Environmental Engineering and Management Journal *August 2014, Vol.13, No. 8, 2109-2118*
http://omicron.ch.tuiasi.ro/EEMJ/

"Gheorghe Asachi" Technical University of Iasi, Romania

COMBINED ULTRASONIC IRRADIATION AND AEROBIC BIODEGRADATION TREATMENT FOR OLIVE MILLS WASTEWATERS

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Abstract

In this study, the reduction of phenolic compounds and other organic pollutants from greenish black (GB) and dark brown (DB) olive mill wastewater (OMW) was investigated. Ultrasonic irradiation in combination with aerobic biodegradation was adopted as the treatment technique. Operational parameters such as the duration of ultrasonic irradiation, ultrasonic power intensity and ultrasonic frequency were tested to determine their effects on phenol, BOD, and COD degradations. It was found that a time interval of 90 minutes of continuous exposure of OMW to ultrasonic field lead up to 81% degradation of the total phenol at 25°C. In addition, the results showed that ultrasonic field affects significantly BOD of OMW. In contrast, there was no significant dependency between COD degradation and ultrasound intensity. It was demonstrated that phenol degradation can be modelled adequately according to first-order kinetics model with rate constant, *k,* of around 0.0083 and 0.0077 min^{-1} for (GB) and (DB) OMW samples, respectively. In the aerobic degradation step, the COD was consumed according to Grau kinetic model. The order of COD degradation rate, is about n=1.13 and 1.27, whereas, the Grau kinetic constant, K=0.0218 and 0.0149 h^{-1} for GB and DB OMW, respectively. The maximum COD removal efficiency achieved was about 80%. It can be concluded that sonication energy plays a significant role on enhancement the efficiency of the biodegradation of OMW by contributing positively in the reduction of the toxic phenolic compounds.

Key words: biodegradation, olive mills wastewater, phenols, ultrasound irradiation

Received: June, 2014; Revised final: July, 2014; Accepted: July, 2014

1. Introduction

Olive mills wastewater (OMW) is a major contributor to the worldwide industrial pollution especially in the Mediterranean countries. As far as Jordan is concerned, the annual quantity of olive mills wastewater (OMW) effluents exceeds 300,000 m^3. This wastewater requires a suitable and inclusive management approach, because OMW usually contains high loads of chemical oxygen demand (COD) (Lafi et al., 2009). In addition, OMW contains a relatively high concentration of polyphenols. Accordingly, OMW is strongly phytotoxic and represents a serious environmental threat (El Hajjouji et al., 2008). For this reason, improved-techniques and suitable processes are needed to eliminate the potentially toxicity of polyphenols and to remove the COD. These processes should be adequate in both technical and economical considerations.

It is familiar that aerobic and anaerobic biological treatment processes are quite efficient

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methods for traditional wastewater like sewage, sludge and various industrial organic wastes. However, these treatment methods cannot be applied to treat fresh OMW due to the strong inhibitory effects of polyphenols. For this reason, several studies have been conducted to reduce the impact of toxic phenols during the treatment process of OMW. Accordingly, several treatment processes including: chemical, physical and biological or combinations of them (El Hajjouji et al., 2008; Francioso et al., 2007; Uğurlu and Karaoğlu, 2011) have emerged during the last two decades. Among these techniques, membrane separation processes have appeared firstly as a promising technique to the treatment of various agricultural wastewater streams (Iaquinta et al., 2009; Ochando-Pulido et al., 2012; Stoller and Chianese, 2006). However, membrane fouling is one of the main drawbacks that usually associate with this technique and therefore limits its applicability (Ergüder et al., 2000; Stoller, 2011; Stoller and Bravi, 2010). Subsequently, advanced oxidation processes (AOPs) such as ozonation (Andreozzi et al., 1998; Benitez et al., 1997), photo-catalysis (Amat et al., 2003), hydrogen peroxide/ferrous iron oxidation (Rivas et al., 2001), and wet air oxidation (Debellefontaine et al., 1994; Mantzavinos et al., 1996) have been applied to degrade polyphenols.

The general oxidative mechanism in these AOPs is based on the formation of hydroxyl radicals ($HO^{\bullet}$), which is considered as a powerful oxidizing agent. Recently, ultrasound irradiation has received increasing attention and was used to degrade organic pollutants found in wastewater (Khoufi et al., 2004). It is known those ultrasounds frequencies belong to the high-energy region are in the range of 18 to 10 MHz. Accordingly, under irradiation by ultrasound energy several chemical and physical effects are expected to occur if organic compounds present in wastewater. These effects comprise of bond breaking, cyclic formation, growth and successive collapse of micro-bubbles formed in a fraction of small time interval. In addition, very high temperatures and pressures are generated within an imploding bubble and consequently, huge quantities of energy are liberated over small area. In this way, ultrasonic irradiation provokes the generation of $HO^{\bullet}$ radicals through thermal dissociation of water (Pang et al., 2011).

