coagulants and volumes of produced chemical sludge are given in Table 2. Among the after acid cracking and three chemicals used in this study, $FeCl_3 \cdot 6H_2O$ resulted in best COD, phenol, suspended solids and oil and grease removal for olive oil mill effluents. COD removal at a $FeCl_3 \cdot 6H_2O$ dosage of 4000 mg/L resulted in an effluent COD of 38,000 mg/L (67%), phenol of 1560 mg/L (72%), suspended solids of 150 mg/L (>99%) and oil and grease of 100 mg/L (>99%) (at pH 9). COD of 39,100 mg/L (66%), phenol of 1730 mg/L (69%), suspended solids of 210 mg/L (>99%) and oil and grease of 180 mg/L (>99%) removal efficiencies were observed in experiments using $FeSO_4 \cdot 7H_2O$ with a dose of 4000 mg/L (at pH 10). While COD removal at a $Al_2(SO_4)_3 \cdot 18H_2O$ dosage of 5000 mg/L resulted in an effluent COD of 41,400 mg/L (64%), phenol of 2100 mg/L (63%), suspended solids of 290 mg/L (>99%) mg/L and oil and grease of 220 mg/L (>99%) (at pH 8). Industrial wastewater supernatants from remaining from all coagulation pre-treatment were then used in activated sludge inhibition tests.

Generally, the amount and the characteristics of the sludge produced during the coagulation–flocculation process are highly dependent on the specific coagulant used and on the operating

conditions [48]. During the chemical treatment experiments, tremendous amount of chemical sludge generation was observed. Volumetrically, chemical sludge generation was about 450–500 mL per liter of influent.

3.2. Fenton and Fenton-like processes

Fenton and Fenton-like oxidation processes can be most suitably applicable to removal of most organics with good energy efficiency. Parameters, affecting the Fenton process, are operating pH, Fe(II) and H_2O_2 concentrations [49–51]. The optimum pH for the Fenton process is given as 3 [52–54], but it has been reported that up to pH 5 results in high pollutant removal efficiencies.

The high efficiencies of COD and other organic parameters removal can be reached by using Fenton and Fenton-like processes with oxidation and coagulation [55]. Parameters, affecting the Fenton and Fenton-like processes, are operating pH and dosages of $FeSO_4$, $FeCl_3$ and H_2O_2 [49,53]. The optimum pH has been observed to be 3 in the majority of the cases [53,56] and hence is recommended as the operating pH. Also, the oxidation potential of hydroxyl radicals ($^\bullet OH$) is known to decrease with an increase in the pH. At low pH, H_2O_2 is stabilized as $H_3O_2^+$ [56] and moreover, the reaction between $OH^\bullet$ and H^+ becomes important [54] and the regeneration of Fe^{2+} by reaction of Fe^{3+} with H_2O_2 is inhibited [57]. On the other hand, the decrease on the oxidation yield of the process at higher pH values is due to the precipitation of Fe^{3+} as $Fe(OH)_3$, hindering the reaction between Fe^{3+} an H_2O_2, and therefore the regeneration of Fe^{2+}. Besides, $Fe(OH)_3$ catalyzes the decomposition of H_2O_2 to O_2 and H_2O, thus decreasing the production of $OH^\bullet$ [58]. Moreover, at high pH values it is possible the formation of highly stable Fe(II) complexes [30,53].

In this study, optimum pH value was determined first. During this determination, pH was adjusted between 2 and 7, and efficiencies of COD and colour removal were observed. Maximum COD and phenol removal efficiencies were obtained at pH 3 (Fig. 1). As it is seen from Fig. 1, at these pH values (500 mg/L (1.79 mM) $FeSO_4 \cdot 7H_2O$ and 500 mg/L (15 mM) H_2O_2 dosages) COD and phenol removal efficiencies for olive oil mill wastewater was calculated as 21 and 23% for Fenton process and 24 and 26% for Fenton-like processes, respectively.

