Enhancement of olive mill wastewater biodegradation by homogeneous and heterogeneous photocatalytic oxidation

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ABSTRACT

Olive mills wastewater (OMW) is characterized by its high organic content and refractory compounds. In this study, an advanced technology for the treatment of the recalcitrant contaminants of OMW has been investigated. The technique used was either photo-Fenton as homogeneous photocatalytic oxidation or UV/semi-conductor catalyst (such as TiO_2, ZrO_2 and FAZA) as heterogeneous photocatalytic oxidation for treatment of OMW. For both the processes, the effect of irradiation time, amounts of photocatalysts and semi-conductors, and initial concentration of hydrogen peroxide has been studied. At the optimum conditions, photo-Fenton process achieved COD, TOC, lignin (total phenolic compounds) and total suspended solids (TSSs) removal values of 87%, 84%, 97.44% and 98.31%, respectively. The corresponding values for UV/TiO_2 were 68.8%, 67.3%, 40.19% and 48.9%, respectively, after 80 min irradiation time. The biodegradability expressed by BOD_5/COD ratio for treated wastewater was ranged from 0.66 to 0.8 compared to 0.19 for raw wastewater indicating enhancement of biodegradation.

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1. Introduction

Demand for olive oil is rapidly expanding worldwide due to its healthy image. Olive oil has gained an increasing popularity due to its oleic acid content, which may affect plasma lipid/lipoprotein profiles and richness in antioxidants, which may prevent some human diseases [1,2]. Olive oil production is an important economic activity of Middle East countries. Unfortunately, this activity leads to the generation of significant amounts of both solid and liquid wastes composed of many complex colored and recalcitrant compounds with high organic loads [3,4].

Biological treatment of OMW is a challenge because of the presence of biologically resistant macromolecule compounds such as tannins, polyalcohol, polysaccharides, pectin, proteins, and a number of monocyclic and polymeric aromatic molecules generally referred to as phenolic compounds in OMW [5–7].

Municipal wastewater treatment plants had to be shut down during the olive campaign period due to discharges of untreated OMW with high organic and recalcitrant content into the sewage [8]. Several methods were tested for the treatment of OMW such as mechanical, physical, chemical, biological and thermal methods. An advisable single treatment method that is economically viable has not been suggested yet.

One of the most promising OMW treatment technologies is the advanced oxidation processes (AOPs) which based on the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals, have been used with an increasing interest due to their high oxidant power. Among the AOPs, the homogeneous photo-Fenton ($Fe^{2+/3+}$/H_2O_2/UV) reaction [9–11] and titanium dioxide-mediated heterogeneous photocatalytic (TiO_2/UV-A) treatment process [12–14] have shown recently great promise for the treatment of industrial wastewater, groundwater and contaminated air. These photocatalysts are capable of absorbing in the near-UV spectral region (300 nm < λ < 400 nm) to initiate radical reactions.

AOPs are very promising methods for the remediation of contaminated wastewaters containing non-biodegradable organic pollutants. Although AOPs generally can produce high quality effluent and cheaper than incineration or wet oxidation technologies, nevertheless, one of the major drawbacks of these AOPs is that their operating costs exceed those of biological treatment. One interesting alternative that is gaining importance among the potential techniques for non-biodegradable or toxic wastewater treatment is the combination of a photocatalytic oxidation with a subsequent biological step. In this way the use of one of the photocatalytic oxidation techniques, the expensive part of the global procedure is reduced to the attainment of a non-toxic and/or biodegradable solution, being the rest of the organic matter removed in the biological step. Previous studies have attempted the strategy of combining chemical and biological processes to treat contaminants in wastewater. Many reports have focused on the study of new chemical

oxidation technologies as a pre-treatment for non-biodegradable or toxic wastewater combined with a conventional biological treatment [15–17]. These results suggest potential advantages for water treatment. Recently, very attractive combined systems have been proposed to treat different kinds of industrial wastewater [18–21].

In UV/TiO$_2$, photo generated holes are generated when TiO$_2$ particles are irradiated with UV light. Hydroxyl radicals are formed mainly in the oxidation of OH$^-$ or H$_2$O by these photogenerated holes, and are principally responsible for the destruction of organic species. Oxygen acts primarily as an efficient electron trap, preventing the recombination of electrons and photogenerated holes [22]. The mechanism of photo-Fenton process was previously described [9,15].

This work evaluates the feasibility of enhancing the biological treatment of the OMW employing the homogeneous photocatalytic oxidation and the heterogeneous photocatalytic oxidation as pre-treatment step. The influence of irradiation time, pH, and initial amounts of both H$_2$O$_2$ and Fe^{2+} ions on photo-Fenton process was investigated. For photocatalytic oxidation (UV/TiO$_2$), the effect of catalyst type, pH, catalyst dose and irradiation time was investigated.

2. Materials and methods

2.1. Composition of olive mill wastewater

The olive mill wastewater (OMW) used in this work was collected from El-Salhia Olive Mills Company, an olive oil processing plant near El-Asamalia in the East of Egypt, operating with a continuous three-phase centrifugation process. Before performing photocatalytic oxidation processes, the OMW was filtered, diluted two times with tap water, settled for 1 h and stored at −15 °C in plastic cans. After these procedures, the OMW chemical oxygen demand was reduced to 117,860 mg/L. For each reaction, a new frozen sample was used in order to avoid initial composition discrepancies between them. Table 1 presents the physiochemical characteristics of OMW.