These hydroxyl radicals can initiate numerous reaction pathways inside the bubble or at the bubble–liquid interface (Atanassova et al., 2005; Thompson and Doraiswamy, 1999). This would result in direct destruction of hydrophobic volatile compounds inside the cavitation bubbles (Sponza and Oztekin, 2013). On the other hand, hydrophilic organic compounds are ultimately disintegrated during the reaction with the hydroxyl radicals (Andreozzi et al., 1998). Consequently, ultrasonic energy has been successfully used to degrade many organic pollutants including Bisphenol-A (BPA) (Guo and Feng, 2009), chlorinated hydrocarbons (González-García et al., 2010), aromatic compounds (Zhang et al., 2011). Atanassova et al. (2005) applied the sonochemical energy to reduce the antioxidant activity of olive mill wastewater. They reported that the reduction in antioxidant activity increased by increasing the ultrasound power and frequency. Recently, Gianico et al. (2013) subjected olive husks to ultrasonic energy in order to increase the organic matter solubility in the solution. They found that sonication energy caused the solubility of olive husks to increase by about 22%.

However, despite of its promising effects, sonication energy has not been used to degrade phenolic compounds in real OMW, neither as a single treatment process nor with other combined treatment processes. Accordingly, this study is devoted to investigate the effect of sonication energy on phenolic compounds of OMW then to subject the sonicated wastewater to an aerobic biodegradation process. The ultrasonic irradiation prior anaerobic biodegradation of OMW is a novel process configuration that has not been addressed previously (Oller et al., 2011). At the present study, the influence of ultrasound time, power, and frequency on the total phenol, COD and BOD concentrations are investigated. The ultrasound treated wastewater is then subjected to an aerobic biodegradation process using acclimated biomass.

2. Materials and methods

2.1. Olive mills wastewater (OMW)

The OMW employed in this investigation was collected from two olive mills in the north side of Jordan. The first sample was obtained from an open disposal pond and was highly concentrated due to successive water evaporation and was of greenish black (GB) color.

The second sample was a dark brown (DB) that obtained from a closed disposal pond. The main physical and chemical properties of these wastewater samples before dilution are presented in Table 1. Due to high concentrations of GB and DB, they were diluted using distilled water by the ratio of wastewater to distilled water of about 1 to 12.5.

Table 1. Physical, chemical, and biological characteristics of OMW used in the present study

Parameter	***Sample***	
Color	Greenish Black (GB)	Dark Brown (DB)
pH	5.2	5.6
Density; g/L	1.08	1.1
Dissolved COD; g/L	180	121
BOD_5 ; g/L	8.9	22
Total solids (TS); g/L	91.2	72
Total phenolic compounds; g tannic acid/L	5.5	4.5

2.2. Treatment procedure

A schematic diagram of the apparatus used to perform the combined sonication and biodegradation experiments is shown in Fig. 1. Ultrasound of various frequencies ranging from 200 to 400 kHz was emitted from an ultrasonic flat plate transducer (ELAC Nautik, Inc., Kiel, Germany) into a glass vessel with a volume of 700 mL, immersed in the water jacket, and connected to the water cooler. This ultrasound frequency range was determined experimentally to have notable degradation of the phenolic compounds exit in the OMW samples.The acoustic energy density to the reactor was near 7 W/cm^2.

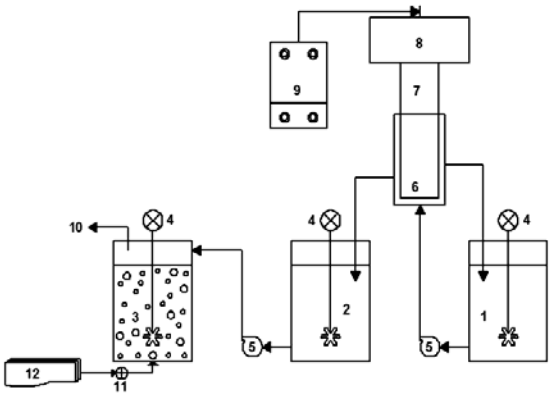

Fig. 1. A schematic diagram for the experimental apparatus: 1-wastewater tank, 2-sonicated wastewater tank, 3-biodegradation bioreactor, 4-mixers, 5-pumps, 6-ELAC-system, 7-cooling jacket, 8-cooling system, 9-ultrasound energy source, 10-off gases, 11-gas filter, 12-compressor

During the experiments, a feed of OMW was pumped from the mixed tank to the sonication glass vessel. At designated times; 0.5 mL samples were withdrawn every 15 and 30 minutes for COD and BOD measurements, respectively, using a 0.1 mL glass syringe (Gastight 1001, Hamilton Corp.). The total sample volumes were too small and did not exceed 1% of the initial wastewater volume in the reactor. After the completion of the sonication time, the treated wastewater was collected in the neutralizer tank where pH was adjusted to be 7 by 0.1 M NaOH solution.

