

Contents lists available at ScienceDirect

# Journal of Hazardous Materials



journal homepage: www.elsevier.com/locate/jhazmat

# Augmentation of biodegradability of olive mill wastewater by electrochemical pre-treatment: Effect on phytotoxicity and operating cost

# F. Hanafi<sup>a,b,\*</sup>, A. Belaoufi<sup>a</sup>, M. Mountadar<sup>b</sup>, O. Assobhei<sup>a</sup>

<sup>a</sup> Laboratoire de Biotechnologies marine et de l'environnement, Faculté des Sciences, Université Chouaib Doukkali, El Jadida, Morocco <sup>b</sup> Unité de Chimie Analytique et Sciences de l'Environnement, Faculté des Sciences, Université Chouaib Doukkali, El Jadida, Morocco

### ARTICLE INFO

Article history: Received 31 January 2011 Received in revised form 28 February 2011 Accepted 28 February 2011 Available online 6 March 2011

Keywords: OMW Pre-treatment Electrocoagulation Biological treatment Phytotoxicity

#### ABSTRACT

In order to exploit the fertilizer value of olive oil mill wastewaters (OMW), a novel method has been developed for its treatment. OMW effluents were pre-treated first by electrocoagulation using aluminum electrode and then by a biological process using a selected strain of *Aspergillus niger* van Tieghem. The effect of treatments was assessed through COD removal, reduction of total phenols, and decrease of phytotoxicity using durum wheat (*Triticum durum*) seeds. This sequential treatment scheme was capable of reducing concentration of organics, phenolics and phytotoxicity. The goal of this investigation was achieved, the phytotoxicity was completely removed and the germination index was 106% of OMW after sequential treatment. It can be concluded that the sequential process of OMW treatment might serve for the production of a fertilizer which is able to improve the growth of plants. These results are encouraging in the context of developing a low-budget technology for the effective management of OMW.

© 2011 Elsevier B.V. All rights reserved.

# 1. Introduction

Olive mill wastewater (OMW) accrues in the production of olive oil during winter and consists of olive fruit extract and added process water. Its annual production is in the range of some million cubic meters throughout the European Union. Analytical parameters reported in the literature vary by several hundred percent, as the composition depends on a broad variety of factors such as type of olives and press system. Nevertheless, OMW could be described as a wastewater with high organic load (typically 10–30 g/l TOC), high COD (up to 150 g/l reported), high salt concentration and acidic pH. The generation of huge amounts of OMW in a short time during the press season is the first problem. Second, OMW contains polyphenols up to several grams per litre, which are phytotoxic and toxic to bacteria used in common biological wastewater treatment plants [1]. Furthermore, the low pH and the polyphenols' complexing abilities raise the solubility of heavy metals in the environment [2].

Treated OMW may find use as a raw material in various biotechnological processes. Since OMW contains various compounds potentially useful for diverse plants, an attractive application is its use as a fertilizer. Biological treatment methods have been recognized as overall economical and effective processes [3]. However, the presence at high concentration of aromatic, phenolic and polyphenolic compounds, which are toxic to many microorganisms, inhibits the efficiency of biodegradation processes [3,4].

In order to facilitate the degradation of toxic or nonbiodegradable organic substances, many researchers have proposed combined methods comprising chemical and biological treatment steps. A common approach refers to the oxidation of the wastewater using a strong oxidative agent, such as ozone [5], Fenton's reagent, a mixture of hydrogen peroxide and ferrous or ferric iron [6], a combination of UV radiation and hydrogen peroxide as well as photo-Fenton [7]. These methods are based on the creation of very reactive oxidizing free radicals, especially hydroxyl radicals.

Electrochemical oxidation has been shown to be an effective technique for removing pollutants from OMW. Many anodes such as Ti/RuO<sub>2</sub> [8], Ti/IrO<sub>2</sub> [9], Ti/Pt [10], Ti/Ta/Pt/Ir [11], boron-doped diamond [12], iron and aluminum electrodes [13,14] have been widely investigated.

In this study, electrocoagulation was used as a pre-treatment step for the oxidation of the recalcitrant organic compounds or metabolites of those that could not be oxidized biologically. The main advantages of electrocoagulation over other conventional techniques, such as chemical coagulation, are "in situ" delivery of reactive agents, no generation of secondary pollution, removal of the smallest colloidal particles, flotation of the pollutant to the top of the solution where it can be easily removed and compact equipment [15]. The use of electrocoagulation as a primary treatment process offers the advantage of reducing the time consumed dur-

<sup>\*</sup> Corresponding author at: B.P. 20, Faculté des Sciences, Université Chouaib Doukkali, 24000 El Jadida, Morocco. Tel.: +212 523 373 254/671 974 333; fax: +212 523 342 187.

