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Electrochemical treatment of olive mill wastewater: Treatment extent and effluent phenolic compounds monitoring using some uncommon analytical tools

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Abstract
Problems related with industrials effluents can be divided in two parts: (1) their toxicity associated to their chemical content which should be removed before discharging the wastewater into the receptor media; (2) and the second part is linked to the difficulties of pollution characterisation and monitoring caused by the complexity of these matrixes. This investigation deals with these two aspects, an electrochemical treatment method of an olive mill wastewater (OMW) under platinized expanded titanium electrodes using a modified Grignard reactor for toxicity removal as well as the exploration of the use of some specific analytical tools to monitor effluent phenolic compounds elimination. The results showed that electrochemical oxidation is able to remove/mitigate the OMW pollution. Indeed, 87% of OMW color was removed and all aromatic compounds were disappeared from the solution by anodic oxidation. Moreover, 55% of the chemical oxygen demand (COD) and the total organic carbon (TOC) were reduced. On the other hand, UV-Visible spectrophotometry, Gaz chromatography/mass spectrometry, cyclic voltammetry and ¹³C Nuclear Magnetic Resonance (NMR) showed that the used treatment seems efficaciously to eliminate phenolic compounds from OMW. It was concluded that electrochemical oxidation in a modified Grignard reactor is a promising process for the destruction of all phenolic compounds present in OMW. Among the monitoring analytical tools applied, cyclic voltammetry and ¹³C NMR are among the techniques that are introduced for the first time to control the advancement of the OMW treatment and gave a close insight on polyphenols disappearance.

Key words: olive mill wastewater; electro-oxidation; polyphenols; cyclic voltammetry; GC/MS; ¹³C NMR
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Introduction
Researches dealing with industrial effluents are faced usually to two problems: to find a suitable method for the detoxification of these effluents and to look for the appropriate analytical tools to characterise, quantify accurately the initial pollution load and monitor efficiently its removal. Within this frame, among the industrial effluents that are giving harsh task to environmental researches, olive mill wastewater (OMW), being the most polluting agro-alimentary by-product constitutes a real major environmental threat particularly in Mediterranean countries where nearly 30 million m³ of OMW are generated each year (Casa et al., 2003). The general characteristics of this effluent is its acidic pH, the dark-brown to black colour (Hamdi, 1993), the high load of organic substances including sugars, tannins, phenolic compounds, polyalcohols,pectins and lipids (Vlyssides et al., 1998). Among these organic substances, phenolic fraction characterized by its great variety and complexity is regarded as the most embarrassing part of OMW (Belaid et al., 2002; De Marco et al., 2007). In this way, several studies show that phenolic compounds are the main responsible for the toxicity (Paixão et al., 1999) and the phytotoxicity (Komilis et al., 2005) of OMW rendering its bio-treatment a challenging task. This fact is probably one of the reasons letting most of the generated OMW is being directly discharged into the environment without any treatment rather than just stoked in open artificial ponds for natural evaporation (Kapellakis et al., 2006). Along with this evaporation treatment-technique, different attempts to decontaminate OMW including biological (Ergüder et al., 2000; Assas et al., 2002; Fadil et al., 2003; Tziotzi