At fixed pH (pH 3 for Fenton and Fenton-like experiments) and constant H_2O_2 concentration of 500 mg/L (15 mM), varied dosages between 500 and 3500 mg/L were experienced to determine optimum $FeSO_4 \cdot 7H_2O$ (0.1–0.7 M) and $FeCl_3 \cdot 6H_2O$ (0.1–0.73 M) dosage
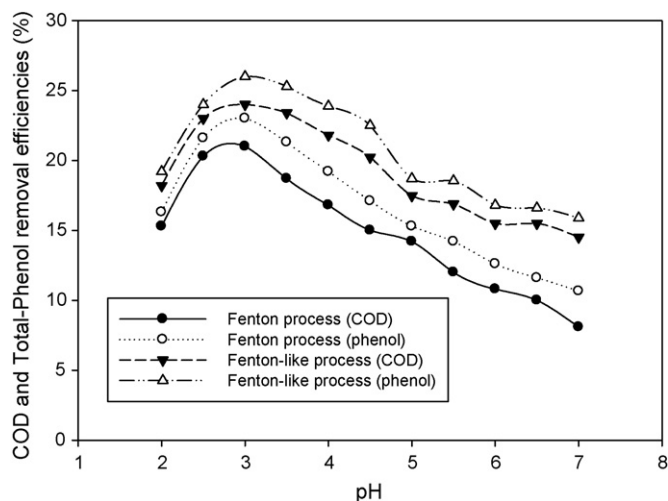
Fig. 2. Effect of $FeCl_3$ and $FeSO_4$ concentrations on COD and total-phenol removal efficiencies during Fenton and Fenton-like processes (pH 3 and $C_{H_2O_2} = 500$ mg/L).

for Fenton and Fenton-like processes. In literature, usually the rate of degradation increases with an increases in the concentration of ferrous ions [50,53,56] though the extent of increase is sometimes observed to be marginal above a certain concentration as reported by Kang and Hwang [51] and Rivas et al., Lin et al. [39]. Efficiency of COD removal due to the constant concentration of hydrogen peroxide and varied dosages of $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ was illustrated in Fig. 2. As a result, optimum Ferric salt dosages were determined as follows: $C_{FeSO4} = 3000$ mg/L (10.74 mM) for Fenton process and $C_{FeCl_3} = 2500$ mg/L (8.93 mM) for Fenton-like process in this study.

Determination of optimum H_2O_2 dosage is another important parameter for Fenton process which has a crucial role in deciding the overall efficiency of the degradation processes. The residual hydrogen peroxide contributes to COD and hence excess amount is not recommended [49,50]. Optimum H_2O_2 dosage determination studies were conducted at determined constant $FeSO_4 \cdot 7H_2O$ dosages and pH values. Varying dosages of H_2O_2 (between 500 mg/L (15 mM) and 4000 mg/L (115 mM)) were applied. Efficiencies of the COD removal at varied dosages of H_2O_2 and constant concentrations of $FeSO_4$ were illustrated in Fig. 3.