E-mail address: hanafi\_fatiha1@yahoo.fr (F. Hanafi).

<sup>0304-3894/\$ -</sup> see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2011.02.087

Table 1	
---------	--

Characteristics of the OMW used in this study.

Parameter (mg/l)	Value
рН	4.68
Conductivity (EC) (mS/cm)	3.24
Chemical oxygen demand (COD)	28,500
Polyphenols	4500
Chlorides (Cl <sup>-</sup> )	1040
Sodium (Na <sup>+</sup> )	1072
Potassium (K <sup>+</sup> )	424
Calcium (Ca <sup>2+</sup> )	77.89
Magnesium (Mg <sup>2+</sup> )	37.60
Absorbance (395 nm)	13

ing biodegradation and improves the economic feasibility of the treatment process. Aerobically treatment using *Aspergillus niger* was used as a secondary treatment step. The *Aspergillus* genus has been used successfully for the bioremediation of green table olive wastewater, which is also characterized by high organic and phenolics content, and satisfactory removal efficiencies have already been reported [16]. Moreover, the phytotoxicity of the resulting liquid phase to durum wheat (*Triticum durum*) seeds was also evaluated and a preliminary cost analysis was conducted.

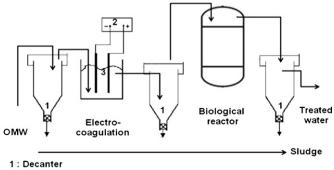
# 2. Experimental

#### 2.1. Characteristics of olive mill wastewater

OMW was obtained from an olive oil continuous processing plant located in Marrakech (southern Morocco). The main characteristics of this OMW are presented in Table 1.

## 2.2. Electrochemical cell

The electrochemical cell has two aluminum plates, one serving as a cathode and the other as anode (Fig. 1). The total effective electrode area was 18 cm<sup>2</sup> (4.5 cm × 4 cm) and the spacing between electrodes was 2.8 cm. The electrodes were connected to a digital DC power supply (4A, 30 V). For each run, 100 cm<sup>3</sup> of OMW were placed into the electrolytic cell without stirring. This electrolysis process lasted 15 min at 250 A/m<sup>2</sup> and without adjustment of pH. The OMW samples contained relatively high amounts of Cl<sup>-</sup> (1040 mg/l) and had high conductivity (3.24 mS/cm) (Table 1). For electrocoagulation process, the presence of Cl<sup>-</sup> in OMW solution was reported to increase the anodic dissolution rate of Al, either by the incorporation of Cl<sup>-</sup> to the oxide film or by the participation of Cl<sup>-</sup> in the metal dissolution reaction [17].



<sup>2 :</sup> DC power

Fig. 1. Schematic representation of sequential treatment process.

#### 2.3. Strain, inoculum and cultures conditions

The strain used in the OMW treatment experiments was isolated from OMW using the agar plate technique and classified by DSMZ (Braunschweig, Germany) as A. niger van Tieghem (DSM 24787). A fungus was maintained through periodic transfer at 4 °C on potatodextrose (2.4%) agar plates in the presence of 0.5% yeast extract. Before using in the biodegradation experiments, the strain was first precultivated during 2 days at 28 °C under agitation (rotary shaker - 150 rpm) in 50 ml of the liquid version of OMW-based medium supplemented with 0.35% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and 0.065% KH<sub>2</sub>PO<sub>4</sub> (w/v), contained in 250 ml Erlenmeyer flasks. The fungus was grown in the form of pellets. Liquid cultures were conducted in duplicate, in Erlenmeyer flasks containing 50 cm<sup>3</sup> of OMW supplemented uniformly with 0.35% (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and 0.065% KH<sub>2</sub>PO<sub>4</sub> (w/v). The flasks were inoculated with 500 mg dry weight fungal biomass per litre OMW and incubated in a rotary shaker at 150 rpm and 28 °C. The growth was followed as dry weights of mycelium following the filtering of the samples through glass microfibres (GF/A Whatman Inc.) and drying 105 °C [18].

# 2.4. Phytotoxicity measurement

The phytotoxic behaviour of the liquid phase to durum wheat (*T. durum*) seeds was assessed using the bioassay described by Mosse et al. [19].

# 2.5. Analytical methods

Before analysis the samples were filtered on glass microfibres (GF/A Whatman Inc.). Chemical oxygen demand (COD) and total Kjeldahl nitrogen (TKN) were determined according to APHA standards methods. Total phenolic content was determined according to the Folin–Ciocalteau method [20]. Decolorisation was assayed by the measurement of absorbance at 395 nm (CARY 1E VARIAN spectrophotometer) [4]. Heavy metals (P, K, Na, Mg, Ca, Cu, Zn, Fe and Al) were detected by spectrometry ICP-AES.