2.2. Chemicals used

Analytical grade photocatalysts TiO$_2$ (anatase), ZrO$_2$, FeSO$_4$·7H$_2$O were supplied by Merck. Mixed Al–Fe pillared clays (called FAZA) were prepared as method mention by Barrault et al. [23]. The specific characterization of catalysts used in this study mention, titanium oxide (TiO$_2$-A) (pure anatase, particle size of 0.02 μm, with a BET surface area of 10 m^2/g), zirconium oxide (ZrO$_2$) (average particle diameter 0.03 μm, specific surface area of 9.8 m^2/g) and FAZA (particle size 0.14 mm, and specific areas according to BET of 240 m^2/g). A.R. grade chemicals H$_2$SO$_4$, NaOH and H$_2$O$_2$ (30%) were used without any purification and were provided by Merck.

Table 1
Characterization of diluted raw wastewater with tap water by factor of 2 after settling 1 h.

Parameter	Wastewater
TSS (mg/L)	8510
COD (mg/L)	117,860
BOD$_5$ (mg/L)	22,500
BOD$_5$/COD	0.19
TOC (mg/L)	44,250
Oil and grease (mg/L)	6847
Lignin (phenol index) (mg/L)	19,161
Phenol (mg/L)	6294

Fig. 1. Schematic diagram of photocatalytic oxidation system experimental set-up.

2.3. Description of the photo-reactor

A laboratory photocatalytic oxidation unit was used for the batch experiments. The schematic diagram of the experimental set-up used is shown in Fig. 1. It consists of an external stirred vessel of 1 L with a variable speed stirrer, combined with a cylindrical photo reactor (0.85 L), made from quartz, with a coaxial and immersed medium pressure UV mercury lamp was used as the UV emitter and light source (Heraeus TQ150, input energy of 150 W) emitting a polychromatic radiation in the range from 100 to 280 nm wavelength. The lamp emitted a power of 6.2 W in the UV-C (100 nm < λ < 280 nm) range (indication Heraeus), corresponding to 1.32 × 10^{-5} Einstein s^{-1}. The UV lamp is equipped with a cooling water jacket to maintain the temperature of the reaction of wastewater at room temperature. There is one cooling circle for cooling UV lamp. The UV system is placed positioned coaxial inside the reactor vessel. The UV system is made from quartz glass, which is available for the transfer of UV irradiation. The reaction chamber is filled with the wastewater, which is between the reactor walls and UV lamp system. The reactor was designed for different flow rates, organic loads, re-circulation rates, and oxidant addition rates. Mixing was accomplished by means of a closed external circulating loop through the illuminated part of the photo-reactor by the use of a peristaltic pump. The flow system was assembled with polytetrafluorethylene or glass tubing and connectors.

2.4. Reactor runs

The laboratory unit was filled separately with 0.85 L of wastewater under study. The optimum conditions for either photo-Fenton or UV/TiO$_2$ treatment as a pre-treatment step for biological treatment were investigated for OMW. In the photochemical oxidation, the pH of the industrial wastewater was adjusted to the desired value with H$_2$SO$_4$ or NaOH addition before start-up, and kept at the same value during the reaction. Then appropriate amount of photocatalyst was added into the mixing vessel and was re-circulated in batch mode through the illuminated part of the photo-reactor by means of peristaltic pump for 10 min. For photo-Fenton process, the desired volume of H$_2$O$_2$ was injected to the solution. The time at which the UV lamp was turned on was considered time zero simultaneously with starting the addition of hydrogen peroxide for photo-Fenton process. The solution was circulated at a flow rate of 180 L h^{-1}. After 60 min reaction time the lamp was turned off. The pH of the photo-treated effluent was adjusted to 7 and the photocatalytic oxidation effluents were centrifuged before the determination of BOD$_5$ and the determination of the other parameters.

2.5. Analytical methods

Samples were taken periodically at regular time intervals from the reaction vessel and were determined immediately to avoid further reaction. As reported in the literature [24], Fenton and photo-Fenton reactions cannot proceed at pH > 10. Therefore, for photo-Fenton process, the reaction was stopped instantly by adding NaOH to the reaction samples before H_2O_2 analysis. One drop of $Na_2S_2O_3$ (0.1N) was also added to each sample to decompose any residual hydrogen peroxide and prevent hydrogen peroxide from reacting with organic substrates during the analysis. Hydrogen peroxide was detected by a modified iodometric titration method according to APHA [25]. The physical and chemical characteristics of the diluted wastewater by factor 2 by distilled were determined according to APHA [25]. Periodically, liquid samples of 1 ml were withdrawn from the reactor for determination of a total organic carbon (TOC) using Phoenix TOC (Model 8000). Three reproducible runs (<2%) were considered.

3. Results and discussion

3.1. Characterization of raw wastewater and non-biodegradability indicators

The physiochemical characteristics of raw wastewater listed in Table 1. The OMW effluents exhibit high COD (117,860 mg/L), low BOD (22,500 mg/L), high TOC (44,250 mg/L) and high phenol index levels (19,161 mg/L). The ratio of BOD_5/COD in wastewater is normally used to express the biodegradability of the wastewater. When the ratio of BOD_5/COD is more than 0.3, the wastewater has a better biodegradability. Whereas the ratio is less than 0.3, the wastewater is difficult to be biodegraded [26]. The non-biodegradability of a wastewater have to be confirmed before apply a photocatalytic oxidation treatment, since classical biological treatments are, at the present, the cheapest and most environmentally compatible. Table 1 shows that the ratio of BOD_5/COD of the wastewater is 0.19 (<0.3). This indicates that, the wastewater is poorly biodegradable and cannot be biodegraded by biological treatment.

3.2. Photocatalytic oxidation processes as pre-treatment step

3.2.1. Homogeneous photocatalytic oxidation (photo-Fenton process)

In this work, photo-Fenton process was selected as a homogeneous photocatalytic oxidation pre-treatment step. The effect of several parameters such as pH, initial amount of Fe^{2+}, initial concentration of H_2O_2 and the irradiation time were investigated to determine the optimum operating conditions for removal of TOC and COD.