Experiments in the aerobic biological treatment step were conducted in the 6 L stirred tank digester with a working liquid volume of 4.5 L. Air was continuously fed to the bioreactor from the compressor through the gas filter and a gas sparger at the bottom of the tank with a constant flow rate of approximately 180 L/h. The main purpose of sparged air is to improve the mixing of the tank contents which facilitate the uptake of substrate by the microbial community in the aerobic biodegradation process.

Activated sludge from a wastewater treatment plant was used as biomass. Initially, 1.5 g/L biomass was added to 2 L of the treated wastewater and 2 L of the distilled water. Furthermore, quantities of NH_4Cl, K_2HPO_4, $MgSO_4$, and $CaCl_2$, and $NaNO_3$ of 0.1 M solutions were added to the tank in order to have COD:N:P ratio of about 100:5:1. This step is necessary to maintain the biomass activity inside the reactor. During the first four days of running the experiment, about one liter of the reactor content was taken every day and replaced by the same amount of fresh ultrasound treated water solution.

Continuous monitoring of microbial biomass concentration was performed to guarantee normal microbial growth and activity. It was assumed that five days run is fair enough for biomass to acclimate the treated wastewater effectively, thereby achieving steady-state condition. Consequently, the bioreactor was supplied by the sonicated wastewater of the two types only.

2.3. Measurement and analysis

One millilitre of the activated sludge was added to each sample of the sonicated wastewater and incubated at temperature of 20 ^oC in a Sapromat (Volth). During the incubation process, BOD_5 and BOD_{20} were determined after 5 days of BOD test (1992). In addition, COD was measured according to the standard method (APHA, 1992). The total phenol content was determined according to the Folin–Ciocalteau method (Vazquez et al., 1974).

3. Degradation mechanism and kinetics

3.1. Sonication degradation mechanism

The $OH^{\bullet}$ radicals, formed during the cavitation in the aqueous medium, initiate phenol degradation in the liquid medium. This is due to the physiochemical properties of phenol, which has low vapour pressure and hydrophilic nature. These properties have dramatic effect on the cavitational collapse.

Recently, different phenol removal mechanisms and metabolites have been reported. Pétrier et al. (1994) studied the sonochemical degradation of phenol in aqueous solution and found hydroquinone, catechol, and benzoquinone as reaction products. Anju et al. (2012) indicated that the hydroxyl radicals were involved in the phenol degradation reactions. They showed that $OH^{\bullet}$ radicals produced from H_2O dissociation inside bubble during the collapse that diffused in the aqueous medium. The concentration of hydroxyl radicals obtained after the collapsed bubbles was very high. The maximum concentration that could be obtained is nearly 4 mM. Nevertheless, Currell et al. (1963) indicated that sonochemical degradation of phenol occurs partially by pyrolysis inside the bubbles during ultrasonic irradiation.

The chemical reactions that usually occur in the sonochemical systems are exceedingly complicated with nineteen forward/backward reaction mechanisms occurring in a pure water system alone. Seven of these reactions, for most of

the chemical kinetics take place during sonication are summarized by Gong and Hart (1998) as given by Eqs (1-7):

$$H_2O \Leftrightarrow H^{\cdot} + OH \quad (1)$$

$$H^{\cdot} + H^{\cdot} \Leftrightarrow H_2 \quad (2)$$

$$OH^{\cdot} + OH^{\cdot} \Leftrightarrow H_2O_2 \quad (3)$$

$$H^{\cdot} + O_2 \Leftrightarrow HO_2^{\cdot} \quad (4)$$

$$H^{\cdot} + HO_2^{\cdot} \Leftrightarrow H_2O_2 \quad (5)$$

$$HO_2^{\cdot} + HO_2^{\cdot} \Leftrightarrow H_2O_2 + O_2 \quad (6)$$

$$HO_2^{\cdot} + OH^{\cdot} \Leftrightarrow H_2O_2 + H \quad (7)$$

After the formation of the hydroxyl radicals, they attacked the Ortho and Para positions of the phenol ring followed by additional oxidation to quinones, ring opening and oxidation to di-acids as shown in Fig. 2 (Bremner et al., 2011). The final steps resulted in the formation of smaller molecules including the oxidative resistant acetic and formic acids. Under certain conditions complete decomposition can occur (Sun et al., 2013).

