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# Electrochemical oxidation of olive oil mill wastewaters

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## Abstract

The electrochemical oxidation of olive oil mill wastewaters over a titanium–tantalum–platinum–iridium anode was investigated. Batch experiments were conducted in a flow-through electrolytic cell with internal recycle at voltage of 5, 7 and 9 V, NaCl concentrations of 1%, 2% and 4%, recirculation rates of 0.4 and 0.62 L/s and initial chemical oxygen demand (COD) concentrations of 1475, 3060, 5180 and 6545 mg/L. The conversion of total phenols and COD as well as the extent of decolorization generally increased with increasing voltage, salinity and recirculation rate and decreasing initial concentration. In most cases, nearly complete degradation of phenols and decolorization were achieved at short treatment times up to 60 min; this was accompanied by a relatively low COD removal that never exceeded 40% even after prolonged (up to 240 min) times. The consumption of energy per unit mass of COD removed after 120 min of treatment was found to be a strong function of the operating conditions and was generally low at high initial concentrations and/or reduced salinity. The acute toxicity to marine bacteria *Vibrio fischeri* decreased slightly during the early stages of the reaction and this was attributed to the removal of phenols. However, as the reaction proceeded toxicity increased due to the formation of organochlorinated by-products as confirmed by GC/MS analysis. The toxicity to *Daphnia magna* increased sharply at short treatment times and remained quite high even after prolonged oxidation.

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**Keywords:** Electrolysis; Olive mill; Toxicity; Treatment; Wastewater

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## 1. Introduction

Olive mill wastewaters (OMW) constitute a serious environmental problem in the Mediterranean Sea region due to the unique features associated with this type of agro-waste, namely seasonal and localized production (typically between December and March), low flowrates (between 10 and 100 m<sup>3</sup>/d) and high and diverse organic

load. This may reach values as high as 220 g/L chemical oxygen demand (COD) and mainly consists of phenols, lipids, sugars and tannins; the former with concentrations that reach up to 10 g/L are known to be biorecalcitrant. Mulinnacci et al. (2001) who analyzed OMW samples from Spain, Italy, France and Portugal reported that the phenolic fraction mainly consisted of compounds such as tyrosol and hydroxytyrosol at concentrations up to about 130 mg/L, caffeic acid up to 4 mg/L and cinnamic acid derivatives up to 118 mg/L with the phenolic composition being a strong function of the effluent origin. For instance, the total polyphenolic

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content varied from as low as 25 mg/L to as high as 4 g/L for the French and Italian samples, respectively. Therefore, it is not surprising that research efforts have been directed towards the development of efficient treatment technologies including several physical, chemical and biological processes as well as various combinations of them; these technologies have recently been reviewed by Mantzavinos and Kalogerakis (2005).

Electrochemical technologies such as electrooxidation, electrocoagulation and electroflotation have been widely used in water and wastewater treatment and several applications have been recently reviewed by Chen (2004). Electrooxidation over anodes made of graphite, Pt, TiO<sub>2</sub>, IrO<sub>2</sub>, PbO<sub>2</sub>, several Ti-based alloys and, more recently, boron-doped diamond electrodes in the presence of chloride ions (typically NaCl) has been employed for the decontamination of various organic-containing effluents. In the case of electrocoagulation, disposable iron or aluminum electrodes are employed and electrochemically leach in the solution with the dissolved metals serving as coagulants. In the case of dissolving iron electrodes, hydrogen peroxide can be added externally in the solution, thus simulating a Fenton-like reaction.

Although the electrochemical oxidation of various synthetic and actual industrial effluents has been given considerable attention, relatively few studies report the use of this technology to treat OMW. Israilides et al. (1997) investigated the electrooxidation of OMW over a Ti–Pt anode at 15 V and 100 A and reported a 93% COD reduction (initial COD was 178 g/L) after 600 min of treatment. In a recent work, Giannes et al. (2003) studied the effect of varying voltage and salinity on OMW oxidation over a Ti–Ta–Pt–Ir anode. They also reported that the ecotoxicity to marine and fresh-water bacteria remained practically unchanged following treatment. Other than these studies, OMW electrocoagulation over iron and aluminum electrodes was found capable of reducing the organic load as well as decolorizing OMW (Adhoum and Monser, 2004; Inan et al., 2004), while an electro-Fenton process was studied for the treatment of synthetic solutions containing various OMW polyphenols (Khoufi et al., 2004). In other studies, Longhi et al. (2001) reported that electrooxidation of a synthetic effluent containing various OMW polyphenols and acids over a PbO<sub>2</sub> anode was capable of reducing substantially the phenolic content of the effluent and this was accompanied by a low total organic carbon removal. The electrooxidation of coumaric acid, a representative of the polyphenolic fraction typically found in OMW, over several different anodes has also been reported in the literature (Saracco et al., 2001).

The aim of this work was to investigate the electrochemical oxidation of OMW over a Ti–Ta–Pt–Ir anode regarding the effect of various operating conditions such

as voltage, electrolyte concentration, initial concentration and sample pre-conditioning on the conversion of COD, phenols and color. The effect of treatment on OMW acute ecotoxicity and its possible relationship to reaction by-products was also investigated.

## 2. Materials and methods

### 2.1. Olive mill wastewaters (OMW)

The effluent used in this study was taken from a three-phase olive mill located in the region of Chania, Western Crete, Greece. The effluent was subject to several consecutive filtrations to remove most of the suspended solids (TSS) and its main properties, prior to and after filtration, are given in Table 1. Unless otherwise stated, experiments were carried out with the filtered OMW which was then diluted with water to achieve the desired initial concentration (e.g. samples diluted 5, 10 and 20 times were used in various runs). An additional experiment was performed using the original, unfiltered OMW in order to examine the effect of increased solids concentration on the process; in this case, the sample was diluted 20 times with water.

