



Electrochemical oxidation of model compounds and olive mill wastewater over DSA electrodes: 1. The case of Ti/IrO₂ anode

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ABSTRACT

The electrochemical oxidation of olive mill wastewater (OMW) and model compounds over a Ti/IrO₂ anode was studied by means of cyclic voltammetry and bulk electrolysis. Experiments were conducted at 1300 mg/L initial COD, 0–1.23 V vs SHE and 1.4–1.54 V vs SHE potential windows, 50 mA/cm² current density, 0–25 mM NaCl, 60–80 °C temperature and acidic conditions. The reactivity of model compounds decreases in the order phenol ≈ p-coumaric acid > cinnamic acid > caffeic acid. Partial and total oxidation reactions occur with the overall rate following zero-order kinetics with respect to COD and increasing with temperature. Oxidation of OMW at 43 Ah/L, 80 °C and in the presence of 5 mM NaCl leads to complete color and phenols removal, elimination of ecotoxicity but moderate (30%) COD reduction. Similar performance can be achieved at 6 Ah/L in the presence of 15 mM NaCl. In the absence of salt, the respective color and phenols removal (at 6 Ah/L) is less than 10%. Excessive salinity (25 mM), although does not change color, phenols and COD removal, has an adverse effect on ecotoxicity.

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1. Introduction

The foodstuff processing industry based on olive oil extraction is an economically important activity for many regions of the Mediterranean Sea area. This process results in large quantities of recalcitrant olive mill wastewaters (OMW) whose chemical oxygen demand (COD) may reach values as high as 220 g/L and suspended solids up to 190 g/L depending on various factors such as olive variety, harvesting time, climatic conditions and the oil extraction process. The phytotoxicity and strong antibacterial action of OMW have been attributed to the phenolic content that also appears to vary regarding its composition and concentration. More than thirty phenolic compounds have been identified in OMW at concentrations ranging from 0.5 to 24 g/L. The presence of these recalcitrant organic compounds constitutes one of the major obstacles in the detoxification of OMW [1].

Therefore, increasing concern has been expressed about the effective treatment and safe disposal of OMW in the environment. 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 [2]. Advanced oxidation processes have been employed in an attempt to reduce the organic load and bio-recalcitrance of these wastewaters. More specifically, electrochemical meth-

ods have attracted a great deal of attention basically due to the increased efficiencies that can be achieved using easy to operate and control, compact bipolar electrochemical reactors. In particular, the industrial use of dimensionally stable anodes (DSA) for wastewater treatment has led to technological solutions, thus reducing operational and investment costs [3].

Several studies report the use of DSA for the oxidation of model aqueous solutions containing polyphenolic compounds typically found in OMW with emphasis on titanium based on different oxides such as IrO₂, RuO₂, SnO₂ [4–10]. On the other hand, only few report the anodic oxidation of actual OMW over DSA. Panizza et al. [11] studied the electrochemical treatment of OMW over a Ti/TiRuO₂ anode. Electrolysis for 30 h at 5 A current intensity and in the presence of 5 g/L NaCl yielded complete removal of COD, aromatics and color. Besides, Un et al. [12,13] achieved almost complete removal of COD, phenols, turbidity and oil-grease after 8 h of treatment over a Ti/RuO₂ anode at 135 mA/cm² current density, 2 M NaCl and 20 °C. Moreover, other traditional electrodes have been used for the treatment of OMW. Israilides et al. [14] investigated the electrooxidation of OMW over a Ti/Pt anode. They found that electrolysis for 10 h at 4% (w/v) NaCl and 0.26 A/cm² reduced COD, total organic carbon (TOC) and the total phenolic content by 93, 80 and 99% respectively. A Ti anode covered by a thin film of Ta/Pt/Ir alloy has also been studied for OMW treatment. Giannis et al. [15] reported 71% COD removal after 8 h of electrolysis at 3% (w/v) NaCl and 16 V, while color and turbidity were completely removed after short periods of treatment. Besides, Gotsi et al. [16] found that complete decolorization and phenol degradation were achieved at treatment times up

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Table 1
Properties of raw OMW used in this study.

| Property | Before centrifugation | After centrifugation |
|----------------------|-----------------------|----------------------|
| COD (g/L) | 47 | 40 |
| TOC (g/L) | 16.9 | 14 |
| Total phenols (g/L) | 8.1 | 3.5 |
| Total solids (g/L) | 50.3 | 0.6 |
| pH | 4.6 | 4.4 |
| Conductivity (mS/cm) | 17 | 18 |

to 1 h. However, COD removal never exceeded 40% after 4 h of electrolytic treatment. Belaid et al. [17] in a recent study report 90% decolorization and nearly 85% removal of phenols at high current densities using a two compartments type electrochemical reactor separated by a cation-exchange membrane equipped with electrodes from platinized expanded N type titanium (0.85 g of Pt/dm²). Moreover, electrocoagulation over iron and aluminium electrodes was found capable of reducing organic load as well as decolorizing OMW [12,13,18–20].

