

Article

Removal of Recalcitrant Compounds from Winery Wastewater by Electrochemical Oxidation

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Abstract: The electro-oxidation of recalcitrant compounds, phthalic acid, tyrosol, and catechin was studied in simulated and real winery wastewater samples using a boron-doped diamond (BDD) anode. In the simulated samples, catechin, although presenting a higher removal rate than that of phthalic acid and tyrosol, attained lower combustion efficiency, indicating that this compound is readily converted into other products rather than being completely oxidized. On the other hand, phthalic acid was easily mineralized. Regarding the electro-oxidation assays performed with the spiked winery wastewater, recalcitrant compounds and overall organic load removal rates increased with applied current density (j), but the removal efficiency of recalcitrant compounds decreased with the increase in j , and the specific energy consumption was significantly raised. The increase in treatment time showed to be a feasible solution for the WW treatment at lower j . After 14 h treatment at 300 A m^{-2} , phthalic acid, tyrosol, and catechin removals above 99.9% were achieved, with a chemical oxygen demand removal of 98.3%. Moreover, the biodegradability index was increased to 0.99, and toxicity towards *Daphnia magna* was reduced 1.3-fold, showing that the electro-oxidation process using a BDD anode is a feasible solution for the treatment of winery wastewaters, including phthalic acid, tyrosol, and catechin degradation.

Keywords: catechin; tyrosol; phthalic acid; phenolic compounds; wine industry effluents; electro-oxidation; BDD anode; toxicity; *Daphnia magna*



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1. Introduction

The industrial production of wine involves the consumption of large volumes of water, with approximately 70% being discharged as wastewater [1]. Winery wastewater (WW) is usually characterized by high salinity and organic load with many different organic compounds, such as organic acids, sugars, alcohols, and recalcitrant high-molecular-weight compounds [1–5]. Disposal in the water courses of this saline and highly polluted WW poses a serious environmental concern, with harmful effects on water quality and ecosystems [1,6–8].

The presence of recalcitrant and toxic compounds that are very difficult to degrade through ordinary biological treatment processes is one of the major problems caused by WW [3]. Among the various recalcitrant and toxic compounds that can be found in WW, phenolic compounds, present in the stems, seeds, and skins of grapes, and which are formed and transformed during the winemaking process, are the most representative [9]. Phenolic compounds, such as catechin, tyrosol, gallic acid, phthalic acid, myricetin, and quercetin, were identified in WW [4,9–11]. According to the literature, these compounds are the main ones responsible for WW coloration and toxicity, and their resistance to biological degradation and consequent persistence in the treated WW is of great concern [9,11].

The presence of recalcitrant compounds combined with high WW variability and strength impacts the ability of wastewater treatment plants to provide effective WW treatment [11,12]. Ioannou et al. [13] analyzed the advantages and disadvantages of different

treatment processes applied to WW treatment, and concluded that, considering the organic matter that cannot be degraded by conventional processes, only a strong oxidizing agent can degrade the recalcitrant and toxic compounds.

Hydroxyl radicals (HO^\bullet) are a highly reactive oxidizing species that reacts unselectively and instantaneously with organic compounds present in wastewater, leading to their degradation and mineralization [14]. Treatment processes based on the generation of this radical species are called advanced oxidation processes (AOPs) and are widely studied for industrial wastewater treatment [3,5,14–20]. Amor et al. [14] performed a review study on the treatment of recalcitrant agroindustrial wastewater by AOPs. The authors found that, regardless of wastewater type or its physicochemical characteristics, treatment performance was significantly enhanced when an AOP was applied. In the specific case of the phenolic compounds, AOPs effectiveness in its degradation was also shown. Amaral-Silva et al. [21] attained complete degradation of the entire phenolic content of elderberry-juice-processing wastewater by applying a Fenton process.

Electrochemical oxidation (EO) is one of the most studied AOPs due to its versatility, easy operation, and high efficiency in the degradation of recalcitrant compounds, especially when boron-doped diamond anodes (BDD) are used [22–24]. According to the literature, the high oxygen-evolution potential presented by the BDD associated with weak BDD(HO^\bullet) adsorption leads to high amounts of hydroxyl radicals available to oxidize organic compounds and mineralize them more effectively than other anode materials can [22–24]. Winery wastewater treatment by EO using a BDD anode was studied by Candia-Onfray et al. [2]. Almost complete mineralization of the organic compounds was achieved, and the authors concluded that EO using a BDD anode can be successfully applied to remove the organic matter from WW.

There are several studies in the literature that describe WW treatment by EO, but with the focus on the removal of macropollutants [2,5,18,19,24]. The degradation of specific recalcitrant and toxic compounds, such as some phenolic compounds that are present in WW, was disregarded in these studies, as well as the ecotoxicological evaluation of the EO process in the treatment of this kind of wastewater. In the present study, the degradation of the recalcitrant and toxic compounds phthalic acid, tyrosol, and catechin through EO using a BDD anode was assessed in simulated and real WW samples. In a novel approach, the influence of different WW constituents, namely, inorganic ions, carboxylic acids, alcohols, and sugars, on the removal efficacy of recalcitrant compounds was evaluated, using simulated WW samples. The influence of applied current density and the ecotoxicological performance of the process was also assessed using real WW samples spiked with the recalcitrant compounds under study.

2. Materials and Methods

2.1. Synthetic Samples

Synthetic WW samples were prepared as 0.1 g L^{-1} aqueous solutions of different recalcitrant compounds, phthalic acid (PhA), tyrosol (T), or catechin (C), in the presence of different WW constituents, namely, inorganic ions (PhA_1, T_1, and C_1), inorganic ions + carboxylic acids (PhA_2, T_2, and C_2), inorganic ions + carboxylic acids + alcohols (PhA_3, T_3, and C_3), and inorganic ions + carboxylic acids + alcohols + sugars (PhA_4, T_4, and C_4). Synthetic samples containing the mixture of the three recalcitrant compounds (M_1, M_2, M_3, and M_4), 0.1 g L^{-1} each, were also studied. The concentration of 0.1 g L^{-1} of recalcitrant compound was chosen considering the maximal tyrosol concentration reported in the literature for WW, 0.06 g L^{-1} [11], and the maximal total polyphenol concentration, 1.45 g L^{-1} , reported for WW by Mosse et al. [4]. Regarding the composition in inorganic ions, carboxylic acids, alcohols, and sugars, they were chosen to simulate a WW at extreme conditions according to the maximal concentrations reported for the main WW constituents [4].