Fig. 1. Effect of pH on COD and phenol removal during Fenton and Fenton-like processes ($C_{FeCl_3} = 500$ mg/L, $C_{FeSO_4} = 500$ mg/L and $C_{H_2O_2} = 500$ mg/L).
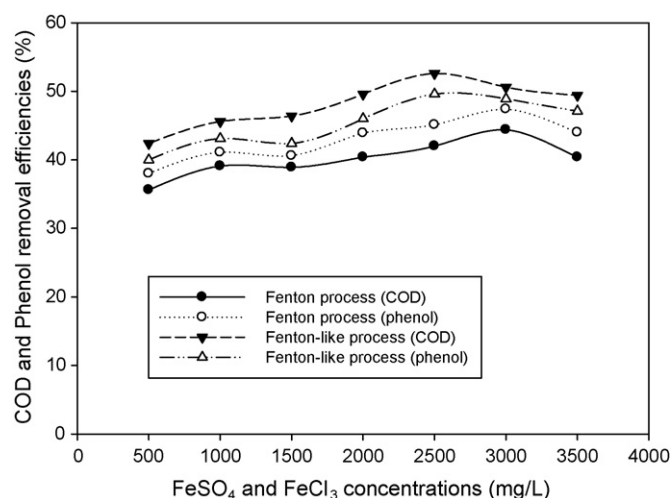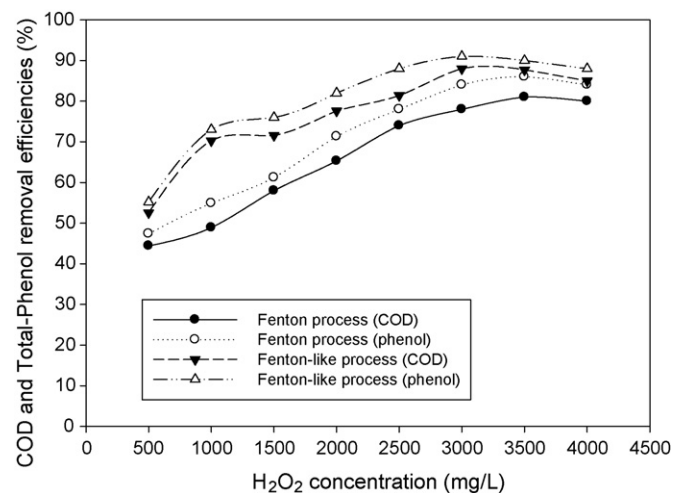
Fig. 3. Effect of H_2O_2 concentration on COD and total-phenol removal efficiencies during Fenton and Fenton-like processes (Fenton process (pH 3 and $C_{FeSO_4} = 3000$ mg/L) (81% COD removal, 86% phenol removal, 350 mL/L sludge volume), Fenton-like process (pH 3 and $C_{FeCl_3} = 2500$ mg/L) (88% COD removal, 91% phenol removal, 300 mL/L sludge volume)).
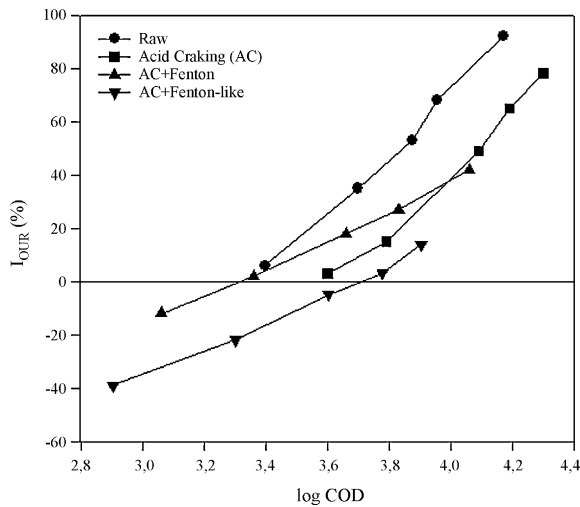
Fig. 4. Inhibition values for raw, chemical pre-treated, and Fenton and Fenton-like processes applied OOMW.

As it is seen from Fig. 3, optimum conditions for Fenton and Fenton-like processes were determined as pH 3, $C_{H_2O_2} = 3500\,mg/L$ (100 mM) and $C_{FeSO_4} = 3000\,mg/L$ (10.74 mM) (81% COD removal, 86% phenol removal, 350 mL/L sludge volume), and pH 3, $C_{H_2O_2} = 3000\,mg/L$ (90 mM) and $C_{FeCl_3} = 2500\,mg/L$ (8.93 mM) (88% COD removal, 91% phenol removal, 300 mL/L sludge volume), respectively. Supernatants from Fenton and Fenton-like experiments were used in activated sludge inhibition tests. In literature, the optimum Fe^{2+}:H_2O_2 molar ratios for Fenton oxidation are given in the range of 1:5 and 1:10 [59]. In this study, Fe^{2+}:H_2O_2 molar ratios for Fenton oxidation are obtained in the range of 1:10.

After the Fenton and Fenton-like experiments, almost the same coagulation–flocculation process chemical dosages were used. The removal efficiencies obtained from Fenton-like process experiments were shown higher total-phenol and COD removal efficiencies and slightly lower sludge volumes than the coagulation/flocculation process. On the other hand Fenton-like process sludge was more compact than the coagulation–flocculation process sludge.

3.3. Activated sludge inhibition tests

Raw, acid cracking applied, coagulated and Fenton and Fenton-like-treated effluents of olive oil mill wastewater were subjected to activated sludge inhibition tests.