3.2.1.1. Effect of pH. The pH value has a decisive effect on the oxidation potential of $OH^{\bullet}$ radicals because of the reciprocal relation of the oxidation potential to the pH value ($E^0 = 2.8$ V and $E^{14} = 1.95$ V). Furthermore, the concentration of inorganic carbon and the hydrolytic speciation of Fe (III) species are strongly affected by the pH value [27]. Therefore, the role of pH in the photo-assisted Fenton reaction must be determined. The % removal of TOC and COD degradation of OMW by photo-Fenton treatment as a function of pH are shown in Fig. 2. The experiments were carried out at pH ranged from 2 to 5 at constant amount of Fe^{2+} (0.3 g/L), H_2O_2 (4 g/L) and irradiation time of 120 min. The results clearly indicate that the extent of degradation decreases with the increase in pH value for pH > 3. This demonstrates that the most effective pH value for degradation of OMW by photo-Fenton treatment is 3. This is consistent with Kuo [28]. More Fe(OH)$^+$ is formed at pH 2–4 and the
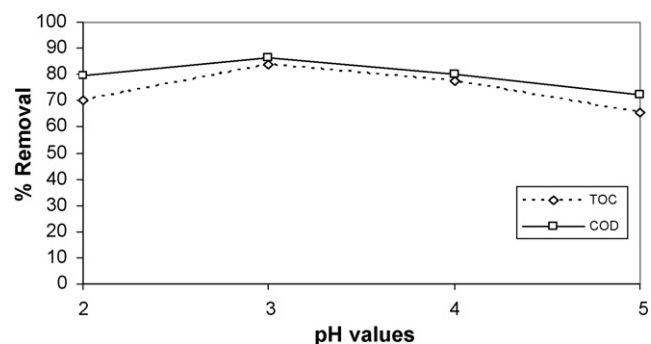
Fig. 2. Effect of pH values on TOC and COD removal rate of OMW treatment by photo-Fenton process. [Initial TOC = 44,250 mg/L and initial COD = 11,780 mg/L.]

activity of Fe(OH)$^+$ is higher than Fe^{2+} in the photo-Fenton reactions. This may be the reason for the optimal removal of TOC and COD in this range. At acidic pH values, it has been shown that hydrogen peroxide decomposes to produce $OH^{\bullet}$ radicals. For pH values above 4, the removal strongly decreases because at higher pH values iron precipitates as hydroxide, which reduces the transmission of the radiation into the water in the photo-Fenton treatment [29]. Another reason for the inefficient removal at pH > 3 is due to the dissociation and auto-decomposition of H_2O_2 [30]. Maximum TOC and COD removals of 84% and 86.5%, respectively, were obtained with the photo-Fenton treatment within 60 min at pH 3.

3.2.1.2. Effect of irradiation time. The photo-treatment time must be as short as possible to avoid a high electricity consumption, which represents about 60% of the total operational cost when using electric light sources [26]. However, if the fixed pre-treatment time is too short, the intermediates remaining in solution could still be structurally similar to initial biorecalcitrant compounds and therefore, non-biodegradable. Furthermore, at short photo-treatment times, the residual H_2O_2 concentration may be high enough to inhibit the biological stage of the coupled reactor. This oxidant is not required for all the photochemical processes, but whenever utilized it has to be eliminated before the biological stage. Fig. 3 indicates that the optimum irradiation time was 60 min at constant pH (3), initial Fe^{2+} (0.3 g/L) and initial H_2O_2 (4 g/L). Within this time, about 84% and 86.5% removal of TOC and COD of the wastewater, respectively, were achieved.

3.2.1.3. Effect of the initial hydrogen peroxide concentration. To elucidate the role of H_2O_2 concentration on the photocatalytic degradation of OMW in the photo-Fenton system, some experiments are carried out by varying the initial H_2O_2 concentrations at constant initial pH (3), initial Fe^{2+} (0.3 g/L) and irradiation time
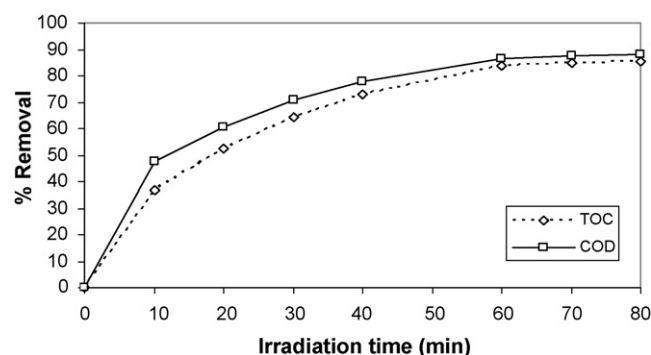

