Electrochemical treatment of olive mill wastewaters: Removal of phenolic compounds and decolourization

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Abstract

Olive mill wastewaters (OMW) characterized by their dark brown colour and their very high content of phenolic compounds constitute an environmental concern, particularly in Mediterranean countries where the production of olive oil is important. In this investigation, OMW were electrolyzed at platinized expanded titanium electrodes in a modified Grignard reactor divided into two cylindrical compartments separated by a cation-exchange membrane. Results show better than 90% decolourization and nearly 85% removal of phenols, as established by gas chromatography/mass spectrometry, at high current intensity. This process can easily be monitored by cyclic voltammetry at a boron-doped diamond electrode. A significant reduction of chemical oxygen demand and total organic carbon was observed. The electrodes are not passivated and the ohmic potential drop is very low. Electrochemical oxidation in a modified Grignard reactor is a promising process for the destruction of phenolic compounds present in OMW.

1. Introduction

Olive oil extraction is a vital industrial activity in the Mediterranean region where cultivation of olive trees is widespread [1]. This activity plays a crucial role in the economy of several "olive-countries", but generates a considerable amount of undesirable aqueous liquid waste called "olive mill wastewaters" (OMW), causing environmental damage.

OMW are usually acidic and vary in colour from dark-red to black, depending on their state of degradation and the prevailing climate [2]. They contain a high concentration of phenolic compounds, up to several grams per litre, which are considered to be harmful to micro-organisms [3, 4]. Attempts to treat OMW have so far involved physical, chemical and physicochemical processes. Physical treatment via heating the acidified OMW in order to precipitate polyphenols did not lead to convincing results [2]. Wet air oxidation catalysed by hydrogen peroxide [5, 6] or by ozone oxidation coupled with H_2O_2 or UV [7–10] has high operating costs and is a sophisticated technology requiring qualified operators. Moreover, these processes are still in their infancy and require further development. Physicochemical methods, such as coagulation and flocculation based on the addition of chemical reagents (Fe₂SO₄, Al₂SO₄,...) able to convert the soluble pollutants and the colloidal particles into a solid waste, may in turn create handling and disposal problems.

Recently, attention has turned to the electrochemical treatment of wastewaters, in which recalcitrant compounds are destroyed by direct or indirect anodic oxidation based on the generation of hydroxyl radicals, ozone, etc. [11, 12]. Different new anode materials have been tested and more compact reactors are being developed. Gotsi et al. [13] have described the electrochemical oxidation over a Ti-Ta-Pt-Ir anode of OMW diluted 5-20 times, with the addition of sodium chloride. They claim complete degradation of phenols and total decolourization after only 60 min of treatment. Chemical oxygen demand (COD) reduction, however, was relatively low and did not exceed 40%. They also reported that the toxicity of the treated OMW was increased; this was related to the generation of organochlorine by-products. Panizza and Cerisola [14] investigated the electrochemical oxidation of OMW in a one-compartment flow cell over a Ti/TiRuO₂ anode in the presence of NaCl. They reported 80% COD reduction and almost total removal of colour and aromatic compounds.

In the present work OMW were treated electrochemically in a modified Grignard reactor described

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elsewhere [15] but under different operating conditions. The Grignard reactor has been efficiently used on a large scale (1200 l) for the oxidation of galacturonic acid to insoluble galactaric acid [16]. The ohmic potential drop was minimized by the use of expanded metal electrodes close to a separating cation-exchange membrane. It was expected that the membrane would maintain moderate acidic conditions, avoiding tar deposition at the anode.