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et al., 2007; Gonçalves et al., 2009), physical (Hamdi, 1993), chemical (Chakchouk et al., 1994; Lin and Wu, 1996; Beltrán et al., 1999) and physico-chemical (Ginos et al., 2006) processes have been explored. Unfortunately, none of these processes is currently applied in the actual field due either to the recalcitrance and toxicity of the organic load content in OMW, cost effectiveness or the drawback of the technique such as the production of a solid waste that needs to be handled, transported and safely disposed. To overcome these difficulties, most of emerging treatment technologies are focusing on the in situ generation of a powerful chemical oxidant, the hydroxyl radical, known by its ability to destroy and detoxify a wide range of organic pollutants (Zhang et al., 2006; Kallel et al., 2009). Among these emerging technologies, electrochemical processes based on electro-oxidation or electro-Fenton phenomenon are nowadays considered the most promising methods for the treatment of various kinds of wastewaters (tannery, textile, diary, landfill leachate and other industrial wastewater) (Chen, 2004; Rajkumar et al., 2004). Moreover, due to the growing development of more efficient electrodes, electrochemical oxidation is being able to destroy several organic pollutants practically recalcitrant compounds such as polyphenols and fatty acids. For instance, some researchers (Israelides et al., 1997; Gotsi et al., 2005; Panizza et al., 2006) have studied electrochemical oxidation of OMW using several types of electrodes with the addition of sodium chloride up to 4% and claimed complete degradation of polyphenols and total discoloration of OMW. Gotsi et al. (2005) reported that although a high discoloration and polyphenols reduction rates were achieved, the toxicity of OMW was increased during its electrochemical treatment and was related to the generation of organochlorine by-products. Belaid et al. (2006) have investigated electrochemical treatment of a diluted and a raw OMW in batch scale without addition of sodium chloride and reported important discoloration level, elevated polyphenols removal efficiency and no toxic by-products were generated. Nonetheless, an important quantity of “foam” was formed and somehow has to be dealt with. Regarding the other side of the problem, OMW pollution was usually controlled by some common and broad analytic tools such COD-meter, BOD-meter, TOC-analysers and UV-Visible spectrophotometry (Khoufi et al., 2007; Lucas et al., 2009). For example, the phenolic fraction was frequently monitored by Folin test or UV absorbance (Panizza et al., 2006; Gonçalves et al., 2009) which are not really specific to phenols besides that they are time consuming, needing several preparations and requires high dilution to respect Beer-Lambert law. In fact, the Folin method uses one standard of phenol (catechol or other) to quantify a wide range of phenolic compounds. Identification of phenolic compounds can be also done using chromatographic methods even though is it usually restricted to some compounds due to the preselection of phenolic standards which are not easily always found at hand (De Marco et al., 2007; Iamarino et al., 2009). Moreover, it is worth noting that although gas chromatography coupled to mass spectrometry presents the advantage of being able to identify unknown chemical compounds. It can be said that it is just restricted to low molecular weight and volatile compounds such as phenolic monomers in this case (Belaid et al., 2006; Knupp et al., 1996). Compounds with a relatively high molecular weight as phenolic polymers are excluded from this measurement and identification.

Keeping this in mind, this investigation focuses, thus, on the electrochemical treatment of a raw OMW using a modified Grignard reactor as well as on the monitoring of the phenolic fraction removal by using uncommon analytical tools. To do so, the ex-batch operating mode was shifted to a dynamic scale to overcome foam nuisance. Pollution abatement was monitored using the classic analytic methods such as, UV-Visible spectrophotometry and Gas chromatography/mass spectrophotometry (GC/MS). In addition, new tools, the cyclic voltammetry and C$^{13}$ NMR covering the whole ranges of phenols (monomers and polymers) were newly applied in this area to assess the behaviour and the elimination of these toxic.

1 Materials and methods

1.1 Origin of the olive mill wastewater

Olive mill wastewater was obtained from a three phase decanter manufacturer from Sfax prefecture, Tunisia. Samplers were transported to the laboratory and kept in a dark place at temperature of about 4°C to avoid further degradation.

1.2 Electrochemical treatment methodology

Electrochemical experiments were conducted in a cylindrical reactor operated in a flow mode (Fig. 1). The reactor cell consisted of two cylindrical electrodes separated by a cationic exchange membrane type IONAC MC 3470. To minimize the ohmic potential drop, the distance between the electrodes was kept below 5 mm. To have a large active surface, the electrodes were laboratory made of

![DC power source](https://www.jesc.ac.cn/)

**Fig. 1** Electrochemical reactor.
expanded platinized titanium N type (0.85 g of Pt(dm)). A direct current variable from 0 to 10 A was supplied from a current generator, type CLES 35-10 (Convergie). The 500 mL of fresh OMW were circulated through the anode compartment using a small pump with a flow rate of 2 mL/min. The cathode compartment was filled with 200 mL of 0.5 mol/L H₂SO₄ solution to ensure good electrical conductivity. All experiments were performed at room temperature (25–28°C) without addition of any external electrolyte.

1.3 Analytical techniques

The general characteristics of OMW such as COD, TOC, pH, electric conductivity, suspended matter, organic and minerals matter were carried out according to the Standard Methods for Examination of Wastewater (JIS, 1998). Total phenols content was estimated based on Folin-Ciocalteau method (Box, 1983). Color fading was monitored via measuring the absorbance at 395 nm as described by Flouri et al. (1996) and Sayadi et al. (1996) and discoloration rates (R) were determined by Eq. (1)

\[ R = \frac{A_{395t} - A_{3950}}{A_{3950}} \times 100 \]  \hspace{1cm} (1)

where, \( A_{395t} \) is absorbance at 395 nm of the raw OMW \((t = 0)\) and \( A_{395t} \) absorbance at 395 nm of treated OMW for a time \( t \).