Fig. 3. Effect of the irradiation time on TOC and COD removal rate of OMW treatment by photo-Fenton process. [Initial TOC = 44,250 mg/L and initial COD = 11,780 mg/L.]
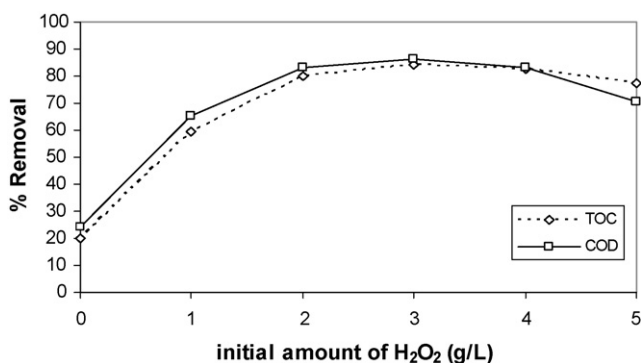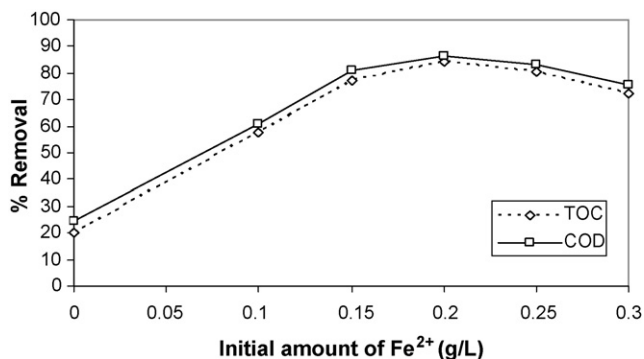
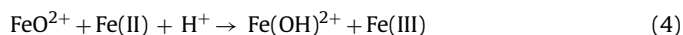**Fig. 4.** Effect of the initial hydrogen peroxide concentration on TOC and COD removal rate of OMW treatment by photo-Fenton process. [Initial TOC = 44,250 mg/L and initial COD = 11,780 mg/L.]

of 60 min. As shown in Fig. 4, the degradation efficiency represented by %TOC and %COD removals is demonstrated when H_2O_2 concentration increases from 0 to 3 g/L, which is explained by the effect of the additionally produced $OH^\bullet$ radicals. However, above this H_2O_2 concentration, the reaction rate levels off and sometimes is negatively affected, by the progressive increase of the hydrogen peroxide. This may be due to auto-decomposition of H_2O_2 to oxygen and water and recombination of $OH^\bullet$ radicals (Reactions (1) and (2)). Excess of H_2O_2 will react with $OH^\bullet$ competing with organic pollutants and consequently reducing the efficiency of the treatment, the H_2O_2 itself contributes to the $OH^\bullet$ radicals scavenging capacity. It is found that, the optimal H_2O_2 concentration is 3 g/L for the treatment of the wastewater under study with 84% TOC and 86.5% COD removals, respectively, after 60 min irradiation time. This dose considered less than dose of H_2O_2 used by Gernjak et al. [27], since their optimum dose of H_2O_2 was 5 g/L.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{1}$$

$$OH^\bullet + H_2O_2 \rightarrow HO_2^\bullet + H_2O \tag{2}$$

3.2.1.4. Effect of the initial amount of Fe^{2+}. To further elucidate the role of Fe^{2+} concentration on the mineralization of the effluent, a series of experiments varying the concentration of iron and keeping fixed the other parameters, at initial pH (3), initial H_2O_2 (3 g/L) and irradiation time of 60 min. Fig. 5 shows the % removal of TOC and COD (i.e., mineralization process) as a function of Fe^{2+} concentration. As can be seen, the TOC and COD removals were mainly influenced by Fe^{2+} concentration. Maximum observed degradation was obtained with Fe^{2+} concentration of 0.2 g/L with 84% and 86.5% TOC and COD removals, respectively. This dose considered less than dose of Fe^{2+} used by Gernjak et al. [27] (0.26 g/L). Nevertheless,

Fig. 5. Effect of the initial amount of Fe^{2+} on TOC and COD removal rate of OMW treatment by photo-Fenton process. [Initial TOC = 44,250 mg/L and initial COD = 11,780 mg/L.]
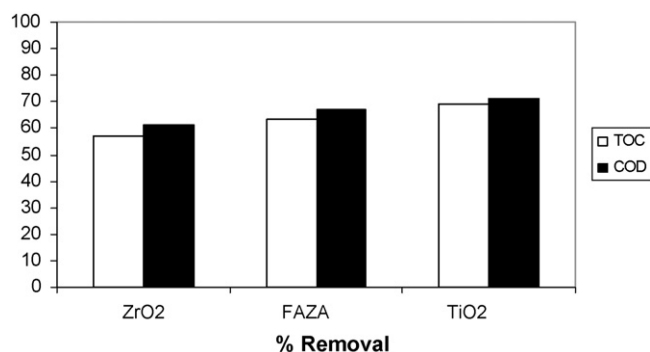
Fig. 6. Effect of the semi-conductor catalyst on TOC and COD removal rate of OMW treatment by heterogeneous photocatalytic oxidation processes. [Initial TOC = 44,250 mg/L and initial COD = 11,780 mg/L.]

an excess of ferrous ions in the system produced a decrease in degradation rate. The possible formation of futile intermediate iron (IV) species (ferryl iron FeO^{2+}) could be the cause of this negative behavior, producing a possible side reaction that interferes with the formation of hydroxyl radicals that are critical for the oxidation of organic matter (Reactions (3)–(5)) [9,31,32].

$$H_2O_2 + Fe(II) \rightarrow FeO^{2+} + H_2O \tag{3}$$

$$FeO^{2+} + Fe(II) + H^+ \rightarrow Fe(OH)^{2+} + Fe(III) \tag{4}$$

$$Fe(OH)^{2+} + H^+ \rightarrow Fe(III) + H_2O \tag{5}$$

3.2.2. Heterogeneous photocatalytic oxidation
3.2.2.1. Catalyst selection. Catalysts in the form of metal oxides (TiO_2, ZrO_2) and composite catalyst from Fe–Al (FAZA) were examined as semi-conductor catalysts during the heterogeneous photocatalytic oxidation. Fig. 6 represents the efficiencies of these selected catalysts on % removal of TOC and COD of OMW after 60 min irradiation time at constant pH value of 4. The amount of catalysts in the terms of catalyst ion concentration used in the reactor was 2 g/L. TiO_2 shows a maximum observed photocatalytic activity and is the most efficient one among the three catalysts used, for both TOC and COD removals. Thus, TiO_2 was selected as the catalyst used in this study for treatment of OMW by using heterogeneous photocatalytic oxidation.