2. Materials and methods

2.1. Electrochemical cell

Electrochemical experiments were carried out in a modified Grignard reactor shown in Figure 1. It consists of two compartments separated by a cation-exchange membrane, type IONAC MC 3470. The electrochemical cell is cylindrical with concentric electrodes placed around the axis of the stirrer. To minimize the ohmic potential drop, the distance between the electrodes was kept below 5 mm [17] and, to ensure a high degree of phenol removal, the electrodes were made of platinized expanded N type titanium (0.85 g of Pt dm^{-2}). The active surface of the anode was about 2.8 dm². A direct current supplier, type CLES 35-10 (Convergie), variable from 0 to 10 A, was used. The anode compartment was filled with 300 ml of fresh OMW which was mechanically stirred throughout electrolysis. The cathode compartment was filled with 200 ml of 1 M NaOH solution to ensure good electrical conductivity. In order to minimize the energy consumption no attempt was made to thermoregulate the reactor. All experiments were performed at room temperature (25-28 °C) without addition of external electrolyte. Table 1 summarizes the experimental conditions and the main parameters monitored.



Fig. 1. Schematic diagram of the electrochemical reactor.

Table 1.	Parameters	monitored	during	the	electrolysis	of	OMW	V
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Parameter	OMW dilution	Current/A		
		7.0	8.4	9.8
Decolouration (measured at 395 nm)	50	+	+	+
	10	+	+	+
	1	+	+	+
Phenolic compounds removal efficiency	50	+	+	+
	10	+	+	+
	1	+	+	+
COD	50	+	+	+
	10	+	+	+
	1	+	+	+
TOC	1	-	-	+

+ measured parameter, - : non-measured parameter.

2.2. Analytical techniques

All determinations for the characterization of OMW, listed in Table 2, were carried out according to the Standard Methods for Examination of Wastewater [18], except for total phenols, which were measured using the Folin–Ciocalteau method [19]. Colour disappearance was monitored by absorbance measurements at 395 nm [20]. Phenolic compounds were monitored by measuring the absorbance at 280 nm [21] using 4-methylcatechol as standard, by cyclic voltammetry and by Gas chromatography/mass spectrometry (GC/MS).

2.2.1. Cyclic voltammetry

Voltammetric measurements were carried out in a conventional three-electrode cell using a EG&G potentiostat/galvanostat model 273 controlled by Research Electrochemistry software 4.30. The working electrode was made of Si/boron-doped diamond (BDD) (area 0.1 cm^2) and the counter-electrode was a platinum disc. Potentials are referenced to a saturated calomel electrode (SCE). All experiments were performed at room temperature (25–28 °C) on degassed OMW samples after acidification with 1 M H₂SO₄ solution.

2.3. GC/MS analysis

Phenolic and possible chlorinated compounds were monitored as follows: 40 ml of OMW was acidified to pH 2 by the addition of concentrated hydrochloric acid. Phenols were then extracted with ethyl acetate. The

Table 2. Main characteristics of OMW

Parameter	Value
рН	5.2
Electric conductivity (mS cm^{-1})	17.5
$COD (g l^{-1})$	42.0
$\Gamma OC (g l^{-1})$	13.0
Suspended solids (g l ⁻¹)	13.7
Minerals matter (g l^{-1})	15.0
Organic matter $(g l^{-1})$	20.0
Phenolic compounds (g l^{-1})	5.6

organic phase was concentrated at 40 °C to about 1 ml and silylized by the addition of N,O-bis(trimethylsilyl)acetamide (BSA). The resulting trimethylsilyl derivatives were analysed by GC/MS (Hewlett-Packard 6980/ HP5973MSD) as described by Belaid et al. [22].

3. Results and discussion

3.1. Characteristics of OMW

The main characteristics of the OMW are shown in Table 2. This effluent is acidic, has an electrical conductivity of 17.5 mS cm⁻¹, a chemical oxygen demand (COD) of 42 g l⁻¹ and a total organic carbon content (TOC) of 13 g l⁻¹. Total phenol content is about 5.6 g l⁻¹. The mineral composition of OMW (Table 3) indicates significant salinity associated with the presence of potassium, sodium and calcium cations as well as bicarbonate, chloride and sulphate anions. The OMW also contain minor amounts of iron and zinc, but no toxic metals such as lead or cadmium. Several other organic compounds including sugars, tannins, pectins and lipids are also found in OMW, as reported by Belaid et al. [22] and Ergüder et al. [23].