### 2.2. Electrochemical degradation experiments

Experiments were conducted in an electrolytic cell comprising a stainless steel 316 L cathode and a titanium (grade II/VII) anode covered by a thin film of tantalum, platinum and iridium alloy. The cathode was 50 mm in diameter and 25 cm long hollow cylinder in the center of which was housed the anode which, in turn, was 8.2 cm long with a diameter of 25 mm. A schematic of the experimental set-up is shown in Fig. 1. In a typical run, the diluted effluent was mixed with the appropriate amount of NaCl, batch loaded in a vessel and continuously pumped in the cell through a peristaltic pump; the rate of recirculation could be adjusted to the desired value through a series of valves. In all cases, the working volume was 10 L. A spiral coil immersed in the liquid and connected to tap water supply was used to remove the heat liberated from the reaction. All experiments were conducted at ambient temperature;

Table 1  
Properties of OMW samples used in this study

Properties	OMW before filtration	OMW after filtration
COD, mg/L	132,700	28,400
Total phenols, mg/L	2790	1520
TSS, mg/L	19,200	840
pH	5.1	5

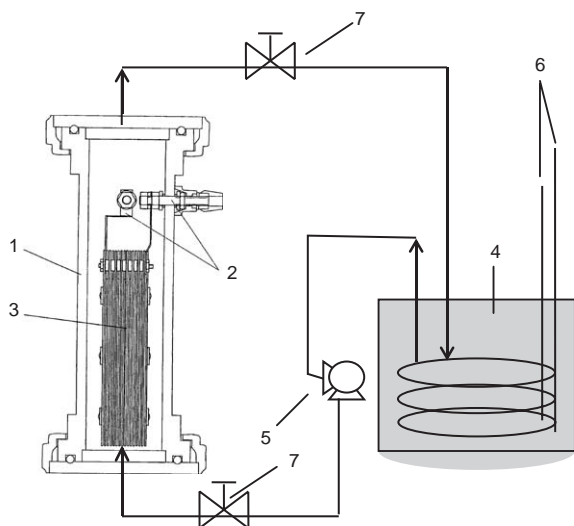


Fig. 1. Schematic of the experimental set-up: (1) cathode; (2) power supply; (3) anode; (4) OMW feed tank; (5) peristaltic pump; (6) coil for cooling water; (7) valves.

nonetheless, temperature was found to increase slowly with treatment time with the extent of temperature rise being dependent of the operating conditions employed (e.g. voltage, salinity, initial OMW concentration, recirculation rate). However, temperature never exceeded 36 °C at the end of each experiment which typically lasted for 120 min (representative temperature-time profile data is shown in Fig. 3b). NaCl was used as the electrolyte at concentrations of 1%, 2% and 4% w/v. Experiments were conducted at voltage values of 5, 7 and 9 V and initial concentrations of filtered OMW of 1475, 3060 and 5180 mg/L COD (these concentrations correspond to dilution factors of about 20, 10 and 5, respectively). For the run carried out with the unfiltered OMW its initial concentration was 6545 mg/L COD.

### 2.3. Chemical oxygen demand (COD)

COD was determined by the dichromate method. The appropriate amount of sample was introduced into commercially available digestion solution containing potassium dichromate, sulfuric acid and mercuric sulfate (Hach Europe, Belgium) and the mixture was then incubated for 120 min at 150 °C in a COD reactor (Model 45600-Hach Company, USA). COD concentration was measured colorimetrically using a DR/2010 spectrophotometer (Hach Company, USA).

### 2.4. Total phenols (TP)

The total phenolic content was determined colorimetrically at 725 nm on a Shimadzu UV 1240 spectro-

photometer using the Folin-Ciocalteu reagent according to the procedures described in detail elsewhere (Atanassova et al., 2005). Caffeic acid was used as standard to quantify the concentration of phenols in OMW.

### 2.5. Color

The extent of decolorization that had occurred during treatment was assessed measuring sample absorbance at 500 nm on a Shimadzu UV 1240 spectrophotometer.

### 2.6. Total suspended solids (TSS)

TSS concentration was determined filtering a well-mixed sample through a Pall (type A/E) glass-fiber filter and then drying the residue retained on the filter at 103 °C for 60 min. The increase in weight of the filter corresponds to TSS.

### 2.7. Liquid-phase microextraction coupled with gas chromatography-mass spectrometry (LPME-GC/MS)

GC/MS analysis was employed to identify primary reaction by-products with emphasis on organochlorinated and other relatively hydrophobic compounds. Prior to GC/MS analysis, the samples were pre-concentrated using a liquid-phase microextraction (LPME) method, a selective tool for the trace analysis of hydrophobic organic compounds in water samples, according to the procedures described in detail elsewhere (Charalabaki et al., 2005). A Shimadzu GC-17A (Version 3) QP-5050A GC/MS system equipped with a 30 m × 0.25 mm, 0.25 μm HP-5MS capillary column (Agilent Technologies) was used for all analyses. The injector was operating at 260 °C in the splitless mode with the split closed for 5 min. Helium (> 99.999% pure) was used as the carrier gas at a flow-rate of 1.2 mL/min. The column oven was initially set at 60 °C for 5 min, then programmed to 300 °C at a 10 °C/min rate, where it was held for 2 min. The interface temperature was set at 310 °C and the detector voltage at 1.50 kV. A 7.5 min solvent cut time was allowed for all analyses. The ionization mode was electron impact (70 eV) and data was collected in the full scan mode ( $m/z$  50–450). For a compound to be considered as a likely reaction intermediate with a certain degree of confidence, its mass spectrum should match that of the GC/MS mass spectrum library by at least 90%.