Phenolic compounds removal was assessed using GC/MS as well as by cyclic voltammetry and nuclear magnetic resonance (NMR) spectroscopy.

1.3.1 GC/MS analysis

Phenolic monomers content and their decay were monitored by GC/MS as follows: 40 mL of OMW was acidified to pH 2 by addition of concentrated HCl. Phenolic monomers were then extracted with ethyl acetate. The organic phase was concentrated to about 1 mL via evaporation at 40°C and then silylated by the addition of N,O-bis(trimethylsilyl) trifluoracetamide (BSTFA). The resulting trimethylsilyl derivatives were analysed by GC/MS as described by Belaid et al. (2002). GC/MS measurements were carried out with Hewlett-Packard 6890 Series GC, Agilent Technology over a HP-5MS fused silica capillary column. Detection was conducted by a mass selective detector with electron impact ionization at 70 eV and 2.9 sec scan time. Obtained mass spectra were compared to the reference compounds stored in Wiley 275L mass spectral library. OMW extract was analyzed first with a full scan mode in order to perceive all compounds presents in the extracted sample, and then the detector was operated in selective ion monitoring (SIM) mode for the identification of the phenolic monomers.

1.3.2 Cyclic voltammetry

Voltammetric measurements were performed in a classic three-electrode cell using a EG&G potentiostat/galvanostat model 273 controlled by Research Electrochemistry software 4.30 for phenols removal monitoring. The working electrode was made of Si/Boron-Doped Diamond (BDD) (area 0.1 cm²) and the counter-electrode was a platinum disc device. The type of electrode used was also reported to be very efficient in terms of electroanalysis which will enhance the sensitivity of the technique (Einaga et al., 2004). Potentials are referenced to a saturated calomel electrode (SCE). All voltammetric measurements were carried out at room temperature (25–28°C) on degassed OMW samples after acidification with 1 mol/L H₂SO₄ solution (Belaid et al., 2006).

1.3.3 Nuclear magnetic resonance spectroscopy

Solid state ¹³C NMR spectra of a dried raw and treated OMW extract as conducted for GC/MS measurements were acquired at 75.47 MHz on a BRUKER WB-300 spectrometer. Magic Angle Spinning sequence was applied at 8000 Hz spinning rate, the pulse repetition rate was set to 5 sec and the scan number was fixed at 1096 scans. The chemical shift scale of the NMR spectra given in parts per million (ppm) was referred to Tetramethylsilane (TMS).

2 Results and discussion

2.1 General characteristics of OMW

Olive mill effluents can be easily identified by their dark brown colour and specifically their unpleasant odour. The analyses performed on this effluent (Table 1) demonstrate that it is principally characterised by a slightly acidic (pH around 5.2), an electrical conductivity of around 15.1 mS/cm and a high pollution load composed of organic matter (22 g/L) and mineral matter (12 g/L). The COD and TOC values far exceed the authorised standards limits and were 65 and 25 g/L respectively. Assay of polyphenols (polymers and monomers) using the Folin-Ciocalteau method leads to an estimated value of around 5.6 g/L thought to be the origin of OMW toxicity and therefore should be removed.

2.2 Evolution of OMW characteristics during electrochemical treatment

Electrochemical experiments were performed at room conditions on a raw OMW. During the treatment, the

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.27</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>15.1</td>
</tr>
<tr>
<td>Suspension solids (g/L)</td>
<td>11.9</td>
</tr>
<tr>
<td>Minerals matter (g/L)</td>
<td>12.2</td>
</tr>
<tr>
<td>Organic matter (g/L)</td>
<td>22.2</td>
</tr>
<tr>
<td>Fatty matter (g/L)</td>
<td>0.11</td>
</tr>
<tr>
<td>COD (g/L)</td>
<td>65</td>
</tr>
<tr>
<td>TOC (g/L)</td>
<td>25</td>
</tr>
<tr>
<td>Polyphenols (g/L)</td>
<td>5.6</td>
</tr>
</tbody>
</table>
temperature of OMW was found increasing from the ambient one (25–27°C) to a max of 45°C after 2 hr to finally stabilize at this level. In the same time, we noticed an increase in the solution conductivity from 15 to 22 mS/cm due to H\(^+\) ions generation in the anodic compartment causing thus a minimisation of energy loss. Indeed, the ohmic potential drop decreased only from 8 V to 3.5–4.0 V and no significant influence on treatment yield was observed. On the other hand, it is assumed that the continuous circulation of OMW in the electrochemical reactor (Fig. 1) will help keeping the temperature of the solution moderate during the treatment.