#### 3. Results and discussion

#### 3.1. Biological treatment alone

In preliminary experiments different strains have been isolated from OMW. Strain A. niger van Tieghem was selected for its ability to better grow in the acidified OMW (pH 4.68). A. niger is an acid producing organism, therefore changes in the pH of the medium constitute a measure of its activity. Different amounts of A. niger mycelia were used as inoculums in treatment experiments of OMW. The results (data not shown) demonstrate that greater inocula give faster reduction of COD and phenolics up to 500 mg/l (inoculum dry weight/litre of medium) while no significant differences were observed after doubling this amount. Throughout the experiments small, compact and uniform pellets of the fungus were formed. In order to study the effects of fungal treatment on OMW, A. niger were tested in batch cultures of OMW, supplemented uniformly with nitrogen and phosphorus. The maximum reduction of COD and phenolics was 63.5% and 56.44%, respectively, after 10 days of treatment (Fig. 2). This high removal efficiency could be attributed to both degradation and conversion of the phenolic compounds. In fact, the phenolics concentrations did not inhibit the microorganism and the degradation time was enough to allow the fungus to decolorise OMW. This result suggested that the longer retention time prepared the biomass to degrade a larger amount of phenolic after the acclimation of fungus to the high concentration of polyphenols. Similarly, Fadil et al. [21] reported that 52.5% of the phenol compounds was removed by Aspergillus sp. after 7 days of

<sup>3 :</sup> Aluminum electrode

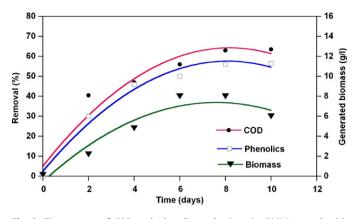


Fig. 2. Time course of COD and phenolics reductions in OMW treated with *Aspergillus niger* van Tieghem.

treatment; this was also accompanied by a significant decrease in the color intensity of the OMW. Aissam et al. [22] argued that the degradation of phenolic compounds was due to the possible action of various enzymes, including those of laccase, tannase and the ligninolytic oxidative enzymes, and demonstrated that the growth of tannase producer *A. niger* HA37 in fourfold-diluted OMW resulted in a 70% degradation of the phenolic compounds. As it can be observed from Fig. 2, up to certain time, biomass concentration increases with time and then decreases. Moreover, it is clear that the maximum value of biomass concentration depends upon the initial substrate concentration. It can be said that such behaviour agrees with the typical decay cycle [23].

In this process the maximum color removal activity was coincidental with the lowest pH value. A. niger cause about 65% decrease of absorbance at 395 nm, after 2-4 days in the culture medium. Hamdi et al. [24] reported that the decreased color intensity of the OMW was possibly due to both the degradation of some phenolic compounds and the adsorption of the polyphenols and tannins onto the fungal mycelium. Fountoulakis et al. [25] reported that during the first 7 days there was no significant decolorisation of OMW, although most of the total phenol fraction was degraded at that time. Color reduction started on the 7th day. It is possible that the phenolic compounds that were degraded in that time were responsible for the dark color of the waste. After 10 days incubation, the color removal activity decreased and the final pH increased. A significant correlation between discoloration and pH profiles was observed. Qin et al. [26] noticed that the color of green tea catechins changed from light brown to dark brown with pH increases. Moreover, they are more stable and not oxidized in acid solutions. In fact, when the pH exceeds 6, phenolic compounds polymerize and give dark polymers which adsorb strongly to proteins [27].

## 3.2. Electrocoagulation of OMW

The purpose of this part of study was directed to treat the OMW by electrocoagulation process. During this process, when direct current passed through the Al anodes, Al<sup>3+</sup> correspondingly dissolved and combined with hydroxyl ions in the water. They formed metal hydroxyls ions, which are partly soluble in water under definite pH values and play the role of coagulant.

During electrocoagulation treatment, pH increased from 4.68 to 7.6, which may be attributed to the smaller production of H<sup>+</sup> than OH<sup>-</sup> as was explained by Israilides et al. [28] and the reduction in phenol concentration. Indeed, phenols are acids in liquids, and their removal from a solution reduces its acidity. The pH value of electrocoagulated OMW can be considered favourable for bio-treatment. After electrocoagulation, the COD of OMW drops to approximately 60.7% of the initial value (Fig. 3). This result

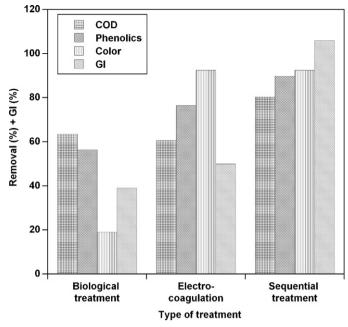


Fig. 3. Comparison of the quality of the OMW after different treatments: biological, electrocoagulation and sequential treatment.