### 2.8. Assessment of acute toxicity

The luminescent marine bacteria *V. fischeri* and the crustacean *D. magna* were used to assess the acute ecotoxicity of OMW samples prior to and after electrochemical treatment. The inhibition of *V. fischeri*

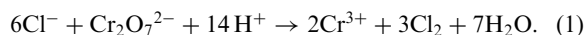
exposed to OMW samples for 15 and 30 min was measured using a Microtox 500 Analyzer (SDI, USA) according to the Microtox 45% Basic Test (Microbics Corporation, Microtox Manual, 1992, A Toxicity Testing Handbook, vols. 1–5, Carlsbad, CA, USA). For each sample, its  $EC_{50}$  value was determined by applying several dilutions; this value alongside the respective confidence intervals were computed using the MicrotoxOmni software.

The toxicity tests on *D. magna* were carried out using a commercial toxicity test Daphtoxkit F magna provided by Microbittest Inc. Experiments with Daphtoxkit F are based on the immobilization of the crustacean *D. magna* due to the action of substances present in samples. The ephippia of *D. magna* were hatched from dormant eggs in 3 days under continuous illumination (6000 lux) at 20 °C. Twenty neonates were used for each dilution of the samples in a series of 4 wells, each of these containing 10 mL sample and 5 neonates. The neonates (younger than 24 h) were exposed to the samples for 24 h at 20 °C in the dark. After the exposure period, the immobilized organisms were counted and the results are expressed as % immobilization of the exposed organisms. All the toxicity tests were performed in duplicate.

### 3. Results and discussion

#### 3.1. Effect of salinity on COD measurement

The standard COD measurement is known to be affected by a number of inorganic substances which are outlined in the Standard Methods for the Examination of Water and Wastewater (APHA, 1998, 20th Edition). Of these, chloride may have a significant positive effect on the test which is due to its reaction with potassium dichromate as follows:



The commercially available COD digestion solutions used in this study counterbalance chloride interference at chloride concentrations up to 0.2% due to the presence of mercuric sulfate. However, this concentration is far lower than that used in electrochemical degradation experiments; therefore, it was decided to estimate the effect of salinity on the COD test. This was done measuring the COD content of OMW samples at various salt concentrations as well as without salt. Fig. 2 shows the effect of salinity on COD at an initial OMW concentration of 1475 mg/L COD since most of the runs were performed at this concentration. As seen, the discrepancy between the measured COD values with and without salt ( $COD_1$  and  $COD_2$ , respectively) increases

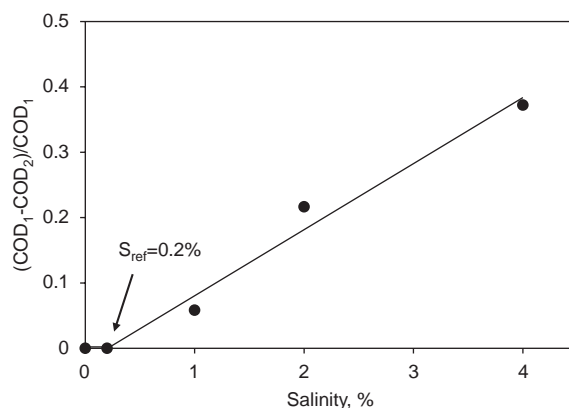


Fig. 2. Effect of salinity on COD measurement.

linearly with percent salinity ( $S$ ) as follows:

$$\left( \frac{COD_1 - COD_2}{COD_1} \right) = \begin{cases} 0 & \text{for } S \leq S_{ref}, \\ 0.1 S - 0.02 & \text{for } S > S_{ref}, \end{cases} \quad (2)$$

where  $S_{ref}$  corresponds to the maximum chloride concentration that is compensated due to the presence of mercury sulfate, i.e. 0.2%.

Eq. (2) was used to account for the effect of chloride interference on COD measurement. The corrected values were then used to perform mass balances and compute process efficiency in terms of specific energy consumption. It should be emphasized that Eq. (2) can only give a rough estimate rather than a precise determination of the actual COD value since chloride concentration changes throughout the reaction due to the formation and subsequent degradation of chlorinated organics, evolution of gaseous chlorine, etc.

Similar tests at different initial OMW concentrations showed that chloride interference decreases considerably with increasing COD concentration and decreasing salinity. For instance, for the electrochemical degradation runs performed at 2% salinity and initial COD values of 3060 and 5180 mg/L the discrepancy between  $COD_1$  and  $COD_2$  was always less than 3%.

#### 3.2. Effect of operating conditions on degradation

Fig. 3a shows the effect of varying voltage on COD, TP and color conversion as a function of treatment time at 4% salinity. As clearly seen, conversion increases with increasing voltage from 5 to 7 to 9 V. Nearly complete removal of phenols and decolorization can be achieved within the first 15–30 min at 7 and 9 V and 60 min at 5V; nonetheless, COD removal is significantly slower with only about 5%, 25% and 35% conversion being achieved after 120 min at 5, 7 and 9 V, respectively. It should be pointed out that all experiments were performed at OMW ambient, unbuffered pH which

