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ORIGINAL PAPER

DSA electrochemical treatment of olive mill wastewater on Ti/RuO_2 anode

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Abstract The electrochemical oxidation of olive mill wastewater (OMW) over a Ti/RuO_2 anode was studied by means of cyclic voltammetry and bulk electrolysis and compared with previous results over a Ti/IrO_2 anode. Experiments were conducted at 300–1,220 mg L^{-1} initial chemical oxygen demand (COD) concentrations, 0.05–1.35 V versus SHE and 1.39–1.48 V versus SHE potential windows, 15–50 mA cm^{-2} current densities, 0–20 mM NaCl, Na_2SO_4, or $FeCl_3$ concentrations, 80 °C temperature, and acidic conditions. Partial and total oxidation reactions occur with the overall rate being near first-order kinetics with respect to COD. Oxidation at 28 Ah L^{-1} and 50 mA cm^{-2} leads to quite high color and phenols removal (86 and 84%, respectively), elimination of ecotoxicity, and a satisfactory COD and total organic carbon reduction (52 and 38%, respectively). Similar performance can be achieved at the same charge (28 Ah L^{-1}) using lower current densities (15 mA cm^{-2}) but in the presence of various salts. For example, COD removal is less than 7% at 28 Ah L^{-1} in a salt-free sample, while addition of 20 mM NaCl results in 54% COD reduction. Decolorization of OMW using Ti/RuO_2 anode seems to be independent of the presence of salts in contrast with Ti/IrO_2 where addition of NaCl has a beneficial effect on decolorization.

Keywords Cyclic voltammetry · DSA · Electrolysis · OMW · Phenols · Ti/RuO_2

1 Introduction

Olive oil extraction is an agro-industrial activity of great economic importance to many regions of the Mediterranean Sea area with serious environmental implications associated with the generation of large quantities of recalcitrant wastewaters (olive mill wastewater (OMW)) as has been discussed in detail in previous report [1]. Moreover, a number of efficient treatment technologies including physical, chemical, and biological processes were reported where specific attention was given on advanced oxidation processes [1, 2]. The latter have been widely employed over the past years in an attempt to reduce the organic load and bio-recalcitrance of these wastewaters. The industrial use of dimensionally stable anodes (DSA) for wastewater treatment has led to technological solutions, thus reducing operational and investment costs [3]. Such DSA-type materials have been used for the oxidation of model aqueous solutions containing phenolic compounds typically found in OMW with emphasis on titanium based on different oxides such as IrO_2, RuO_2, SnO_2 [4–9]. As has already been emphasized [1], only few of these investigations have dealt with the DSA oxidation of actual OMW. Ti/TiRuO_2, Ti/Pt, and Ti/Ta/Pt/Ir anodes have been employed by Panizza and Cerisola [10], Israilides et al. [11], Giannis et al. [12], and Gotsi et al. [13] to investigate the electrooxidation of OMW. Moreover, electrocoagulation over iron and aluminum electrodes was found capable of reducing organic load as well as decolorizing OMW [14–16]. In general, the use of Ti/IrO_2 and Ti/RuO_2 "active" [17] anodes has merely been reported in the literature. Ti/IrO_2 anode was used for OMW electrooxidation in a previous study [1], while the only published work (to the best of our knowledge) using Ti/RuO_2 was carried out by Un et al. [14, 15]. They reported almost complete

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removal of initial chemical oxygen demand (COD), phenols, turbidity, and oil-grease after 7 h of treatment over a Ti/RuO_2 anode at 135 mA cm^{-2} current density, 2 M NaCl, and 20 °C. In the present study, the efficiency of a Ti/RuO_2 anode to treat OMW was studied regarding the effect of applied current density, type, and concentration of salt and initial COD on performance as evaluated by means of COD, total organic carbon (TOC), phenols, and color removal, as well as energy consumption. The results are also compared to those of our previous study on Ti/IrO_2 anode [1].

2 Experimental and analytical

2.1 Materials

2.1.1 DSA preparation

The Ti/RuO_2 working electrode was prepared by thermal decomposition of 150 mM $RuCl_3$ (Fluka 84050, 41%) metal precursor dissolved in isopropanol (Fluka, 99.5%), on a disc-shaped titanium support. The precursor of $RuCl_3$ before the dilution in isopropanol was treated with 10% HCl, stirred, and heated at 80 °C for 24 h. Procedures for titanium substrate pre-treatment and anode deposition are described elsewhere [1]. The final RuO_2 loading was 0.4 mg cm^{-2}.

2.1.2 Effluent and aromatic compounds

Olive mill wastewater was provided by a three-phase olive oil mill located in Chania, W. Crete, Greece. Following centrifugation to remove 99% of its solids, OMW contained 40 g L^{-1} COD, 14 g L^{-1} TOC, and 3.5 g L^{-1} total phenolic content (TPh) [1]. The effluent was then diluted with 1 M $HClO_4$ solution in ultrapure water to achieve an initial COD concentration in the range 300–1,220 mg L^{-1}.

p-Coumaric acid ($C_9H_8O_3 \geq 98\%$), caffeic acid ($C_9H_8O_4 \geq 97\%$), and cinnamic acid ($C_9H_8O_2 \approx 99\%$) were purchased from Fluka, while phenol ($C_6H_6O \geq 99\%$) was purchased from Sigma–Aldrich.

