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# Optimal conditions for olive mill wastewater treatment using ultrasound and advanced oxidation processes

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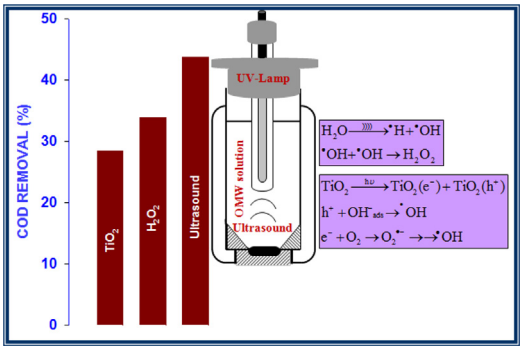
## HIGHLIGHTS

- Optimal conditions for ultrasound and advanced oxidation processes are studied.
- The use of ultrasound, UV and the $TiO_2$ catalyst is effective on OMW oxidation.
- $TiO_2$ can be efficiently used in the sonophotocatalytic oxidation of OMW.
- The main active radicals for OMW oxidation were the OH radicals.

## GRAPHICAL ABSTRACT

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## ABSTRACT

The treatment of olive mill wastewater (OMW) in Jordan was investigated in this work using ultrasound oxidation (sonolysis) combined with other advanced oxidation processes such as ultraviolet radiation, hydrogen peroxide ($H_2O_2$) and titanium oxide ($TiO_2$) catalyst. The efficiency of the combined oxidation process was evaluated based on the changes in the chemical oxygen demand (COD). The results showed that 59% COD removal was achieved within 90 min in the ultrasound /UV/$TiO_2$ system. A more significant synergistic effect was observed on the COD removal efficiency when a combination of US/UV/$TiO_2$ (sonophotocatalytic) processes was used at low ultrasound frequency. The results were then compared with the COD values obtained when each of these processes was used individually. The effects of different operating conditions such as, ultrasound power, initial COD concentration, the concentration of $TiO_2$, frequency of ultrasound, and temperature on the OMW oxidation efficiency were studied and evaluated. The effect of adding a radical scavenger (sodium carbonate) on the OMW oxidation efficiency was investigated. The results showed that the sonophotocatalytic oxidation of OMW was affected by the initial COD, acoustic power, temperature and $TiO_2$ concentration. The sonophotocatalytic oxidation of OMW

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Radicals
COD

increased with increasing the ultrasound power, temperature and $H_2O_2$ concentration. Sonolysis at frequency of 40 kHz combined with photocatalysis was not observed to have a significant effect on the OMW oxidation compared to sonication at frequency of 20 kHz. It was also found that the OMW oxidation was suppressed by the presence of the radical scavenger. The COD removal efficiency increased slightly with the increase of $TiO_2$ concentration up to certain point due to the formation of oxidizing species. At ultrasound frequency of 20 kHz, considerable COD reduction of OMW was reported, indicating the effectiveness of the combined US/UV/$TiO_2$ process for the OMW treatment.



## 1. Introduction

The Mediterranean area is the source of more than 95% of olive trees cultivated worldwide (Russo et al., 2016). According to International Olive Oil Council, the annual production rate of olive oil has increased by around 70% from about one million tonnes in 1990 up to more than 2.3 in 2016 (Guarino et al., 2019). There are nearly 750 million productive olive trees in the world and the majority of them are located in the Mediterranean countries. These countries are responsible for more than 90% of the global production of olive oil (Galliou et al., 2018). The Mediterranean countries are producing more than $30 \times 10^6\ m^3$ of olive mill wastewater (OMW) annually [Vaidya et al., 2019]. Jordan is the home to some of the oldest olive trees in the world. Olive planting has expanded with subsequent increasing olive production capacity from 73,000 tons in 1990 to 191,000 ton in 2004 and 175,000 ton in 2011. These also corresponded to olive oil production of 11,000 tons in 1990, 29,000 tons in 2004 and 27,000 tons in 2011 (Elnenay et al., 2017). The considerable increase in olive oil industry is responsible for the generation of the wastes by either the press process or the three-phase process, which are the most widely applied technologies for producing olive oil (Borja et al., 2006). Despite the fact that the OMW is produced seasonally and in smaller quantities compared to other forms of waste (i.e., domestic sewage); the adverse impacts of OMW on the environment are quite high (Aharonov-Nadborny et al., 2018; Koutsos et al., 2018). Therefore, a special attention has been directed to find a proper treatment and safe disposal of its wastes over the last years (Al-Addous et al., 2017).

The waste of OMW is very complex and contains a wide variety of pollutants. The main characteristics include, strong offensive smell, high COD and BOD, high concentrations of polyphenol, high concentration of total solids and acidic pH (Al Bsoul et al., 2019). These characteristics are greatly influenced by many parameters such as the harvesting time, type of olives, use of fertilizers, phase of maturity, and weather conditions. The direct discharge of OMW effluent into natural water bodies has been forbidden in many countries and an extensive research to develop sustainable and effective technologies of treatment is critically needed.

There are several OMW treatment techniques studied to minimize the environmental impacts of OMW disposal. The effective treatment of OMW typically requires the use of the several technologies that combine chemical, biological and physical processes. The common treatment options currently used to remove solids, colour, odour and to reduce the initial polluting charge are: 1) filtration (Ochando-Pulido and Martinez-Ferez, 2018), 2) membrane separation (Pulido, 2016; Ochando-Pulido and Martinez-Ferez, 2017; Tawalbeh et al., 2018), 3) adsorption (Abdelhay et al., 2018; Al Bsoul, 2014), 4) extraction (Messikh et al., 2015; Chiha et al., 2016), 5) coagoflocculation (Rytwo et al., 2013), 6) settling, and 7)biological processes that involve microbial decomposition of chemicals in OMW (Ashkanani et al., 2019).

Different pretreatment and treatment methods are proposed to decrease the undesirable effects of OMW. The olive mill solid residue proved to be an efficient adsorbent for removal of phenol due to the large amount of phenolic compounds in OMW (Luo et al., 2019). After phenol detoxification, traditional wastewater treatment processes will be able to reduce OMW pollution load to permitted levels. Therefore, pre-treatment of OMW before disposal is required to protect water resources. According to Al-Khatib et al. (2009), 84% of COD removal from diluted OMW was achieved by Up-Flow Anaerobic Sludge Bed (UASB) and physical treatment using $FeCl_3$, CaO and $Ca(.OH)_2$, where improved concrete workability and compressive strength were achieved. The remaining oil was recovered from the solid waste (more than 5% of waste) by using a Soxhlet device (El-Hamouz et al., 2007). The solid waste was successfully transformed into activated carbon to adsorb chromate ion from water (Abdel-Ghani et al., 2016). Different from what has been studied in the literature, the current work aims at studying the enhancement of the photocatalysis efficiency using an ultrasound (US)-assisted photocatalytic oxidation (US/UV/$TiO_2$) or sonophotocatalytic oxidation. To the best of the authors' knowledge, such combination of treatment processes has not yet been reported in the literature. The focus will be directed into the determination of an effective treatment method that is capable of significantly increasing the degradations of OMW.

This work aims at investigating the effectiveness of US/UV/$TiO_2$ for OMW oxidation at different conditions including the initial COD concentration, the concentration of the nano-sized metal oxides, hydrogen peroxide concentration of ($H_2O_2$), concentration of radical scavenger, ultrasound frequency, power and temperature. The current research hypothesis relies on the merit of utilizing ultrasound as a powerful oxidation technique in combination with advanced oxidation processes (AOPs) to enhance the generation of radicals. The use of ultrasound has a positive effect on mass transfer and surface reactions. Furthermore, it appears that this combination is promising in water decontamination and for the complete oxidation of the organic matter.