Although the electrochemical oxidation of OMW has been given considerable attention, the use of DSA like Ti/IrO₂ has never been attempted before. The aim of this work was to study the behavior of Ti/IrO₂ anode for the electrochemical oxidation of model solutions containing various aromatic compounds (p-coumaric, cinnamic, caffeic acids) typically found in OMW as well as actual OMW. Moreover phenol, despite the fact that it is not contained in OMW, was studied as a model compound since it is a typical precursor for the formation of many polyphenolic compounds found in OMW. For this purpose, cyclic voltammetry and bulk electrolysis were carried out to explore the activity of Ti/IrO₂ anode under different experimental conditions.

2. Experimental and analytical

2.1. Materials

2.1.1. DSA preparation

The Ti/IrO₂ working electrode was prepared by thermal decomposition of 250 mM H₂IrCl₆ (Acros Organics, 40%) metal precursor dissolved in isopropanol (Fluka, 99.5%), on a disc-shaped titanium support. The titanium substrate was sandblasted to ensure good adhesion of the deposit on its surface. Following sandblasting, the substrate was treated using a 1 M oxalic acid solution to clean its surface from residual sands. The substrate was then dried in an oven at 70 °C and weighed. The precursor solution was spread on the titanium substrate forming a thin film layer on the electron surface. Afterwards, the sample was treated in an oven for 10 min to allow solvent evaporation. This step was followed by treatment in the furnace for the thermal decomposition of the precursor solution at 500 °C in air for 10 min. The same procedure was repeated five times and, after the last IrO₂ coating, the electrode remained at 500 °C for 1 h. The final IrO₂ loading was 0.4 mg/cm².

2.1.2. Actual effluent and model phenolic solutions

OMW was provided by a three-phase olive oil mill located in Chania, W. Crete, Greece. The effluent was subjected to centrifugation for 15 min at 3500 rpm to remove most of its solids. The effluent has a strong olive oil smell and a dark black-brown color with maximum absorbance in the visible region at 450 nm. Its main properties before and after centrifugation are given in Table 1. Experiments with OMW were conducted at about 1300 mg/L initial COD (the effluent was diluted with 1 M HClO₄ solution in ultrapure water).

p-Coumaric acid (C₉H₈O₃ ≥ 98%), caffeic acid (C₉H₈O₄ ≥ 97%) and cinnamic acid (C₉H₈O₂ ≈ 99%) were purchased from Fluka, while phenol (C₆H₆O ≥ 99%) was purchased from Sigma–Aldrich. These four compounds were used to prepare model aqueous solu-

tions whose initial COD was about 1300(±5%) mg/L, thus matching the COD of the diluted OMW. All compounds were dissolved in 1 M HClO₄ electrolyte. It should be noted that cinnamic acid (which is the parent molecule of p-coumaric and caffeic acids) is an aromatic rather than phenolic compound; however and for the sake of clarity, all model solutions will be referred to as phenolic.

2.2. Cyclic voltammetry

Cyclic voltammetry (CV) was carried out in a conventional three-electrode cell using a computer-controlled potentiostat (AMEL 2053) with a function generator (AMEL 7800). Ti/IrO₂ electrode was used as the working electrode, Hg/Hg₂SO₄·K₂SO₄ (saturated) as reference electrode and Pt wire as counter electrode. At each voltammetric measurement, several scans were obtained in order to study two potential windows, one between 0 and 1.23 V vs SHE (i.e. before oxygen evolution) and another between 1.4 and 1.54 V vs SHE. The electrolyte was either 1 M HClO₄ or one of the solutions of the model compounds described above. Solutions were magnetically stirred for 20 min to ensure complete mixing.