points out the ability of the electrolysis process to eliminate soluble compounds present in OMW. The concentration of phenolics was significantly reduced during the electrocoagulation. Removal efficiency was about 76.44% for total polyphenols. Kavitha and Palanivelu [29] reported that in electro-Fenton, biodegradable aliphatic compounds such as acetic acid and oxalic acid were identified as the major products during the degradation of synthetic phenol. However, transformation of phenolic polymers to simple phenolic compounds was not demonstrated. Crude OMW was highly colored due to its high content of polyaromatic compounds. In the beginning of the electrolysis treatment, the color intensity of the effluent increased as a result of phenolic compounds polymerization [30]. However, color intensity decreased to 92.44% of the initial color at the end of treatment. During the electrolysis treatment, a part of the solute and particle matter present in OMW turned out to be a suspended solid that could reach between 6 and 7 g/l at the end of the electrolysis reaction. The colloids were precipitated with aluminum which was continuously dissolved into the wastewater from the aluminum anodes, as governed by the Faraday's law. These total suspended solid were rapidly eliminated by simple sedimentation. The temperature of the electrolysed solution increased in the first 15 min, from 22 to 48 °C, suggesting that the electrochemical decomposition of the wastewater was completed in this period.

The pH, COD, coloration and phenolics removal were consistently very good. Indeed, the effluent quality of the pre-treated OMW by electrocoagulation process was rather excellent. It could be directly fed as influent to aerobic treatment.

#### 3.3. Sequencing electrocoagulation and biological processes

Coupling chemical and biological processes has received a lot of attention in recent years as a promising treatment alternative for effluents that are too toxic to treat biologically. The underlying principle behind process integration is that a chemical pretreatment stage may be capable of converting most of the biorecalcitrant pollutants, commonly found in industrial effluents, to more readily biodegradable intermediates followed by a biological treatment step to convert these intermediates to biomass, biogas and water. Chemical pretreatment usually comprises a mild advanced oxidation process aiming at the partial rather than complete mineralization; consequently, treatment costs associated with this step are relatively small. In the present study, a combination of electrocoagulation and biodegradation processes aims to evaluate the performance of this combined sequence on OMW phytotoxicity.

In the sequential process represented in Fig. 1 (electrocoagulation pre-treatment plus biological treatment), global removals of 78.5%, 91.6% and 92.44% were obtained for COD, total phenolic content and color, respectively, higher than those obtained in the single aerobic process, as shown in Fig. 3. From the global efficiency, 41.82% of COD elimination was accomplished by the electrocoagulation treatment and 36.68% by the biological treatment. Likewise for the phenolic content elimination, 54.08% was accomplished by the electrocoagulation treatment and 37.52% by the biological treatment. The electrocoagulation proved to be very efficient in terms of color removal. Levels above 92.44% in color reduction were found after short time treatment (15 min). Not only the removal efficiency of all parameters studied was higher after sequential treatment but also the retention time for aerobic treatment was shortened. The incubation time was significantly reduced from 10 days for single biological treatment to 2 days for OMW previously treated by electrocoagulation. This implies that pretreatment by electrocoagulation improves the following aerobic process. The reason for this may be attributed to the fact that electrocoagulation oxidizes the phenolic compounds which are inhibitors of aerobic microorganisms. Indeed, a drastic decrease (from 4500 to 1060 mg/l) of the total phenolics was observed during the electrocoagulation. While, the single electrocoagulation process is not sufficient to remove all the subsisting compounds and the electrocoagulated samples are still toxic towards durum wheat (T. durum) seeds. Therefore, the achieved effluent quality, after the sequential treatment, related to COD and phenolics offers farmers another possibility to spread OMW during the winter months.

#### 3.4. Sludge characteristics

The sludge production is another important parameter in characterizing the electrocoagulation process. Table 2 shows the composition of the sludge. The generated sludge from electrocoagulation was characterized by the high organic matter (68.5%), carbon (34%) and nitrogen contents (0.95%). Moreover, Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> concentrations were also very high. The destabilization and the precipitation of the colloids have led to salts accumulation in the OMW sludge. Also, the high concentration of Al confirms that the aluminum was in the aqueous solution inducing particle destabilization and oxidation. After 15 min electrocoagulation, the Na<sup>+</sup>,  $K^+$  and  $Mg^{2+}$  concentrations were 29.670, 10.830 and 3.267 (g/kg), respectively. Jarboui et al. [30] while studying the performance of OMW evaporation reported that during storage time, Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> concentrations increase. In OMW, the most abundant ion is potassium characterized by its high solubility and hence the possibility of its infiltration through clay-sandy layers [31]. Heavy metal concentrations (0.01788 g/kg for Cu and 0.0983 g/kg for Zn) were extremely low with regard to the standard legal limits (i.e. 1 g/kg for Cu, and 3 g/kg for Zn; Council Directive 86/278/CEE). The pH of sludge was 6.7. According to Lasaridi et al. [32] compost should have a pH value within the range of 6.0-8.5 to ensure compatibility with most plants. Furthermore, the germination index of sludge was very high and reached 153%.