Samples with inorganic salts contained sodium sulfate anhydrous ($\geq 99\%$), 1.85 g L^{-1} , calcium sulfate dihydrate ($\geq 99\%$), 2.23 g L^{-1} , and potassium chloride ($\geq 99\%$), 0.13 g L^{-1} .

Samples PhA_2, T_2, C_2, and M_2, besides the inorganic salts, contained carboxylic acids: L(+)-tartaric acid ($\geq 99.5\%$), 0.53 g L^{-1} , lactic acid solution ($\geq 85\%$), 0.35 g L^{-1} , acetic acid glacial ($\geq 99.8\%$), 0.66 g L^{-1} , succinic acid ($\geq 99\%$), 0.08 g L^{-1} . Samples PhA_3, T_3, C_3, and M_3, were prepared like samples PhA_2, T_2, C_2, and M_2, with the addition of alcohols: ethanol ($\geq 99.8\%$), 5 g L^{-1} , glycerol solution (83.5%–89.5%), 0.32 g L^{-1} , methanol ($\geq 99.9\%$), 0.02 g L^{-1} . Samples PhA_4, T_4, C_4, and M_4, were prepared like samples PhA_3, T_3, C_3, and M_3, with the addition of sugars: maltose ($\geq 99\%$), 13.2 g L^{-1} , glucose ($\geq 99\%$), 2.7 g L^{-1} , D(–)fructose ($\geq 99\%$), 1.5 g L^{-1} . All the reagents were purchased from Sigma-Aldrich (Lisbon, Portugal). The composition and physicochemical characteristics of the different synthetic samples prepared are presented in Supplementary Material Table S1.

2.2. Winery Wastewater

The winery wastewater used in this study was collected in December 2020 from a winemaking company in Portugal before being submitted to any treatment, and was kept refrigerated until its use. WW characterization is presented in Table 1. Since, in the collected WW, the concentration of the studied recalcitrant compounds (phthalic acid, tyrosol, and catechin) was very low and near the limit of quantitation of the used analytical procedure, WW samples were fortified with the recalcitrant compounds at a concentration of 0.1 g L^{-1} each. The characterization of the fortified WW is also presented in Table 1.

Table 1. Characterization of studied winery wastewater before and after being fortified with recalcitrant compounds.

Parameter	Collected WW	Fortified WW
COD (g L^{-1})	5.14 ± 0.07	5.7 ± 0.1
BOD ₅ (g L^{-1})	3.3 ± 0.3	2.3 ± 0.1
BOD ₅ /COD	0.65	0.39
EC _{50-48 h} (%)	64.8 ± 0.4	15.9 ± 0.8
Toxic units	1.54	6.31
TOC (g L^{-1})	1.48 ± 0.05	1.64 ± 0.04
IC (mg L^{-1})	26 ± 7	23 ± 8
TN (mg L^{-1})	4.1 ± 0.6	5 ± 1
Phthalic acid (mg L^{-1})	0.14 ± 0.02	100 ± 1
Tyrosol (mg L^{-1})	0.79 ± 0.05	99.9 ± 0.9
Catechin (mg L^{-1})	<0.10	100 ± 1
pH	4.8 ± 0.1	4.1 ± 0.1
EC ($\mu\text{S cm}^{-1}$)	223 ± 17	243 ± 13

2.3. Electrochemical Oxidation Experiments

EO experiments were performed in an undivided cylindrical cell containing 230 mL of the sample and operating in batch mode with stirring (250 rpm). The anode, a commercial BDD electrode purchased from Neocoat (La Chaux-de-Fonds, Switzerland), and the cathode, a stainless-steel plate, both with an immersed area of 10 cm^2 , were placed in parallel with an interelectrode gap of 0.3 cm and centered on the electrochemical cell. The power supply, a GW, Lab DC, model GPS-3030D (0–30 V, 0–3 A), was purchased from ILC (Lisbon, Portugal). The duration of the experiments was 6 h except otherwise stated, with samples being collected every hour for monitoring.

EO experiments using the synthetic samples were performed at an applied current density (j) of 300 A m^{-2} . For the degradation of WW fortified with the recalcitrant compounds, the influence of j , 300, 500, 700, and 900 A m^{-2} was evaluated. Because the WW presented a low electrical-conductivity (EC) value, EO experiments performed at 500, 700, and 900 A m^{-2} required the addition of a supporting electrolyte, Na_2SO_4 0.25 g L^{-1} . To assess the influence of the presence of the supporting electrolyte, EO experiments at 300 A m^{-2} were run with and without the addition of Na_2SO_4 0.25 g L^{-1} . Aiming to achieve the Portuguese chemical oxygen demand (COD) legal discharge limit (150 g L^{-1}),

the degradation of WW fortified with the recalcitrant compounds at 300 A m^{-2} was prolonged for 14 h. A graphical representation of the performed EO experiments is presented in Supplementary Material Figure S1.

All experiments were performed in triplicate, with reproducibility found in all studied experimental conditions. Results presented in Section 3 correspond to the mean values from different replicas.

2.4. Analytical Methods

COD determinations were performed according to the closed reflux and titrimetric method [25]. Biochemical oxygen demand (BOD_5) evaluation followed the respirometric method described elsewhere [26]. Total organic carbon (TOC), inorganic carbon (IC), and total nitrogen (TN) were measured in a Shimadzu TOC-VCPH analyzer combined with a TNM-1 unit purchased from Izasa Scientific (Carnaxide, Portugal).

Phthalic acid, tyrosol, and catechin concentrations were determined by high-performance liquid chromatography (HPLC) utilizing a Shimadzu 20A Prominence HPLC system equipped with diode array detector SPD-M20A, column oven CTO-20AC, and an LC-20AD SP pump, all purchased from Izasa Scientific (Carnaxide, Portugal). We used an RP-18 reversed-phase Purospher STAR column ($250 \times 4 \text{ mm}$ (i.d.), $5 \mu\text{m}$), purchased from VWR International (Amadora, Portugal). The elution was performed isocratically with a mixture of phosphoric acid aqueous solution (0.1%):acetonitrile, 85:15 (v/v), at a flow rate of 1 mL min^{-1} and $35 \text{ }^\circ\text{C}$. The detection wavelength was 195 nm for phthalic acid, 192 nm for tyrosol, and 202 nm for catechin. All used chemicals were HPLC-grade and supplied by Sigma-Aldrich (Lisbon, Portugal). Solutions were prepared with ultrapure water obtained from a Milli-Q system (Merck, Lisbon, Portugal).