2.3. Bulk electrolysis

Electrochemical experiments were conducted in a batch type, laboratory scale electrolytic cell purchased from Metrohm. The electrochemical reactor was a single-compartment cell comprising a Ti/IrO₂ anode with an active working area of 12.5 cm² and a zirconium cathode enclosed in a porous porcelain pot; stirring was provided by a magnetic bar. The temperature remained constant by means of a temperature control system. A condenser was used to prevent liquid evaporation at increased temperatures. The volume of the reaction mixture was 110 mL. All experiments were carried out in acidic conditions, using 1 M HClO₄ solution as the main electrolyte. During each electrolytic run samples of 3 mL were drawn from the reactor at certain time intervals, filtered with a 0.45 μm filter to remove residual solids and analyzed in terms of COD, total phenolic content (TPH), TOC and color. Representative runs were performed in triplicate to check for reproducibility which was found to be quite good, within ±5%. Instantaneous current efficiency (ICE) of the anodic oxidation computed from COD values according to the following equation:

$$ICE = \frac{COD_0 - COD_t}{8I\Delta t} FV \quad (1)$$

where COD₀ (g/L) and COD_t (g/L) correspond to concentrations at $t=0$ and $t=t$ (s) respectively, I is the applied current (A), F is the Faraday constant (96,487 C/mol), V is the liquid holdup (L) and 8 is the equivalent mass of oxygen (g/eq).

2.4. Analytical measurements

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). TPH was determined colorimetrically at 765 nm on a Shimadzu UV 1240 spectrophotometer using the Folin-Ciocalteu reagent according to a modified micromethod described in detail elsewhere [21]. TOC was monitored using a Shimadzu 5050A TOC analyzer. Sample absorbance was scanned in the 400–800 nm wavelength band on a Shimadzu UV 1240 spectrophotometer. Changes in sample absorbance at 450 nm were monitored to assess the extent of decolorization that had taken place during treatment.

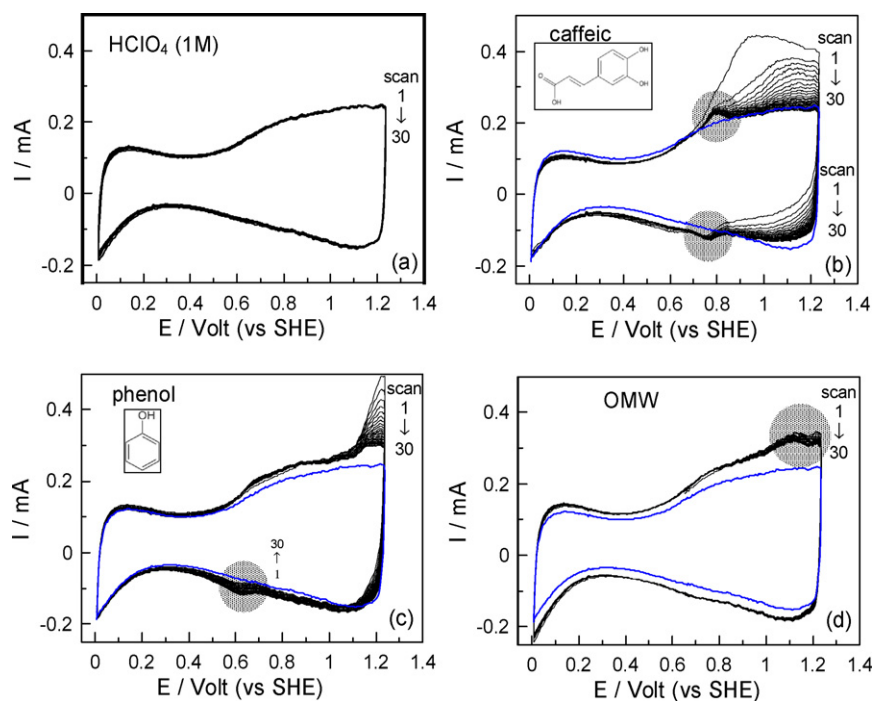


Fig. 1. Cyclic voltammograms over Ti/IrO₂ anode using 1 M HClO₄ electrolyte (a) without organics; (b) with 4.51 mM caffeic acid; (c) with 5.8 mM phenol; (d) with OMW at 1300 mg/L COD. Evolution of cyclic voltammograms with increasing number of polarization cycles (scan 1 → 30); scan rate = 20 mV/s; T = 30 °C; potential window = 0–1.23 V vs SHE. The steady state voltammogram of HClO₄ (Fig. 1a) is shown also in figs. b, c and d. (For interpretation of the references to color in the text related to the figure, the reader is referred to the web version of the article.)

The luminescent marine bacteria *V. fischeri* were used to assess the acute ecotoxicity of samples before and after treatment. The inhibition of bioluminescence of *V. fischeri* exposed to samples for 15 min at 15 °C was measured using a LUMISTox analyzer (Dr. Lange, Germany) and the results were compared to an aqueous control. For BOD₅ measurements, samples were diluted appropriately, inoculated with 1% activated sludge and changes in dissolved oxygen concentration were monitored.