3.2. Electrochemical treatment of OMW

3.2.1. OMW decolourization and toxicity reduction

Figure 2(a–c) shows the decline in the colour of undiluted OMW, and of samples diluted 10-fold and 50-fold, respectively, versus time at different currents. In all runs, the colour intensity decreases, leading to a nearly colourless liquid at the end of treatment. These figures also show that decolourization is faster the higher the dilution and the current. The impact of current is very significant during the first 2 h of treatment. Since the dark brown colour of OMW reflects its high load in polyphenols, as reported by Hamdi [2], its decolourization suggests that these compounds, responsible for its toxicity, are destroyed by electrochemical oxidation. Experiments on the germination of corn seeds (data not shown), watered with raw and treated OMW, demonstrate that the latter is not phytotoxic. Indeed, only

Table 3. Mineral composition of OMW

Element	Concentration		
K^+ (g l ⁻¹)	2.8		
$Ca^{2+}(gl^{-1})$	1.0		
$Mg^{2+}(gl^{-1})$	0.3		
$Na^{+}(gl^{-1})$	1.3		
HCO^{3-} (g l^{-1})	5.2		
SO_4^{2-} (g l^{-1})	1.5		
$Cl^{-}(g l^{-1})$	3.0		
Cu^{2+} (mg l ⁻¹)	0.5		
Fe^{2+} (mg l ⁻¹)	9.8		
Zn^{2+} (mg l ⁻¹)	4.6		
Mn^{2+} (mg l ⁻¹)	0.9		



Fig. 2. Decolourization during electrolysis at different currents, OMW dilution. (a) undiluted OMW, (b) dilution factor 10, (c) dilution factor 50. $\Delta - I$: 7.0 A; $\blacklozenge - I$: 8.4 A; $\circ - I$: 9.8 A.

seeds watered with treated OMW germinated. This preliminary result supports the practice of using treated OMW for irrigation under some circumstances.

3.2.2. *Effect of the electrochemical treatment* on COD and TOC reduction

COD and TOC are considered to be the two main parameters for pollution control. Figure 3a–c shows that the COD is reduced for the undiluted as well as for the diluted OMW samples, at all currents, indicating that organic compounds are effectively oxidized. The highest COD reduction (65%) was achieved with the 50fold diluted sample (Figure 3c) using a current of 9.8 A. Under the same conditions, COD reduction for the undiluted sample does not exceed 40% (Figure 3(a)).

For the TOC (Figure 4) the best reduction is about 45% for undiluted OMW after a 5-h treatment at 9.8 A. The drop in TOC values suggests that CO₂ is formed at the same time as other organic intermediates. Similar results were found by Boye et al. [24] and by Gandini et al. [25] who succeeded in breaking carboxylic acids down to CO₂ and H₂O. Moreover, Rodrigo et al. [26]



Fig. 3. COD reduction during electrolysis at different currents, OMW dilution. (a) undiluted OMW, (b) dilution factor 10, (c) dilution factor 50. $\Delta - I$: 7.0 A; $\blacklozenge - I$: 8.4 A; $\circ - I$: 9.8 A.

stated that 93% of the carbon initially present in their samples was converted to CO_2 via an electrochemical process using a BDD electrode.

3.2.3. *Monitoring the degradation of phenolic compounds* As mentioned earlier, the degradation of phenolic compounds was monitored during the electrolysis of



Fig. 4. TOC reduction during electrolysis of undiluted OMW at different currents. $\Delta - I$: 7.0 A; $\blacklozenge - I$: 8.4 A; $\circ - I$: 9.8 A.

OMW using UV–visible spectrometry and cyclic voltammetry. Phenols and possible toxic by-products were detected by GC/MS.