Ecotoxicity towards *Daphnia magna* was evaluated through Daphtoxkit F microbiotest DM230921 purchased from Ambifirst (Moita, Portugal). The concentration responsible for 50% of immobilization, EC_{50} , was calculated using the standard data-processing method Daphtoxkit F spreadsheet by measuring the number of immobilized *D. magna* neonates exposed to different dilutions of the WW samples. Toxicity results expressed in terms of toxicity units (TU) were determined according to Equation (1) [27].

$$\text{TU} = \frac{100}{\text{EC}_{50}(\%)} \quad (1)$$

pH was measured with a HANNA pH meter (HI 931400), and electrical conductivity with a Mettler Toledo conductivity meter (SevenEasy S30K), both purchased from MT Brandão (Oporto, Portugal).

3. Results and Discussion

3.1. Electro-Oxidation of Synthetic Samples

Figure 1 presents the variation in time of phthalic acid, tyrosol, and catechin concentrations, during the EO experiments run with the synthetic samples at 300 A m^{-2} .

Sample composition influences the removal rate of the recalcitrant compounds, and catechin presented the highest removal rate in all the studied experimental conditions, meaning that catechin is more easily degraded than phthalic acid or tyrosol is. Since catechin presents a more complex molecular structure than that of other studied pollutants (Supplementary Material Figure S2), this was not expected. According to the literature, the first oxidation step of this molecule, 2-(3,4-dihydroxyphenyl)-3,4-dihydro-2H-1-benzopyran-3,5,7-triol, may be: (i) the formation of a ketone group in the C6 of the benzopyran structure, followed by the formation of catechuic acid and 2,4,6-trihydroxybenzoic acid (Supplementary Material Figure S3a) [28,29]; (ii) the formation of a semiquinone followed by the formation of quinone 4-(3,5,7-trihydroxy-3,4-dihydro-2H-1-benzopyran-2-yl)cyclohexa-3,5-diene-1,2-dione (Supplementary Material Figure S3b) [30]; or (iii) the formation of an intramolecularly cyclized derivative when in the presence of reactive oxygen species (Supplementary Material Figure S3c) [31]. In all cases, the first catechin

oxidation product was not detected at the HPLC conditions for catechin detection, explaining the fast catechin concentration decay. Regarding PhA and T, with only one aromatic ring, complete electro-oxidation must be easier after ring cleavage, since this step leads to smaller byproducts than those from C. This fact is corroborated by combustion efficiency η_C that may be determined according to Equation (2), where TOC and COD are in mg L^{-1} , n is the number of electrons transferred to the electrode in the complete oxidation of the organic compound (Equation (3)), and x is the number of carbon atoms in the organic molecule [32].

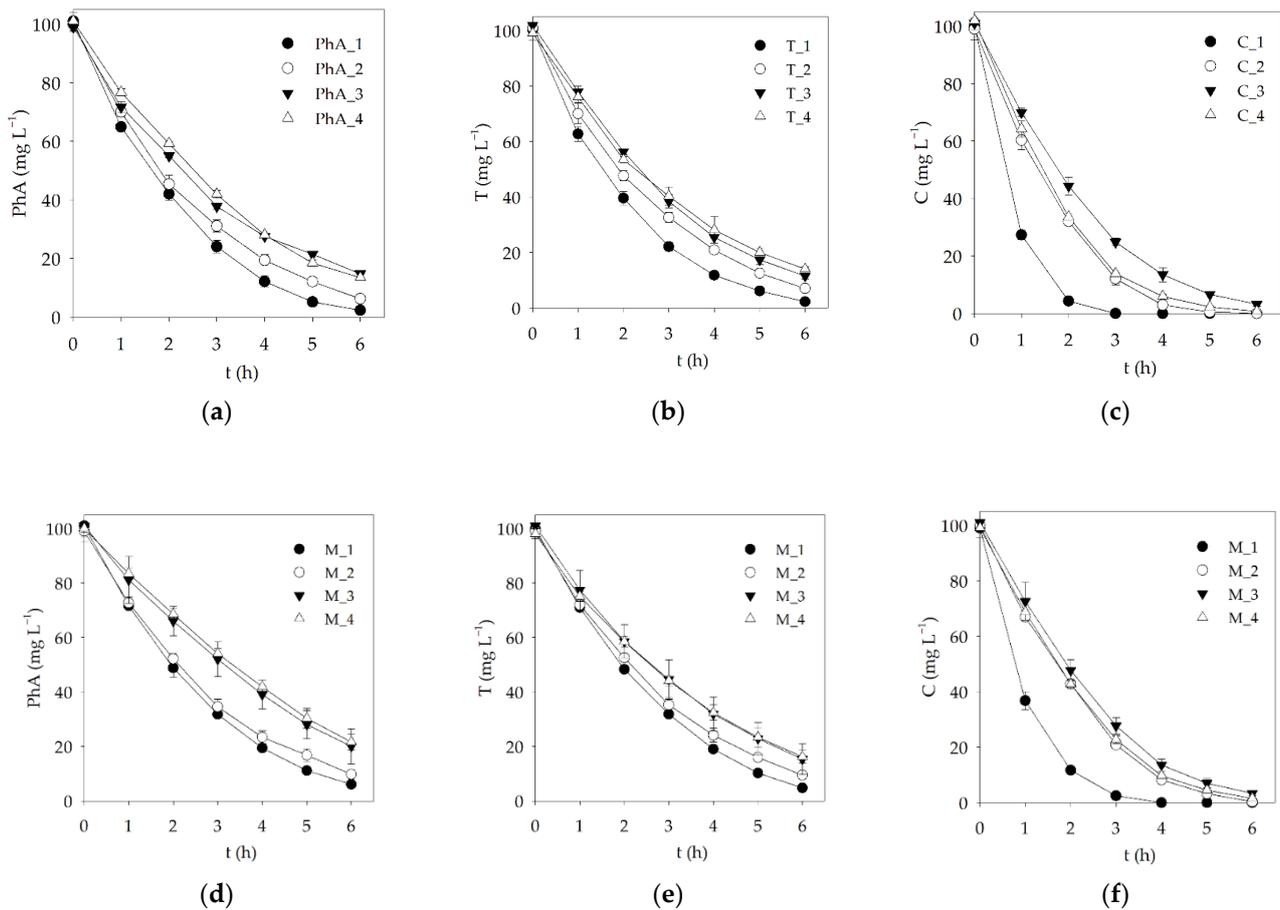
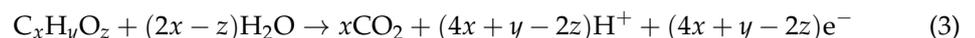