3. Results and discussion

3.1. CV measurements

The electrochemical activity of Ti/IrO₂ electrode was studied using aqueous solutions of 1 M HClO₄ with or without organic content. CV was carried out at two different potential windows (i.e. 0–1.23 V vs SHE where no oxygen evolution takes place and 1.4–1.54 V vs SHE). Fig. 1 shows cyclic voltammograms of four solutions, namely the electrolyte alone, OMW at 1300 mg/L initial COD, 4.51 mM caffeic acid and 5.8 mM phenol; for the two model phenolic solutions, the initial concentration, in terms of COD, is similar to that of actual OMW. Fig. 1a shows the behavior of the electrode under many cycles in the region 0–1.23 V vs SHE using 1 M HClO₄ only. Besides the fact that there is no oxygen evolution (as it would be expected), electrode stability on repeated scans is quite remarkable. The shape of the voltammogram does not change by increasing the scan number, while a pair of anodic and cathodic peaks appears at about 1.1 V vs SHE due to the oxidation of IrO₂ to IrO₃ and the reduction of IrO₃ to IrO₂ respectively. Fig. 1b shows cyclic voltammograms for caffeic acid oxidation. The anode displays a significant and rapidly changing catalytic activity. Oxidation and reduction peaks can be observed in the scans. Amongst them a high oxidation peak around 0.97 V vs SHE (due to oxidation of the acid) which decreases dramatically after the second scan, whereas a pair of anodic and cathodic peaks around

0.8 vs SHE and 1.1 V vs SHE remains after stabilization of the system. It is worth noticing that following an infinite (theoretically) number of scans, the system will probably reveal the same behavior as in the case where no organic compound is added in the electrolyte (see blue line corresponding to 1 M HClO₄). According to recent reports concerning the stability of DSA-type electrodes [22,23], this rapid decrease of catalytic activity can predominantly be attributed to polymeric product deposition at the electrode surface and, to a lesser extent, to the organic concentration decrease in the micro-area near the working electrode. The above argument is strengthened from the fact that the last voltammogram of Fig. 1b was reproducible repeating one or more scans with a fresh caffeic acid solution but without cleaning the electrode. Besides, according to previous reports, Ti/IrO₂ may be considered as a typical example of “active” electrode (the redox potential of the IrO₃/IrO₂ couple, 1.35 V vs SHE, is close to the standard potential of O₂ evolution, 1.23 V vs SHE) and, thus, it is suitable for electrosynthesis or partial oxidation reactions. The fact that caffeic acid is relatively recalcitrant to electrochemical oxidation (as will be shown in following paragraphs) may be related to electrode deactivation due to polymeric compounds being formed and deposited on the electrode surface (fouling). On the other hand, this type of deactivation is less pronounced for phenol oxidation. As seen in Fig. 1c, the system is stabilized after the first 10 cycles and this is consistent with the fact that phenol is more readily electrochemically oxidized (as will also be shown in following paragraphs). The appearance of the pairs of anodic and cathodic peaks around 0.8 and 1.1 V for the case of caffeic acid (Fig. 1b) and around 0.6 V for the case of phenol is a direct proof for intermediate products formation (which could be for example phenoxy radicals talking for the case of phenol oxidation or products of quinine-like structure) during the oxidation. Regarding OMW, its voltammogram shown in Fig. 1d is comparable to that of the electrolyte in the absence of organic compounds (see blue line in Fig. 1d). Although one would expect to see several oxidation and reduction peaks due to the redox reactions of the

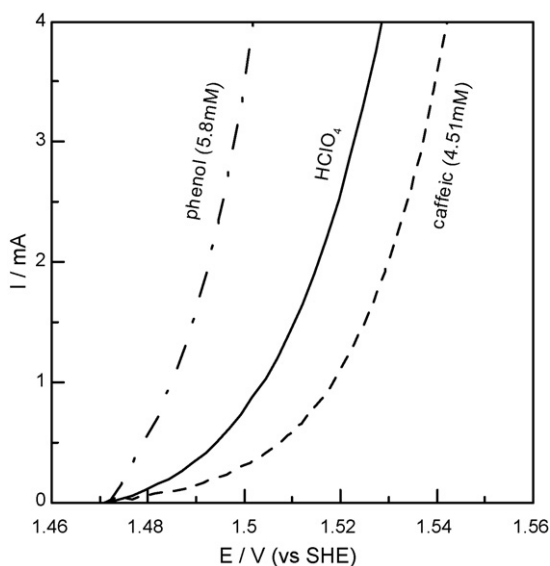


Fig. 2. Cyclic voltammograms over Ti/IrO₂ anode using 1 M HClO₄ electrolyte with 5.8 mM phenol or 4.51 mM caffeic acid. Potential window = 1.4–1.54 V vs SHE; other conditions as in Fig. 1.

various components present in OMW, this is not the case. A possible explanation would involve both the formation of polymeric deposits deactivating the electrode and the low rate of oxidation reactions due to absence of oxygen evolution.