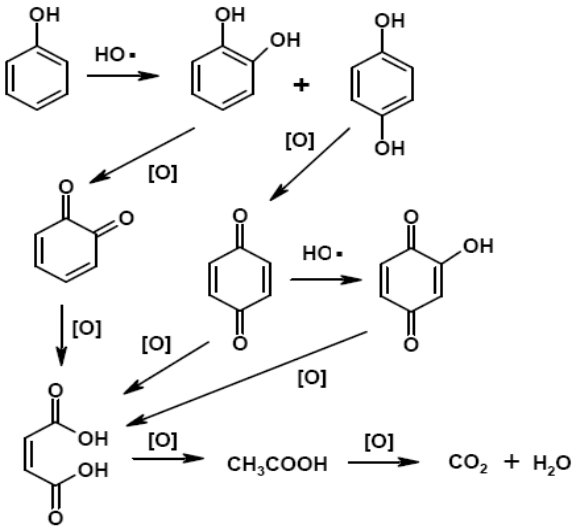

Fig. 2. Degradation mechanism of phenol under ultrasound treatment proposed by Bremner et al. (2011)

3.2. Sonication degradation kinetics

The application of ultrasound energy is expected to intensify chemical and biological processes both in terms of increasing the conversion as well as the rate of a chemical or biological reaction. If ultrasound source is applied in a frequency and intensity range that creates cavitation, it will promote sonochemical transformation of the pollutants into a simple chemical structure of better water-soluble properties.

Consequently, the chemical reaction kinetics and the mass transfer of the produced substances will not represent limiting factors in the biodegradation step (Siripattanakul-Ratpukdi, 2014). Moreover, the presence of toxic constituents like polyphenols, at high concentrations will significantly inhibit the microbial activity and reduces their ability to degrade the organic pollutants (Chiha et al., 2010). For these reasons, the degradation of phenolic compounds represents an essential pretreatment step in order to intensify the biodegradation process.

The determination of the kinetics and mechanism of phenolic compounds degradation is a very essential step for the modeling of the degradation process. Some researchers reported some degradation method including advanced oxidation processes and ultrasonic energy (Chiha et al., 2010; Hong-guang et al., 2011; Qiao et al., 2013; Serpone et al., 1994; Zhang et al., 2011). However, most of these studies have used synthetic phenol solution rather than a real wastewater. Chiha et al. (2010) used several kinetic models including Langmuir-type mechanism described by Eq. (8) to predict the sonochemical degradation of some phenolic non-volatile organic compounds. They analyzed the degradation data using a kinetic model developed by Okitsu et al. (2005). They found that the expression given by Eq. (9) can describe the degradation data as given by Eqs. (8, 9):

$$r = \frac{kKC_0}{1 + KC_0} \quad (8)$$

$$r = K_b + \frac{kKC_0}{1 + KC_0} \quad (9)$$

where r is the degradation rate (M min^{-1}), k is the pseudo rate constant (M min^{-1}), K is the equilibrium constant (min^{-1}) and C_o (M) is the pollutant initial concentration, K_b is a constant representing the rate of decomposition in the bulk liquid (M min^{-1}).

Subsequently, Qiao et al. (2013) investigated the sonochemical effects on the degradation of caffeic acid and sinapic acid under ultrasound treatment. They reported that the experimental data obtained were well fitted by pseudo zero-order kinetics for operating temperature in the range -5 to 25°C. On the other hand, Hong-guang et al. (2011) and Zhang et al. (2011) found that the first-order kinetic model defined by the following Eq. (10) successfully described the ultrasonic degradation of organic matters in aqueous media:

$$\ln[C/C_0] = kt \quad (10)$$

where k is an apparent rate constant, and C_0 and C are the initial concentration and concentration at time t, respectively.

In this investigation, the integral method was used to estimate the kinetic parameters of phenol degradation in which trial-and-error procedure was performed (Chiha et al., 2010). The squared

correlation coefficient, R^2, was used to measure the goodness of the fitting between the experimental data and the corresponding predicted one. The kinetic model for reaction rate and concentration can be described by Eqs. 11 and 12, respectively:

$$-dC/dt = k\,C^n \tag{11}$$

$$C^{1-n} = C_0^{1-n} + (1-n)kt \;\; ; \;\; n \neq 1 \tag{12}$$

where C is the phenol concentration (mg. L^{-1}), t is the contact time (min), C_o is the initial phenol concentration (mg.L^{-1}), k and n are the reaction constant and reaction order, respectively.

3.3. Biological treatment kinetics

In the biological degradation step the organic load is aerobically consumed by the activated sludge cells and converted mainly to carbon dioxide. The COD decomposition rate in this step could be described by the following model proposed by Grau et al. (1975) that used activated sludge to treat multi component organic load:

$$q = K\left(COD/COD_o\right)^n \tag{13}$$

where K and n are the kinetic parameters of the decomposition process and q is the specific rate of *COD* decomposition defined as:

$$q = -\left[dCOD/dt\right]/X \tag{14}$$

where X is the biomass density (g/L), t is the time (h). In order to evaluate the kinetic parameters, Eq. (13) can be linearized to the following form:

$$\ln q = \ln K + n\ln\left(COD/COD_0\right) \tag{15}$$

A plot of ln q against ln(COD/COD_0) will give a straight line of slope n and intercept of ln$K$.