EC_{20}, EC_{50} and EC_{90} values of raw ($EC_{20CODRaw} = 2990 \pm 20\,mg/L$, $EC_{50CODRaw} = 5489 \pm 34\,mg/L$, $EC_{90CODRaw} = 12{,}302 \pm 76\,mg/L$), and treated samples ($EC_{20AcidCrakingCOD} = 6754 \pm 53\,mg/L$, $EC_{50AcidCrakingCOD} = 12{,}742 \pm 86\,mg/L$, $EC_{90AcidCrakingCOD} = 29{,}332 \pm 124\,mg/L$, and $EC_{20AC+FentonCOD} = 4785 \pm 25\,mg/L$) of OOMW effluent were determined from $\ln COD$ versus I_{OUR} (%) data plots and given in Fig. 4, respectively. It can be clearly seen from the figures that some samples show negative I_{OUR} values. Negative I_{OUR} values show that inhibitory effect of wastewater samples on activated sludge mixture is not occurred. According to these data, evaluated un-pre-treated samples have toxic and inhibitory effects on activated sludge mixture and these effluents almost cannot be treated by means of classical biological processes. Acid cracking and physicochemical treatment positively affected the biodegradability of OOMW effluent and inhibition on activated sludge was considerably removed. But, inhibition on activated sludge cannot be completely removed by means of physicochemical treatment. On the other hand, toxicity can be almost removed using Fenton and Fenton-like processes. For the determination of appropriate process for OOMW, main results of this study were summarized in Table 3 and operating costs of applied processes were presented. In conclusion, Fenton-like process generally resulted in higher phenol, COD and toxicity removal efficiencies.

Even though acid cracking + Fenton-like process among other processes studied in this paper was found to give the best results (93% COD and 95% total-phenol removal), use of acid cracking and chemical treatment. But, these removal efficiencies are still not enough for discharge regulations [43].

Inhibition on activated sludge was not removed by chemical treatment. But, there is almost no inhibitory effect of Fenton and Fenton-like reagent applied samples on activated sludge mixture was determined. Following the AC and Fenton and Fenton-like pre-treatment alternatives, OOMW can be discharged to central canal systems for final treatment in centralized wastewater treatment plants.

3.4. Cost evaluation

All processes were evaluated in terms of their operating costs (on the basis of chemical requirements) and their cost profiles were compared (Table 4). Operating costs of all investigated processes were found reasonable except ozonation. Therefore, for the protection of centralized wastewater treatment plants, chemical treatment of Fenton-like process can be used as a pre-treatment alternative for OOMW prior to discharge into sewage. Within this framework, this present investigation can be accepted as a

Table 3
Results of studied processes on OOMW.

Process	COD removal (%)	Total-phenol removal (%)	pH	$C_{H_2SO_4}$ (mg/L)	$C_{H_2O_2}$ (mg/L)	C_{FeSO_4} (mg/L)	C_{FeCl_3} (mg/L)
Acid cracking (AC)	46	37	2	9583	–	–	–
AC + chemical treatment	67	72	9	–	–	–	4000
AC + Fenton process	90	91	3	–	3500	3000	
AC + Fenton-like process	93	95	3	–	3000	–	2500

Table 4
Operating costs for the studied processes.[a,b]

Reagents	Basis	Cost (€)	Process	Treatment Cost (€/m³)
FeSO$_4$·7H$_2$O	kg	0.41	Acid cracking (AC)	1.60
FeCl$_3$·6H$_2$O	kg	0.38	AC + coagulation with FeCl$_3$	3.57
H$_2$O$_2$	kg	0.48	AC + Fenton	4.81
Electricity	kW/h	0.116	AC + Fenton-like	4.29
H$_2$SO$_4$	kg	0.32		
NaOH	kg	0.30		

[a] Cost of labor and sludge disposal not included.
[b] Treatment costs were calculated for 30 m³/d flow rate.

feasibility study for the pre-treatment of olive oil mill wastewater before discharge to the sewage.

4. Conclusions

In this study, acid cracking, chemical treatment and Fenton and Fenton-like processes were applied on olive oil mill wastewaters. These wastewater samples have toxic nature and high resistance toward degradation by activated sludge microorganisms. Acute toxicities of raw and evaluated samples on activated sludge microorganisms were determined using respiration inhibition test [41]. The following conclusions can be drawn from this study.