CV experiments were also carried out at 1.4–1.54 V vs SHE potential window (oxygen evolution regime) as high current densities are usually employed to oxidize organic molecules. The respective voltammograms for phenol and caffeic acid are shown in Fig. 2. In the case of phenol, there is a clear shift to the onset of oxygen evolution to lower potentials which is an indication that phenol would be readily oxidized under oxygen evolution conditions. This is a totally different behavior compared to phenol being oxidized over a Pt electrode as reported in a previous study [4]. Unlike phenol, caffeic acid exhibits a shift to higher potential values and this is consistent with the fact that caffeic acid is resistant to electrochemical oxidation. In either case though, the effect of the organic compound on the onset of oxygen evolution is a direct proof that current densities sufficient for oxygen evolution can affect significantly oxidation rates.

Cyclic voltammograms were also taken for cinnamic and p-coumaric acids. The former exhibited a behavior close to caffeic acid

(rapid deactivation on repeated scans), while the latter a behavior similar to phenol (slow deactivation).

3.2. Bulk electrolysis

3.2.1. Oxidation of phenolic compounds

The electrochemical oxidation of phenolic compounds was carried out at a current density of 50 mA/cm² and 60 or 80 °C temperature. This current density was selected in order to operate at the oxygen evolution regime where oxidation reactions take place through the mechanisms shown in Fig. 3 [24]. Fig. 4a shows the extent of COD removal as a function of the charge passed during the electrochemical oxidation of phenolic substances at 80 °C. Phenol and p-coumaric acid are readily oxidizable with COD removal being 60% at 28 Ah/L, while the respective phenolic content of the solution (measured as TPh) is reduced by 93 and 87% (data not shown). For cinnamic and caffeic acids, COD removal is as low as 25 and 5% respectively at 28 Ah/L. The fact that caffeic acid is recalcitrant to oxidation (TPh is reduced by 60% at 28 Ah/L) may be explained by the electrode surface fouling as explained in the previous paragraphs. On the other hand, the susceptibility of phenol to oxidation is consistent with its behavior during cyclic voltammetry at conditions of oxygen evolution. These results are also consistent with the instantaneous current efficiency (ICE) of the anodic oxidation computed from COD values according to Eq. (1). ICE values are shown in Fig. 4b. Phenol and p-coumaric acid have ICE values expectedly greater than those of caffeic and cinnamic acids that are more resistant to oxidation. The level of ICE values (i.e. about 0.1 for phenol and p-coumaric acid) is in good agreement with values reported elsewhere [4] for similar organic compounds and anodes.

Fig. 4c shows COD- and TOC-time profiles for phenol during oxidation at 60 and 80 °C. As clearly seen, oxidation is favored at increased temperatures, while COD reduction is always greater than TOC reduction and this discrepancy is more pronounced at lower temperatures. These results imply that the substrate is converted to intermediates which are eventually mineralized to carbon dioxide and water. However, reaction by-products appear to be more recalcitrant to total oxidation and this is reflected to lower TOC removal rates. Interestingly, TOC and COD appear to decrease nearly linearly with charge (or time), thus implying a near zero-order rate with respect to the organic content. Similar results were obtained for p-coumaric and cinnamic acids (data not shown), i.e. their electrochemical oxidation proceeds through partial and total oxidation reactions to yield various aromatic intermediates [4,25] and CO₂ respectively. These findings are in

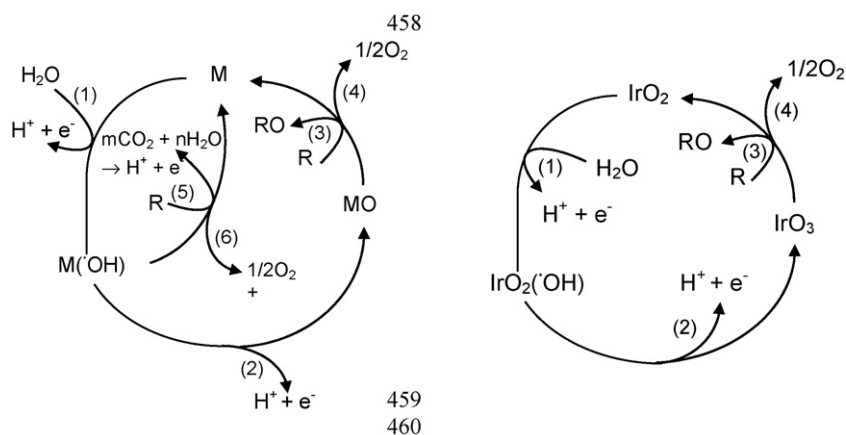


Fig. 3. Proposed scheme (adapted from reference [24]) of the electrochemical oxidation of organic compounds on active (reactions 1, 2, 3, 4) and non-active (reactions 1, 5, 6) anodes. *Left:* Generic mechanism; *Right:* The case of Ti/IrO₂. Reproduced by permission of The Electrochemical Society.