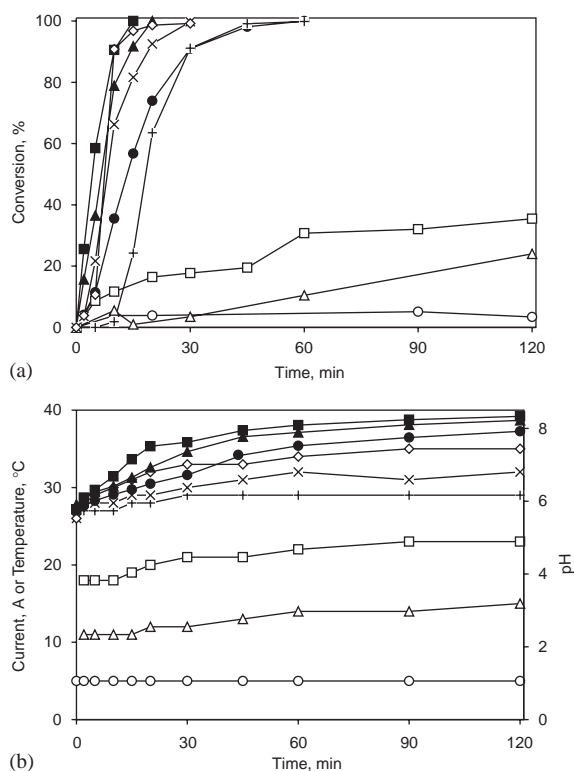


Fig. 3. (a) Effect of voltage on conversion. -○- COD, 5 V; -△- COD, 7 V; -□- COD, 9 V; -●- TP, 5 V; -▲- TP, 7 V; -■- TP, 9 V; -+- color, 5 V; -X- color, 7 V; -◇- color, 9 V. (b) Change of current, temperature and solution pH (on secondary axis) for various voltages. -○- current, 5 V; -△- current, 7 V; -□- current, 9 V; -●- pH, 5 V; -▲- pH, 7 V; -■- pH, 9 V; -+- temperature, 5 V; -X- temperature, 7 V; -◇- temperature, 9 V. Other conditions: salinity, 4%; initial COD, 1475 mg/L; recirculation rate, 0.62 L/s.

was monitored throughout the reaction; Fig. 3b shows the change of solution pH as well as current and temperature as a function of time for various voltages. As seen, pH increases gradually during the reaction with the degree of pH rise being dependent of the operating conditions employed (e.g. voltage, salinity, initial OMW concentration, recirculation rate). However, the final pH value never exceeded 8.5 at the conditions in question. Similar results were obtained by Israilides et al. (1997) who reported that the electrochemical oxidation of OMW over a Ti–Pt anode was accompanied by a pH increase from 4 to about 8; this increase was attributed to the increased formation of hydroxyl anions in the solution. It is well documented that pH does not have a significant effect on the electrochemical degradation of organics over titanium anodes in the range 3–10 (Rajkumar and Palanivelu, 2003, 2004; Chiang et al., 1995); therefore, no action was taken to adjust or buffer the pH of the solution.

Fig. 4 shows the effect of varying salinity on COD, TP and color conversion as a function of treatment time at 9 V. As seen from Figs. 3a and 4, conversion increases with increasing salinity and this is more pronounced for phenols and color removal. For instance, complete conversion of phenols occurs after 15, 30 and 45 min of treatment at 4%, 2% and 1% salinity, respectively. Conversely, COD conversion remains as low as 25% after 120 min at 1% salinity and increases to about 35% at 2% and 4% salinity. The beneficial effect of increasing salinity on the electrochemical degradation of OMW over a similar anode was also reported by Giannes et al. (2003) who found that treatment for 300 min at 16 V led to about 20%, 40% and 50% COD removal at 1.5%, 2% and 3% salinity, respectively.

To assess the extent to which phenols degradation contributes to overall COD conversion, the measured concentration of total phenols was converted to equivalent COD considering that phenols are represented by caffeic acid. Fig. 5 shows the removal of total COD as well as that of COD due to phenols as a function of salinity and treatment time at 9 V. During the early stages of the reaction, total COD removal appears to be predominantly due to the degradation of phenols. For instance, the ratio of equivalent phenolic COD to total COD conversion is about 90%, 80% and 70% after 10 min of reaction at 1%, 2% and 4% salinity, respectively. As the reaction proceeds, other organic compounds also undergo oxidation and this explains why the relative contribution of phenols degradation decreases. For example, the phenolic COD removal at 1% salinity increases from about 55 to 108 mg/L with increasing treatment time from 10 to 30 min; however, the respective ratio of phenolic COD

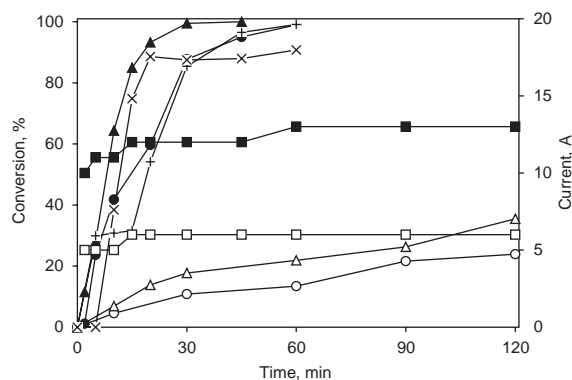


Fig. 4. Effect of salinity on conversion and current change (on secondary axis). -○- COD, 1% NaCl; -△- COD, 2% NaCl; -●- TP, 1% NaCl; -▲- TP, 2% NaCl; -+- color, 1% NaCl; -X- color, 2% NaCl; -□- current, 1% NaCl; -■- current, 2% NaCl. Other conditions: voltage, 9 V; initial COD, 1475 mg/L; recirculation rate, 0.62 L/s.