3.2.3.1. UV-visible absorbance. Figure 5 shows typical examples of selected UV-visible spectra of a 100-fold diluted OMW sample and the same after a 5-h treatment. The spectrum of the untreated sample shows high absorbance at around 225 and 280 nm corresponding to conjugated aromatic compounds and ascribed to the socalled E and B bands in the benzene ring, respectively. In contrast, these bands are absent from the spectrum of electrochemically treated OMW, suggesting that all aromatic compounds are oxidized. This assumption is supported by the mechanism for the electrochemical destruction of benzene derivatives proposed by Martinez-Huitle et al. [27]. The visible spectrum (375–600 nm) of the treated sample also shows no residual absorbance, i.e. the OMW are totally decolourized. This result is in good agreement with those of Panizza and Cerisola [14] in previous studies on the electrochemical oxidation of OMW.

3.2.3.2. Kinetics of phenolic compound degradation. Figure 6c shows a significant reduction in phenolic compound concentration in the 50-fold diluted OMW mainly during the first 2 h at all currents. Thereafter degradation proceeds insignificantly and stabilizes at about 98% at the end of treatment. For the more concentrated OMW samples (Figure 6(a, b)), the removal of phenols is slower and reaches high levels only after 4 h.

As a typical example, conversion of Figure 6(a) to a logarithmic scale gives Figure 7, corresponding to the kinetics of phenol degradation. The curves follow the equation:

$$\frac{dC}{C} = -kdt$$

integration of which gives:

$$\mathrm{Ln}C_t = -kt + \mathrm{Ln}C_0$$



Fig. 5. UV–Visible spectra of untreated and 4-h treated OMW samples, dilution factor 100. • – Untreated OMW; \circ – 4-h treated OMW.



Fig. 6. Phenolic compound reduction during electrolysis at different currents, OMW dilution. (a) undiluted OMW, (b) dilution factor 10, (c) dilution factor 50. $\Delta - I$: 7.0 A; $\bullet - I$: 8.4 A; $\circ - I$: 9.8 A.

where C_0 and C_t are the initial concentration and the concentration at time t of phenolic compounds, respectively; k is the apparent rate constant. From these equations, it can be deduced that the kinetics are first-order with a rate constant (k) proportional to the current (I). The calculated ratios k/I related to



Fig. 7. First-order kinetics for phenolic compound removal during electro-oxidation of undiluted OMW at different currents. $\Delta - I$: 7.0 A; $\blacklozenge - I$: 8.4 A; $\circ - I$: 9.8 A.

Table 4. First-order rate constants for phenolic compound electrooxidation

OMW	Current (A)	$k (h^{-1})$	$\tfrac{k}{I} \left(\mathbf{h}^{-1} \mathbf{A}^{-1} \right)$	$t_{1/2} = \frac{\mathrm{Ln}_2}{k} (\mathrm{h})$
Undiluted	7	0.348	4.96×10^{-2}	1.99
	8.4	0.417	4.96×10^{-2}	1.66
	9.8	0.484	4.93×10^{-2}	1.43
Diluted/10	7	0.440	6.30×10^{-2}	1.57
	8.4	0.576	6.85×10^{-2}	1.20
	9.8	0.653	6.66×10^{-2}	1.06
Diluted/50	7	1.146	16.37×10^{-2}	0.60
	8.4	1.353	16.11×10^{-2}	0.51
	9.8	1.611	16.43×10^{-2}	0.43

Figure 6(a) (undiluted OMW), are about $4.9 \times 10^{-2} \text{ h}^{-1} \text{ A}^{-1}$ for all currents. Similar kinetic behaviour is obtained for the 10-fold diluted OMW where the k/I is about $6.5 \times 10^{-2} \text{ h}^{-1} \text{ A}^{-1}$ (Table 4).

This result agrees with that of Polcaro et al. [28] who found that the logarithm of phenol concentration was always a linear function of time, indicating first-order kinetics. Comparable results were also reported by Panizza and Cerisola [14] who found that OMW COD reduction followed pseudo-first-order kinetics. This first-order kinetic trend was also noted by Martinez-Huitle et al. [27] for the oxidation of chloranilic acid.