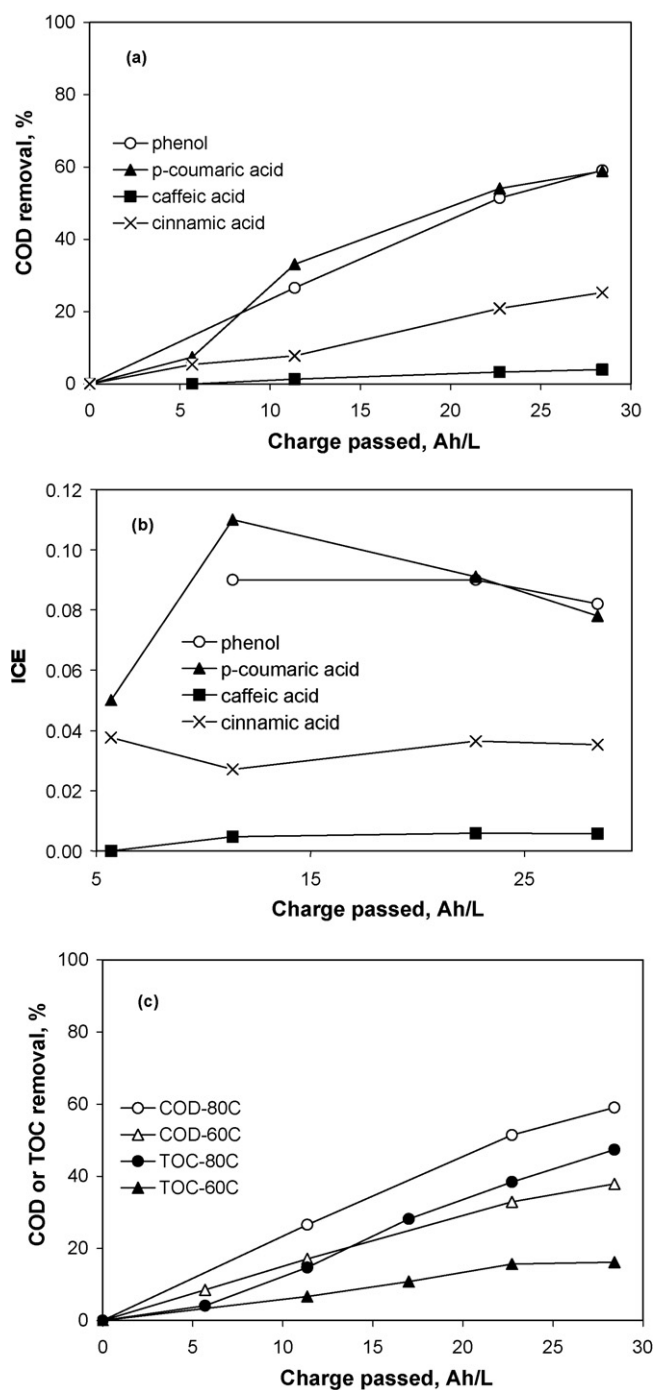


Fig. 4. Electrochemical oxidation of model phenolic solutions at 50 mA/cm². (a) Change of COD as a function of substrate and charge at 80 °C; (b) ICE values as a function of substrate and charge at 80 °C; (c) comparison between COD and TOC and effect on temperature for phenol oxidation.

agreement with the generic electrochemical oxidation mechanism originally proposed by Cominellis [24] as illustrated in Fig. 3. In brief, anodic water discharge yields hydroxyl radicals (reaction 1) that are adsorbed onto the active anode (M) to form the higher metal oxide (M(OH*)) (reaction 2). The organic substrate (R) is then selectively converted to more oxidized intermediates (reaction 3), while the higher metal oxide is decomposed to liberate oxygen (reaction 4). For non-active anodes, total oxidation may become the dominant reaction pathway (reaction 5) with simultaneous oxidation of radicals to yield oxygen (reaction 6). In this work, Ti/IrO₂, a typical active anode, seems to follow the