#### 3.5. Germination index

Durum wheat (*T. durum*) is often cultivated in the same Mediterranean environment where olive is widespread. In many olive growing areas the period when OMW is available can overlap with winter cereals sowing times and the amount of OMW to be disposed of can be considerably high. It is therefore useful to use durum wheat (T. durum) seeds for testing the phytotoxicity of treated OMW. Before the treatment process, the GI was zero percent, indicating phytotoxicity of the raw OMW. However, the decrease of phenolics occurred during the electrocoagulation, biological process and sequential treatment contributed to the detoxification of the OMW (Fig. 3.). Ginos et al. [33] who studied the phytotoxic properties of OMW to lettuce seeds reported that phytotoxicity decreased considerably following treatment with lime and cationic polyelectrolytes, and this was attributed to the removal of phenols and other phytotoxic species from the liquid phase. Similar decrease was described to be responsible for toxicity reduction during composting progress [34]. Our results support these previous findings. The GI was 39% after biological treatment, 50% after electrocoagulation and 106% after sequential treatment. Wheareas, for the sludge formed after electrocoagulation, the GI value was very promising about 153%. According to Paredes et al. [35], GI value above 50% indicates that the soil amendment used would not hurt plants while Lasaridi et al. [32] considered that compost experimented with GI value below 80% is phytotoxic. Nevertheless, other researchers characterized a non-phytotoxic and stable substrate with GI in the range of 66-100% [36]. The European Commission decision on the eco-label does not specify any limit value for GI. As a consequence, such sequential treatment would mitigate OMW phytotoxicity, therefore this wastewater can be spread at dates close to winter cereal sowing. Likewise, the sludge formed after electrocoagulation, has a substantial richness of organic matter and absence of phytotoxicity suitable for soil amendment as organic fertilizer.

#### 3.6. Energy consumption and preliminary cost evaluation

Treatment costs for the three technologies studied were evaluated. Investment costs were not taken into account. Only the cost of energy, electrode and nutrient necessary for the treatment was considered. Electrochemical treatment efficiency is usually assessed in terms of specific energy consumption (SEC). This is defined as the amount of energy consumed per unit mass of organic removed. At 250 A/m<sup>2</sup>, the SEC was about 3.35 kWh/kg COD<sub>removed</sub> [Eq. (1)], while COD, phenolics and dark color removals were 60.7%, 76.44% and 92.44%, respectively. Electrochemical pretreatment usually comprises a mild advanced oxidation process aiming at the partial rather than complete mineralization; consequently, specific energy consumption and treatment costs associated with this step are relatively small.

In the case of the aerobic biological treatment, stirring and aeration require the greatest amounts of energy. After 10 days incubation period, the SEC average was 10,070 kWh/kg COD<sub>removed</sub> [Eq. (3)], and led to about 63.5% and 56.44% COD and phenolics removal, respectively.

In the sequential treatment the SEC was about 6517 kWh/kg COD<sub>removed</sub>. The biological treatment was enhanced by electrochemical pretreatment and the incubation period during biological treatment was significantly reduced. It passed from 10 days for biological treatment alone to 2 days for pretreated effluent. Likewise the pretreatment reduced the SEC by about 35% (from 10,070 kWh/kg COD<sub>removed</sub>).

For electrocoagulation, the evaluation of the cost should consider the specific energy consumption, the electrode consumption and the treatment cost of the sludge that is generated. This set of values should be determined experimentally. The generated sludge was characterized by the high organic matter, phosphorus, nitrogen and nutrients. The GI of generated sludge was around 153% indicating that the sludge can be used as organic fertilizer without any treatment. The SEC was 3.35 kWh/kg COD<sub>removed</sub> [Eq. (1)]

#### Table 2

Characteristics of sludge generated from electrocoagulation of OMW (D.M.: dry matter, O.M.: organic matter, C: carbon, T.N.: total nitrogen, GI: germination index; all nutrients are expressed in g/kg).