Figure 1. Decay in time of phthalic acid, tyrosol, or catechin concentrations during EO experiments ($j = 300 \text{ A m}^{-2}$) performed with synthetic samples with different compositions: (a) PhA in PhA_1 to PhA_4; (b) T in T_1 to T_4, (c) C in C_1 to C_4; (d–f) PhA, T and C, respectively, in mixtures of PhA + T + C.

$$\eta_C = \frac{32}{12} \times \frac{n}{4x} \times \frac{d\text{TOC}}{d\text{COD}} \quad (2)$$



For this calculation, it is necessary to attain the slope of the TOC vs. COD plot (Figure 2) for the different electrodegradation assays run with PhA, T or C solutions in the presence of the inorganic ions (PhA_1, T_1, and C_1, respectively). The calculated combustion efficiencies are presented in Table 2. This table also contains the theoretical TOC vs. COD slope obtained by calculating TOC and COD with the concentration of organic molecules determined by HPLC (Figure 1).

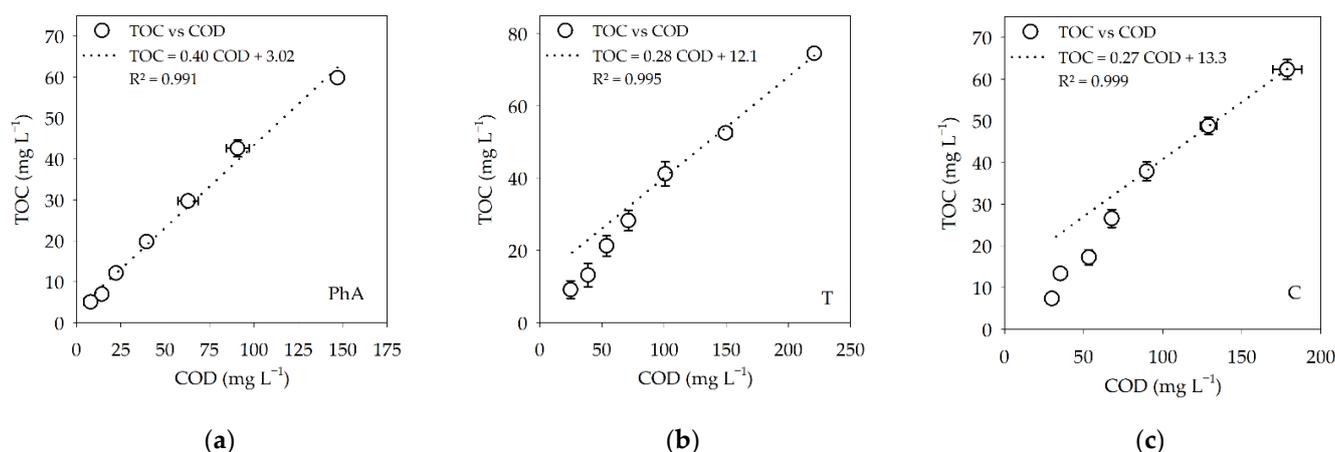


Figure 2. TOC vs. COD plots for EO assays performed with (a) PhA, (b) T, and (c) C in the presence of inorganic ions.

Table 2. Results from application of Equations (2) and (3) to experimental data obtained in EO assays performed with solutions PhA_1, T_1, and C_1.

Compound	<i>n</i>	<i>x</i>	TOC vs. COD Slope		η_c Exp.
			Experimental	Theoretical	
PhA_C ₈ H ₆ O ₄	30	8	$y = 0.40x + 3.02$; $R^2 = 0.991$ (0–6 h)	0.40	1.00
T_C ₈ H ₁₀ O ₂	38	8	$y = 0.28x + 12.1$; $R^2 = 0.995$ (0–2 h)	0.31	0.89
C_C ₁₅ H ₁₄ O ₆	62	15	$y = 0.27x + 13.6$; $R^2 = 0.999$ (0–2 h)	0.36	0.74

In fact, although catechin presented the highest removal rate, it showed the lowest combustion efficiency, meaning that the molecule is quickly converted into another product rather than being completely oxidized. A different pathway was presented by phthalic acid with a constant combustion efficiency of 1, meaning that the molecule was converted into carbon dioxide and water without accumulating byproducts. Regarding tyrosol, after 2 h, the presence of byproducts had to be significant, although it presented high combustion efficiency during this first period. Comparing the TOC vs. COD slope obtained from experimental TOC and COD values or from concentrations determined by HPLC showed: (i) for PhA, slopes were equal, meaning that this molecule was easily converted into H₂O and CO₂, and any byproduct that may have been formed rapidly suffered complete oxidation; (ii) regarding T, the experimental and theoretical slopes were similar, which corroborates the high combustion efficiency; (iii) for C, the theoretical slope was much higher, pointing to a quick conversion of C into byproducts rather than its complete oxidation. Considering that, of the studied recalcitrant compounds, catechin has the most complex molecular structure, its lower combustion efficiency may have been due to mass transport limitations to the anode surface, which favors oxidation in bulk instead of oxidation on the anode surface [18]. According to the literature, during the EO process, when chloride is present in the solution, as in the case of the prepared synthetic samples, active chlorine species that are formed promote the indirect oxidation of organic compounds in the bulk of the solution, which favors the partial oxidation (conversion) of organic compounds instead of their complete mineralization [18].

For all studied recalcitrant compounds, the highest removal rate was observed for solutions containing only the recalcitrant compound(s) and inorganic salts, since there were no other organic compounds in solution to compete with the recalcitrant compounds oxidation. With the sequential addition of the carboxylic acids and alcohols, a decrease in the removal rate of the recalcitrant compounds was observed, which was consistent with the increase in organic load content. However, the final addition of the sugars, which increased the COD from approximately 12 to 32 g L⁻¹, presented a differentiated

effect on the removal rate of the different recalcitrant compounds. When compared to the degradation in the presence of ions + carboxylic acids + alcohols, the addition of sugars increased the catechin removal rate; for phthalic acid and tyrosol, no significant change was observed. Since catechin degradation may involve the formation of radical species, there is the possibility of this radical species reacting with sugars to rapidly originate byproducts that are not detected.