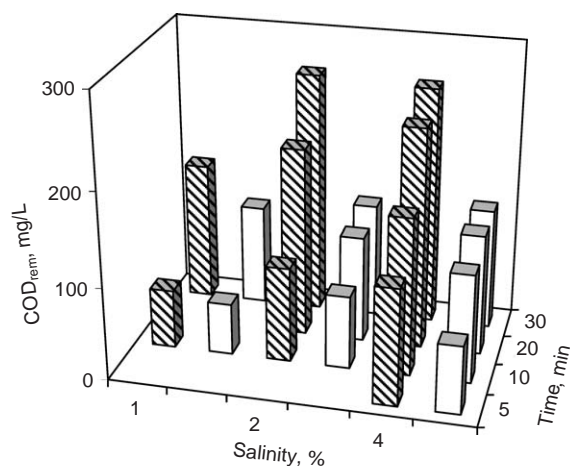


Fig. 5. Concentration of total COD (hatched bars) and equivalent phenolic COD (white bars) removed as a function of salinity and treatment time. Other conditions: voltage, 9 V; initial COD, 1475 mg/L; recirculation rate, 0.62 L/s.

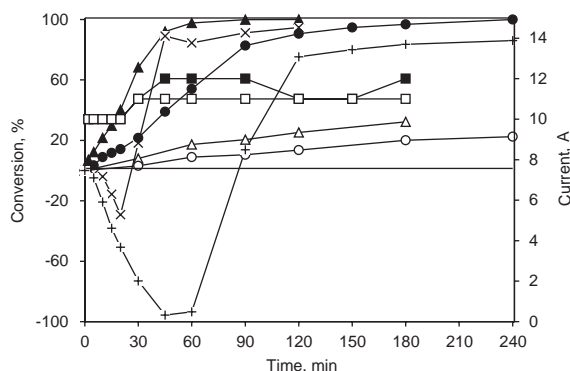


Fig. 6. Effect of initial concentration on conversion and current change (on secondary axis). -○- COD, initial COD: 5180 mg/L; -△- COD, initial COD: 3060 mg/L; -●- TP, initial COD: 5180 mg/L; -▲- TP, initial COD: 3060 mg/L; -+- color, initial COD: 5180 mg/L; -X- color, initial COD: 3060 mg/L; -□- current, initial COD: 5180 mg/L; -■- current, initial COD: 3060 mg/L. Other conditions: voltage: 9 V; salinity: 2%; recirculation rate: 0.62 L/s.

to total COD conversion decreases from about 90% to 70%.

Fig. 6 shows the effect of initial OMW concentration on COD, TP and color conversion at 2% salinity and 9 V. As seen from Figs. 5 and 6, conversion decreases with increasing OMW concentration; for instance, 15%, 25% and 35% COD conversion was recorded after 120 min at 5180, 3060 and 1475 mg/L of initial COD, respectively, while complete phenols degradation occurred after about 180, 60 and 30 min, respectively. Interestingly, sample color during the early stages of the reaction was found to increase and this was more

pronounced for the experiment conducted at the higher concentration. This is believed to be due to the oxidative polymerization of phenols and tannins originally present in the sample yielding dark colored organic compounds (Adhoum and Monser, 2004; Assas et al., 2002).

Fig. 7 shows the change of COD and phenols conversion with time at a recirculation rate of 0.4 L/s, 4% salinity and 9 V. As seen from Figs. 3a and 7, increasing recirculation from 0.4 to 0.62 L/s has practically no impact on phenols removal since complete degradation occurs within 10–15 min in either case. However, the extent of COD conversion substantially increases from about 15% to 35% after 120 min at 0.4 and 0.62 L/s, respectively. This can be explained by the synergistic effect of (a) increased production of oxidants and (b) the fact that a greater number of organics flow through the cell in a single pass, both of which occur at increased flow-through velocities, thus leading to increased degradation rates (Kraft et al., 1999). In a final experiment, a diluted sample was subject to electrochemical treatment at 4% salinity and 9 V without filtering the solids and the results are also shown in Fig. 7. Nearly complete degradation of phenols occurred after 180 min of treatment and this was accompanied by about 30% COD removal.

### 3.3. Mechanisms of electrochemical degradation

Two mechanisms are thought to be responsible for organic matter (R) electrochemical degradation, namely: (a) direct anodic oxidation where the pollutants are adsorbed on the anode surface (S) and destroyed by the anodic electron transfer reaction and (b) indirect oxidation in the liquid bulk which is mediated by the

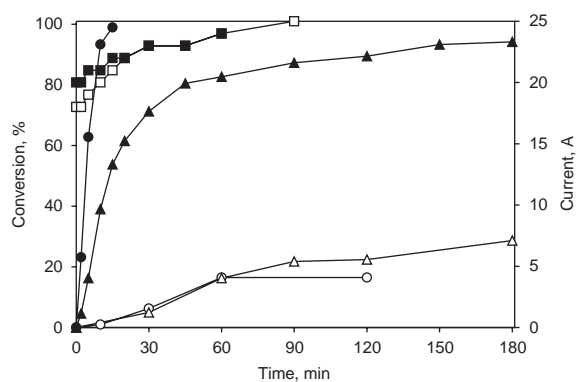
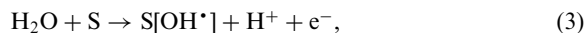
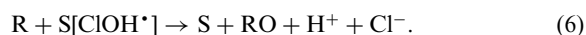
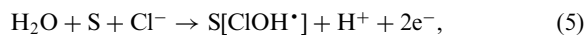


Fig. 7. Effect of recirculation rate and OMW pre-conditioning on conversion and current change (on secondary axis). -○- COD, filtered OMW, 0.4 L/s rate; -△- COD, unfiltered OMW, 0.62 L/s rate; -●- TP, filtered OMW, 0.4 L/s rate; -▲- TP, unfiltered OMW, 0.62 L/s rate; -□- current, filtered OMW, 0.4 L/s rate; -■- current, unfiltered OMW, 0.62 L/s rate. Other conditions: voltage: 9 V; salinity: 4%; initial COD: 1475 mg/L for filtered OMW and 6545 mg/L for unfiltered OMW.