For the most dilute OMW (50-fold), the kinetics were first-order only during the first 2 h where k/I is about 16.2×10^{-2} h⁻¹ A⁻¹ (Table 4). During the remaining time, the kinetic behaviour changes, probably due to the fact that most of the phenols are already destroyed (Figure 6(c)). Given the fact that the rate constants depend only on current, it seems likely that the degradation is controlled by indirect oxidation via the production of some oxidizing species, such as CIO, CI and particularly OH as suggested by Comninellis [12] and Simond et al. [29].

3.2.3.3. Cyclic voltammetry at BDD elecа trode. Figure 8(a-d) shows the voltammograms of untreated OMW and OMW electrochemically treated for different times (1, 2 and 4 h (s), respectively). That for untreated OMW (Figure 8(a)) shows a large anodic current peak between 0.7 and 1.7 V attributable to all the phenolic compounds initially present. After 1 h (Figure 8(b)), the intensity of this peak decreases nearly 2fold due to phenol degradation. As the electrolysis progresses, the anodic current peak continues to decrease gradually (Figure 8(c)) and disappears completely after 4 h (Figure 8(d)) corresponding to virtually complete removal of phenols. It can be concluded that cyclic voltammetry at a BDD electrode is a straightforward means of following phenol degradation. No sample dilution, for example, is required, in contrast to the spectrophotometric method. This method may therefore be used *in situ* as a means monitoring phenol oxidation in automated electrochemical systems. The electrochemical destruction of aromatic compounds at a BDD electrode is reported to be a very efficient process, when a large electrode is used [25-28].



Fig. 8. Cyclic voltammograms of untreated and treated OMW at a 0.1 cm^2 BDD electrode, scan rate 20 mV s⁻¹. (a) untreated OMW, (b) c and d: treated OMW for 1, 2 and 4 h(s), respectively.

3.2.3.4. Detection of phenolic compounds by GC/MS. Figure 9 shows the chromatogram of untreated OMW, corresponding to the monomeric phenol derivatives listed in Table 5. Figure 10 presents the chromatogram of an OMW sample electrochemically



Fig. 9. GC/MS chromatogram of untreated OMW.

treated for 4 h. Comparison suggests that the treatment has almost completely eliminated the phenols. Indeed, nearly all peaks related to phenols are absent from the chromatogram of the treated sample. Moreover, even upon magnification of this chromatogram, only small traces can be observed. One peak, ascribed to 4hydroxybenzoic acid, was identified. This compound may be an intermediate in the electro-oxidation of polyphenols. It has been reported that carboxylic acids are usually formed as intermediates in the oxidation of aromatic derivatives [27-29]. GC/MS analysis also established the absence of chlorinated compounds. Ross et al. [30] demonstrated that small amounts of such compounds can be removed from solution by electrooxidation. Also, Körbahti et al. [31] observed that mono-, di- and tri-substituted chlorinated phenols produced in the electrolysis of phenolic compounds are consumed thereafter by destruction and/or polymerization. However, Gotsi et al. [13] detected organochlorine by-products in electrochemically treated OMW, increasing toxicity. This feature may be related to the relatively high amount of the electrolyte (10–40 g l^{-1} of NaCl) added to the raw OMW.

Of course, using GC/MS, we could only monitor the degradation of low-molecular weight phenols. However, results obtained by UV-visible absorption and cyclic voltammetry at a BDD electrode suggest that high-molecular weight phenols are also destroyed by our electrochemical treatment.

3.2.4. Potential difference between the electrodes and the ohmic potential drop

In each run the potential difference between the cathode and the anode (Figure 11) decreases slightly up to 30 min, then stabilizes at about 3 V during the remaining time. This means that there was no passivation of the electrodes, a phenomenon which is commonly observed with phenols, as reported by Rodrigo et al. [26].

The ohmic potential drop is thus moderate and is related to the presence of the membrane and the reduced distance between the electrodes. In order to maintain the conductivity of the medium and minimize the ohmic potential drop, Israilides et al. and Gotsi et al. [12, 13] used significant amounts of supporting electrolyte which induced the production of toxic chlorinated compounds. Other electrolytes such as Na₂SO₄, H₂SO₄, NaOH and their mixtures have also been tested [32, 33].