2.2.1 Discoloration of OMW during electrolysis

During electrolysis, the visual observation shows that the blackish-brown color of the OMW was turning to yellowish, and then gradually disappears to obtain finally an almost colourless solution (Fig. 2).

Moreover, the spectrum of the raw OMW presented in Fig. 3 shows high absorbance at around 225 and 280 nm corresponding to conjugated aromatic compounds and ascribed to the so-called E and B bands in the benzene ring, respectively. However, the UV-Visible spectrum of the treated OMW at a current density of 3.5 A/dm\(^2\) demonstrates a progressive reduction of the absorbance at the above mentioned wavelengths. The spectrum of treated OMW for 10 hr (Fig. 3) indicates an almost total disappearance of the aromatic compounds and discoloration was achieved via electrophilic cleavage of the chromophoric group.

Figure 4 illustrates the evolution of OMW discoloration rate versus electrolysis time at different current densities. It can be noticed that in all runs, color removal was increasing leading to a nearly colourless effluent at the end of treatment with a discoloration rate of 90% under a current density of 3.5 A/dm\(^2\).

2.3 Monitoring of OMW pollution during electrolysis via COD and TOC

The COD and TOC are two common parameters that can be used to see the effect of electrolysis on the clean-up of OMW and to monitor the organic charge in wastewater. Compared to color removal (Fig. 5a), COD reduction seems advancing slower and attained a max of 55% after 10 hr of electrolysis under a current density of 3.5 A/dm\(^2\) (Fig. 5a) suggesting that the ability of electrochemical treatment in term of discoloration is higher than that of the oxidation of the organic matter.

As to TOC evolution presented in Fig. 5b, it shows almost a similar trend to that of COD (Fig. 5a). The TOC reduction rates are proportional to the treatment time and the applied current density with a maximum value being around 50% recorded after 10 hr of OMW electrolysis under 3.5 A/dm\(^2\) current density. It is worth noting that Rajkumar and Palanivelu (2004) reported that the oxidation of certain phenolic compounds occurs in two stages; the first one is rapid and leads to the formation of some stable intermediates in addition to water and carbon dioxide. However, the second stage representing the further oxidation of these intermediates is very slow and needs longer time and more severe conditions to reach a total mineralisation. Anyhow, the most important is that mother toxic phenolic compounds were destroyed.

Also the combination of the COD and TOC results enables us to determine the average oxidation state of carbon (AOSC) according to the following Eq. (2) (Stumm et al., 1981; Mantzavinos et al., 2000): 

\[
\text{AOSC} = 4 - \left(\frac{1.5 \text{ COD}}{\text{TOC}}\right)
\]

Given that methane corresponds to the least oxidised state of carbon, the AOSC value is equal to (–4), whereas the highest degree of oxidation of carbon (AOSC = +4) corresponds to carbon dioxide. Variations in AOSC versus time at different current densities are illustrated in Fig. 6. These graphs demonstrate that the AOSC values was increasing in proportion with the applied current density and
2.4 Monitoring of phenolic compounds oxidation during electrolysis

Since the blackish brown colour of the OMW reflects its polyphenols content (Saez et al., 1992), the change in colour along the treatment means that these compounds were among the targets of the electrochemical oxidation. To confirm this assumption and demonstrate the performance of the electrochemical treatment in terms of phenolic compounds removal, we monitored the evolution of these compounds using different analytical tools.

2.4.1 GC/MS determination and identification of phenolic monomers

Analysis of raw OMW-extract by GC/MS in full SCAN mode (Fig. 7) led to identify carboxylic acids, fatty acids and 18 phenolic monomers among them neutral phenolic compounds and phenolic acids (Table 2).