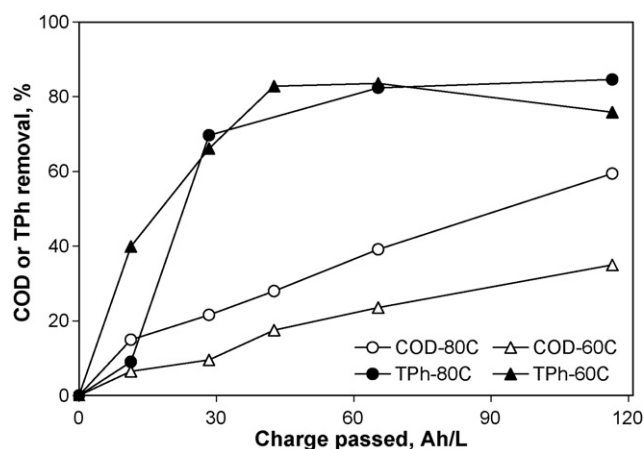


Fig. 5. Effect of temperature on COD and TPh removal during electrochemical oxidation of OMW at 50 mA/cm².

generic scheme as partial oxidation reactions occur to a considerable degree.

3.2.2. Oxidation of OMW

The electrochemical oxidation of OMW in 1 M HClO₄ electrolyte was studied at temperatures of 60 and 80 °C and the results are shown in Fig. 5. It is obvious that OMW oxidation is more efficient at increased temperatures reaching 85 and 60% TPh and COD reduction respectively at 116 Ah/L of charge passed at 80 °C; the respective values for the run at 60 °C are 75 and 35%. COD conversion appears to vary linearly with treatment time, thus implying that the reaction is pseudo-zero order concerning COD, i.e.:

$$-\frac{d\text{COD}}{dt} = k \Leftrightarrow \text{COD}_0 - \text{COD}_t = kt \quad (2)$$

where k is an apparent reaction constant incorporating the concentration of oxidants that, at given operating conditions, are electrogenerated at a constant rate.

If the data of Fig. 5 are plotted in the form of Eq. (2), straight lines (not shown) passing through the origin fit the experimental results well (the coefficient of the linear fitting, r , is 0.96) and from the slopes of the straight lines the computed k values are 52 and 26 mg/(L h) at 80 and 60 °C respectively. At the level of relatively high organic concentrations studied, the reaction seems to be under electrochemical kinetic control and the rate does not depend on COD as the organics to oxidants concentration ratio is expected to be relatively high and the reaction is not limited by organics mass transfer. If the data of Fig. 4 are treated in a similar fashion, respective kinetic constants can be computed for the oxidation of model compounds as follows: 146 (0.99), 95 (0.99), 144 (0.98), 60 (0.99) and 10 mg/(L h) (0.99) for phenol at 80 °C, phenol at 60 °C, p-coumaric acid at 80 °C, cinnamic acid at 80 °C and caffeic acid at 80 °C respectively with numbers in brackets corresponding to fitting coefficients. Interestingly, although OMW and model solutions have a common initial COD, rates are substantially different implying that the complex matrix of actual effluents should be taken into consideration.

In an attempt to enhance treatment efficiency, it was decided to modify effluent conductivity through the addition of NaCl. In the presence of sodium chloride, chlorohydroxyl radicals can be formed on the anode surface and then oxidize the organic compound [6,14–16,26]. Moreover, reactions between radicals and water can yield free chlorine and hypochlorite as primary oxidants as well as chlorine dioxide as a secondary oxidant. All these oxidants are quite stable and migrate in the bulk solution where they oxidize the organic compound. A series of experiments were carried out