Parameter	рН	D.M. (%)	O.M. (%)	C (%)	T.N. (%)	Р	К	Na
Sludge	6.7	66	68.5	34	0.9546	4.407	10.830	29.670
Parameter Sludge	Mg 3.267	Ca 2.903	Cu 0.01788		Zn 0.0983	Fe 1.082	Al 16.190	GI (%) 153

and electrode consumption was 0.066 kg Al/kg COD<sub>removed</sub> [Eq. (2)]. The electrocoagulation average operational costs are in the range of  $\in$  0.396/kg COD<sub>removed</sub> [13] (electrical energy price: 0.1007  $\in$ /kWh and electrode materiel price: 0.8843  $\in$ /kg of aluminum).

Specific energy consumptions (SEC) can be expressed as:

$$SEC = \frac{U \times l \times t}{(COD_0 - COD_t) \times V}$$
(1)

where SEC is the specific energy consumption (kWh/kg of  $COD_{removed}$ ); *U* is applied voltage (25 V); *I* is current intensity (0.9 A); *t* is retention time (0.25 h),  $COD_0$  is chemical oxygen demand before treatment (28.5 g/L);  $COD_t$  is chemical oxygen demand after treatment (11.2 g/L); and *V* is the volume of the treated wastewater (0.1 L).

And electrodes consumption was 1.1 g/L (experimental value).

$$C_{\text{electrode}} = \frac{1.1}{(\text{COD}_0 - \text{COD}_t)}$$
(2)

where  $C_{\text{electrode}}$  is the electrodes consumption (kg Al/kg COD<sub>removed</sub>); COD<sub>0</sub> is chemical oxygen demand before treatment (28.5 g/L); and COD<sub>t</sub> is the chemical oxygen demand after treatment (11.2 g/L).

For the aerobic biological process (10 days incubation period), the estimation of the operating cost should include both the energy cost for stirring (kWh/kg  $COD_{removed}$ ) and the cost of the nutrient required to fungal growth (nitrogen and phosphorus). The price of  $(NH_4)_2SO_4$  and  $KH_2PO_4$  was  $\in 25/kg$  and  $\in 30/kg$ , respectively (Morocco market 2010). Consequently, the total cost required for the treatment was  $\in 1017/kg COD_{removed}$  [Eq. (4)], of which 98% is for the energy. For the biological treatment, the cost of nutrients can be ignored compared with the stirring cost. This, therefore, is the key to reducing the cost of the detoxification of OMW.

The specific energy consumptions (SEC) for aerobic treatment can be expressed as:

$$SEC = \frac{(P_{stir} \times t)}{(COD_0 - COD_t) \times V}$$
(3)

where SEC is the specific energy consumption (kWh/kg of  $COD_{removed}$ );  $P_{stir}$  is the required power of the stirrer (38 W); t is retention time (240 h),  $COD_0$  is chemical oxygen demand before treatment (28.5 g/L),  $COD_t$  is chemical oxygen demand after treatment (10.41 g/L); and V is the volume of the treated wastewater (0.05 L).

The stirring cost ( $\epsilon$ /kg COD<sub>removed</sub>) is the product of the SEC (kWh/kgCOD<sub>removed</sub>) and the prices of electricity ( $\epsilon$ /kWh).

The total aerobic operating cost ( $\varepsilon/kg\ \text{COD}_{\text{removed}})$  can be expressed as:

Total aerobic operating 
$$cost = cost(SEC) + cost(Nutrient)$$
 (4)

For the sequential treatment, the cost should consider the specific energy consumption (for electrocoagulation and stirring), the electrode consumption and the cost of the nutrient required to fungal growth. Energy for stirring cost was  $\in$ 651.7/kg COD<sub>removed</sub> + the energy cost for electrocoagation was  $\in$ 0.337/kg COD<sub>removed</sub> + the nutrient cost was  $\in$ 10/kg COD<sub>removed</sub> + the electrode consumption cost was  $\in$ 0.058/kg COD<sub>removed</sub>. The total cost was calculated

between  ${\in}662/kg$  COD\_{removed} and  ${\in}750/kg$  COD\_{removed}; 98.5% of which was consumed by the biological unit.

When the investment costs are compared, it is easy to note that using electrocoagulation as a pre-treatment had a significant impact on the investment cost. The energy consumptions in the biological treatment process held significant portion of operation costs compared to the electrochemical treatment process. The removal efficiency (in terms of average values) recorded during the sequential process was 80.35%; 89.73% and 92.44% COD, phenolics and dark color, respectively (Fig. 3). The goal of this investigation was achieved, the phytotoxicity was completely removed and the GI was 106% after sequential treatment. Therefore, OMW can be spread into agricultural land.