The identification of the phenolic compounds present in OMW was based on mass spectra of references stored in the instrument data base (Wiley 275). However, to confirm this data-based identification, further efforts were done taking into consideration of the obtained fragments and the following information: (1) the mass spectrum of a phenolic compound is usually characterised by the presence of the molecular ion [M]⁺. This is because the presence of an aromatic core in the structure of the molecule gives greater stability to the molecular ion, even after ionisation by electron impact (De Hoffmann et al., 2005); (2) the [(CH₃)₃Si]⁺ ion with an m/z = 73 is always present in the mass spectrum meaning that silylation reaction was complete; (3) if the molecule contains more than (CH₃)₃SiO- group, the [(CH₃)₂Si-O-Si(CH₃)₂]⁺ ion with an m/z = 147 is systematically observed in the mass spectrum; (4) the [M-(OSiMe₃)]⁺ ion is generally present in the mass spectra of phenolic acids (Plessi et
al., 2006); compounds with an ethanol group, such as tyrosol, hydroxytyrosol, homovanillyl alcohol, vanilethane diol and 3,4-dihydroxyphenylglycol, can undergo alpha cleavage (Knupp et al., 1996). This result is due to the formation of a characteristic ion derived from cyclic tropylium corresponding to the [M-(OSiMe₃)]⁺ fragment.

In addition, the measurement of the same sample (raw OMW-extract) under the same conditions using the SIM mode in which only the molecular ions of the phenolic compounds are taken into account was conducted. The result presented in Fig. 8 shows a better resolution of the chromatogram. The different peaks related to the identified phenols are illustrated therein and their names are listed in Table 2.

On the other hand, extracts of the electrolysed OMW for 2, 4, 6, 8 and 10 hr at a current density of 3.5 A/dm² were also analysed by GC/MS under the same operating conditions described above. Careful examination of the obtained chromatograms (data not shown but partially presented in Table 3) reveals the gradual disappearance of all phenolic monomers peaks identified in the raw OMW. It is important to note the absence of chlorinated derivatives-

Fig. 7 GC/MS chromatogram of raw OMW full scan mode.

Fig. 8 GC/MS chromatogram of raw OMW in SIM mode. (1)-(18) phenolic compounds and their names are listed in Table 2.
### Table 2 Molecular weight and characteristic of identified phenolic compounds in raw OMW

<table>
<thead>
<tr>
<th>Identified phenolic compounds</th>
<th>RT (min)</th>
<th>MW (M⁺)</th>
<th>Main fragments M⁺ of the TMS derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 1,2-Dihydroxybenzene (Catechol)</td>
<td>15.35</td>
<td>254</td>
<td>239, 166, 151, 136, 73 (100%)</td>
</tr>
<tr>
<td>(2) 1,3-Dihydroxybenzene (Resorcinol)</td>
<td>17.53</td>
<td>254</td>
<td>239 (100%), 217, 147, 133, 117, 101, 73</td>
</tr>
<tr>
<td>(3) 1,4-Dihydroxy-2,5-dimethylbenzene</td>
<td>19.19</td>
<td>282 (100%)</td>
<td>267, 193, 179, 147, 91, 73</td>
</tr>
<tr>
<td>(4) 1,2-Dihydroxypropenylbenzene</td>
<td>21.03</td>
<td>294 (100%)</td>
<td>279, 205, 147, 73</td>
</tr>
<tr>
<td>(5) 3-Hydroxybenzoic acid</td>
<td>21.68</td>
<td>282</td>
<td>267 (100%), 223, 207, 193, 73</td>
</tr>
<tr>
<td>(6) 4-Hydroxyphenylethanol (Tyrosol)</td>
<td>21.82</td>
<td>282</td>
<td>267 (100%), 223, 193, 179, 73</td>
</tr>
<tr>
<td>(7) 4-Hydroxybenzoic acid</td>
<td>23.23</td>
<td>282</td>
<td>267 (100%), 223, 193, 179, 147, 126, 117, 85, 73</td>
</tr>
<tr>
<td>(8) 4-Hydroxyphenylacetic acid (PHPA)</td>
<td>23.52</td>
<td>296</td>
<td>281, 252, 217, 192, 179, 164, 147, 133, 73 (100%)</td>
</tr>
<tr>
<td>(9) 4-Hydroxy-3-methoxyphenethyl alcohol (Homovanillyl alcohol)</td>
<td>25.05</td>
<td>312</td>
<td>297, 282, 229 (100%), 179, 73</td>
</tr>
<tr>
<td>(10) 4-Hydroxyphenylpropionic acid</td>
<td>26.13</td>
<td>310</td>
<td>295, 192, 179 (100%), 73</td>
</tr>
<tr>
<td>(11) 4-Hydroxy-3-methoxybenzoic acid</td>
<td>26.33</td>
<td>312</td>
<td>297 (100%), 282, 253, 223, 193, 126, 73</td>
</tr>
<tr>
<td>(12) 3,4-Dihydroxyphenyl alcohol (Hydroxytyrosol)</td>
<td>26.41</td>
<td>370</td>
<td>355, 323, 281, 267 (100%), 193, 179, 147, 103, 73</td>
</tr>
<tr>
<td>(13) 4-Hydroxyphenylacetic acid (Para coumaric acid)</td>
<td>26.74</td>
<td>308</td>
<td>355, 311, 281, 267, 256, 223, 193, 166, 138, 73</td>
</tr>
<tr>
<td>(14) 4-Hydroxy-3-methoxyphenylethylene glycol (Vanilic acid)</td>
<td>27.69</td>
<td>400</td>
<td>297 (100%), 147, 73 (100%)</td>
</tr>
<tr>
<td>(15) 2,5-Dihydroxybenzeneacetic acid (Homogentisic acid)</td>
<td>28.43</td>
<td>384 (100%)</td>
<td>369, 341, 267, 252, 237, 147, 73</td>
</tr>
<tr>
<td>(16) 3,4-Dihydroxyphenylglycol (Vanilic acid)</td>
<td>29.84</td>
<td>458</td>
<td>443, 355 (100%), 281, 147, 73</td>
</tr>
<tr>
<td>(17) 3,4-Dihydroxyphenylpropionic acid</td>
<td>30.04</td>
<td>398 (100%)</td>
<td>383, 309, 280, 267, 179, 73</td>
</tr>
<tr>
<td>(18) 3,4-Dihydroxyphenylpropionic acid</td>
<td>30.04</td>
<td>398 (100%)</td>
<td>383, 309, 280, 267, 179, 73</td>
</tr>
</tbody>
</table>