4. Conclusion

OMW were treated by electrochemical oxidation in a modified Grignard reactor. It was found that:

- whatever the dilution factor, decolourization is very significant, reaching nearly 90% at high currents.
- phenolic compound removal is faster at high currents, due to the higher production rate of oxidant radicals, and also depends on the dilution factor.

Table 5. Phenolic compounds detected in untreated OMW

Compound	RT/min	$MW/M^{+\cdot}$	Main fragments of M ⁺⁺ of the TMS derivatives
(1) 1,2-benzenediol (<i>Catechol</i>)	15.35	254	239, 166, 151, 136, 73 (100%)
(2) 1,3-dihydroxybenzene (Resorcinol)	17.53	254	239 (100%), 217, 147, 133, 117, 101, 73
(3) 1,4-dihydroxy-2,5-dimethylbenzene	19.19	282 (100%)	267, 193, 179, 147, 91, 73
(4) 1,2- dihydroxypropenylbenzene	21.03	294 (100%)	279, 205, 147, 73
(5) 4-hydroxyphenylethanol (<i>Tyrosol</i>)	21.82	282	267, 193, 179 (100%), 163, 126, 103, 73
(6) 4-hydroxybenzoic acid	23.23	282	267 (100%), 223, 193, 179, 147, 126, 85, 73
(7) 4-hydroxyphenylacetic acid	23.52	296	281, 252, 217, 192, 179, 164, 147, 73 (100%)
(8) 4-hydroxy-3-methoxyphenethylalcohol (Homovanillyl alcohol)	25.05	312	297, 282, 209 (100%), 179, 103, 73
(9) 4-hydroxy-3-methoxybenzoic acid (Vanillic Acid)	26.33	312	297 (100%), 282, 267, 253, 223, 193, 126, 73
(10) 3,4-dihydroxyphenyl alcohol (Hydroxytyrosol)	26.41	370	355, 323, 281, 267 (100%), 193, 179, 147, 103, 73
(11) 4-hydroxycinnamic acid (para Coumaric Acid)	26.74	308	293, 249, 219, 73 (100%)
(12) 3,4-dihydroxybenzoic acid (Protocatechuic Acid)	27.27	370	355, 311, 281, 267, 256, 223, 193 (100%), 166, 138, 73
(13) 4-hydroxy-3-methoxyphenethylene glycol (<i>Vanilethane diol</i>)	27.69	400	297 (100%), 147, 73 (100%)
(14) 2,5-dihydroxybenzeneacetic acid (Homogentisic Acid)	28.43	384 (100%)	369, 341, 267, 252, 237, 147, 73
(15) 3,4-dihydroxyphenylglycol	29.84	458	443, 355 (100%), 281, 147, 73
(16) 3,4-dihydroxyphenylpropionic acid	30.04	398 (100%)	383, 280, 267, 179, 73

RT: Retention time/min; MW (M⁺⁻): molecular weight; (100%): major fragment.

- phenol removal can be monitored by UV absorption at 280 nm but, more easily, by cyclic voltammetry at a BDD electrode.
- even at prolonged times, the procedure does not completely remove organic compounds. Indeed,



Fig. 10. GC/MS chromatogram of treated (4 h) OMW.



Fig. 11. Typical example of cell voltage variation during electrolysis at 8.4 A. Δ – Untreated OMW; \blacklozenge – Dilution factor: 10; \circ – Dilution factor: 50.

COD and TOC values are never reduced to zero.

- no toxic compounds, such as chlorinated by-products, are detected in the treated OMW.
- the potential difference between the cathode and the anode is stable during electrolysis: electrode passivation does not occur. Also, the ohmic potential drop is lower than in previous studies.

On the basis of these results it can be suggested that electrochemical oxidation of OMW in a modified Grignard reactor is a promising process for the destruction of phenolic compounds and also for colour removal.

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