(i) Raw OOMW have toxic and inhibitory effects on activated sludge mixture and these effluents almost cannot be treated by means of classical biological processes.
(ii) The removal efficiencies obtained from coagulation experiments were shown similar phenol and COD removal efficiencies. FeCl$_3$ resulted in best COD and phenol removal efficiencies. Chemical pre-treatment was positively affected the biodegradability, but inhibition on activated sludge was not removed completely.
(iii) Fenton and Fenton-like processes have shown superior total-phenol and COD removal performance on evaluated samples. Inhibitory effect of Fenton-like and Fenton's reagent applied samples on activated sludge mixture was considerably removed.

Consequently, Fenton-like process showed a satisfactory COD, phenol and toxicity removal performance and to be economically more viable choice for the OOMW before discharge into sewage for the protection of central wastewater treatment plants.

Acknowledgement

References

[1] M. Drouiche, V.L. Mignot, H. Lounicci, D. Belhocine, H. Grib, A. Pausse, N.V. Mameri, A compact process for the treatment of olive mill wastewater by combining UF and UV/H$_2$O$_2$ techniques, Desalination 169 (2004) 81–88.
[2] M. Ahmadi, F. Vahabzadeh, B. Bonakdarpour, E. Mofarrah, M. Mehranian, Application of the central composite design and response surface methodology to the advanced treatment of olive oil processing wastewater using Fenton's peroxidation, Journal of Hazardous Materials 123 (2005) 187–195.
[3] K. Kestioğlu, T. Yonar, N. Azbar, Feasibility of physico-chemical treatment and advanced oxidation processes (AOPS) as a means of pre-treatment olive mill effluent (OME), Process Biochemistry 40 (2005) 2409–2416.
[4] R. Andreozzi, G. Longo, M. Majone, G. Modesti, Integrated treatment of olive oil mill effluents (OME): study of ozonotion coupled with anaerobic digestion, Water Research 32 (1998) 2357–2364.
[5] C.A. Paraskeva, V.G. Papadakis, E. Tsarouchi, D.G. Kanellopoulou, P.G. Koutsoukos, Membrane processing for olive mill wastewater fractionation, Desalination 213 (2007) 218–229.
[6] Project Improlive, Improvements of treatments and validation of the liquid-solid waste from the two phase olive oil extraction. Annex A2: Final report, Fair CT96 1420, 2000.
[7] E. Turano, S. Curcio, M. Paola, V. Calabro, G. Iorio, An integrated centrifugation–ultrafiltration system in the treatment of olive mill wastewater, Journal of Membrane Science 209 (2002) 519–531.
[8] C. Scioli, L. Vollaro, The use of yarowia lipolytica to reduce pollution in olive mill wastewaters, Water Research 31 (1997) 2520–2524.
[9] K. Fadil, A. Chahlaoui, A. Ouahbi, A. Zaid, R. Borja, Aerobic biodegradation and detoxification of wastewaters form the olive oil industry, International Biodeterioration and Degradation 51 (2003) 37–41.
[10] K. Al-Malah, O.J.M. Azzam, N.I. Abu-Lail, Olive mills effluent (OME) wastewater post-treatment using activated clay, Separation Purification Technology 20 (2000) 225–234.
[11] S. Khoufi, F. Aloui, S. Sayadi, Treatment olive mill wastewater by combined process electro-Fenton reaction and anaerobic digestion, Water Research 40 (2006) 2007–2016.
[12] C.J. Israilides, A.G. Vlyssides, V.N. Mourafeti, G. Karvouni, Olive oil wastewater treatment with the use of an electrolysis system, Bioresource Technology 61 (1997) 163–170.
[13] R. Cossu, N. Blakey, P. Cannas, Influence of codisposal of municipal solid waste and olive vegetation water on the anaerobic digestion of a sanitary landfill, Water Science and Technology 27 (1993) 261–271.
[14] A. Dhouib, F. Aloui, N. Hamad, S. Sayadi, Pilot-Plant treatment of olive mill wastewaters by phanerochaete chrysosporium coupled to anaerobic digestion and ultrafiltration, Process Biochemistry 41 (2006) (2006) 159–167.
[15] T.H. Ergüder, E. Güven, G.N. Demirer, Anaerobic treatment of olive mill wastes in batch reactors, Process Biochemistry 36 (2000) 243–248.
[16] M. Gotsi, N. Kalogerakis, E. Psillakis, P. Samaras, D. Mantazavinos, Electrochemical oxidation of olive mill wastewaters, Water Research 39 (2005) 4177–4187.
[17] F. Şengül, Endüstriyel Atık suların Özellikleri ve Arıtılması, D.E.Ü. Mühendislik-Mimarlık, Fakültesi Basım Ünitesi, 1991, İzmir.
[18] C. Paredes, M.P. Bernal, A. Roig, J. Cegarra, Effects of olive mill wastewater addition in composting of agroindustrial and urban wastes, Biodegradation 12 (2001) 225–234.