RT: retention time; MW (M⁺): molecular weight; 100%: major fragment.

### Table 3 Phenolic compounds removal during electrochemical treatment of OMW (current density: J = 3.5 A/dm²)

<table>
<thead>
<tr>
<th>Pᵢ (t) (phenolic compound)</th>
<th>Duration of the treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>(1) Catechol</td>
<td>4.627</td>
</tr>
<tr>
<td>(2) Resorcinol</td>
<td>0.85</td>
</tr>
<tr>
<td>(3) 1,4-Dihydroxy-2,5-dimethylbenzene</td>
<td>0.264</td>
</tr>
<tr>
<td>(4) 1,2-Dihydroxypropenylbenzene</td>
<td>0.316</td>
</tr>
<tr>
<td>(5) 3-Hydroxybenzoic acid</td>
<td>0.003</td>
</tr>
<tr>
<td>(6) Tyrosol</td>
<td>87.234</td>
</tr>
<tr>
<td>(7) 4-Hydroxybenzoic acid</td>
<td>0.660</td>
</tr>
<tr>
<td>(8) 4-Hydroxyphenylacetic acid</td>
<td>0.231</td>
</tr>
<tr>
<td>(9) Homovanillic alcohol</td>
<td>1.853</td>
</tr>
<tr>
<td>(10) 4-Hydroxyphenylpropionic acid</td>
<td>0.267</td>
</tr>
<tr>
<td>(11) Vanilic acid</td>
<td>0.105</td>
</tr>
<tr>
<td>(12) Hydroxytyrosol</td>
<td>2.629</td>
</tr>
<tr>
<td>(13) Para coumaric acid</td>
<td>0.046</td>
</tr>
<tr>
<td>(14) Protocatechuic acid</td>
<td>0.175</td>
</tr>
<tr>
<td>(15) Vanilene diol</td>
<td>0.026</td>
</tr>
<tr>
<td>(16) Homogentisic acid</td>
<td>0.125</td>
</tr>
<tr>
<td>(17) 3,4-Dihydroxyphenylglycol</td>
<td>0.506</td>
</tr>
<tr>
<td>(18) 3,4-Dihydroxyphenylpropionic acid</td>
<td>0.229</td>
</tr>
</tbody>
</table>

Percentage of total phenolic monomers (%) 100 5.075 0.232 0.009 0 0

-: not detected.