4. Results and discussion

4.1. Effect of ultrasound time duration on OMW phenol degradation

In this study, diluted OMW samples were subjected to ultrasonic irradiation for duration up to 90 minutes, the power intensity was approximately 7 W/cm^2 and water bath temperature was 25 °C. The applied ultrasound frequency is kept at 351 kHz and 206 kHz for the greenish black (GB) and dark brown (DB) OMW samples, respectively. Phenol concentration was measured and shown in Fig. 3 as a function of time. It clear in Fig. 3 that phenol concentration decreases notably with ultrasonic irradiation time for both GB and DB OMW samples. For example, after ultrasonic irradiation of 30 minutes, the total phenol percent removal efficiency, defined as [100(C_0-C)/C_0]%, reaches around 53 and 49 % for GB and DB OMW samples, respectively. Also it is clear in the figure that the maximum total phenol removal efficiencies after the whole period (90 min) were 81 and 82% for GB and DB OMWS samples, respectively. These results agree with those of Del Bubba et al. (2004) who used physico-chemically treatment process for OMW and achieved an average phenol removal of 84%.

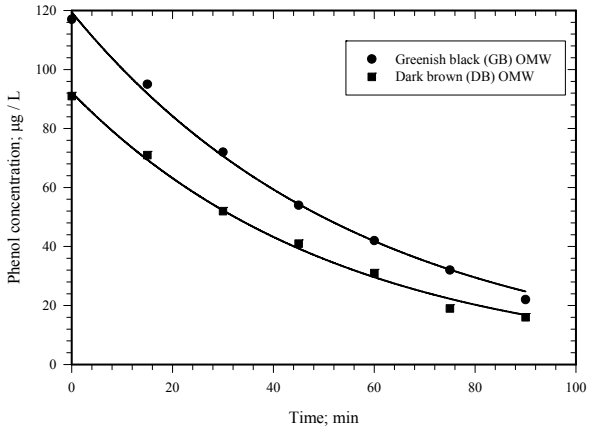

Fig. 3. Variation of phenol concentration in OMW samples with ultrasound time at power intensity: 7 W/cm^2; volume: 700 mL; pH: natural; temperature: 25 ± 1 °C

4.2. Degradation kinetics of phenol under Ultrasound Treatment

The kinetics of phenol degradation was investigated using the integral method. The experimental results were fitted to different kinetic (zero-order, first-order, second-order) models. The fitting to the first order kinetics is given in Fig.4.

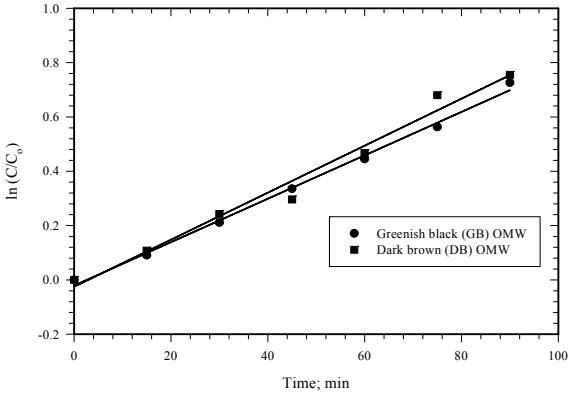

Fig. 4. ln(C/C_0) versus time for the sonochemical degradation of phenol at power intensity: 7W/cm^2; volume: 700 mL; pH: natural; temperature: 25 ± 1 °C

It is evident from Fig. 4 that the degradation kinetics of phenol under the effect of ultrasound energy is well-fitted according to first-order kinetic model for both GB and DB OMW. The squared correlation coefficient, R^2, was 0.993 and 0.978 for GB and DB OMW, respectively.

The degradation rate constant, k, was 0.0083, and 0.0077 min^{-1} for GB and DB OMW,

respectively. From these *k* values, it can be observed that the phenol degradation by ultrasound for GB OMW samples is relatively faster than that of DB OMW. Moreover, the decrease in degradation rate with increasing sonication time can be attributed to the decreased competition for hydroxyl radicals in the bulk solution. These results are consistent with those of Chiha et al. (2010), Hong-Guang et al. (2011), Qiao et al. (2013), and Zhang et al. (2011).

4.3. Effect of ultrasound irradiation on the chemical oxygen demand (COD) of OMW

The variation of COD with time for both GB and DB OMW under the effect of ultrasound irradiation was also measured and plotted in Fig. 5. As illustrated in the Figure, the sonication had practically no significant effect on the COD of OMW. The COD of the GB olive mill wastewater increases by only 7.5%, whereas there is no net change in the COD of the DB olive mill wastewater. In general, the complex aliphatic organic compounds such as fatty acids or olive oil are thought to be unaffected by sonochemical energy since these species are stable and resistant to degradation.