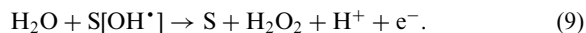
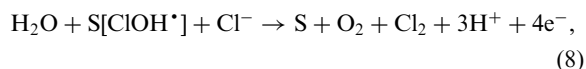
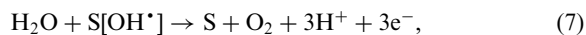
oxidants that are formed electrochemically; such oxidants include chlorine, hypochlorite, hydroxyl radicals, ozone and hydrogen peroxide. Anodic water discharge results in the formation of hydroxyl radicals that are adsorbed on the anode surface and can then oxidize the organic matter (Israilides et al., 1997):



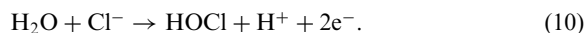
In the presence of NaCl, chlorohydroxyl radicals are also formed on the anode surface and then oxidize the organic matter:



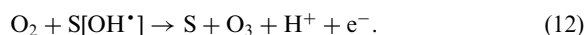
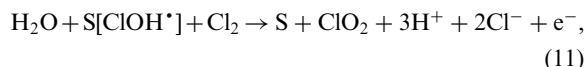
Reactions between water and radicals near the anode can yield molecular oxygen, free chlorine and hydrogen peroxide:



Furthermore, hypochlorite can be formed as follows:



Therefore, direct anodic oxidation of OMW through reactions (4) and (6) results in reduced COD as well as the formation of primary oxidants such as oxygen, chlorine, hypochlorite and hydrogen peroxide. Free chlorine and oxygen can further react on the anode yielding secondary oxidants such as chlorine dioxide and ozone, respectively:



Primary and secondary oxidants are quite stable and migrate in the solution bulk where they indirectly oxidize OMW. The efficiency of direct oxidation depends on the anode activity, the diffusion rate of organics on the anode surface and the applied current density. On the other hand, the efficiency of indirect oxidation depends on the diffusion rate of oxidants in the solution and the pH value (Israilides et al., 1997). At acidic conditions, free chlorine is the dominant oxidizing agent, while at slightly alkaline conditions hypochlorite, chloride ions and hydroxyl radicals are all important. At the conditions employed in this study, pH typically varied between 5 and 8 throughout the course of the

reaction implying that indirect oxidation might have proceeded through various oxidants.

### 3.4. Energy consumption

Electrochemical treatment is undoubtedly an energy-intensive process and its 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 load (e.g. COD) removed. Fig. 8 shows how the cumulative SEC increases with increasing salinity during OMW treatment at 9 V. This happens because an increase in COD removal with salinity is accompanied by a proportionately greater increase in energy consumption. For instance, the cumulative energy consumption after 120 min of treatment was 107 and 228 Wh at 1% and 2% salinity, respectively (this corresponds to a 110% increase), while the respective amount of COD removed was 3.3 and 5.2 g (this corresponds to a 55% increase). For the run at 4% salinity, an energy consumption of 393 Wh was accompanied by a 5.1 g of COD removal. Values of SEC after 120 min of treatment for the runs carried out at various electrolyte concentrations as well as for the rest of the runs of this study are summarized in Table 2. As seen, reduced SEC can be achieved at increased initial concentrations and/or decreased salinities (runs 5, 7–9). It should be noted that for the run at 5 V (run 1), an energy consumption of as little as 50 Wh was accompanied by an insignificant COD reduction of 0.6 g and this explains the rather high SEC value recorded. The last column of Table 2 shows SEC values corresponding to at least 90% removal of phenols. At the conditions employed in this study, phenols were readily oxidizable electrochemically and this is consistent with the low levels of energy consumption shown in Table 2.

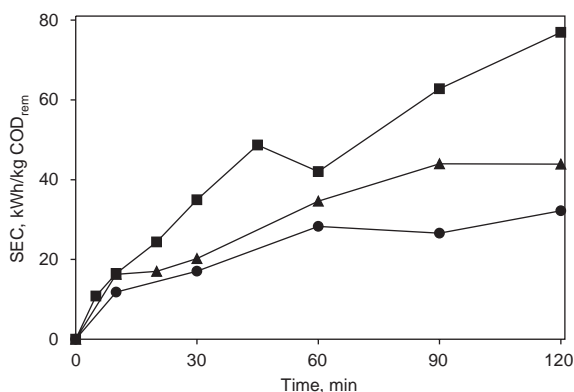


Fig. 8. Specific energy consumption during OMW treatment as a function of salinity. -●- 1% NaCl; -▲- 2% NaCl; -■- 4% NaCl. Other conditions: voltage, 9 V; initial COD, 1475 mg/L; recirculation rate: 0.62 L/s.



Table 2

Specific energy consumption (SEC) during electrochemical treatment at various conditions

Run	Voltage, V	Salinity, %	Initial COD, mg/L	Recirculation rate, L/s	SEC <sup>a</sup> , kWh/kg COD <sub>rem</sub>	SEC <sup>b</sup> , kWh/kg COD <sub>rem</sub>
1	5	4	1475	0.62	82.1	ND
2	7	4	1475	0.62	56.1	ND
3	9	4	1475	0.62	76.9	16.6
4	9	2	1475	0.62	43.9	17.2
5	9	1	1475	0.62	32.2	17.5
6	9	4	1475	0.4	190.8	13.1
7	9	2	3060	0.62	27.1	20.0
8	9	2	5180	0.62	28.3	28.3
9	9	4	6545	0.62	28.1	28.1

Runs 1–8, filtered OMW; Run 9, unfiltered OMW.

ND: Not determined.