3.2. Electro-Oxidation of Winery Wastewater

The characterization of the WW samples before and after being spiked with the recalcitrant compounds (Table 1), confirms the low biodegradability and high toxicity of the recalcitrant compounds in study, reinforcing the need to apply treatment technologies capable of degrading these pollutants into more biodegradable and less toxic compounds. Although both WW samples (before and after being spiked) are classified as toxic, according to the toxicity classification reported by Pablos et al. [27], the toxicity towards *D. magna* of the WW sample increased by 4.1-fold after being spiked with the recalcitrant compounds. The biodegradability index (BOD₅/COD) was reduced from 0.65 to 0.39 with the addition of the recalcitrant compounds. According to the literature, if BOD₅/COD is higher than 0.6, the wastewater is fairly biodegradable; however, if it is lower, biodegradation is relatively slow, and completely inhibited for BOD₅/COD values lower than 0.3 [33].

Comparing this to the average WW characterization reported in the literature [4] shows that, although the TOC value of the WW sample utilized in this study was above the average, the COD and BOD₅ were much lower. The salts content inferred from the EC value, and the concentration in tyrosol in the WW in study were much lower than the average values reported in the literature [4,11]. These differences in WW composition are mainly ascribed to differences in vinification processes and techniques, volume of utilized water, and overall winery design [4].

The electro-oxidation of WW fortified with PhA, T, and C was performed at different applied current densities, 300 to 900 A m⁻², to study the influence of j in the recalcitrant compound removal rate. For experiments performed at j higher than 300 A m⁻², the addition of a supporting electrolyte, Na₂SO₄ 0.25 g L⁻¹, was required due to the low electrical conductivity presented by the WW.

The influence of the supporting electrolyte on EO performance was assessed at 300 A m⁻². The obtained results (Supplementary Material Figure S4) showed that, although COD and TOC removal rates were not significantly affected by the addition of Na₂SO₄, the removal rate of the recalcitrant compounds was slightly decreased, which could be ascribed to the parallel sulfate oxidation that, although in low extent due to the low sulfate concentration, might hinder the oxidation of the recalcitrant compounds.

Figure 3 presents the PhA, T, and C decays vs. electrical charge and time (insets) for EO experiments performed at 300 A m⁻² without supporting electrolyte addition, and at 500, 700, and 900 A m⁻², with the addition of Na₂SO₄ 0.25 g L⁻¹.

For all studied recalcitrant compounds and for a similar applied charge, a decrease in removal efficiency with the increase in j was observed, with the removal of the recalcitrant compounds being more efficient at the lowest applied current (300 A m⁻²). Nonetheless, the decay of recalcitrant compounds with time shows an increase in the removal rate of the compounds with j , which is in accordance with the enhanced production of oxidative species at higher currents, promoting faster compound degradation for comparable treatment time. The decrease in current efficiency with the increase in j regarding recalcitrant compound removal, is probably due to the faster oxidation of other compounds present in solution at higher j , which lead to oxidation byproducts that were rather more degraded than the recalcitrant compounds in study.

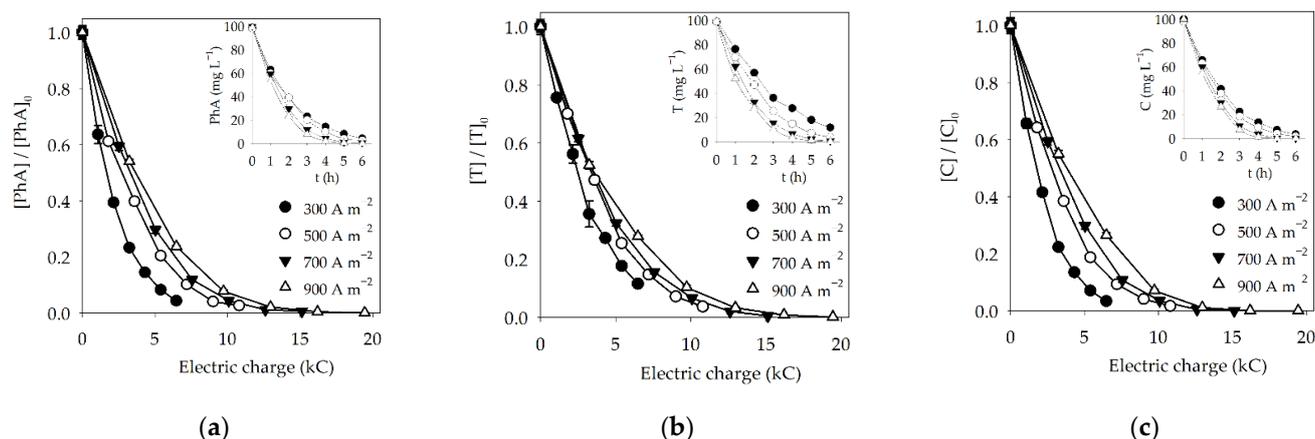


Figure 3. Variation with applied charge and time (insets) of (a) phthalic acid, (b) tyrosol, and (c) catechin concentrations for the EO experiments performed with spiked winery wastewater at different applied current densities.

For all the applied current densities, phthalic acid and catechin presented similar decays, with higher removal rates and efficiencies than those for tyrosol, indicating that phthalic acid and catechin are preferably degraded over tyrosol. Nevertheless, with the increase in j , the difference among tyrosol, phthalic acid, and catechin removal rates diminished. This could have been due to the higher availability of BDD(HO^\bullet) at higher j to simultaneously oxidize the different compounds, but it could also be related with the presence of the sulfate ions that had been added in the experiments performed at 500, 700, and 900 A m⁻². According to the literature, the slower decay of tyrosol could be due to its low reactivity with BDD(HO^\bullet) [34]. In the presence of sulfate ions from the supporting electrolyte addition, indirect oxidation through $\text{SO}_4^{\bullet-}$ and $\text{S}_2\text{O}_8^{2-}$ oxidants may also occur [18]. In the study of the influence of the supporting electrolyte on the EO performance at 300 A m⁻², the experiments performed without sulfate addition attained higher tyrosol removal rate (Supplementary Material Figure S4b). However, this reduction in T removal rate promoted by the presence of sulfate was lower than that observed for PhA and C. This can be ascribed to the formation of $\text{SO}_4^{\bullet-}$ and $\text{S}_2\text{O}_8^{2-}$ from sulfate oxidation, enhanced by the increase in j , which promotes tyrosol oxidation. Either way, at the highest studied j (900 A m⁻²), after 6 h assay, phthalic acid, tyrosol, and catechin concentrations were below 0.10 mg L⁻¹, showing that these recalcitrant compounds could be effectively degraded by EO even when present in real complex wastewater matrices.