3.2.2.2. Effect of initial pH values. The most important parameter that influences the heterogeneous photocatalytic oxidation is solution pH. Previous studies indicate that pH may affect heterogeneous photocatalytic oxidation in a number of ways. First, the charge of the substrate molecules and the surface of the TiO_2 catalyst are both pH dependent [30–33]. The pH changes can influence the adsorption of the substrate molecules onto the catalyst surfaces, an important step for photocatalytic oxidation to takes place. Second, as indicated in Reaction (6), $OH^\bullet$ can be formed by the reaction between hydroxide ion and positive hole. An alkaline condition would thus favor $OH^\bullet$ formation and enhance degradation. Third, the TiO_2 particles tend to agglomerate under acidic condition and the surface area available for substrate adsorption and photon absorption would be reduced [33]. The effect of pH values from 2 to 10 on the heterogeneous photocatalytic oxidation of OMW is shown in Fig. 7. Increase of pH of the wastewater from 2 to 10 increases the %TOC removal from 38.4% to 70.1% at 60 min reaction time and %COD removal from 40.5% to 72.4% at the same reaction time. In this study, the heterogeneous photocatalytic oxidation was observed to be faster in alkaline pH than in acidic pH range. Similar observations have been reported [34–40]. Since there is no wide difference in both %TOC and %COD removals at pH values of 8 and 10, pH 8 was found to be the optimal point under the given experimental conditions (TiO_2, 2 g/L, irradi-
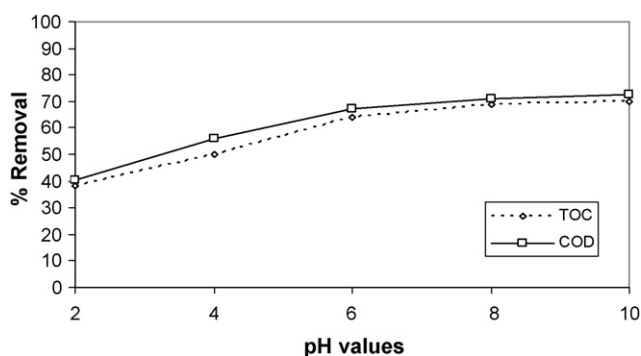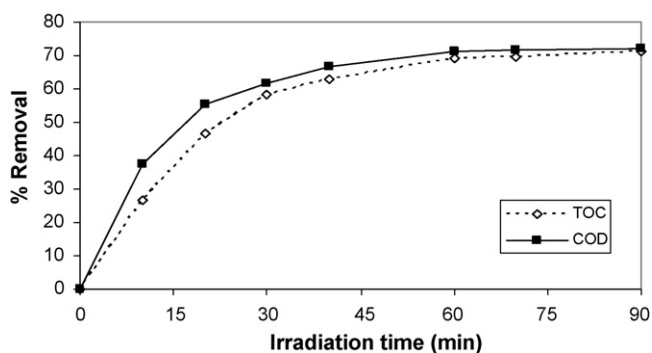
Fig. 7. Effect of pH values on TOC and COD removal rate of OMW treatment by UV/TiO$_2$ process. [Initial TOC = 44,250 mg/L and initial COD = 11,780 mg/L.]

Fig. 9. Effect of initial amount of TiO$_2$ on TOC and COD removal rate of OMW treatment by UV/TiO$_2$ process. [Initial TOC = 44,250 mg/L and initial COD = 11,780 mg/L.]

ation time 60 min). This may indicate that the organic substrates of OMW are highly susceptible to be attacked by ·OH$^\bullet$ despite a weak adsorption of them onto the catalyst. On the other hand, at pH 2–4, agglomeration of TiO$_2$ particles was indeed observed in our study. This might have reduced the availability of catalyst surface for substrates adsorption and photon absorption, thus lowering the heterogeneous photocatalytic oxidation rate at acidic pH.

$$HO_2 + h^+{}_{\upsilon B} \rightarrow OH^\bullet + H^+ \tag{6}$$

3.2.2.3. Effect of irradiation time. OMW (initial COD of 117,860 mg/L and initial TOC of 44,250 mg/L, initial pH value was 8) was treated with UV/TiO$_2$ process. The treatment of OMW by UV/TiO$_2$ process with addition of 2 g/L TiO$_2$ as catalyst at different irradiation time intervals was studied. Fig. 8 shows the concentration-time profile for TOC and COD, respectively, during the UV/TiO$_2$ oxidation process of OMW versus irradiation time. It can be seen that the rate of TOC and COD removals are slower throughout the reaction during the time intervals from 60 to 90 min. The % removal of TOC reached only about 69% and 71.4% for TOC removal after 60 and 90 min irradiation time, respectively. Also, about 71.2% and 71.9% of COD removal was recorded after 60 and 90 min irradiation time, respectively. These results imply the presence of organic compounds in the wastewater that are resistant to further oxidation since both TOC and COD are not completely removed even after 90 min of irradiation time.