## 2. Theory

Advanced oxidation processes (AOPs) have extensively been used for the treatment of wastewater containing non-biodegradable organic compounds (Mirzaei et al., 2017; Al Momani and Jarrah, 2010). They have been also effectively used as pre-treatment methods to eliminate toxic compounds that inhibit biological wastewater treatment processes (Mekki et al., 2013; Almomani et al., 2019). Thus, AOPs as pre-treatment process (prior to conventional biological processes involving microbial decomposition of chemicals in OMW) is currently the most successful technique for OMW treatment (Cesaro et al., 2013; Al-Qodah et al., 2014; Al Momani et al., 2004). Recently, the application of ultrasound irradiation encompassing the oxidation of organic matters received increasing attention in water and wastewater treatment. The process involves cyclical nucleation, expansion and successive disintegrate of microbubbles which is known as cavitations. Acoustic cavitation liberates huge quantities of energy over a small location that forms a localized elevated temperature ($\geq$5000 K) and pressure ($\geq$1000 atm). Thus, sonochemical oxidation in aqueous

phase can be attributed to thermal dissociation of water molecule in the cavities where reactive species such as hydroxyl radicals are produced in cavitation bubble reactions (Pang et al., 2011; Almomani and Baranova, 2013). Moreover, alternative processes include the use of photocatalyst as the nano-sized $TiO_2$ with ultrasound or ultraviolet (UV) radiation in the oxidation of organic matter due to the non-toxicity, stability of the chemical structure, electrical and optical characteristics (Sponza and Oztekin, 2013). Photocatalysis efficiency can be improved using high or low frequency (Uğurlu and Karaoğlu, 2011; ElShafei et al., 2017; Almomani et al., 2016; Moncayo-Lasso et al., 2019). This is due to the remarkable effects of chemical and physical properties of ultrasound in the regeneration of the catalyst surface and the formation of free radicals. Thus, the stability of the chemical structure, non-toxicity, optical and electrical properties of the nano-sized $TiO_2$ and nano-sized ZnO as photocatalyst resulted in their extensive uses with UV radiation in the organic impurity oxidation. Furthermore, when $TiO_2$ photocatalysts are irradiated by US, organic molecules are oxidized by both the excitation of electrons in the band gap of $TiO_2$ (Ahmedchekkat et al., 2011) and ultrasonic splitting of water molecules, according to the following equations:

$$TiO_2 \xrightarrow{h\upsilon} TiO_2(e^-) + TiO_2(h^+) \quad (1)$$

$$h^+ + OH^-_{ads} \rightarrow \cdot OH \quad (2)$$

$$e^- + O_2 \rightarrow O_2^{\cdot -} \rightarrow \cdot OH \quad (3)$$

$$H_2O \xrightarrow{))))} \cdot H + \cdot OH \quad (4)$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \quad (5)$$

where $h^+$ is a hole, $\cdot OH^-$ is a hydroxide ion on the catalyst surface and $e^-$ is an electron (Deepthi et al., 2016). This combined process leads to a continuous cleaning of the photocatalyst by US, which maintains its reactivity for longer sonication times. Hence, the combination of sonolytic process with AOPs can be a new alternative for the oxidation of organic compounds (Safa et al., 2019; Vinu and Madras, 2008; Ai et al., 2010; Luo et al., 2008; Selli et al., 2008).

## 3. Materials and methods

### 3.1. Materials

Hydrogen Peroxide solution (30%, $H_2O_2$) supplied by Sigma-Aldrich (Germany). Sodium carbonate (99.5% pure) supplied by Merck (Germany). The $TiO_2$ Photocatalyst used in this research was Degussa P-25 (80% anatase and 20% rutile, 55 $m^2/g$, crystallite size 25–35 nm, $pH_{PZC}$ = 5.6, analytical grade, non porous). All chemicals were used without additional purification. All solutions were prepared using deionized water.

### 3.2. Olive oil mills wastewater samples (OMW)

The OMW used in this study was taken from an olive mill site located in the northern part of Jordan. The samples were collected from the effluent stored in a closed pool. The OMW was filtered and kept in sealed bottles in a refrigerator at 4 °C in the dark. The range of COD values for OMW samples were between 44800 and 63870 mg/L. The OMW samples used for all sonophotcatalytic experiments were diluted using deionized water (by an appropriate ratio to obtain different initial COD concentrations). The main physical and chemical characteristics of OMW samples before dilution are shown in Table 1. (Each measurement was conducted three times and the

**Table 1**
Physical and chemical characteristics of olive mill wastewater (OMW). Data are shown as mean ± standard error of three replicates.

| Parameter | Value |
|---|---|
| pH | 4.60 ± 0.09 |
| Phenol (g/L) | 1.95 ± 0.06 |
| Total Solids (g/L) | 55.30 ± 2.00 |
| COD (g/L) | 51.25 ± 1.80 |
| $BOD_2$ (g/L) | 8.37 ± 0.25 |
| Density (g/L) | 1.92 ± 0.08 |
| Conductivity (mS/m) | 23.50 ± 0.35 |

Wastewater especially industrial effluents such as olive oil mill wastewaters tend to have very high COD levels, which make this type of wastewaters difficult to be treated by a single process. Nowadays, the attention is directed towards the application of different water treatment methods to maximize efficiency. In this study, the sonophotocatalytic oxidation (US/UV/$TiO_2$) of olive oil mill wastewaters, was studied in conjunction with varying some of the oxidation parameters, to reduce the COD in the OMW. Dilution is necessary for the effective treatment. In practice, this step of treatment is implemented in secondary or tertiary processes.

### 3.3. Reactor

Experiments were performed in a cylindrical reactor equipped with a water jacket. Sonication (Ultrasonic Processor, VCX 750, Germany) frequency of 20 kHz was applied through a horn (40-mm diameter) into a cylindrical double-jacketed Reactor. The output acoustic energy was near 525 W. More details on the experimental setup are provided elsewhere (Ahmedchekkat et al., 2011). The solution temperature was regulated by immersing a thermocouple in the reacting OMW. A 15 W UV lamp with a wavelength of 254 nm, 1 cm-diameter with 20 cm-length, was fixed vertically in the reactor. During treatment, the temperature of the OMW was maintained at 25 °C. Samples were pipetted at different time interval and analyzed immediately. The reproducibility of the measurements was within 1–3% and each data set was repeated three times. The results were reported as a mean value ± standard error.

### 3.4. Procedure

Diluted OMW samples were treated using different process configuration including US, UV, US/UV, US/UV/$TiO_2$ under the same experimental operating conditions. These are 20 kHz Ultrasound frequency; 300 W US power 10 g/L initial COD; 300 mL volume; 0.25 g/L $TiO_2$; 15 W UV power; 4.5 pH and 25 ± 1 °C temperature). OMW Samples were taken periodically, centrifuged at 6000 rpm for 4 min and filtered by syringe filters (Minisart RC25, Sartorious) to remove the $TiO_2$ nanoparticles. Control experiments (with $TiO_2$ only) were run in order to ensure that no significant oxidation of OMW occurred.

### 3.5. Chemical oxygen demand measurement

COD values of the initial and treated samples were determined by Thomas and Mazas method (Thomas and Mazas, 1986), where dichromate solution (Aldrich) was used in an acid solution. A sample of 2 mL of OMW was added and then introduced into commercially available digestion solution (0–15,000 mg/L) to be reacted at 150 °C for 120 min in a thermoreactor (RD 125-Tintometer – Lovibond-Germany). Each experiment was performed in duplicate and the average results are shown in this work.

### 3.6. Statistical analysis

The effects of different parameters on COD concentrations and COD removal efficiencies during the sonophotocatalytic oxidation of OMW were judged based on standard error. All of the experiments were performed in triplicate and the mean value of COD concentration ($\bar{C}$) has been calculated using the following equation:

$$\bar{C} = \frac{\sum_{i=1}^{N} C_i}{N} \tag{6}$$

where N is the number of runs conducted for the same OMW treatment experiment under the same operating conditions and where $C_i$ is the COD concentration obtained from each run. Moreover, the standard error of the mean ($\sigma_c$) was evaluated as follows:

$$\sigma_C = \frac{\sigma}{\sqrt{N}} \tag{7}$$

where $\sigma$ is the standard deviation that is defined by:

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(C_i - \bar{C}\right)} \tag{8}$$

Finally, the COD concentrations are presented as the mean ± standard error ($\bar{C} \pm \sigma_C$) in all error bars in the figures and the uncertainties in the tables.