In addition to recalcitrant compound removal, EO performance at the different studied j was evaluated in terms of organic load removal, pH evolution, biodegradability, and toxicity towards the *D. magna* of the treated samples, and energy consumption. Figure 4 shows COD and TOC decays, and the pH variation vs. electrical charge and time (insets) during the EO assays run at different j .

Contrary to what was observed for the removal of the recalcitrant compounds, COD and TOC decays with applied charge (Figure 4a,b) showed identical trends for the different applied j , indicating similar current efficiencies regarding the overall COD and TOC removals, probably because experiments were run under current control most of the time. This was corroborated by COD and TOC decays with time (insets of Figure 4a,b) that show an increase in removal rates with j , indicating that the process was operating under kinetic control, which is consistent with the high organic load presented by WW. Slightly lower current efficiency was observed for the highest applied j (900 A m⁻²), which might have been due to secondary reactions that were enhanced at higher j , such as oxygen evolution and inorganic ion oxidation [35]. For all studied j , higher COD removal was attained compared to that of TOC, probably due to the formation of low-molecular-mass byproducts with high oxidation degree, which is difficult to oxidize [36]. In a study performed by Lauzurique et al. [24] where industrial winery wastewater was treated by EO using a BDD

anode, carboxylic acids, namely, oxamic, acetic, and propionic acids, were identified in the final electrolyzed samples.

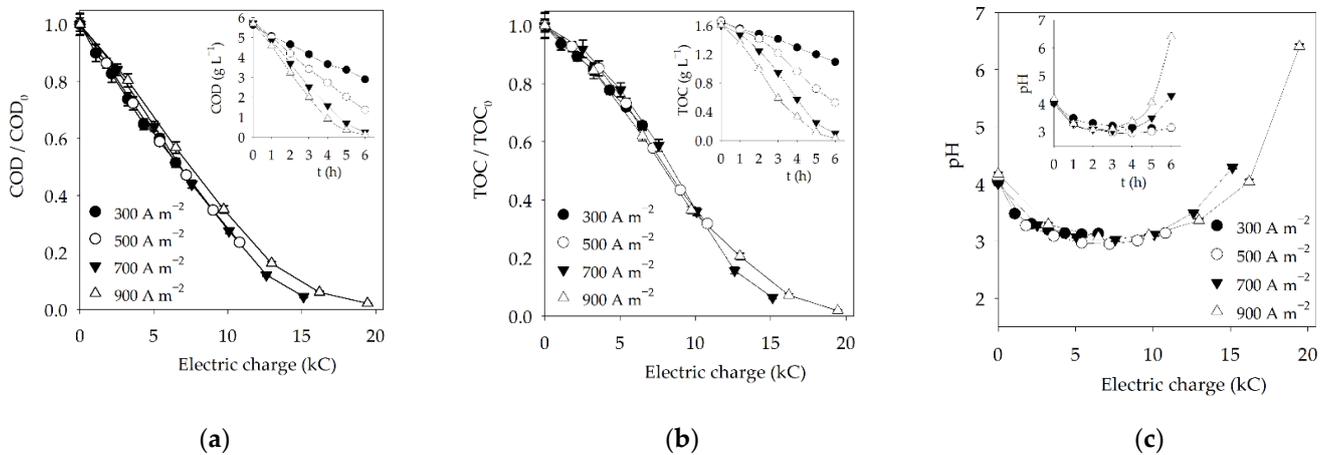


Figure 4. Variation with applied charge and with time (insets) of (a) COD, (b) TOC, and (c) pH for EO experiments performed with spiked winery wastewater at different applied current densities.

Regarding pH variation (Figure 4c), for all the j studied, a regular decrease was observed until the applied charge of approximately 7.5 kC. For applied charges above 7.5 kC, an increase in pH was observed. The decrease in pH observed for lower applied charges could be explained by the formation of carboxylic and inorganic acids, from the oxidation of organic and inorganic compounds, and by the release of H⁺ from redox reactions that may occur [35,37]. The posterior pH increase at higher applied charges could be ascribed to the suppression of reactions that most contribute to H⁺ in solution, and to the occurrence of secondary reactions, such as the hydrogen evolution reaction enhanced by the increase in j and by the decrease in organic matter likely to be oxidized [37–39]. As noticed by Candia-Onfray et al. [2], and Lauzurique et al. [24], the increase in pH during EO treatment is particularly important when WW has an acidic pH, as the one used in this study, since for wastewater discharge in water bodies, a pH between 6.0 and 9.0 is usually required [40].

Figure 5 presents the biodegradability index and ecotoxicity towards the *D. magna* of the final samples obtained after 6 h of EO treatment at the different j studied.

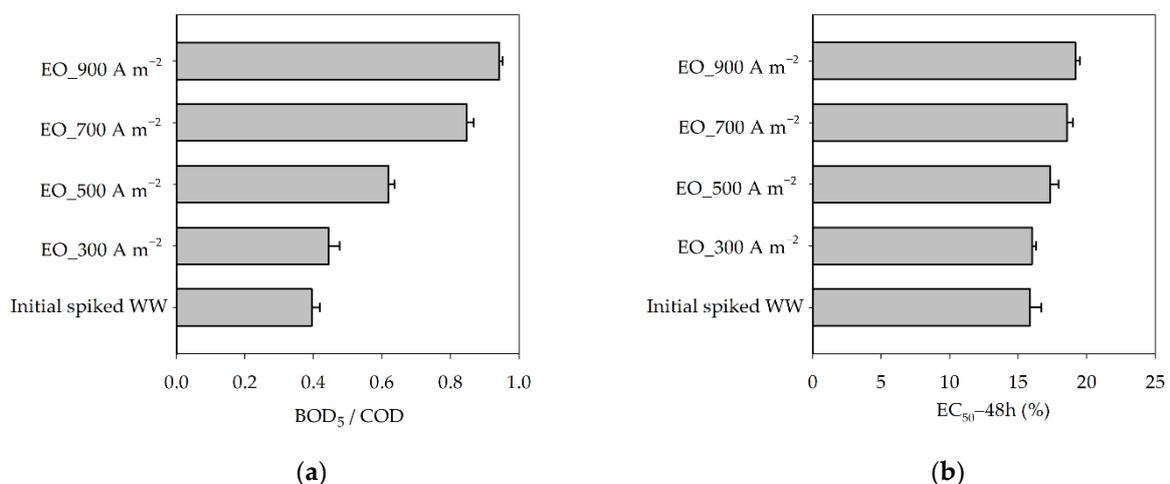


Figure 5. (a) Biodegradability index given by ratio BOD₅/COD; (b) ecotoxicity towards *D. magna* expressed in terms of EC_{50-48 h} (%) for initial WW sample spiked with recalcitrant compounds utilized in the EO experiments, and for final samples obtained after 6 h of EO treatment at different studied applied current densities.