<sup>a</sup>After 120 min of treatment.<sup>b</sup>For  $\geq 90\%$  removal of phenols.

### 3.5. Comparison with other treatment processes

At the conditions employed in this study, electrochemical oxidation generally led to nearly complete degradation of phenols and decolorization after short treatment times (i.e. up to 60 min) and this was accompanied by a relatively low COD removal that never exceeded 40% even after prolonged (i.e. up to 240 min) times. Other than electrolysis, numerous advanced oxidation processes (AOPs) have been employed for OMW treatment. Benitez et al. (1999) reported that ozonation of OMW (with COD varying between 10 and 34 g/L) for 8 h at temperatures between 10 and 40 °C and pH values between 5 and 9 resulted in a moderate COD reduction (between 12% and 28%). This was, however, accompanied by a substantial decrease of the aromatic content of OMW (up to 76%) which was adequate to enhance the subsequent aerobic degradation. Experiments with a more concentrated OMW (COD  $\approx$  60 g/L) showed that ozonation for 8 h led to 6.2% COD and 94.3% total phenols reduction (Benitez et al., 1997). The effect of operating conditions (hydrogen peroxide and iron concentration, reaction temperature) on OMW treatment (COD = 95 g/L) by means of Fenton oxidation was studied by Beltrán-Heredia et al. (2001) who reported COD and total phenols reductions up to about 33% and 94%, respectively after 8 h of treatment. In other studies, Rivas et al. (2001a) found that Fenton treatment of OMW (COD  $\approx$  15 g/L) was capable of reducing the COD content and total phenols by as much as 85–90% and 100%, respectively after 3–4 h at 50 °C. Moreover, the same effluent was subject to sub-critical wet oxidation (Rivas et al., 2001b) for 6 h at 180 °C and 7 MPa total pressure after which 30% COD and 80% total phenols reduction was achieved. Although complete mineralization by means of chemical oxidation is

plausible, this would require harsh treatment conditions and consequently become prohibitively expensive. Rivas et al. (2001c) reported that OMW treatment by super-critical wet oxidation at temperatures up to 500 °C and 25 MPa total pressure was capable of decontaminating completely the effluent in 1–3 min.

Eventually, the viability of any OMW treatment process will be dictated primarily by process economics rather than treatment efficiency. We have recently summarized (Tzagaroulakis et al., 2005) data regarding running costs for various physical, chemical and biological OMW treatments showing that electrochemical oxidation would cost about 0.6–0.75 €/kg COD removed; this is about an order of magnitude greater than the running cost of a combined aerobic–anaerobic treatment process. The respective cost for lime coagulation alone (a typical treatment process in Greece and elsewhere in the Mediterranean) would be in the order of 0.01 €/kg solids removed. However, electrochemical treatment is still less costly than other AOPs; for instance, running costs for Fenton oxidation could be as high as about 2.6 €/kg COD removed presumably due to the high cost of hydrogen peroxide.

### 3.6. Effect of treatment on ecotoxicity and determination of by-products

For the run carried out with the unfiltered OMW, the effect of treatment on acute ecotoxicity was assessed using the marine bacteria *V. fischeri* and the crustaceans *D. magna* and the results are shown in Tables 3 and 4, respectively. The toxicity of the original sample to *V. fischeri* was quite high yielding EC<sub>50</sub> values as low as about 0.5% after 15 or 30 min of exposure time. Treatment for 60 min was capable of partly reducing the toxicity of the original sample with EC<sub>50</sub> values increasing to 1.36% and 1.13% after 15 and 30 min of

Table 3

Change of OMW acute toxicity to *V. fischeri* as a function of treatment time and exposure time

Treatment time, min	15 min exposure time		30 min exposure time	
	EC <sub>50</sub> , %	Confidence range, %	EC <sub>50</sub> , %	Confidence range, %
0	0.47	0.37–0.6	0.5	0.4–0.64
60	1.36	1.17–1.58	1.13	1–1.29
120	0.06	0.05–0.07	0.06	0.05–0.07
180	0.22	0.13–0.38	0.04	0.01–0.14

Treatment conditions: salinity: 4‰; initial COD: 6545 mg/L; voltage: 9 V; recirculation rate: 0.62 L/s.

Table 4

Change of OMW acute toxicity to *D. magna* as a function of treatment time for 24 h exposure time

Treatment time, min	Immobilization, %	Confidence range, %
0	5	2.5–7.5
60	50	45–55
120	40	37.5–42.5
180	25	22.5–27.5

Treatment conditions: salinity: 4‰; initial COD: 6545 mg/L; voltage: 9 V; recirculation rate: 0.62 L/s.

exposure, respectively. This reduction may be due to the substantial degradation of phenols (i.e. about 85% as shown in Fig. 7) that had been achieved after 60 min of treatment. However, at prolonged treatment times toxicity increased substantially and samples treated for 120 or 180 min became more toxic than the original OMW.

For the tests with *D. magna*, original and treated samples had to be diluted 10 times prior to analysis due to the strong toxic effect of the undiluted samples to the bacteria. As seen in Table 4, the diluted, original sample was only partially toxic to *D. magna* with the immobilization being as low as 5%. Nonetheless, treatment for 60 or 120 min resulted in a nearly 10-fold increase in toxicity which was only partly removed after 180 min of reaction; in all cases though, electrochemically oxidized OMW samples were more toxic to *D. magna* than the original, untreated effluent. It is also notable that the ecotoxicity of original and treated OMW samples depends on the sensitivity of the microorganisms used and their response to the various species initially present in the effluent as well as their oxidation metabolites. Saline bacteria appeared to be more sensitive to effluents treated for prolonged treatment times, while daphnids were more sensitive to effluents oxidized for shorter times.