## 4. Results and discussion

### 4.1. Oxidation of OMW using ultrasound alone and in combination with other AOPs.

The oxidation of OMW (indicated by the COD Removal %) was investigated using a variety of AOPs, under the same experimental conditions including (i) Ultraviolet (UV), (ii) sonication (US) (iii) UV + $TiO_2$ and (iv) US + UV + $TiO_2$ combination, as summarized in Table 2. Negligible reduction in OMW COD levels without UV and US was achieved without US and UV. Nevertheless, only 3% oxidation of OMW was obtained after UV treatment of 180 min versus 5% obtained with sonication. Table 2 shows that the oxidation of OMW using UV in the presence of $TiO_2$ achieved only 9% versus 19% under US + UV + $TiO_2$ combination after a treatment of 180 min.

The COD removal percentage values of US, UV/$TiO_2$ and the combination of US/UV/$TiO_2$ were inserted in Eq. (9) to evaluate the synergistic ratio and the obtained synergistic ratio was 1.35. This suggests that a synergistic effect can result from the US + UV + $TiO_2$ combination. The enhancement of the COD removal by US on UV + $TiO_2$ process is related to the enlarged physical effect of ultrasound due to its propagation through the suspended $TiO_2$ nanoparticle and thus prevents the formation of agglomerates throughout the process. Thus, this effect finally enhances the formation of the enhanced amount of **.**OH radicals formed as a result of the increase in the surface area of the catalyst.

**Table 2**
Chemical oxygen demand (COD) removal efficiencies resulted from using a variety of Advanced oxidation processes (AOPs) (olive mill wastewater solution pH = 5.4). Data are shown as mean ± standard error of three replicates.

| Advance oxidation treatment method | COD removal (%) |
|---|---|
| Ultraviolet (UV) | 3 ± 0.06 |
| Ultrasound (US) | 5 ± 0.15 |
| UV + $TiO_2$ | 9 ± 0.21 |
| US + UV + $TiO_2$ | 19 ± 0.47 |

$$\text{Synergy ratio} = \frac{(\text{US/UV/TiO}_2)}{(\text{UV/TiO}_2) + \text{US}} \tag{9}$$

### 4.2. Effect of $TiO_2$ concentration

The obtained results showed that the concentration effect of $TiO_2$ catalyst was considerable on the COD removal. Four different concentrations of $TiO_2$ including 0.25, 0.75, 1 and 2 g/L were studied. The optimum results were obtained at a concentration of 0.75, which was used in all subsequent experiments, as seen in Fig. 1(a). It has been observed that the impact becomes almost constant above 90 min.

Nano-sized $TiO_2$ nanoparticles have a large total surface area and therefore, provide more chances for the organic compounds (COD) to adsorb on the surface. The combination of ultrasound, the photocatalyst $TiO_2$ nanoparticles, and a UV light of 245 nm wavelength will excite and activate the $TiO_2$ nanoparticles to generate **.**OH radicals with oxidative performance. Furthermore, the temperature of the hot spot produced by ultrasonic cavitation in the sonicator can reach 104 °C. This will enhance the production of **.**OH radicals on the surface of the $TiO_2$ nanoparticles. The following steps take place during OMW treatment: (i) mass transfer of the pollutants (COD) from the bulk solution to the surface of nano-sized $TiO_2$, (ii) adsorption of pollutants onto the nano-sized $TiO_2$ surface, and, (iii) initiation of chemical reactions (**.**OH and other radicals) on the surface of the nano-sized $TiO_2$ and iv) desorption of the products from surface to the bulk solution of the OMW in the sonicator (Khoufi et al., 2004). At low $TiO_2$ concentrations, the adsorbed pollutant molecules on nano-sized $TiO_2$ surfaces decrease in the OMW. Therefore, the COD removal percentage has decreased since the organics did not find sufficient available catalytic sites on the surface of the $TiO_2$ nano-particles. Simultaneously, the generation of **.**OH is inhibited so as the formation rate and the number of **.**OH radicals are reduced.

On the other hand, at high $TiO_2$ concentrations, and beyond a concentration of 0.75 mg/L, the COD removal also decreased. In this case, the whole absorbance of system will be affected, higher scattering effect is observed, hence, the reaction rate will decrease. Furthermore, and even in the presence of ultrasound, the capacity and light scattering of $TiO_2$ particles would increase and consequently, the passage of the irradiation though the tested solution will be suppressed.

These results are in a good agreement with those obtained by Ahmed et al. (2015), Gonzalez and Martínez (2008) and Neppolian et al. (2011) where the maximum oxidation of solutions containing organic matter was obtained at an optimal $TiO_2$ concentration.

### 4.3. Effect of initial OMW concentration

The effect of the initial COD concentrations of OMW on the sonophotocatalytic oxidation process was investigated. Three initial COD concentrations of OMW including 1000, 7500 and 10,000 mg/L at 4.98 pH were studied at the identified optimum value of 0.75 g/L $TiO_2$ concentration and illustrated in Fig. 1(b).

The COD removal increased up to 48% as the ultrasound time were increased from 0 to 180 min. The results showed that the COD removal was not fully achieved under the stated conditions. This might be due to the generation of high concentration of intermediate compounds that cannot be further oxidized by **.**OH radicals, hence, accumulated in the system (Sponza and Oztekin, 2013).

The results showed that the removal percentage of COD has decreased with increasing the initial COD concentration of OMW. This was probably caused by the insufficient levels of **.**OH radicals present. This minimizes the contact opportunities between the