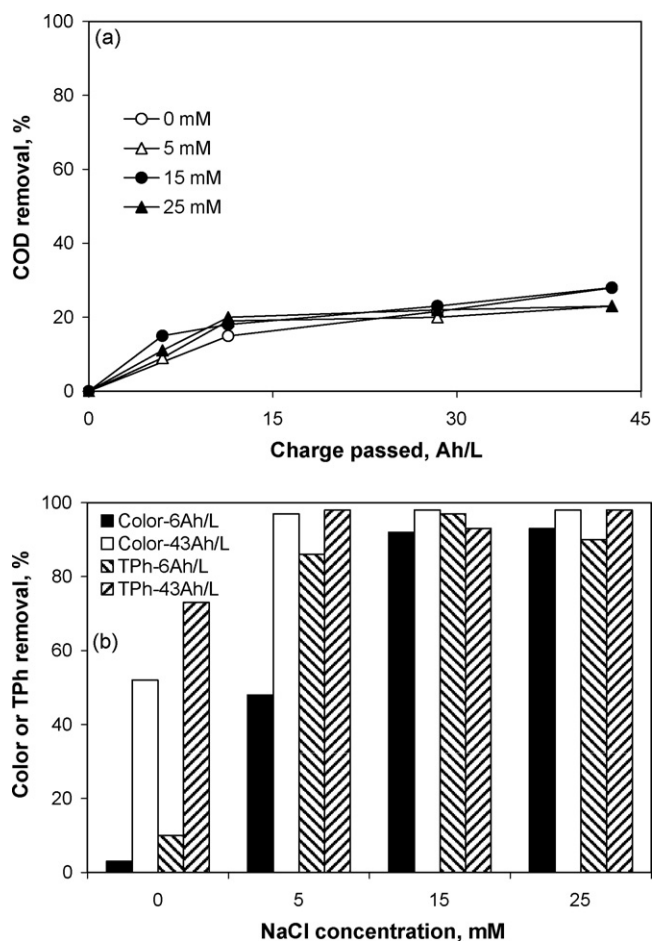


Fig. 6. Effect of NaCl on (a) COD and (b) TPh and color removal during electrochemical oxidation of OMW at 50 mA/cm² and 80 °C.

using NaCl as a supporting electrolyte at concentrations of 5, 15 and 25 mM in the OMW acidic solution. Results are summarized in Fig. 6.

As clearly seen, addition of 5 mM NaCl enhances substantially TPh removal which becomes quantitative even from the early stages of reaction (i.e. at 6 Ah/L). This is accompanied by a comparatively high level of decolorization, thus implying that polyphenols are responsible to a great degree for the effluent's dark color [16]. On the other hand, color removal remains as low as 50% at 43 Ah/L for the run without NaCl. It can be hypothesized that phenolic compounds can be disrupted by a strong oxidizing agent, such as free chlorine, since at acidic conditions free chlorine is expected to be the dominant oxidizing agent in the solution [14]. It is worth noticing that, even at the higher salinity, NaCl does not affect COD removal which remains practically unchanged at about 30%. The fact that (i) COD is a lumped parameter of the organic pollution accounting for several species, other than polyphenols, that may be resistant to oxidation and (ii) free chlorine may not be formed at concentrations high enough to sustain indirect oxidation reactions could explain the observed COD profiles. (The formation of free chlorine was evident owing to its characteristic smell, mainly at the beginning of the treatment.)

Although the addition of 5 mM NaCl (a relatively low concentration that would comply with chlorine sewer discharge limits) is beneficial to process performance, it should be kept in mind that electrolysis is still an energy-intensive treatment technology. For instance, the specific energy consumption after 7.5 h of operation (i.e. 43 Ah/L) at 5 mM NaCl and 80 °C is about 72 kWh/kg COD removed.

Prior to oxidation, the effluent was strongly ecotoxic and non-biodegradable aerobically with its EC₅₀ and BOD₅/COD values being 9% and 2% respectively. However, oxidation at 43 Ah/L with or without 5 mM NaCl eliminated ecotoxicity completely; as at these conditions most of TPh has been converted (Fig. 6b), ecotoxicity appears to be closely related to the effluent's phenolic content. Conversely, aerobic biodegradability remained practically unchanged at the level of the untreated sample. Oxidation at 25 mM NaCl for 43 Ah/L led to an effluent which was nearly as toxic as the untreated one although, at these conditions, TPh removal was again quantitative. This may be due to (i) the formation of some toxic organochlorinated by-products [16] and (ii) osmotic phenomena responsible for breaking cell membranes, both of which would be favored at increased salinity.

4. Conclusions

In this work, the electrochemical oxidation of compounds found in OMW over a Ti/IrO₂ DSA was investigated. The main conclusions can be summarized as follows:

- (1) As corroborated by cyclic voltammetry, the stability and activity of Ti/IrO₂ depend on whether adequate current densities for oxygen evolution are applied or not, as well as on the type of molecule to be oxidized. For instance, as phenolic compounds undergo oxidative polymerization, polymeric deposits may contaminate the anode surface and deactivate it.
- (2) Bulk electrolysis of model compounds and actual OMW showed that degradation proceeds through partial oxidation reactions to intermediates that are eventually mineralized to carbon dioxide and water. Degradation appears to follow zero-order kinetics with respect to lumped organic concentration and increases with increasing temperature.
- (3) Regarding the oxidation of actual effluent, low to moderate levels of COD and TOC decrease are accompanied by ecotoxicity elimination as well as considerable color and phenols removal. The latter is enhanced by the addition of NaCl, thus implying that, in addition to anodic oxidation, indirect bulk electrolysis also happens.

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