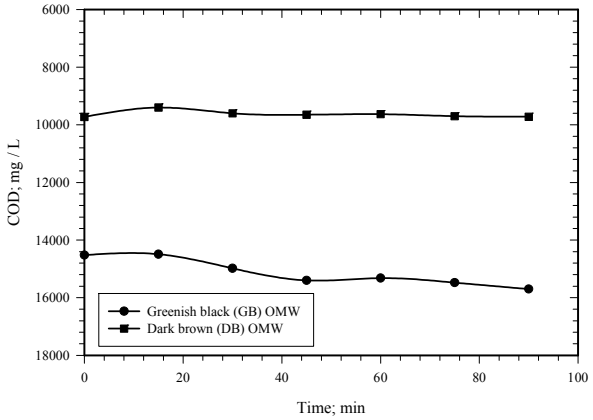

Fig. 5. Variation of the COD of the OMW samples with ultrasound irradiation time at ultrasound power intensity: 7W/cm^2; OMW sample volume: 700 mL; pH: natural; temperature: 25 ± 1 °C; ultrasound frequency: 351 kHz for GB samples and 206 kHz for DB samples

Thus, the effect of the ultrasound energy was primarily on the aromatic compounds like poly phenols rather than aliphatic compounds which is due to the high degree of the unsaturation. However, the concentration of phenolic compounds in OMW is relatively low and varies from 0.05 to 10 g/L depending on the type and source of the wastewater (El Hajjouji et al., 2008). Consequently, the net effect of phenolic compounds degradation on the COD values is considered to be negligible.

4.4. Effect of ultrasound irradiation on the biological oxygen demand (BOD) of OMW

The variation of BOD with time for greenish black (GB) and dark brown (DB) OMW samples under the effect of ultrasound energy was monitored and compared with two reference solutions; water (Reference solution one) and municipal wastewater (Reference solution two). The results are presented in Fig. 6 and Fig. 7.

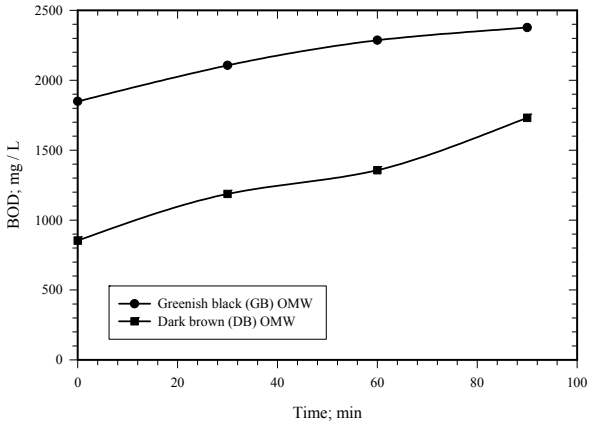

Fig. 6. Variation of the BOD of the OMW samples with ultrasound irradiation time at ultrasound power intensity: 7W/cm^2; OMW sample volume: 700 mL; pH: natural; temperature: 25 ± 1 °C; ultrasound frequency: 351 kHz for GB samples and 206 kHz for DB samples

It is expected that poly phenol degradation by ultrasound energy generally enhances OMW samples biodegradation. Measurements of BOD_5 and BOD_{20} were conducted to see the ability of microorganisms to degrade the sonicated samples. As mentioned above, Fig. 6 illustrates the changes in BOD for the DB and GB OMW as a function of ultrasound irradiation time applied. The initial values of BOD were 1848 and 853mg/L for DB and GB OMW samples, respectively. The corresponding ultrasound frequencies for the DB and GB samples were 206 and 351 kHz, respectively. It can be seen in Fig. 6 that as the irradiation time increases the BOD_5 value increases.

The BOD for GB OMW samples increases more significantly with irradiation time than that observed for DB OMW. For example, the BOD_5 of GB OMW increases about 103% or almost doubled during the first 90 minutes while for that of the DB one, the increase does not exceed 35%. This behaviour could be attributed to the conversion of the suspended BOD to soluble forms as a result of the $OH^{\cdot}$ radicals attack on poly phenols. Therefore, sonication results in transferring a significant portion of the aromatic amines that have a complex structure and are resistant to biodegradation, under aerobic conditions into biodegradable organic species, consequently increasing the BOD (Benitez et al., 1997; El Hajjouji et al., 2008).

Fig. 7(a) and (b) shows BOD–time profile for DB and GB OMW samples exposed to different ultrasound irradiation times in addition to two reference samples of water (Reference solution one) and municipal wastewater (Reference solution two). It is evident from Fig. 7(a) that ultrasonic treatment time had a significant effect on the increase of BOD.

In addition, Fig. 7(a) shows that the BOD continuously increases with time for the sonicated samples. Moreover, the sonication results show a distinct enhancement of the BOD increase at high irradiation time-values. During the 20 days of incubation, BOD_{20} was almost doubled for GB OMW samples treated for 90 minutes than for the untreated samples. Similar behaviour was obtained for the sonicated DB OMW sample shown in Fig. 7(b). The BOD was enhanced with increasing sonication time. The BOD value of water was zero which was used as a reference sample. BOD increased with sonication time due to the higher energy absorbed by the organic compounds leading to an increase in the destruction of complex compounds to form biodegradable matter.