Toxic compounds—ally in the treated OMW considered as toxic compounds. In order to determine the extent of phenolic monomers destruction, we set the following arbitrary ratio Eq. (3):

$$Pᵢ (t) = \frac{Sᵢ (t)}{\sum Sᵢ (0)} \times 100$$  \hspace{1cm} (3)

where, $$Pᵢ (t)$$ is fraction of a remaining phenolic monomer (i) in the OMW after a treatment period (t), $$Sᵢ (t)$$ is the peak surface area of a phenolic monomer (i) after a treatment period (t), $$\sum Sᵢ (0)$$ is the sum of the surface areas of all detected phenolic monomers peaks issued from the raw OMW ($$t = 0$$ min).

Table 3 shows the variations of these percentages along the treatment. Although the number of the identified phenolic compounds was high (18 compounds), tyrosol with a fraction of 87.23%, catechol (4.62%), hydroxytyrosol (2.63%) and homovanillic alcohol (1.85%) were the main components in the raw OMW. After 2 hr of treatment, more than 95% of the total detected phenolic monomers were eliminated. However, a slight increase was observed in the amount of certain compounds, such as resorcinol and 4-
hydroxyphenylacetic acid. This increase might be due to a plausible formation of intermediate compounds caused by the electrooxidation of the high molecular weight polyphenols. Nonetheless after 6 hr of treatment, almost all phenolic monomers even the formed intermediates were removed. Note that, phenolic compounds with a relatively high molecular weight were excluded from this analysis and identification. Therefore, additional measurement using cyclic voltammetry and nuclear magnetic resonance was addressed to see the extent of the electrochemical treatment on these compounds.

2.4.2 Monitoring of total polyphenols using cyclic voltammetry method

As mentioned in the introduction, although UV-Visible spectrophotometry can be used to monitor phenolic compounds present in OMW, its application requires high dilution of the effluent sample. Also, its sensitivity is greatly affected by the accidental presence of matter mainly the suspended particles. To avoid such handicaps and cover the whole phenolic compounds range, we have applied for the first time an easy technique; the cyclic voltammetry on a boron-doped diamond electrode. Hence voltammetric measurements performed on a raw sample of oil mill effluent reveal a large serrated anodic peak between 0.7 and 1.7 V/ECS corresponding to the oxidation of all phenolic compounds types (Fig. 9). Spectrum of the electrolysed OMW demonstrates weakening of the anodic peak as a function of treatment time. For instance, it can be said that after 2 hr of treatment, the disappearance of most phenolic compounds was achieved corroborating with GC/MS results. Figure 10 shows also a slight shift of the anodic peak towards lower potentials probably due to the formation of certain intermediate phenolic compounds that were oxidised at lower potentials. After 4 hr, only tiny traces of phenolic compounds were detected. The voltammogram of OMW treated for 10 hr demonstrates disappearance of all the phenolic fractions initially existing in the effluent.

2.4.3 $^{13}$C NMR monitoring of total polyphenols (monomers and polymers)

The $^{13}$C NMR spectrum of the raw OMW (Fig. 10a) reveals the presence of a broad variety of carbons covering the range of chemical displacement from 0 to 180 ppm. Absorption of these signals was done based on bibliographic data (Zinn et al., 2002; Marche et al., 2003; Marshall et al., 2005; El Hajjouji et al., 2008). Thus, the spectrum shows the presence of aliphatic carbon located in the region of 20 to 50 ppm as well as deshielded aliphatic carbon in the range of 50 to 110 ppm probably corresponding to the alkoxy groups and carbohydrate derivatives. Carbons located between 110 and 160 ppm correspond to aromatic compounds (substituted aromatics and phenol derivatives), whereas those appearing in the last range (160 and 180 ppm) stand for the highly deshielded carbons (carboxyl and/or carboxyl carbon). On the other hand, the obtained $^{13}$C NMR spectra of the treated OMW (Fig. 10b–f) demonstrate a remarkable modification in the composition of the organic matter as a function of electrolysis time in particular the gradual disappearance of the aromatic carbons signals.

To give a full insight on these spectra, we calculated the degree of aromaticity Eq. (4), the degree aliphaticity Eq. (5) and the degree of carboxylicity Eq. (6) in raw and treated OMW defined as followings and according to previous publications (Zinn et al., 2002; Marche et al., 2003, 2005).