3.2.2.4. Effect of initial amount of TiO$_2$. The amount of semiconductor as catalyst is one of the main parameters for the heterogeneous photocatalytic oxidation studies. In order to avoid the use of excess catalyst it is necessary to find out the optimum loading for efficient OMW treatment. The effect of catalyst weight (TiO$_2$-anatase) on the %TOC and %COD removals of OMW was investigated from 0 to 3 g/L of the catalyst, keeping fixed the other

Fig. 8. Effect of irradiation time on TOC and COD removal rate of OMW treatment by heterogeneous photocatalytic oxidation processes. [Initial TOC = 44,250 mg/L and initial COD = 11,780 mg/L.]
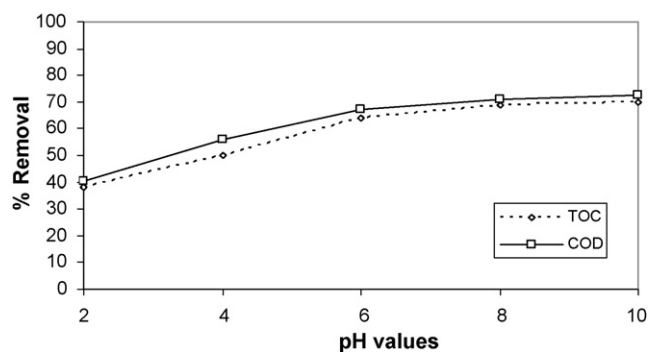
parameters. The results are shown in Fig. 9. The results clearly show that both TOC and COD % removals of OMW were found to be directly proportional to catalyst concentration, indicating a heterogeneous regime. The increase of catalyst weight from 1 to 2 g/L increases the TOC removal from 38.5% to 69% at 60 min irradiation time and COD removal from 45.6% to 71.2% at the same irradiation time. As expected, the removals of TOC and COD were found to increase with the increasing concentration of TiO$_2$ and approaching a limiting value at high concentration. The limiting value (2 g/L) mainly results from the following two factors: (a) aggregation of TiO$_2$ particles at high concentrations, causing a decrease in the number of active surface sites, and (b) increase in opacity and high scattering of TiO$_2$ particles at high concentrations leading to a decrease in the passage of irradiation through the sample [40–42]. In such a condition, part of the catalyst surface probably became unavailable for photon absorption and dye adsorption, thus bringing little stimulation to the catalytic reaction and may be the other reasons for the decrease in both TOC and COD % removals [41–43]. Hence 2 g/L was used as the optimum catalyst dosage for the photocatalytic reaction.

3.3. Biodegradability enhancement

The key question concerning the combined use of either photo-Fenton process or UV/TiO$_2$ process as a pre-treatment step and a biological treatment is to probe that the biodegradability of the photo-treated effluent and, particularly, the BOD$_5$/COD ratio increases during the photo-Fenton and UV/TiO$_2$ processes, approaching the value 0.3 that is considered the quantitative index for organic matter complete biodegradability. Thus, BOD$_5$ and COD determination of the treated wastewater were carried out in order to characterize the evolution of the BOD$_5$/COD ratio. The biodegradability of the treated effluents within 45 and 60 min irradiation time of photo-Fenton and UV/TiO$_2$ reactions was also tested by incubating the pre-treated effluent over a 5-day period as shown in Fig. 10.

After 60 min irradiation time, the final values of BOD$_5$/COD values were 0.8 and 0.66 for photo-Fenton and UV/TiO$_2$ processes, respectively. These results show that the biodegradability can be enhanced by the photocatalytic oxidation converting the non-biodegradable organic substrates into more biodegradable compounds. The ratio of BOD$_5$/COD of the pre-treated homogeneous and heterogeneous photocatalytic oxidation for OMW after 45 min irradiation time increased from initial 0 to 0.4 and 0 to 0.3 for photo-Fenton and UV/TiO$_2$ processes, respectively. The result indicates the biodegradability of photocatalytically treated OMW with both photo-Fenton and UV/TiO$_2$ processes was enhanced. Therefore, the more appropriate photocatalytic treatment time was 45 min for practical wastewater treatment.
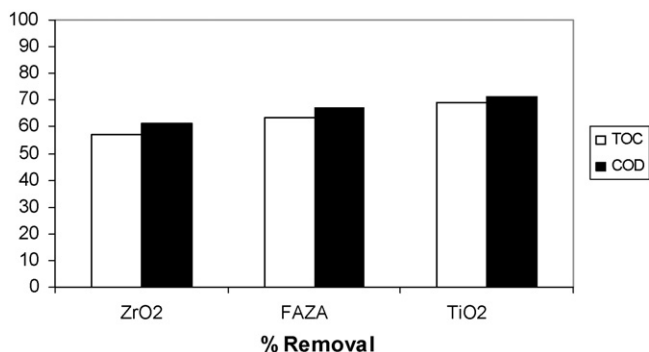
Fig. 10. Biodegradability enhancement of pre-treated photocatalytic effluents of OMW. [Photo-Fenton process: 0.2 g/L Fe^{2+}, 3 g/L H_2O_2, pH = 3; UV/TiO_2: 2 g/L TiO_2, pH = 8.]

Table 2
Characterization of the pre-treated effluents of OMW by using photo-Fenton and UV/TiO_2 processes.

Parameter	Photo-Fenton effluent[a]		Photocatalytic effluent[b]	
	Level	% R[c]	Level	% R[c]
TSS (mg/L)	144	98.31	4,350	48.88
COD (mg/L)	15,321	87.00	33,944	71.20
BOD_5 (mg/L)	12,257	45.52	22,403	0.43
BOD_5/COD	0.80		0.66	
TOC (mg/L)	7,080	84.00	13,718	69.00
Oil and grease (mg/L)	124	98.19	1,663.1	75.71
Lignin (mg/L)	490	97.44	11,460	40.19
Phenol (mg/L)	385	93.88	4,146	34.13

[a] Optimum operating conditions of photo-Fenton treatment method.
[b] Optimum operating conditions of UV/TiO_2 photocatalytic treatment method.
[c] Percent removal.