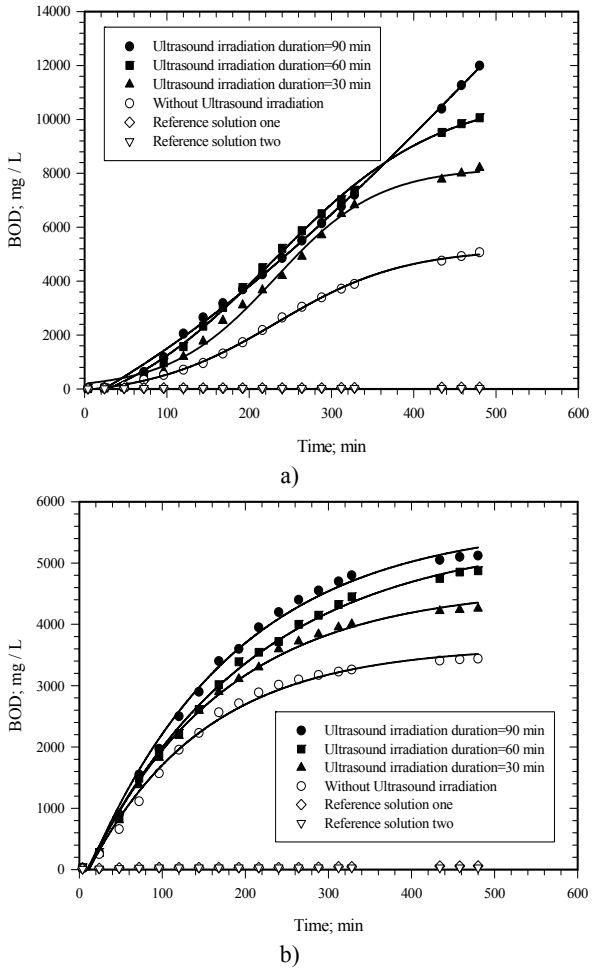

Fig. 7. Variation of the BOD of the OMW samples with time at different ultrasound irradiation time and ultrasound power intensity: 7W/cm^2; OMW sample volume: 700 ml; pH: natural; temperature: 25 ± 1 °C. a) GB OMW samples with ultrasound frequency of 351 kHz; b) DB OMW samples with ultrasound frequency of 206 kHz.

4.5. Aerobic biological treatment process

The sonication process was considered in order to rule out the phenolic inhibition effect in OMW. Consequently, both COD and BOD increase with increasing ultrasound duration and its energy intensity. This gives the opportunity for degradation of other organic compounds. Hence, a biological treatment of sonicated OMW was necessary in order to reduce the COD.

It can be concluded that a combination of ultrasonic degradation and biological treatment of OMW will result in better characteristics of these two processes including economical and technical advantages. Note that before ultrasonic treatment, olive mill wastewater was very toxic and the activated sludge is completely inhibited. However, it was observed that there was slight increase in the COD of untreated wastewater after 24 hours of continuous aeration accompanied by biomass. This behavior could be attributed to the degradation of the deactivated biomass, known as lysis, to generate more COD. In addition, the activated sludge was able to grow and degrade the sonicated wastewater as shown in Fig. 8, which depicts the normalized COD removal values of both DB and GB OMW samples. It is clear from Fig. 8 that COD removal rate of the two samples is significant. For instance, in the first 24 h from startup the COD in the GB and DB samples decreases to 58 and 50% of the initial values, respectively. Moreover, those values decreased to 28 and 20 of the initial values after 72 h of continuous operation. This indicates that the aerobic biological treatment process was able to remove 72 and 80% from GB and DB OMW, respectively.

These results agree with those of Benitez et al. (1999) who investigated the treatment of OMW by ozonation followed by aerobic degradation and achieved 84% COD reduction for initial COD concentration of 22 g/L. The residual COD in the solution is less than 28 and 20% of GB and DB OMW samples could be considered as non-biodegradable organic matter or needs longer aeration period. This non-biodegradable organic material could be removed by other treatment methods such as coagulation. The decomposition rate of COD was the highest in the first 24 h of operation. This behavior could be attributed to the fact that the biomass was more active in this period because the medium was rich with nutrients like P and N. The concentration of these nutrients decreased with the process progress until complete depletion. This suggests the application of fed batch operation to feed the reactor with the necessary nutrients.

The kinetic model proposed by Grau et al. (1975) was used to describe the biological COD degradation.