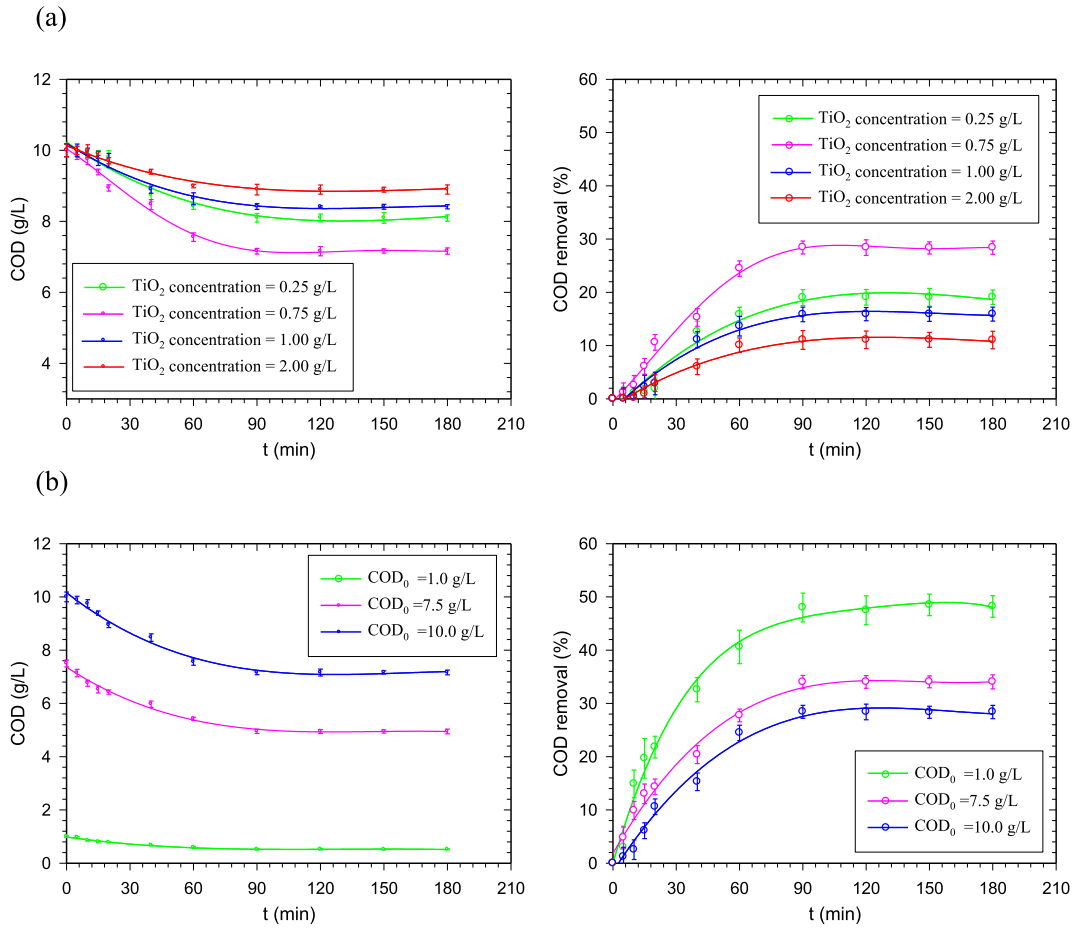


**Fig. 1.** Variations of chemical oxygen demand (COD) concentrations and COD removal efficiencies with time during sonophotocatalytic oxidation of olive mill wastewater (OMW): (a) in the presence of titanium oxide; (b) for different initial COD concentrations in the presence of titanium oxide. Error bars represent mean ± standard error of three replicates.

organic matter and the **.**OH radicals. Thus, leading to a decrease in the removal of COD, as previously reported by (David, 2009). Another possible explanation would be attributed to the shielding effect of the OMW in the solution that is responsible for the decrease in the generation of **.**OH radicals on the $TiO_2$ nanoparticles surface (Wang et al., 2016). Another possible explanation might be attributed to the lack of access into the catalyst sites due to the coverage by the organic compounds (Sponza and Oztekin, 2013).

### 4.4. Effect of hydrogen peroxide concentration

The effect of hydrogen peroxide was investigated using three concentrations of 0, 5 and 10 mmol/L. The results showed that the removal of COD was slightly improved with increasing concentration of $H_2O_2$ as seen in Fig. 2(a). For instance, 33% COD removal was achieved after about 180 min at 300 W with $H_2O_2$, while the respective value without $H_2O_2$ was about 28%. The latter effect can be attributed to the increased production of hydroxyl radicals in the reaction system as a consequence of the addition of oxidizing species, such as $H_2O_2$, during $TiO_2$ photo-oxidation photocatalysis, and thus the oxidation efficiency of OMW increased.

The effect of addition of oxidizing species, such as $H_2O_2$, throughout sonophotocatalysis is attributed to the increase in hydroxyl radicals' formation in the reaction according to Eqs. (10) and (11) (Subramaniam et al., 2018; El Mragui et al., 2019).

$$e^- + H_2O_2 \rightarrow OH- + \cdot OH \quad (10)$$

$$O_2\cdot^- + H_2O_2 \rightarrow \cdot OH + OH^- + O_2 \quad (11)$$

### 4.5. Effect of temperature

The effect of three different temperatures including 25, 35 and 45 °C was investigated at 20 kHz, 300 W, $TiO_2$ concentration of 0.75 g/L and shown in Fig. 2(b). The obtained results showed that the increase in temperature has a positive impact on the COD removal. For instance, the removal percentages at 180 min were 28, 35 and 39% at 25, 35 and 45 °C, respectively. It is generally believed that higher temperatures increase the equilibrium vapour pressure and enhance the bubble production (Galiano et al., 2018). In addition, the reaction rate and the kinetic constant of the sonophotocatalytic oxidation are strongly favored at higher temperatures. Similar results were obtained by Entezari et al. (2005) who investigated the effectiveness of ultrasound assisted catalytic wet peroxide for the removal of 2-chlorophenol from aqueous solution (Entezari et al., 2005).

### 4.6. Effect of ultrasound power

Three ultrasound powers (300, 415 and 525 W) were investigated their impact on the COD removal from OMW and illustrated in Fig. 3(a). The results showed that the COD removals were 28, 35

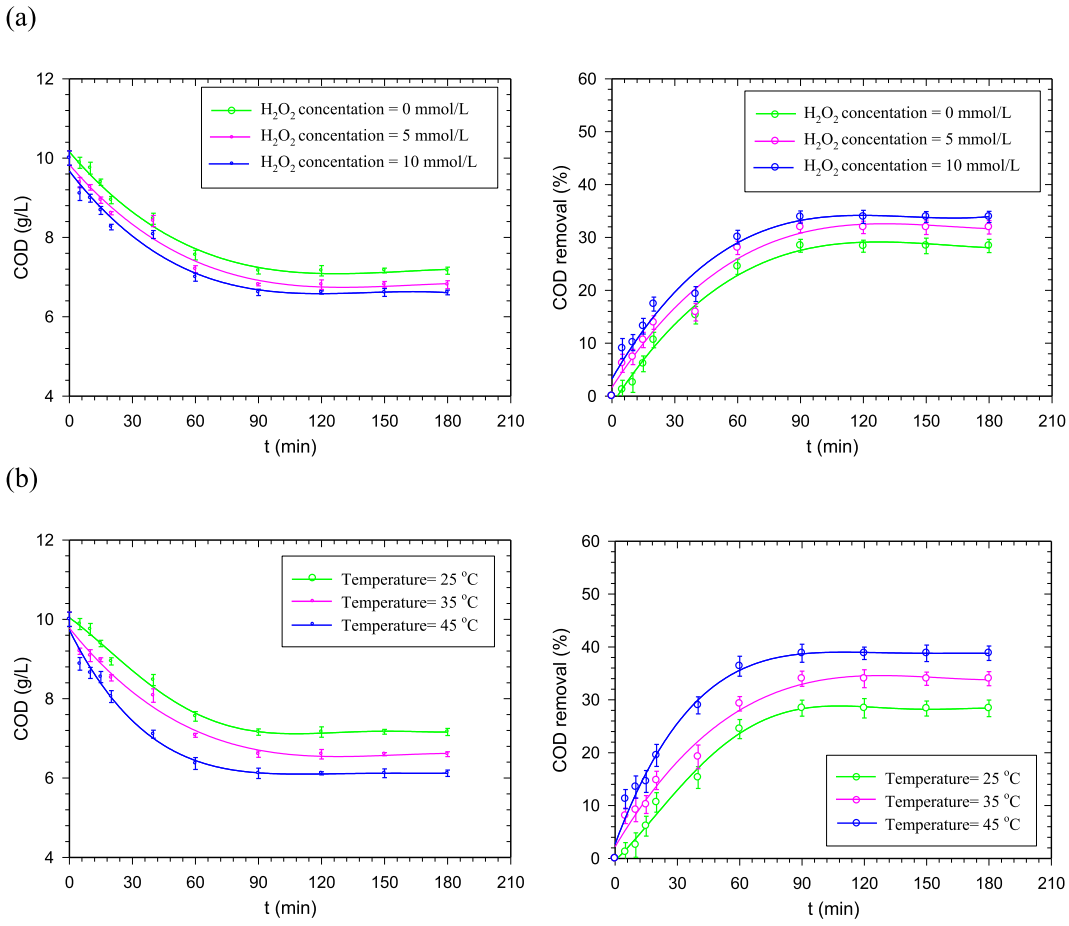


**Fig. 2.** Variations of chemical oxygen demand (COD) concentrations and COD removal efficiencies with time during sonophotocatalytic oxidation of olive mill wastewater (OMW): (a) in the presentence of titanium oxide and hydrogen peroxide; (b) at different operating temperatures. Error bars represent mean ± standard error of three replicates.

and 44%, respectively. It is observed that the removal increased with the increase in power increase and this is due to cavitation and the formation of bubbles and their collapse leading to enhanced production of •OH radicals (Al-Qodah et al., 2014).