Degree of aromaticity:

$$f_A = \frac{C_{Ar}}{(C_{Ar} + C_{Al})} \times 100\% \quad (4)$$

Degree of aliphaticity:

$$f_{Al} = \frac{C_{Al}}{(C_{Ar} + C_{Al})} \times 100\% \quad (5)$$

Degree of carboxylicity:

$$f_{Cb} = \frac{C_{Cb}}{(C_{Ar} + C_{Al})} \times 100\% \quad (6)$$

where, $f_A$ is degree of aromaticity, $f_{Al}$ is degree of aliphaticity, $f_{Cb}$ is degree of carboxylicity, $C_{Ar}$ is aliphatic carbon situated in the range of 0 to 110 ppm, $C_{Ar}$ is aromatic carbon situated in the range of 110–160 ppm, $C_{Cb}$ is carboxylic carbon situated in the range of 160–180 ppm.

Results of this analysis presented in Table 4 demonstrate that the degree of aromaticity in the raw OMW was falling quickly over time to reach 0.91% after 6 hr of treatment. Beyond this time, the aromaticity becomes nil and all detected carbons are in the aliphatic form ($f_{Al} = 100\%$). This result corroborates with our earlier assumption of benzene ring cleavage and is entirely consistent with that obtained cyclic voltammetry, in which the elimination of all phenol compounds after 6 hr of electrolysis was observed. In addition, $^{13}$C NMR demonstrates high carboxylic carbon...
content in the raw OMW extract of around 37%. It should be remembered that at this stage the carboxylic carbon is found in aliphatic form as well as in aromatic form as detected by GC/MS and which revealed the presence of a broad variety of phenolic acids in the raw OMW extract (Table 2). The carboxylic percentage increases as a function of treatment time due to the oxidation process of the organic matter.

2.5 Energy utilisation

The variation of COD as a function of electrolysis time permits monitoring the evolution of the effective current (EC) during treatment Eq. (7) (Azzam et al., 2000; Cañizares et al., 2005).

\[
EC = \frac{(\text{COD}_0 - \text{COD}_t)}{8I\Delta t} \times F \times V \times 100 \quad (7)
\]

where, \(\text{COD}_0\) (g O\(_2\)/L) and \(\text{COD}_t\) (g O\(_2\)/L) are chemical oxygen demand at time \(t = 0\) and time \(t\), respectively, \(V\) (L) is electrolyte volume, \(F\) (96487 C/mol) is Faraday’s constant, \(I\) (A) is current intensity, \(\Delta t\) (sec) is electrolysis time.

Application of this formula enabled monitoring the current efficiency during OMW electrolysis. Figure 11 demonstrates that the anodic current mainly served to oxidise the organic matter during the first 4 hr of treatment.
The maximum values recorded are in the region of 95%, 89% and 81%, respectively, at current densities of 2.5, 3 and 3.5 A/dm² respectively. Although there was no addition of external electrolyte, this high current efficient use might be due to the large electrode surface area thanks to the expanded platinitised titanium used. Beyond this period, a gradual reduction in the current efficiency was observed. This was expected because it is known that the electrochemical treatment leads to small organic molecular fragments, such as acetic acids, epoxides, aldehydes, ketones, etc. leading to a residual COD and that are relatively stable and needs stronger electrochemical conditions to be incinerated. So some current loss under joule effect was noticed.

3 Conclusions

It was demonstrated that electrochemical treatment of a raw OMW in a Grignard reactor equipped with two cylindrical expanded electrodes and separated by a cationic exchange membrane under dynamic scale was conclusive.

(1) The process able to completely remove all variety of phenolic compounds present in the OMW and which are responsible for the toxicity of such kind of wastewater. (2) Although 90% of OMW color was removed, under the used electrochemical conditions, COD and TOC reductions were nearly 55%. (3) Electrochemical treatment of OMW does not produce toxic chlorinated derivatives when electrolysis is conducted without addition of sodium chloride. (4) Monitoring of AOSC demonstrates that average oxidation of carbon stabilises after 4 hr of treatment confirming the formation of stable intermediates. (5) Effective current utilisation reached 95% in the first treatment hours to stabilize later at 60% when most of initial color and phenolic compounds were removed. (6) No foam was observed as noticed in our former study and this was related to the dynamic mode adopted. (7) Most of analytical methods used such UV-Visible, cyclic voltammetry, GC/MS and ¹³C NMR to monitor phenolic compounds load disappearance confirm their total removal and the cleavage of the benzene ring.

References


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