Table 2 presents the time-dependent COD for both GB and DB olive mill wastewater samples. Additional data required to construct a linear plot in order to estimate kinetic model parameters are summarized in the table. Linear trends between ln(q) and ln(COD/COD_o) are presented in Fig. 9. The corresponding values of squared correlation coefficient were closed to unity which indicates the validity of Grau et al. model to describe the degradation kinetic process.

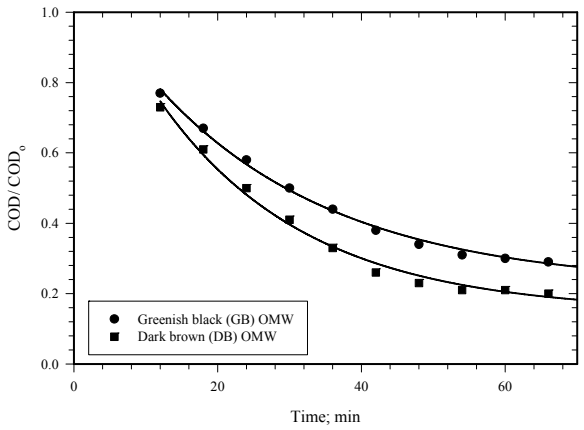

Fig. 8.Variation of dimensionless with time in the biological treatment process at T = 25 ^oC and pH = 7

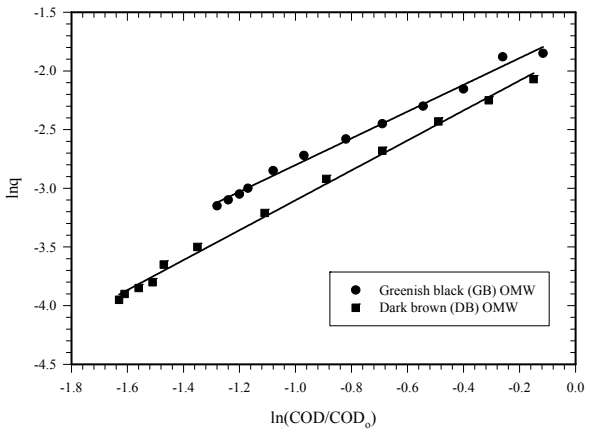

Fig. 9. ln(q) against ln(COD/COD$_o$) against time in the biological treatment unit

Table 2. Time-dependent COD, biomass density, specific COD degradation for (DB) and (GB) OMW during the biodegradation process. Initial COD for GB and DB were 14.7 and 9.7 g/L, respectively

Time (h)	*COD_{GB} (g/L)*	*COD_{DB} (g/L)*	*X_{GB} (g/L)*	*X_{DB} (g/L)*	*$ln[COD/COD0]_{GB}$ (-)*	*$ln[COD/COD0]_{DB}$ (-)*	*lnq_{DB} (-)*	*lnq_{DB} (-)*
0	14.7	9.70	1.50	1.50	0.00	0.00	0.00	0.00
6	12.9	8.34	1.70	1.80	-0.12	-0.15	-1.85	-2.07
12	11.2	7.08	1.90	2.0	-0.26	-0.31	-0.19	-2.25
18	9.70	5.90	2.08	2.20	-0.4	-0.49	-2.15	-2.43
24	8.40	4.95	2.17	2.33	-0.54	-0.69	-2.3	-2.88
30	7.24	4.08	2.26	2.43	-0.69	-0.89	-2.45	-2.92
36	6.37	3.29	2.34	2.52	-0.82	-1.11	-2.58	-3.21
42	5.60	2.71	2.41	2.61	-0.97	-1.35	-2.72	-3.50
48	4.90	2.38	2.47	2.65	-1.08	-1.47	-2.85	-3.65
54	4.50	2.15	2.53	2.70	-1.17	-1.51	-3.00	-2.80
60	4.16	2.05	2.58	2.72	-1.20	-1.56	-3.05	-3.85
66	3.89	1.96	2.60	2.82	-1.24	-1.61	-3.10	-3.9
72	3.64	1.90	2.61	2.82	-1.28	-1.63	-3.15	-3.95

The values of kinetic parameters were as follows: the order of COD degradation, n = 1.13 and 1.27 and kinetic constant, K=0.0218 and 0.0149 h^{-1} for GB and DB OMW, respectively. It should be taken into consideration these parameters are affected by the operating temperature, biomass content, and initial COD.

5. Conclusions

A combined sonochemical and biological degradation treatment process was applied for the removal of phenol and COD from OMW. The obtained results in this investigation prove the applicability of sonication energy as a pre-treatment technology to reduce the content of toxic phenolic compounds**.** To remove all the phenol content from this wastewater, the sonication energy intensity and duration should be increased or the wastewater itself could be diluted more. The biodegradation step was not able to remove all the COD. This suggests the need for a longer residence time in the reactor or a higher cell density.

On the other hand, another treatment method like coagulation could be used to remove the remaining COD after the biological treatment step. In addition, further investigations are required in order to consider the effect of temperature variations during the day or during the season of olive harvesting.

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