### 4.7. Effect of hydroxyl radical scavengers

Sodium carbonate was tested as a scavenger of OH**.** radicals to evaluate the role of such radicals in the OMW oxidation process. OMW containing different concentrations of sodium carbonate was treated for 180 min. Fig. 3(b) shows the COD removal–time profiles of OMW during oxidation at 10 g/L of COD, 20 kHz, 300 W, 0.75 g/L of $TiO_2$ and in the presence of sodium carbonate (as radical scavengers) at a concentration from 0 to 2 mM.

The experimental results revealed that the COD removal was inhibited in the presence of sodium carbonate and the COD removal was lower at higher concentrations of sodium carbonate. The sodium carbonate was used as a scavenger for **.**OH radicals in the bubble. This will prevent the **.**OH radicals accumulation at the interface. The COD removal was observed to be considerably inhibited when sodium carbonate was added. It shows that the hydroxyl radical **.**OH is an active oxidative intermediate with a significant role in the sono-photo-catalytic COD removal process. These results can be supported by a previous study (Al bsoul et al., 2010) performed on the ultrasound oxidation of Mycobacterium sp.6PY1 in the presence of sodium carbonate. The same study (at similar condition) verified the presence of hydrogen peroxide ($H_2O_2$). Therefore, hydrogen peroxide is often used as an indicator for the formation of the oxidizing species (hydroxyl radical) during sonication at 20 kHz versus time. After 60 min, the maximum duration of the sonication experiments, the concentration of hydrogen peroxide in distilled water was 15 μM.

### 4.8. Effect of ultrasound frequency

The effect of two ultrasound frequencies, 20 and 40 kHz, on the COD removal were investigated and shown in Fig. 4. Results showed that the removal was doubled at lower frequency where it reached 28% at 20 kHz, whereas only 14% was observed at 40 kHz. While the number of cavitation bubbles is likely to increase at higher frequency, the sononchemical effect of bubbles may be reduced. This is attributed to the fact that at lower frequency, the US maintains the reactivity of hydroxyl radicals over longer durations of time as a result of a continuous cleaning action of the photocatalyst surfaces (Ola and Maroto-Valer, 2015). In addition, a more energetic collapse of cavitation bubbles is expected to occur at low frequency, rather than at high frequency, because of the larger bubbles radius observed coupled with the shape oscillations (David, 2009).

### 4.9. Oxidation kinetics of OMW under optimum conditions

Three models (zero-order, pseudo first-order, second-order) were studied in this part in an attempt to identify he oxidation kinetic in order to predict the COD removal at any time for the proposed process. The kinetics of COD oxidation was studied via the

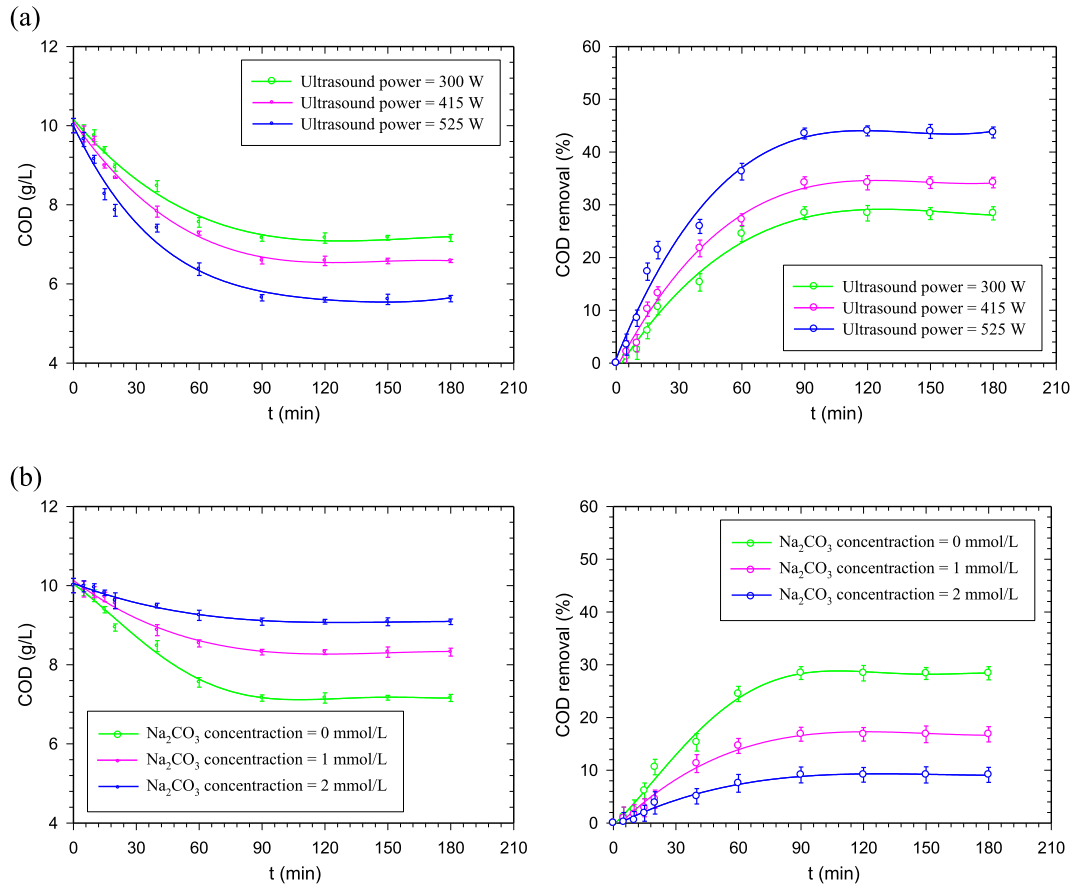


**Fig. 3.** Variations of chemical oxygen demand (COD) concentrations and COD removal efficiencies with time during sonophotocatalytic oxidation of olive mill wastewater (OMW): (a) at different ultrasound power; (b) in the presence of sodium carbonate as radical scavengers. Error bars represent mean ± standard error of three replicates.

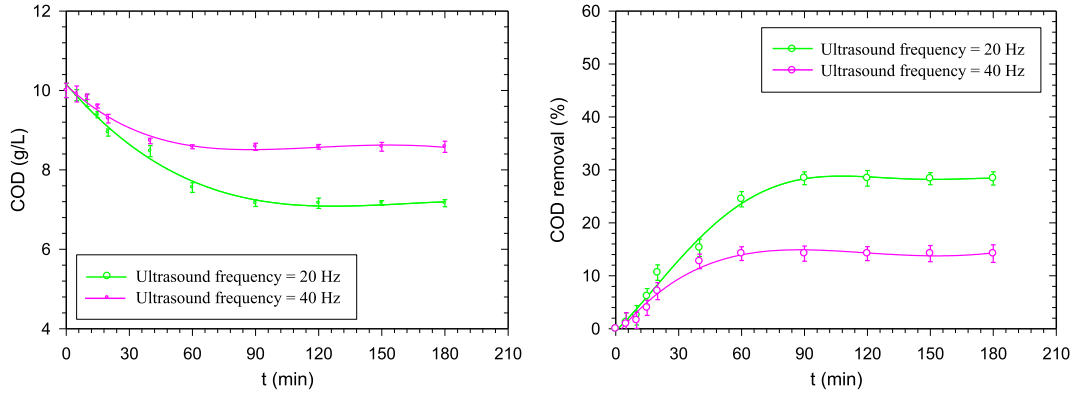


**Fig. 4.** Variations of chemical oxygen demand (COD) concentrations and COD removal efficiencies with time during sonophotocatalytic oxidation of olive mill wastewater (OMW) with two levels of ultrasound frequency. Error bars represent mean ± standard error of three replicates.

integral method. By this method, trial-and-error procedure was used to figure out the reaction order. If the assumed reaction order is correct, the plot of the COD-time data [COD against time (zero-order), ln COD against time (first-order), $COD^{-1}$ against time (second-order)] should give a straight line.