#### 4. Conclusion

Intense research at the international level has shown that physical, chemical and biological processes (either alone or in various combinations) can offer technically sound solutions of OMW treatment. Unfortunately, these high technology treatment options usually entail capital and operating costs which the owners of small-or medium-sized olive mills cannot afford (and consequently refuse) to pick up. Alternatively, OMW reuse for plant irrigation is a relatively inexpensive disposal technique. In this work, the electrocoagulation of OMW coupling with aerobic biological treatment was investigated regarding the effect of this sequential process on OMW characteristics and subsequent phytotoxicity. Pretreatment with electrocoagulation enhanced the subsequent aerobic oxidation process. This sequential treatment scheme was capable of reducing concentration of organics, phenolics and phytotoxicity. These results are encouraging in the context of developing a low-budget technology for the effective management of OMW.

#### Acknowledgment

The authors wish to thank the "Académie Hassan II des Sciences et Techniques".

#### References

- A. Mekki, A. Dhoui, F. Feki, S. Sayadi, Assessment of toxicity of the untreated and treated olive mill wastewaters and soil irrigated by using microbiotests, Ecotoxicol. Environ. Safe. 69 (2008) 488–495.
- [2] C. de-la-Fuente, R. Clemente, I. Martinez-Alcal, G. Tortosa, M.P. Bernal, Impact of fresh and composted solid olive husk and their water-soluble fractions on soil heavy metal fractionation; microbial biomass and plant uptake, J. Hazard. Mater. 186 (2011) 1283–1289.
- [3] G.G. Aggelis, H.N. Gavala, G. Lyberatos, Combined and separate aerobic and anaerobic biotreatment of green olive debittering wastewater, J. Agr. Eng. Res. 80 (2001) 283–292.
- [4] M. Kissi, M. Mountadar, O. Assobhei, E. Gargiulo, G. Palmieri, P. Giardina, Roles of two white-rot basidiomycete fungi in decolourisation and detoxification of olive mill waste water, Appl. Microbiol. Biotechnol. 57 (2001) 221–226.
- [5] F.J. Rivas, F.J. Beltrán, O. Gimeno, Joint treatment of wastewater from table olive processing and urban wastewater. Integrated ozonation—aerobic oxidation, Chem. Eng. Technol. 23 (2000) 177–181.
- [6] F.J. Rivas, F.J. Beltrán, O. Gimero, P. Alvarez, Treatment of brines by combined Fenton's reagent-aerobic biodegradation. II. Process modeling, J. Hazard. Mater. 96 (2003) 277–290.

- [7] F.J. Benitez, J.L. Acero, T. Gonzalez, J. Garcia, Organic matter removal from wastewaters of the black olive industry by chemical and biological procedures, Process Biochem. 37 (2001) 257–265.
- [8] U.T. Un, U. Altay, A.S. Koparal, U.B. Ogutveren, Complete treatment of olive mill wastewaters by electrooxidation, Chem. Eng. J. 139 (2008) 445–452.
- [9] E. Chatzisymeon, A. Dimou, D. Mantzavinos, A. Katsaounis, Electrochemical oxidation of model compounds and olive mill wastewater over DSA electrodes: 1. The case of Ti/IrO<sub>2</sub> anode, J. Hazard. Mater. 167 (2009) 268–274.
- [10] E. Kotta, N. Kalogerakis, D. Mantzavinos, The effect of solids on the electrochemical treatment of olive mill effluents, J. Chem. Technol. Biotechnol. 82 (2007) 504–511.
- [11] M. Gotsi, N. Kalogerakis, E. Psillakis, P. Samaras, D. Mantzavinos, Electrochemical oxidation of olive oil mill wastewaters, Water Res. 39 (2005) 4177–4187.
- [12] E. Chatzisymeon, N.-P. Xekoukoulotakis, E. Diamadopoulos, A. Katsaounis, D. Mantzavinos, Boron-doped diamond anodic treatment of olive mill wastewaters: statistical analysis, kinetic modeling and biodegradability, Water Res. 43 (2009) 3999–4009.
- [13] F. Hanafi, O. Assobhei, M. Mountadar, Detoxification and discoloration of Moroccan olive mill wastewater by electrocoagulation, J. Hazard. Mater. 174 (2010) 807–812.
- [14] S. Khoufi, F. Feki, S. Sayadi, Detoxification of olive mill wastewater by electrocoagulation and sedimentation processes, J. Hazard. Mater. 142 (2007) 58–67.
- [15] M.Y.-A. Mollah, R. Schennach, J.-R. Parga, D.-L. Cocke, Electrocoagulation (EC) science and applications, J. Hazard. Mater. B84 (2001) 29-41.
- [16] A. Kyriacoua, K.E. Lasaridi, M. Kotsoua, C. Balis, G. Pilidis, Combined bioremediation and advanced oxidation of green table olive processing wastewater, Process Biochem. 40 (2005) 1401–1408.
- [17] C.-T. Wang, W.-L. Chou, Y.-M. Kuo, Removal of COD from laundry wastewater by electrocoagulation/electroflotation, J. Hazard. Mater. 164 (2009) 81–86.
- [18] G. Öngen, G. Güngör, B. Kanberoglu, Decolourisation and dephenolisation potential of selected Aspergillus section Nigri strains-Aspergillus tubingensis, in olive mill wastewater, World J. Microbiol. Biotechnol. 23 (2007) 519–524.
- [19] K.P.M. Mosse, A.F. Pattia, E.W. Christend, T.R. Cavagnaroc, Winery wastewater inhibits seed germination and vegetative growth of common crop species, J. Hazard. Mater. 180 (2010) 63–70.
- [20] F. Hanafi, N. Sadif, O. Assobhei, M. Mountadar, Olive oil mill wastewater treatment by means of electrocoaculation with punts aluminium electrodes, J. Water Sci. 22 (2009) 473–485.
- [21] A. Fadil, A. Chahlaoui, A. Ouahbi, A. Zaid, R. Borja, Aerobic biodegradation and detoxification of wastewaters from the olive oil industry, Int. Biodeterior. Biodegrad. 51 (2003) 37–41.