3.4. Characterization of the pre-photo-treated OMW effluents

Table 2 listed the characterization of the pre-treated effluents of OMW by using both photo-Fenton and UV/TiO_2 processes as pre-treatment steps. As shown in Table 2, the concentrations of TOC, COD, TSS, phenols, lignin, oil and grease were reduced by 84%, 87%, 98.31%, 93.44%, 97.44% and 98.19%, respectively, for photo-Fenton process. The corresponding efficiency removals of photocatalytic UV/TiO_2 were 69%, 71.2%, 48.88%, 34.13%, 40.19% and 75.71%, respectively. The BOD_5/COD ratios increased to 0.66 and 0.8 for photocatalytic UV/TiO_2 and photo-Fenton process, respectively. Also, biodegradability tendency was enhanced by the photocatalytic oxidation processes.

4. Conclusions

Raw OMW was determined to be non-biodegradable since the biodegradability test indicated that the BOD_5/COD ratio is about 0.19. The BOD_5/COD ratios of both pre-treated photo-Fenton effluent and photocatalytic UV/TiO_2 were increased to 0.8 and 0.66, respectively. The optimum irradiation time for both processes was 60 min that enhance the economical feasibility of the integrated process. Also, the other optimum operating conditions for both processes were determined. The results showed the efficiencies of both processes to reduce the major recalcitrant substances found in OMW. Phenol and lignin were decreased to 93.44% and 97.44%, respectively, by using photo-Fenton processes but they decreased to 34.1%, 40.19%, respectively, after 60 min UV/TiO_2. The photocatalytic treatment of the final effluent of one of the olive mill industry was successfully achieved with the both processes. The integrated system of photocatalytic oxidation followed by biological treatment

appears to be feasible for treating OMW containing recalcitrant compounds.

References

[1] B. Delplanque, I. Jusselin, B. Le Roy, C. Motta, Interet nutrionnel des huiles d'olive, Oleogineux Corps Gras Lipides 6 (1999) 86–93.
[2] M. Fito, M.I. Covas, R.M. Lamuella-Roventos, J. Vila, J. Orrents, C. De La Torre, Protective effect of olive oil and its phenolic compounds against low density lipoprotein oxidation, Lipids 35 (6) (2000) 633–638.
[3] M.D. Gonzalez, E. Moreno, J. Quevedo, A. Ramos, Studies on antibacterial activity of waste waters from olive oil mills (alpechin): inhibitory activity of phenolic and fatty acids, Chemosphere 20 (1990) 423–432.
[4] G. Tuncel, C. Nergiz, Antimicrobial effect of some olive phenols in a laboratory medium, Lett. Appl. Microbiol. 17 (1993) 300–302.
[5] M. Hamdi, Anaerobic digestion of olive oil wastewaters, Process Biochem. 31 (2) (1996) 105–110.
[6] N. Zouari, Decolourization of olive oil mill effluent by physical and chemical treatment prior to anaerobic digestion, J. Chem. Technol. Biotechnol. 73 (1998) 297–303.
[7] M.I. Badawy, R.A. Wahaab, A.S. El-Kalliny, Fenton-biological treatment processes for the removal of some pharmaceutical from industrial wastewater, J. Hazard. Mater., in press.
[8] N. Azbar, I. Cevilan, I. Turan, Effect of OOMW on central treatment plant and evaluation of the pretreatment requirements, in: N. Azbar, N. Vardar, M. Akýn, I. Cevilan (Eds.), Proceedings of the First International Workshop on Environmental Problems in Olive Oil Production and Solutions, 2002, pp. 1–6.
[9] G. Ruppert, R. Bauer, The photo-Fenton reaction—an effective photochemical wastewater treatment process, J. Photochem. Photobiol. A: Chem. 73 (1993) 75–78.
[10] R.G. Zepp, J. Hoigne, Hydroxyl radical formation in aqueous reactions (pH 3–8) of iron(II) with hydrogen peroxide, Environ. Sci. Technol. 26 (1992) 313–319.
[11] J.M. Herrmann, Heterogeneous photocatalysis: state of the art and present applications, Top. Catal. 34 (1–4) (2005) 45–65.
[12] I. Arslan, I.A. Balcioglu, D.F. Bahnemann, Heterogeneous photocatalytic treatment of simulated dyehouse effluents using novel TiO_2-photocatalysts, Appl. Catal. B: Environ. 26 (2000) 193–206.
[13] I.K. Konstantinou, T.A. Albanis, TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. A review, Appl. Catal. B: Environ. 49 (2004) 1–14.
[14] M.I. Badawy, T.A. Gad-Allah, M.Y. Ghaly, A. Lopez, Combination of photocatalytic and biological processes as an integrated system for treatment and recovery of industrial wastewater containing pesticides, Afinidad 63 (526) (2006) 478–487.
[15] B.S. Ska-Sobecka, M. Tomaszewska, A.W. Morawski, Removal of micropollutants from water by ozonation/biofiltration process, Desalination 128 (2005) 151–157.
[16] M. Kitis, C.D. Adams, J. Kuzhikannil, G.T. Daigger, Effects of ozone/hydrogen peroxide pretreatment on aerobic biodegradability of nonionic surfactants and polipropylene glycol, Environ. Sci. Technol. 34 (11) (2000) 2305–2310.
[17] M.I. Badawy, M.E.M. Ali, Fenton's peroxidation and coagulation processes for the removal of combined industrial and domestic wastewater, J. Hazard. Mater. B 136 (2006) 961–966.
[18] F.A. El-Gohary, M.I. Badawy, M.A. El-Khateeb, A.S. El-Kalliny, Integrated treatment of olive mill wastewater (OMW) by the combination of Fenton's reaction and anaerobic treatment, J. Hazard. Mater. 162 (2–3) (2009) 1536–1541.
[19] A. Marco, S. Esplugas, G. Saum, How and why to combine chemical and biological processes for wastewater treatment, Water Sci. Technol. 35 (4) (1997) 321–327.
[20] J.P. Scott, D.F. Ollis, Integration of chemical and biological oxidation processes for water treatment: review and recommendations, Environ. Prog. 14 (2) (1995) 88–103.
[21] M. Lapertot, S. Ebrahimi, S. Dazio, A. Rubinelli, C. Pulgarin, Photo-Fenton and biological integrated process for degradation of a mixture of pesticides, J. Photochem. Photobiol. A: Chem. 186 (2007) 34–40.
[22] C.H. Wu, Photodegradation of C.I. Reactive Red 2 in UV/TiO_2-based systems: effects of ultrasound irradiation, J. Hazard. Mater., in press.
[23] J. Barrault, M. Abdellaoui, C. Bouchoule, A. Majesté, J.M. Tatibouët, A. Louloudi, N. Papayannakos, N.H. Gangas, Catalytic wet peroxide oxidation over mixed (Al–Fe) pillared clays, Appl. Catal. B: Environ. 27 (4) (2000) 225–230.
[24] C. Hu, W. Yizhong, Decolorization and biodegradability of photocatalytic treated azodyes and wool textile wastewater, Chemosphere 39 (1999) 2107–2115.
[25] APHA, AWWA, Standard Methods for the Examination of Water and Waste Water, 20th ed., WPCF, New York, 1998.
[26] V. Sarria, S. Parra, M. Invernizzi, P. Peringer, C. Pulgarin, Photochemical–biological treatment of a real industrial biorecalcitrant wastewater containing 5-amino-6-methyl-2-benzimidazolone, Water Sci. Technol. 44 (2001) 93–101.