The correlation coefficients, $R^2$, were used to find the fitting between data obtained experimentally and the predicted data and the best correlation coefficient ($R^2$) was selected. The general equation for reaction rate and the integral form that shows the concentration (COD) profile can be described by Eqs. (12) and (13), respectively:

$$-\frac{dC}{dt} = kC^n \tag{12}$$

$$C^{1-n} = C_0^{1-n} + (1-n)kt; n \neq 1 \tag{13}$$

where $C$ is the COD of OMW at any time (mg/L), $t$ is the treatment time (min), $C_0$ is the initial COD of OMW (mg/L), $k$ and $n$ are the kinetics constants. The integrated form of a rate expression proposed for the COD oxidation kinetics is certainly the predicted oxidation kinetic equation.

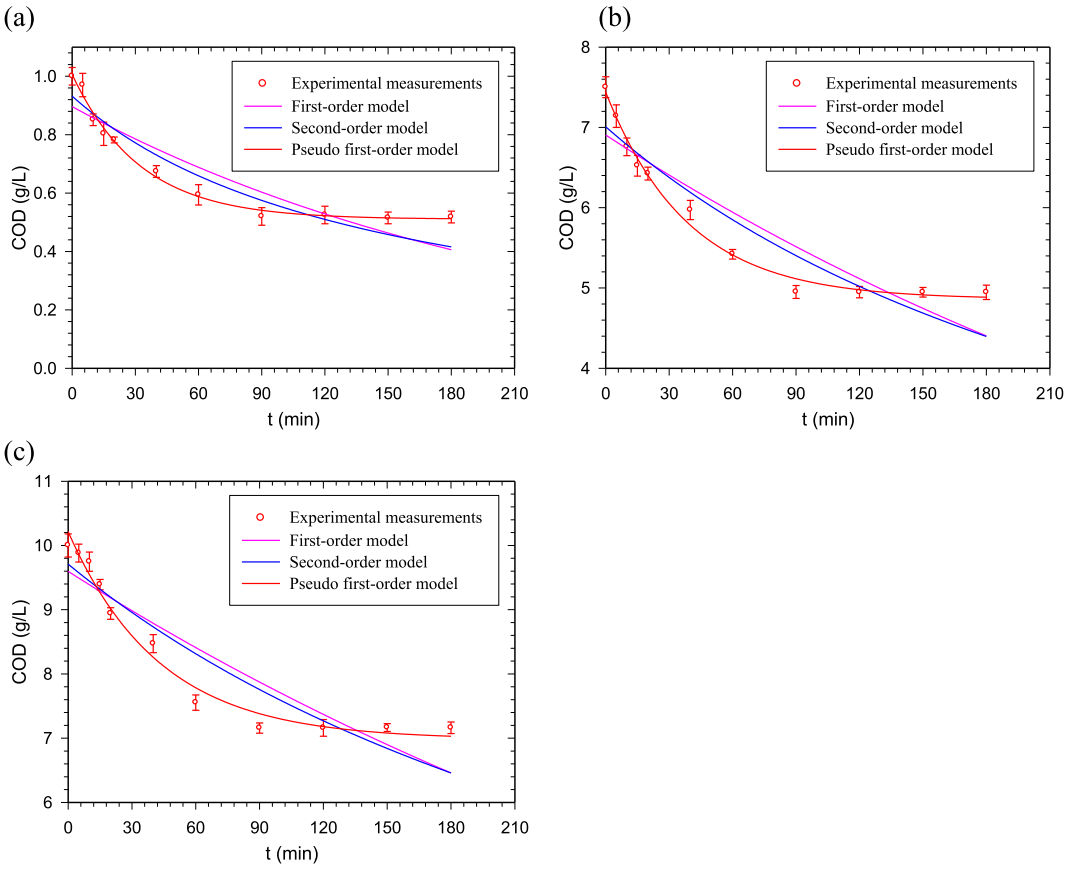


**Fig. 5.** Experimental and predicted chemical oxygen demand (COD) concentrations for first, second, and pseudo first order models for different initial COD concentrations (a) 1.0 ± 0.03 g/L (b) 7.5 ± 0.13 g/L (c) 10 ± 0.18 g/L with time during sonophotocatalytic oxidation of (olive mill wastewater) OMW in the presence of titanium oxide. Error bars represent mean ± standard error of three replicates.

At this stage, the oxidation kinetics of OMW under sonophotocatalysis treatment was studied for a large initial COD range of 1–10 g/L. The experimental operating conditions were selected under the optimum operating conditions that maximize the COD removal efficiency including US frequency: 20 kHz; US power: 525 W, $TiO_2$ concentration: 0.75 g/L; temperature: 45 ± 1 °C. For the following initial COD concentrations (10, 7.5 and 1 g/L), the COD removal % under the optimum operating conditions of the sonophotocatalytic oxidation of OMW was 48, 52 and 59% respectively.

The kinetics of COD oxidation was studied via the integral method. The experimental data were analyzed using different kinetic (first order, pseudo first-order, second-order) models. The fitting to the first order kinetics is shown in Fig. 5. Results show that pseudo first-order kinetic model was found to fit well for the COD oxidation kinetics.

As shown in Table 3, the regression coefficient, $R^2$, was 0.9911, 0.9903 and 0.9808 for initial COD of 1, 7.5 and 10 g/L, respectively. The oxidation rate constant, $k$, was 0.0309, 0.0257 and 0.0232. For OMW with initial COD of 1, 7.5 and 10 g/L, respectively. From these $k$ values, it can be seen that the oxidation by sonophotocatalysis for OMW samples is relatively faster when the initial COD concentration decreased. From Fig. 5 it can be observed that the oxidation

**Table 3**
Kinetic models tested. Initial concentrations are shown as mean ± standard error of three replicates.

| $C_{0,exp}$ (g/L) | First-order model | | | | |
|---|---|---|---|---|---|
| | | $C_{0,cal}$ (g/L) | $k_1$ ($min^{-1}$) | $R^2$ (–) | |
| 1.0 ± 0.03 | | 0.896 | 0.0044 | 0.8279 | |
| 7.5 ± 0.13 | | 6.905 | 0.0025 | 0.8368 | |
| 10.0 ± 0.18 | | 9.598 | 0.0022 | 0.8323 | |
| $C_{0,exp}$ (g/L) | Second-order model | | | | |
| | | $C_{0,cal}$ (g/L) | $k_2$ ($L.g^{-1}.min^{-1}$) | $R^2$ (–) | |
| 1.0 ± 0.03 | | 0.932 | 0.0074 | 0.8919 | |
| 7.5 ± 0.13 | | 7.008 | 0.0005 | 0.8755 | |
| 10.0 ± 0.18 | | 9.710 | 0.0003 | 0.8668 | |
| $C_{0,exp}$ (g/L) | $C_{e,exp}$ (g/L) | Pseudo first-order model | | | |
| | | $C_{0,cal}$ (g/L) | $k_1$ ($min^{-1}$) | $R^2$ (–) | $C_{e,cal}$ (g/L) |
| 1.0 ± 0.03 | 0.518 ± 0.02 | 1.007 | 0.0309 | 0.9911 | 0.510 |
| 7.5 ± 0.13 | 4.946 ± 0.09 | 7.439 | 0.0257 | 0.9903 | 4.860 |
| 10.0 ± 0.18 | 7.162 ± 0.09 | 10.216 | 0.0232 | 0.9808 | 6.981 |

rate decrease with increasing treatment time. The latter effect may be attributed to the decreased of the hydroxyl radicals' competition in the bulk solution. These results are a good agreement with those of Chiha et al. (2010) and Al-Qodah et al. (2014).

## 5. Future research perspectives

The experimental results of the current study will be helpful in the design and operation of olive mill wastewater treatment units. The combined treatment method reported in this work can be adopted effectively to treat other industrial wastewater effluents in Jordan. Future research perspectives should be directed toward the application of such combined approach with other advanced oxidation techniques in an attempt to improve the overall oxidation efficiency.