For all applied j , an increase in BOD₅/COD and EC_{50–48 h} values was observed, compared to that of the initial WW sample spiked with the recalcitrant compounds, indicating that the oxidation products from the EO treatment are more biodegradable and less toxic towards *D. magna* than the original compounds. BOD₅/COD and EC_{50–48 h} values both increased with j , which was in accordance with the higher oxidation degree of the degradation products at higher j . However, whereas the biodegradability index significantly increased with j , the reduction in toxicity towards *D. magna* was less pronounced. At 900 A m⁻², a BOD₅/COD of 0.94 was attained, which indicates that almost the entire organic load of the sample was biodegradable. Nevertheless, toxicity towards *D. magna* was 5.22 TU, corresponding to a decrease of 1.09 TU, compared to the initial sample. These results indicate that, although the additional organic oxidation at higher j resulted in the formation of more biodegradable byproducts, they were still toxic towards *D. magna*. Acetic and propionic acids, identified in the literature as endproducts in WW treatment by EO using a BDD anode [24], presented EC_{50–48h} values towards *D. magna* of 18.9 and 22.7 mg L⁻¹, respectively, although they are readily biodegradable under aerobic and anaerobic conditions [41,42].

Considering all obtained results at the different studied j , it can be concluded that, for 6 h of EO treatment, the best results were attained at the highest applied j (900 A m⁻²). Besides removing recalcitrant compounds in more than 99.9%, EO treatment at 900 A m⁻² for 6 h led to samples with COD (124 mg L⁻¹) and pH (6.40) in compliance with the Portuguese legal discharge limits (COD ≤ 150 mg L⁻¹; 6.0 ≤ pH ≤ 9.0 [40]), TOC concentration of 31 mg L⁻¹, biodegradability index of 0.94, and 1.2-fold reduction in toxicity towards *D. magna*. Nevertheless, the higher the applied current in EO process, the higher the electric energy consumption and consequently the treatment cost, which can make the treatment process unfeasible [24].

Specific energy consumption E_{sp} in kWh (kg COD)⁻¹ attained at each j was calculated by means of Equation (4), where U is cell voltage in V resulting from the applied current intensity I in A, Δt is the duration of the treatment in s, V is the volume of treated wastewater in L, and ΔCOD is the removed COD in mg L⁻¹ during Δt . Obtained results showed an increase in E_{sp} with j , mainly due to the increase in cell voltage. At 300, 500, 700 and 900 A m⁻², E_{sp} values were 47, 51, 63 and 88 kWh (kg COD)⁻¹, respectively. The close E_{sp} values achieved at 300 and 500 A m⁻² were because, at 500 A m⁻², Na₂SO₄ 0.25 g L⁻¹ was added to the sample, which increased electrical conductivity and consequently decreased cell voltage. On the other hand, the high E_{sp} value observed at 900 A m⁻² compared to that obtained at lower j could be explained by the decrease in overall current efficiency at that j (Figure 4a), as described above.

$$E_{sp} = \frac{U \times I \times \Delta t}{3.6 \times V \times \Delta COD} \quad (4)$$

Recalcitrant compounds removal was more efficient in terms of applied charge at the lowest studied j , and the lowest E_{sp} was also achieved at 300 A m⁻², without the addition of supporting electrolyte being necessary. EO experiments were performed at these experimental conditions, with treatment time prolonged until the COD had been reduced to values below the Portuguese legal discharge limit (150 mg L⁻¹), which was 14 h. Figure 6 displays the phthalic acid, tyrosol, catechin, COD and TOC decays with time, and pH variation, and Table 3 presents the final attained values for the evaluated parameters after 14 h treatment.

Electric energy consumption E in kWh m⁻³ was calculated by means of Equation (5), where U is the average cell voltage in V resulting from the applied current intensity I in A, Δt is the duration of the treatment in h, and V is the volume of treated wastewater in L.

$$E = \frac{U \times I \times \Delta t}{V} \quad (5)$$

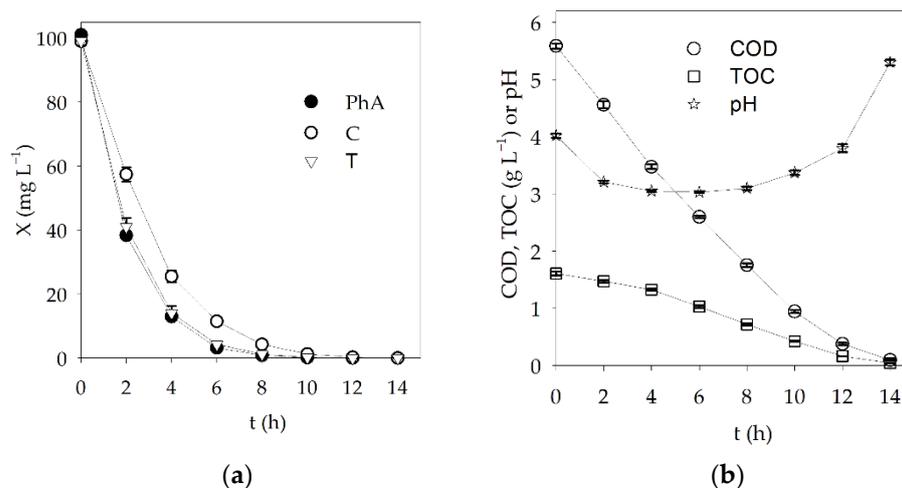


Figure 6. Variation with time of (a) PhA, T and C; and (b) COD, TOC, and pH for EO experiments performed with spiked winery wastewater at 300 A m⁻² for 14 h.

Table 3. Characterization of winery wastewater treated by EO, at 300 A m⁻² for 14 h, and energy consumption attained by the treatment.