[19] R. Sarika, N. Kalogerakis, D. Mantzavinos, Treatment of olive mill effluents. Part II. Complete removal of solids by direct flocculation with poly-electrolytes, Environment International 31 (2005) 297–304.
[20] A. Ginos, T. Manios, D. Mantzavinos, Treatment of olive mill effluents by coagulation–flocculation–hydrogen peroxide oxidation and effect on phyto-toxicity, Journal of Hazardous Materials B133 (2006) 135–142.
[21] S. Filidei, G. Masciandaro, B. Ceccanti, Anaerobic digestion of olive mill effluents: evaluation of wastewater organic load and phytotoxicity reduction, Water Air Soil Pollution 145 (2003) 79–94.
[22] I. Sabbah, T. Marsook, S. Basheer, The effect of pretreatment of anaerobic activity of olive mill wastewater using batch and continuous systems, Process Biochemistry 39 (2004) 1947–1951.
[23] C. Paredes, J. Cegarra, A. Roig, M.A. Sanchez-Monedero, M.P. Bernal, Characterisation of olive mill wastewater (alpechin) and its sludge for agricultural purposes, Bioresource Technology 67 (1998) 111–115.
[24] A. Rozzi, F. Malpei, Treatment and disposal of olive mill effluents, International Biodeterioration and Biodegradation 47 (1996) 135–144.
[25] T.U. Ün, S. Ugur, A.S. Koparal, Ü. Bakır Ogutveren, Electrocoagulation of olive mill wastewaters, Separation and Purification Technology 52 (2006) 136–141.
[26] 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 UF and UV/H2O2 techniques, Desalination 169 (2004) 81–88.
[27] P. Canepa, N. Marignetti, U. Rognini, S. Calgari, Olive mills wastewater treatment by combined membrane processes, Water Research 22 (1988) 1491–1494.
[28] S. Doğruel, T. Olmez-Hanci, Z. Kartal, I. Arslan-Alaton, D. Orhon, Effect of Fenton oxidation on the particle size distribution of organic carbon in olive mill wastewater, Water Research 43 (2009) 3974–3983.
[29] H. Lee, M. Shoda, Removal of COD and color from livestock wastewater by the Fenton method, Journal of Hazardous Materials 153 (2008) 1314–1319.
[30] P. Bautista, A.F. Mohedano, M.A. Gilarranz, J.A. Casas, J.J. Rodriguez, Application of Fenton oxidation to cosmetic wastewaters treatment, Journal of Hazardous Materials 143 (2007) 128–134.
[31] X. Wang, S. Chen, X. Gu, K. Wang, Pilot study on the advanced of landfill leachate using a combined coagulation, Fenton oxidation and biological aerated filter process, Waste Management 29 (2009) 1354–1358.
[32] X. Wang, G. Zeng, J. Zhu, Treatment of jean-wash wastewater by combined coagulation, hydrolysis/acidification and Fenton oxidation, Journal of Hazardous Materials 153 (2008) 810–816.
[33] C. Walling, Fenton's reagent revised, Acc. Chem. Res. 8 (1975) 125–131.
[34] G. Üstün, S.K. Akal Solmaz, A. Birgül, Regeneration of industrial district wastewater using of Fenton process and ion exchange—a case study, Resources, Conservation and Recycling 52 (2007) 425–440.
[35] P. Canizares, J. Lobato, R. Paz, M.A. Rodrigo, C. Saez, Advanced oxidation processes for the treatment of olive-oil mills wastewater, Chemosphere 67 (2007) 832–838.
[36] E. Bettazzi, M. Morelli, S. Caffaz, C. Caretti, E. Azzari, C. Lubello, Olive mill wastewater treatment: an experimental study, Water Science and Technology 54 (2006) 17–25.
[37] A. Ginos, T. Manios, D. Mantzavinos, Treatment of olive mill effluents by coagulation–flocculation–hydrogen peroxide oxidation and effect on phyto-toxicity, Journal of Hazardous Materials 133 (2006) 135–142.
[38] J. Beltran-Heredia, J. Torregrosa, J. Garcia, J. Dominguez, J. Tiermo, Degradation of olive oil mill wastewater by the combination of Fenton's reagent and ozonation processes with an anaerobic biological treatment, Water Science and Technology 44 (2001) 103–108.
[39] F.J. Rivas, F.J. Beltr án, O. Gimeno, J. Frades, Treatment of olive oil mill wastewater by Fenton's reagent, Journal of Agricultural and Food Chemistry 49 (2001) 1873–1880.
[40] OECD, Guideline for Testing of Chemicals: Activated Sludge, OECD 209 Respiration Inhibition Test, Organization of Economic Cooperation and Development, Paris, 1993.
[41] ISO 8192, Water Quality––Oxygen Demand Inhibition Assay by Activated Sludge, 1995.
[42] C. Gendig, G. Domogala, F. Agnoli, U. Pagga, U.J. Strotmann, Evaluation and further development of the activated sludge respiration inhibition test, Chemosphere 52 (2003) 143–149.