In general, the ecotoxicity of the final effluent was higher than that of the starting sample regardless the microorganisms involved and this was suspected to be

due to the formation of organochlorinated compounds during electrochemical oxidation. To confirm this hypothesis, samples drawn prior to and after treatment were analyzed by means of LPME-GC/MS and representative chromatograms are shown in Fig. 9. It should be pointed out that the LPME-GC/MS protocol employed in this study mainly aimed at identifying relatively hydrophobic compounds such as chlorinated organics; consequently, more hydrophilic constituents of OMW could not be detected. Several phenolic and other aromatic compounds are present in the original sample, namely: 2-methyl phenol (0.90), 2-ethyl phenol (0.91), 2-methoxy-4-methyl phenol (0.91), phenethyl alcohol (0.94), benzyl alcohol (0.90) and trimethoxy benzene (0.93) with numbers in brackets showing match factors of each compound's mass spectrum to that of the GC/MS library. Other compounds include butyric acid (0.90), 2,2-dimethyl decane (0.91) and cyclohexane carboxylic acid, methyl ester (0.92). The presence of phthalates is most likely due to contamination from the plastic containers where OMW was stored. With the exception of benzyl alcohol, other phenolic and aromatic compounds originally present in the sample do not appear at detectable concentrations after 60 min of treatment and this is consistent with the reduced concentration of total phenols recorded. A significant peak corresponding to 1,4-dichloro-2,5-dimethoxy benzene (0.90) appears in the 60-min chromatogram implying the formation of organochlorinated compounds. This is more pronounced after 180 min of treatment where several other chlorinated benzene derivatives and alkanes are present in the reaction mixture, namely: benzyl chloride (0.92), trichloronitro methane (0.90), hexachloro ethane (0.95), trichloroethyl benzene (0.90), trichloro ethane (0.92), tetrachloro ethane (0.90), chlorocyclohexane (0.93) and trichloroacetyl chloride (0.94). The presence of these chlorinated compounds as well as of others that could not be positively identified due to their low concentrations is thought to be responsible for the increased levels of sample toxicity shown in Tables 3 and 4. Due to their high hydrophobic partition coefficient in octanol/water, chlorinated organics easily accumulate in living

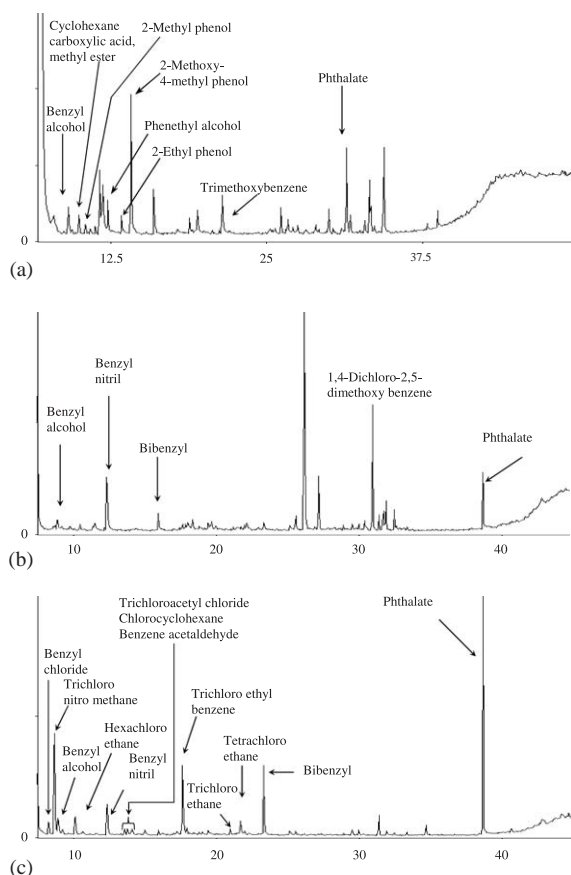


Fig. 9. LPME-GC/MS chromatograms of samples taken before and after electrochemical treatment: (a) original sample; (b) after 60 min; (c) after 180 min. Treatment conditions: salinity, 4‰; initial COD, 6545 mg/L; voltage, 9 V; recirculation rate: 0.62 L/s.

organisms and have serious deleterious effects. Toxicity usually increases with increasing degree of chlorination and this is associated with an increase in lipophilicity, thus leading to a greater potential for uptake by the organism. For instance, the  $EC_{50}$  value for unicellular seaweed exposed to monochlorinated benzene derivatives is in the order of 300 mg/L and decreases to about 1 mg/L for tetrachlorinated derivatives. A possible way to restrict the formation of harmful chlorinated organics would be to perform electrolysis under alkaline conditions where chlorine is predominantly converted to hypochlorite; the latter, despite its strong oxidizing ability, is a relatively weak chlorination agent.

#### 4. Conclusions

The conclusions drawn from this study can be summarized as follows:

- (1) Electrochemical oxidation of OMW is capable of degrading its phenolic content and decolorizing it at short treatment times and low-energy consumption. However, this is accompanied by a relatively low degree of mineralization. Treatment efficiency, in terms of both conversion and specific energy consumption, is affected by the operating conditions employed, i.e. voltage, salinity, recirculation rate, initial concentration.
- (2) Although the ecotoxicity of the untreated effluent to *V. fischeri* is quite high, it partly decreases after short treatment and this appears to be due to the degradation of the phenolic content of OMW. Unfortunately, at prolonged electrochemical oxidation times the formation of organochlorinated by-products leads to increased levels of toxicity. The toxicity of the untreated effluent to *D. magna* is relatively low but it increases substantially even at short oxidation times. It appears that proper evaluation of sample ecotoxicity would require a battery of bioassays of different sensitivity taking into account the type of the receiving water body.

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