Parameter	WW after Treatment
COD (mg L ⁻¹)	97 ± 2
BOD ₅ (mg L ⁻¹)	96 ± 3
BOD ₅ /COD	0.99
EC _{50-48 h} (%)	20.4 ± 0.6
Toxic units	4.90
TOC (mg L ⁻¹)	41 ± 3
IC (mg L ⁻¹)	2.1 ± 0.5
TN (mg L ⁻¹)	3.8 ± 0.3
Phthalic acid (mg L ⁻¹)	<0.10
Tyrosol (mg L ⁻¹)	<0.10
Catechin (mg L ⁻¹)	<0.10
pH	5.30 ± 0.06
EC (μS cm ⁻¹)	205 ± 11
E _{sp} (kWh (kg COD) ⁻¹)	53
E (kWh m ⁻³)	292

After 12 h treatment at 300 A m⁻², phthalic acid and catechin concentrations were below 0.10 mg L⁻¹, but, for tyrosol, a concentration below 0.10 mg L⁻¹ was only attained after 14 h assay. Regarding COD, a regular linear decay was observed until the 10th hour of treatment, which is typical of an electrochemical reaction controlled by current. After that time and due to the reduction in COD, different behavior was observed, since part of the process is diffusion-controlled. On the other hand, DOC decay was slower in the first hours of assay, since during the initial period of EO, most of the organics are partially oxidized rather than completely mineralized. pH variation followed the same trend as that observed for EO experiments run at higher j , with an initial decrease until approximately the 5th hour assay and a subsequent increase until the end of the treatment. Nevertheless, the final pH after 14 h treatment (5.30) was below the Portuguese legal discharge limit ($6.0 \leq \text{pH} \leq 9.0$ [40]).

When compared to the 6 h treatment at 900 A m⁻², the 14 h treatment at 300 A m⁻² attained similar results, with less 22% of applied charge. COD removal, biodegradability index, and EC_{50-48 h} after 14 h treatment at 300 A m⁻² were even slightly higher than those obtained for the 6 h treatment at 900 A m⁻². However, although the biodegradability index of the treated sample was close to 1, which indicated that the sample was highly

biodegradable, toxicity towards *D. magna*, although reduced, was still high, indicating that the few oxidation byproducts that remained in the solution presented ecotoxicity towards *D. magna*.

As expected, the specific energy consumption of the 14 h treatment at 300 A m^{-2} ($53 \text{ kWh (kg COD)}^{-1}$) was much lower than that of the 6 h treatment at 900 A m^{-2} ($88 \text{ kWh (kg COD)}^{-1}$), although in the EO treatment performed at 300 A m^{-2} , no supporting electrolyte was added. The electric energy consumption attained for the 14 h treatment at 300 A m^{-2} (292 kWh m^{-3}) was much higher than that reported in the literature for WW treatment by EO with BDD anode (96 kWh m^{-3}) [2]. Nevertheless, in the treatment described in the literature, a supporting electrolyte, 50 mM of Na_2SO_4 ($\sim 7.1 \text{ g L}^{-1}$), was added to the WW, which increased the electrical conductivity, and consequently reduced the cell potential and decreased energy consumption. Although the addition of salts is described as beneficial for the EO process [2], the salt cost and the logistics of this additional operation need to be considered besides the final conductivity of the sample.

4. Conclusions

Electrochemical oxidation with a BDD anode is effective in the degradation of phthalic acid, tyrosol, and catechin in winery wastewater.

Experiments performed with synthetic samples showed that the composition of wastewater influences the removal of recalcitrant compounds by EO:

- The presence of carboxylic acids and alcohols decreases the removal rate of the recalcitrant compounds. However, when sugars are added, no significant decrease in the removal rates was observed. In fact, the presence of sugars showed to be beneficial for catechin removal.
- Independently of sample composition, catechin is more rapidly degraded than phthalic acid and tyrosol are. However, it presented the lowest combustion efficiency, meaning that the molecule is quickly converted into another product rather than being completely oxidized. Conversely, phthalic acid is easily mineralized, and any byproduct that may be formed rapidly suffers complete oxidation.

The electro-oxidation of real WW samples spiked with PhA, T, and C showed that these recalcitrant compounds could be successfully removed from real matrices, with the efficiency of the process being dependent on the applied current density:

- Although the removal rate of recalcitrant compounds increases with the applied current density, removal efficiency decreases with the increase in j , probably due to the enhancement of parallel oxidation reactions at higher j .
- The increase in j also promotes higher COD and TOC removal along with an increase in the biodegradability index and a reduction in the toxicity towards *D. magna*. Nevertheless, the specific energy consumption was significantly increased.

The increase in treatment time proved to be a feasible solution for WW electro-oxidation at lower j , enabling complete WW treatment at optimized efficiency and without requiring the addition of reagents. After 14 h treatment at 300 A m^{-2} , a treated sample was obtained with PhA, T, and C concentrations below 0.10 mg L^{-1} , a COD of 97 mg L^{-1} , a biodegradability index of 0.99, and 1.3-fold reduction in toxicity towards *D. magna*.

Ecotoxicological evaluation showed that EO treatment leads to WW samples that are less toxic towards *D. magna* than the original ones are. Still, the nontoxic level was not attained, which was ascribed to the presence of oxidation endproducts, such as acetic and propionic acids that, although readily biodegradable, present toxicity towards the model organism.

Study findings revealed the potential of EO for the degradation of recalcitrant compounds in winery wastewater, providing a feasible environmentally friendly solution for the management of this kind of wastewater. Different electrode materials, cell configurations, and experimental conditions should be further investigated to reduce the energetic costs and the ecotoxicity of the treated wastewater.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w14050750/s1>, Table S1: Composition and physicochemical characteristics of the synthetic samples used in the experiments; Figure S1: Graphical representation of the EO experiments performed; Figure S2: Molecular structure of (a) phthalic acid; (b) tyrosol; and (c) catechin; Figure S3: Degradation pathways for catechin degradation according to the literature: (a) adapted from Hopper and Mahadevan and from Vuong et al. [28,29]; (b) adapted from Janeiro and Brett [30]; and (c) adapted from Shishido et al. [31]; Figure S4: Decay in time of (a) phthalic acid; (b) tyrosol; (c) catechin; (d) COD; (e) TOC; and (f) pH, for the EO experiments performed with spiked winery wastewater, at an applied current density of 300 A m^{-2} , with and without the addition of supporting electrolyte, Na_2SO_4 0.25 g L^{-1} .

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