[27] W. Gernjak, M.I. Maldonado, S. Malato, J. Caceres, T. Krutzler, A. Glaser, R. Bauer, Pilot-plant treatment of olive mill wastewater (OMW) by solar TiO$_2$ photocatalysis and solar photo-Fenton, Solar Energy (2004) 567–572.

[28] W.G. Kuo, Decolorizing dye wastewater with Fenton's reagent, Water Res. 26 (1992) 881.

[29] M.I. Badawy, M.Y. Ghaly, T.A. Gad-Allah, Advanced oxidation processes for the removal of organophosphorus pesticides from wastewater, Desalination 194 (2006) 166–175.

[30] B.C. Faust, J. Hoigne, Photolysis of Fe(III)-hydroxyl complexes as sources of OH radicals in clouds, fog and rain, Atoms Envion. 24A (1) (1990) 79–89.

[31] E. Lipczynska-Kochany, Degradation of aqueous nitrophenols and nitrobenzene by means of the Fenton reaction, Chemosphere 22 (1991) 529–536.

[32] M.Y. Ghaly, G. Härtel, R. Mayer, R. Haseneder, Photochemical oxidation of p-chlorophenol by UV/H$_2$O$_2$ and photo-Fenton process. A comparative study, Waste Manage. 21 (2001) 41–47.

[33] K.H. Chan, W. Chu, The dose and ratio effects of Fe(II) and H$_2$O$_2$ in Fenton's process on the removal of atrazine, Environ. Technol. 24 (2003) 703–710.

[34] M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, Chem. Rev. 93 (1993) 341–357.

[35] N.C.G. Tan, J.L. Opsteeg, G. Lettinga, J.A. Field, Mineralization of azo dyes under integrated anaerobic/aerobic conditions, in: R. Fass, Y. Flashner, S. Reuveny (Eds.), Novel Approaches for Bioremediation of Organic Pollution, Plenum, New York, USA, 1999, pp. 83–93.

[36] W.Z. Tang, H. An, Photocatalytic degradation kinetics and mechanism of Acid Blue 40 by TiO$_2$/UV in aqueous solution, Chemosphere 31 (1995) 4171–4183.

[37] K. Hustert, R.G. Zepp, Photocatalytic degradation of selected azo dyes, Chemosphere 24 (1992) 335–342.

[38] A.M. Fathy, J.Y. Farah, M.Y. Ghaly, Effect of catalyst type and dose on solar photocatalytic oxidation for the degradation of zenafix yellow reactive dye aqueous solution, Afinidad 63 (524) (2006) 308–314.

[39] A. Mills, S. Morris, Photo mineralization of 4-chlorophenol sensitized by titanium dioxide: a study of the initial kinetics of carbon dioxide photogeneration, Photochem. Photobiol. A: Chem. 71 (1993) 75–83.

[40] R. Terazian, N. Serpone, Heterogeneous photocatalysed oxidation of creosote components: mineralization of xylenols by illuminated TiO$_2$ in oxygenated aqueous media, J. Photochem. Photobiol. A: Chem. 89 (1995) 163–175.

[41] M.Y. Ghaly, J.Y. Farah, A.M. Fathy, Enhancement of decolorization rate and COD removal from dyes containing wastewater by the addition of hydrogen peroxide under solar photocatalytic oxidation, Desalination 217 (2007) 74–84.

[42] M.S.T. Goncalves, A.M.F. Oliveira-Campos, E.M.M.S. Pinto, P.M.S. Plasência, M.J.R.P. Queiroz, Photochemical treatment of solutions of azo dyes containing TiO$_2$, Chemosphere 39 (1999) 781–786.

[43] J. Lea, A.A. Adesina, The photo-oxidative degradation of sodium dodecyl sulfate in aerated aqueous TiO$_2$ suspension, J. Photochem. Photobiol. A: Chem. 118 (1998) 111–122.