[43] Anonymous, Turkish Water Control Regulation, Environmental Ministry of The Turkish Republic, 2004.

[44] I. Arslan-Alaton, F. Gurses, Photo-Fenton-like and photo-Fenton-like oxidation of procaine penicillin g formulation effluent, Journal of Photochemistry and Photobiology A: Chemistry 165 (2004) 165–175.

[45] T. Yonar, G. Kaplan Yonar, K. Kestioğlu, N. Azbar, Decolorisation of textile effluent using homogeneous photochemical oxidation processes, Coloration Technology 121 (2005) 258–264.

[46] G.E. Üstün, S.K.A. Solmaz, Color and cod removal from organized industrial district (OIR) wastewater by Fenton process, Fresenius Environmental Bulletin 15 (2006) 508–511.

[47] APHA–AWWA–WEF, Standard Method for the Examination of Water and Wastewater, 19th ed., American Public Health Association, Washington, DC, 1995.

[48] O.S. Amuda, I.A. Amoo, Coagulation/flocculation process and sludge conditioning in beverage industrial wastewater treatment, Journal of Hazardous Materials 141 (2007) 778–783.

[49] D.L. Sedlak, A.W. Andren, Oxidation of chlorobenzene with Fentons reagent, Environmental Science and Technology 25 (1991) 777–782.

[50] S.H. Lin, C.C. Lo, Fenton process of treatment desizing wastewater, Water Research 31 (1997) 2050–2056.

[51] Y.W. Kang, K.Y. Hwang, Effect of reaction conditions on the oxidation efficiency in the Fenton process, Water Research 34 (2000) 2786–2790.

[52] F.K. Nesheiwat, A.G. Swanson, Clean contaminated sites using Fenton's reagent, Chemical Engineering Progress 96 (2000) 61–66.

[53] 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 Research 35 (2001) 1338–1343.

[54] W.Z. Tang, C.P. Huang, 2,4 Dichlorophenol oxidation kinetics by Fenton's reagent, Environmental Technology 17 (1996) 1371–1378.

[55] R. Chen, J. Pignatello, Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds, Environmental Science and Technology 31 (1997) 2399.

[56] B.G. Kwon, D.S. Lee, N. Kang, J. Yoon, Characteristics of p-chlorophenoloxidation by Fenton's reagent, Water Research 33 (1999) 2110–2118.

[57] J.J. Pignatello, Dark and photoassisted iron (3+)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, Environmental Science and Technology 26 (1992) 944–951.

[58] C. Höfl, G. Sigl, O. Specht, I. Wurdack, D. Wabner, Oxidative degradation of AOX and COD by different advanced oxidation processes. A comparative study with two samples of a pharmaceutical wastewater, Water Science and Technology 35 (1997) 257–264.

[59] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment. I. Oxidation technologies at ambient condition, Advances in Environmental Research 8 (2004) 501–551.