## 6. Conclusions

In this work, a study for the removal efficiency of COD from OMW was conducted. The results showed that the combination of AOPs such as US, UV, $H_2O_2$ in the presence of catalyst ($TiO_2$ nanoparticles) was more efficient for the removal of COD than using the individual AOPs. This was attributed to the higher amount of **.**OH radicals generated. The presence of $H_2O_2$ showed a slight effect on the enhancement of COD removal from OMW. The rate of COD removal was evaluated and the results revealed that the rate of COD removal decreased with increasing initial concentration of COD in OMW. A maximum COD removal rate was achieved at 0.75 g/L of $TiO_2$ as opposed to the other investigated values of 0.25, 1 and 2 g/L. It was noticed that the use of a higher frequency US did not show a significant improvement on the removal rate of COD. However, the results showed that the removal rate at frequency of 20 kHz was higher than that at 40 kHz. This study also reported that the presence of scavengers such as sodium carbonate inhibited the removal of COD from OMW. The analysis of the oxidation data showed that the pesudo first order model is an excellent representation of the sonophotocatalytic oxidation. The kinetic study performed in this research revealed that the data follow the first order model with regression coefficient in the range of 0.98 to 0.99.

## Declaration of Competing Interest

The authors declare that they is no conflict of interest.

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## References

Abdel-Ghani, N.T., El-Chaghaby, G.A., Elgammal, M.H., Rawash, E.S.A., 2016. Optimizing the preparation conditions of activated carbons from olive cake using KOH activation. Xinxing Tan Cailiao/New Carbon Mater. 31, 492–500.

Abdelhay, A., Al Bsoul, A., Al-Othman, A., Al-Ananzeh, N., Jum'h, I., Al-Taani. A., 2018. Kinetic and thermodynamic study of phosphate removal from water by adsorption onto (Arundo donax) Reeds, Adsorp. Sci. Technol. 36, 46–61.

Aharonov-Nadborny, R., Tsechansky, L., Raviv, M., Graber, E.R., 2018. Mechanisms governing the leaching of soil metals as a result of disposal of olive mill wastewater on agricultural soils. Sci. Total Environ. 630, 1115–1123.

Ahmed, S.M., El-Zomrawy, A.A., Al-Kamali, A.S.N., Ghaleb, K.A.S., 2015. Ponceau 6R dye decoloration and chromate reduction simultaneously in acid medium. Arab. J. Chem. 8, 500–505.

Ahmedchekkat, F., Medjram, M.S., Chiha, M., Al-Bsoul, A.M.A., 2011. Sonophotocatalytic oxidation of Rhodamine B using a novel reactor geometry: effect of operating conditions. Chem. Eng. J. 178, 244–251.

Ai, Z., Li, J., Zhang, L., Lee, S., 2010. Rapid decolorization of azo dyes in aqueous solution by an ultrasound-assisted electrocatalytic oxidation process. Ultrason. Sonochem. 17, 370–375.

Al-Addous, M., Alnaief, M., Class, C., Nsair, A., Kuchta, K., Alkasrawi, M., 2017. Technical possibilities of biogas production from olive and date waste in Jordan. BioResources 12 (4), 9383–9395.

Al Bsoul, A., 2014. The use of eucalyptus leaves as adsorbent for copper ion removal. Desalin. Water Treat. 52, 7838–7844.

Al Bsoul, A., Hailat, M., Abdelhay, A., Tawalbeh, M., Jum'h, I., Bani-Melhem, K., 2019. Treatment of olive mill effluent by adsorption on titanium oxide nanoparticles. Sci. Total Environ. 688, 1327–1334.

Al Bsoul, A., Magnin, J.P., Commenges-Bernole, N., Gondrexon, N., Willison, J., Petrier, C., 2010. Effectiveness of ultrasound for the destruction of Mycobacterium sp. strain (6PY1). Ultrason. Sonochem. 17, 106–110. https://doi.org/10.1016/j.ultsonch.2009.04.005.

Al-Khatib, A., Aqra, F., Al-Jabari, M., Yaghi, N., Basheer, S., Sabbah, I., Al-Hayek, B., Mosa, M., 2009. Environmental pollution resulting from olive oil production. Bulg. J. Agric. 15, 544–551.

Almomani, F., Al Ketife, A., Judd, S., Shurair, M., Bhosale, R.R., Znad, H., Tawalbeh, M., 2019. Impact of $CO_2$ concentration and ambient conditions on microalgal growth and nutrient removal from wastewater by a photobioreactor. Sci. Total Environ. 662, 662–671.

Almomani, F., Baranova, E.A., 2013. Kinetic study of electro-Fenton oxidation of azo dyes on boron-doped diamond electrode. Environ. Technol. 34, 1473–1479.

Al Momani, F., Gonzalez, O., Sans, C., Esplugas, S., 2004. Combining photo-Fenton process with biological sequencing batch reactor for 2,4-dichlorophenol degradation. Water Sci. Technol. 49, 293–298.

Almomani, F.A., Bhosale, R.R., Kumar, A., Kennes, C., 2016. Removal of volatile sulfur compounds by solar advanced oxidation technologies and bioprocesses. Sol Energy 135, 348–358.

Al Momani, F.A., Jarrah, N., 2010. Treatment and kinetic study of cyanobacterial toxin by ozone, J. Environ. Sci. Health – Part A Toxic/Hazard. Substances Environ. Eng 45, 719–731.

Al-Qodah, Z., Al-Bsoul, A., Assirey, E., Al-Shannag, M., 2014. Combined ultrasonic irradiation and aerobic biooxidation treatment for olive mills wastewaters. Environ. Eng. Manage. J. 13, 2109–2118.

Ashkanani, A., Almomani, F., Khraisheh, M., Bhosale, R., Tawalbeh, M., AlJaml, K., 2019. Bio-carrier and operating temperature effect on ammonia removal from secondary wastewater effluents using moving bed biofilm reactor (MBBR). Science of the Total Environment 693, 133425. https://doi.org/10.1016/j.scitotenv.2019.07.231.

Borja, R., Raposo, F., Rincon, B., 2006. Treatment technologies of liquid and solid wastes from two-phase olive oil mills. Grasas Y Aceites 57 (1), 32–46. https://doi.org/10.3989/gya.2006.v57.i1.20.

Chiha, M., Ahmedchekkat, F., Al-Bsoul, A., 2016. Removal of chromium (III) from aqueous solutions using an advanced extraction technique (AET). Desalin. Water Treat. 57, 5567–5578.

Chiha, M., Merouani, S., Hamdaoui, O., Baup, S., Gondrexon, N., Pétrier, C., 2010. Modeling of ultrasonic oxidation of non-volatile organic compounds by Langmuir-type kinetics. Ultrason. Sonochem. 17, 773–782.

Cesaro, A., Naddeo, V., Belgiorno, V., 2013. Wastewater treatment by combination of advanced oxidation processes and conventional biological systems. J. Bioremed. Biodegrad. 4, 8. https://doi.org/10.4172/2155-6199.1000208.

David, B., 2009. Sonochemical degradation of PAH in aqueous solution. Part I: Monocomponent PAH solution. Ultrason. Sonochem. 16, 260–265.

Deepthi, S., Venkatesan, J., Kim, S.K., Bumgardner, J.D., Jayakumar, R., 2016. An overview of chitin or chitosan/nano ceramic composite scaffolds for bone tissue engineering. Int. J. Biol. Macromol. 93, 1338–1353.

El-Hamouz, A., Hilal, H.S., Nassar, N., Mardawi, Z., 2007. Solid olive waste in environmental cleanup: oil recovery and 156 carbon production for water purification. Environ. Eng. Manage. J. 84, 83–92.

El Mragui, A., Daou, I., Zegaoui, O., 2019. Influence of the preparation method and ZnO/(ZnO + $TiO_2$) weight ratio on the physicochemical and photocatalytic properties of ZnO-$TiO_2$ nanomaterials. Catal. Today 321–322, 41–51.

Elnenay, A.E.M.H., Nassef, E., Malash, G.F., Magid, M.H.A., 2017. Treatment of drilling fluids wastewater by electrocoagulation. Egypt. J. Pet. 26, 203–208.