- [22] H. Aissam, F. Errachidi, M.J. Penninckx, M. Merzouki, M. Benlemlih, Production of tannase by Aspergillus niger HA37 growing on tannic acid and olive mill waste water, World J. Microbiol. Biotechnol. 21 (2005) 609–614.
- [23] S. Aiba, A.E. Humphrey, N.F. Millis, Biochemical Engineering, Academic Press, New York, 1973.
- [24] M. Hamdi, A. Khadir, J.L. Garcia, The use of Aspergillus niger for the bioconversion of olive mill waste-waters, Appl. Microbiol. Biotechnol. 34 (1991) 828–831.
- [25] M.S. Fountoulakis, S.N. Dokianakis, M.E. Kornaros, G.G. Aggelis, G. Lyberatos, Removal of phenolics in olive mill wastewaters using the white-rot fungus Pleurotus ostreatus, Water Res. 36 (2002) 4735–4744.
- [26] Y.Z. Qin, Z. Anqi, T. David, H. Yu, C. Zhen-Yu, Stability of green tea catechins, J. Food Chem. 45 (1997) 4624–4628.
- [27] J.A. Field, G. Lettinga, Treatment and detoxification of aqueous spruce bark extracts by Aspergillus niger, Water Sci. Technol. 24 (1991) 127–137.
- [28] C.J. Israilides, A.G. Vlyssides, V.N. Mourafeti, G. Karvouni, Olive oil wastewater treatment with the use of an electrolysis system, Bioresour. Technol. 61 (1997) 163–170.
- [29] V. Kavitha, K. Palanivelu, The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol, Chemosphere 55 (2004) 1235–1243.
- [30] R. Jarboui, F. Sellami, C. Azri, N. Gharsallahb, E. Ammar, Olive mill wastewater evaporation management using PCA method case study of natural degradation in stabilization ponds (Sfax Tunisia), J. Hazard. Mater. 176 (2010) 992–1005.
- [31] R. Jarboui, F. Sellami, A. Kharroubi, N. Gharsallah, E. Ammar, Olive mill waste water stabilization in open air ponds: impact on clay-sandy soil, Bioresour. Technol. 99 (2008) 7699–7708.
- [32] K. Lasaridi, I. Protopapa, M. Kotsou, G. Pilidis, T. Manios, A. Kyriacou, Quality assessment of composts in the Greek market: the need for standards and quality assurance, J. Environ. Manage. 80 (2006) 58–65.
- [33] A. Ginos, T. Manios, D. Mantzavinos, Treatment of olive mill effluents by coagulation-flocculation-hydrogen peroxide oxidation and effect on phytotoxicity, J. Hazard. Mater. 133 (2006) 135–142.
- [34] C. Fausto-Cereti, F. Rossini, F. Federici, D. Quaratino, N. Vassilev, M. Fenice, Reuse of microbially treated olive mill wastewater as fertilizer for wheat (Triticum durum Desf.), Bioresour. Technol. 91 (2004) 135–140.
- [35] C. Paredes, M.P. Bernal, J. Cegarra, A. Roig, Biodegradation of olive mill wastewater sludge by its co-composting with agricultural wastes, Bioresour. Technol. 85 (2002) 1–8.
- [36] S. Hachicha, J. Cegarra, F. Sellami, R. Hachicha, N. Drira, K. Medhioub, E. Ammar, Elimination of polyphenols toxicity from olive mill wastewater sludge by its co-composting with sesame bark, J. Hazard. Mater. 161 (2009) 1131–1139.