ElShafei, G.M.S., Yehia, F.Z., Eshaq, G., ElMetwally, A.E., 2017. Enhanced degradation of nonylphenol at neutral pH by ultrasonic assisted-heterogeneous Fenton using nano zero valent metals. Sep. Purif. Technol. 178, 122–129.

Entezari, M.H., Heshmati, A., Sarafraz-yazdi, A., 2005. A combination of ultrasound andinorganic catalyst: removal of 2-chlorophenol from aqueous solution. Ultrason. Sonochem. 12, 137–141.

Galiano, F., André Schmidt, S., Ye, X., Kumar, R., Mancuso, R., Curcio, E., Figoli, A., 2018. UV-LED induced bicontinuous microemulsions polymerisation for surface modification of commercial membranes – enhancing the antifouling properties. Sep. Purif. Technol. 194, 149–160.

Galliou, F., Markakis, N., Fountoulakis, M.S., Nikolaidis, N., Manios, T., 2018. Production of organic fertilizer from olive mill wastewater by combining solar greenhouse drying and composting. Waste Manage. 75, 305–311.

Gonzalez, A.S., Martínez, S.S., 2008. Study of the sonophotocatalytic oxidation of basic blue 9 industrial textile dye over slurry titanium dioxide and influencing factors. Ultrason. Sonochem. 15, 1038–1042.

Guarino, F., Falcone, G., Stillitano, T., De Luca, A.I., Gulisano, G., Mistretta, M., Strano, A., 2109. Life cycle assessment of olive oil: a case study in southern Italy. J. Environ. Manage. 238, 396–407.

Khoufi, S., Aouissaoui, H., Penninckx, M., Sayadi, S., 2004. Application of electro-Fenton oxidation for the detoxification of olive mill wastewater phenolic compounds. Water Sci. Technol. 49, 97–102.
Koutsos, T.M., Chatzistathis, T., Balampekou, E.I., 2018. A new framework proposal, towards a common EU agricultural policy, with the best sustainable practices for the re-use of olive mill wastewater. Sci. Total Environ. 622–623, 942–953.
Luo, T., Ai, Z., Zhang, L., 2008. Fe@$Fe_2O_3$ core–shell nanowires as iron reagent. 4. Sono–Fenton oxidation of pentachlorophenol and the mechanism analysis. J. Phys. Chem. C 112, 8675–8681.
Luo, Q.-X., Guo, L.-P., Yao, S.-Y., Bao, J., Liuand, Z.-T., Liu, Z.-W., 2019. Cobalt nanoparticles confined in carbon matrix for probing the size dependence in Fischer-Tropsch synthesis. J. Catal. 369, 143–156.
Mekki, A., Dhouib, A., Sayadi, S., 2013. Effects of olive mill wastewater application on soil properties and plants growth. Int. J. Recycl. Org. Waste Agric. 2, 15. https://doi.org/10.1186/2251-7715-2-15.
Messikh, N., Chiha, M., Ahmedchekkat, F., Al Bsoul, A., 2015. Application of radial basis function neural network for removal of copper using an emulsion liquid membrane process assisted by ultrasound. Desalin. Water Treat. 56, 399–408.
Mirzaei, A., Chen, Z., Haghighat, F., Yerushalmi, L., 2017. Removal of pharmaceuticals from water by homo/heterogonous Fenton-type processes – a review, Chemosphere 174, 665–688.
Moncayo-Lasso, A., Torres- Palma, R.A., Martínez-Pachón, D., Hernández, F., Botero-Coy, A.M., Ibáñez, M., Serna-Galvis, E.A., 2019. Degradation of seventeen contaminants of emerging concern in municipal wastewater effluents by sonochemical advanced oxidation processes. Water Res. 154, 349–360.
Neppolian, B., Ciceri, L., Bianchi, C.L., Grieser, F., Ashokkumar, M., 2011. Sonophotocatalytic oxidation of 4-chlorophenol using $Bi_2O_3/TiZrO_4$ as a visible light responsive photocatalyst. Ultrason. Sonochem. 18, 135–139.
Ochando-Pulido, J.M., Martinez-Ferez, A., 2017. Experimental design optimization of reverse osmosis purification of pretreated olive mill wastewater. Sci. Total Environ. 587–588, 414–422.
Ochando-Pulido, J.M., Martinez-Ferez, A., 2018. Operation setup of a nanofiltration membrane unit for purification of two-phase olives and olive oil washing wastewaters. Sci. Total Environ. 612, 758–766.
Ola, O., Maroto-Valer, M.M., 2015. Review of material design and reactor engineering on $TiO_2$ photocatalysis for $CO_2$ reduction Oluwafunmilola. J. Photochem. Photobiol. C 24, 16–42.
Pang, Y.L., Abdullah, A.Z., Bhatia, S., 2011. Review on sonochemical methods in the presence of catalysts and chemical additives for treatment of organic pollutants in wastewater. Desalination 277, 1–14.
Pulido, J., 2016. A review on the use of membrane technology and fouling control for olive mill wastewater treatment. Sci. Total Environ. 563–564, 664–675.
Russo, C., Cappelletti, G.M., Nicoletti, G.M., Di Noia, A.E., Michalopoulos, G., 2016. Comparison of European olive production systems, Sustainability 8, 825; DOI: 10.3390/su8080825.
Rytwo, G., Lavi, R., Rytwo, Y., Monchase, H., Dultz, S., König, T.N., 2013. Clarification of olive mill and winery wastewater by means of clay-polymer nanocomposites. Sci. Total Environ. 442, 134–142.
Safa, S., Nasirizadeh, N., Dehghani, M., Ghaneian, M.T., 2019. Removal of reactive blue 19 dye from aqueous solutions using sonochemistry process in presence of $TiO_2$ nanoparticle. J. Mazandaran Univ. Med. Sci. 27, 147–161.
Selli, E., Bianchi, C.L., Pirola, C., Cappelletti, G., Ragaini, V., 2008. Efficiency of 1, 4-dichlorobenzene oxidation in water under photolysis, photocatalysis on $TiO_2$ and sonolysis. J. Hazard. Mater. 153, 1136–1141.
Sponza, D.T., Oztekin, R., 2013. Treatment of the olive mill industry wastewater with ultrasound and some nano-sized metal oxides. J. Chem. Eng. Process Technol. 4, 9. DOI: 10.4172/2157-7048.1000147.
Subramaniam, M.N., Goh, P.S., Lau, W.J., Ng, B.C., Ismail, A.F., 2018. AT-POME colour removal through photocatalytic submerged filtration using antifouling PVDF-TNT nanocomposite membrane. Sep. Purif. Technol. 191, 266–275.
Tawalbeh, M., Al Mojjly, A., Al-Othman, A., Hilal, N., 2018. Membrane separation as a pre-treatment process for oily saline water. Desalination 447, 182–202.
Thomas, O., Mazas, N., 1986, La mesure de la DCO dans les milieux faiblement pollués. Analusis 14, 300–302.
Uğurlu, M., Karaoğlu, M., 2011. $TiO_2$ supported on sepiolite: preparation, structural and thermal characterization and catalytic behaviour in photocatalytic treatment of phenol and lignin from olive mill wastewater. Chem. Eng. J. 166, 859–867.
Vaidya, V., Carota, E., Calonzi, D., Petruccioli, M., D'Annibale, A., 2019. Production of lignin-modifying enzymes by Trametes ochracea on highmolecular weight fraction of olive mill wastewater, a byproduct of olive oil biorefinery. New Biotechnol. 50, 44–51.
Vinu, R., Madras, G., 2008. Kinetics of sonophotocatalytic oxidation of anionic dyes with nano-$TiO_2$. Environ. Sci. Technol. 43, 473–479.
Wang, F., Wang, C., Yu, Z., Xu, K., Li, X., Fu, Y., 2016. Two multifunctional Mn(II) metal-organic frameworks: synthesis, structures and applications as photocatalysis and luminescent sensor. Polyhedron 105, 49–55.