2.2 Cyclic voltammetry

Cyclic voltammetry (CV) was carried out in a conventional three-electrode cell using a computer-controlled potentiostat (μ-Autolab III). Ti/RuO_2 electrode was used as the working electrode, $Hg/Hg_2SO_4{\cdot}K_2SO_4$ (sat) as reference electrode (MSE) and Pt wire as counter electrode. At each voltammetric measurement, several scans were obtained in order to study two potential windows, one between 0.05 and 1.35 V versus SHE and another between 1.39 and 1.48 V versus SHE. The electrolyte was either 1 M $HClO_4$ or organic solutions of phenol, caffeic acid, *p*-coumaric acid, cinnamic acid, or actual OMW in 1 M $HClO_4$. Caffeic, *p*-coumaric, and cinnamic acids were chosen as representatives of the polyphenolic fraction typically found in OMW, while phenol as a precursor for the formation of the various phenolics in OMW. Solutions were magnetically stirred for 20 min to ensure complete mixing.

2.3 Bulk electrolysis

Electrochemical experiments were conducted in the same batch type, laboratory scale electrolytic cell described elsewhere [1]. All experiments were carried out in acidic conditions, using 1 M $HClO_4$ solution as the main electrolyte and at a constant temperature of 80 °C. 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, TOC, TPh, and color.

2.4 Analytical measurements

Chemical oxygen demand was determined by the dichromate method. TOC was measured on a Shimadzu 5050A TOC analyzer. TPh was determined colorimetrically at 765 nm on a Shimadzu UV 1240 spectrophotometer using the Folin–Ciocalteau reagent according to a modified method described in detail elsewhere [18]. Changes in sample absorbance at 510 nm were monitored on a Shimadzu UV 1240 spectrophotometer to assess the extent of decolorization that had taken place during treatment. The luminescent marine bacteria *Vibrio fischeri* were used to assess the acute ecotoxicity of samples before and after treatment. Details on analytical protocols are given elsewhere [1].

The relative contribution of partial and total oxidation reactions to overall COD removal was assessed computing the efficiency of partial oxidation, ε, as follows [19]:

$$\varepsilon = \frac{\mathrm{COD_0(TOC/TOC_0) - COD}}{\mathrm{COD_0 - COD}}, \tag{1}$$

where COD_0 and TOC_0 are initial concentrations. Moreover, changes in COD were employed to compute instantaneous current efficiency, ICE, of the anodic oxidation as follows [1]:

$$\mathrm{ICE} = \frac{\mathrm{COD_0 - COD}_t}{8I\Delta t}FV, \tag{2}$$

where I is the applied current (A), F the Faraday constant (96,487 C/mol), V the liquid holdup (L), COD (g L^{-1}), and 8 is the equivalent mass of oxygen (g eq^{-1}).

3 Results and discussion

3.1 CV measurements

The electrochemical activity of Ti/RuO_2 electrode was studied using aqueous solutions of 1 M $HClO_4$ with or without organic content. CV was carried out at two different potential windows (i.e., 0.05–1.35 V versus SHE where no oxygen evolution is expected to occur and 1.39–1.48 V versus SHE). Figure 1 shows cyclic voltammograms of four solutions, namely the electrolyte alone (shaded voltammograms), OMW at 1,220 mg L^{-1} initial COD, 3 mM caffeic acid, and 3 mM phenol. Besides the fact that there is no oxygen evolution (as would be expected), it is worth noting that both the total charge of the double layer and the shape of the voltammogram are totally stable on many repeated scans. The well-known two pairs of peaks between 0.7 and 1.1 V versus SHE [20, 21] attributed to the Ru_2O_3/RuO_2 and the Ru_2O_3/Ru couples can be observed in the CV of the electrolyte alone although they can hardly be distinguished due to the noise during the CV. The pronounced reduction peak observed near 0.1 V versus SHE, as has already been proposed by Galizzioli et al. [20], is probably due to the solid-state reduction of RuO_2, i.e., to penetration of atomic hydrogen into the lattice. Figure 1a shows cyclic voltammograms for phenol oxidation (first and last scan) and, as clearly seen, the anode displays a significant but rapidly changing catalytic activity. The oxidation peak at 1.2 V versus SHE can be attributed to phenol oxidation; on repeated scans, the peak size decreases, thus indicating likely anode deactivation. Figure 1b shows CV for caffeic acid oxidation, where anode deactivation is also evident. It is worth noting that for caffeic acid oxidation over Ti/RuO_2 no reduction peak was observed in the region of 0.76–1.35 V versus SHE contrary to the case of Ti/IrO_2 [1] where two pairs of anodic and cathodic peaks (at 0.8 and 1.1 V versus SHE) were observed. The broad oxidation peak observed at around 1.2 V versus SHE tends to be negligible after 20 cycles. It is obvious that following a theoretically infinite number of scans either for phenol or caffeic acid oxidation, the system will probably reveal the same behavior as in the case where no organic compound is added to the electrolyte.

Similar to the case of Ti/IrO_2 [1] and 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. This is supported from the fact that both Ti/IrO_2 and Ti/RuO_2 are comparably “active” electrodes (their redox potential is close to the standard potential of O_2 evolution) and, thus, they are suitable for electrosynthesis or partial oxidation reactions.

Regarding OMW, its voltammogram shown in Fig. 1c is comparable to that of the electrolyte in the absence of

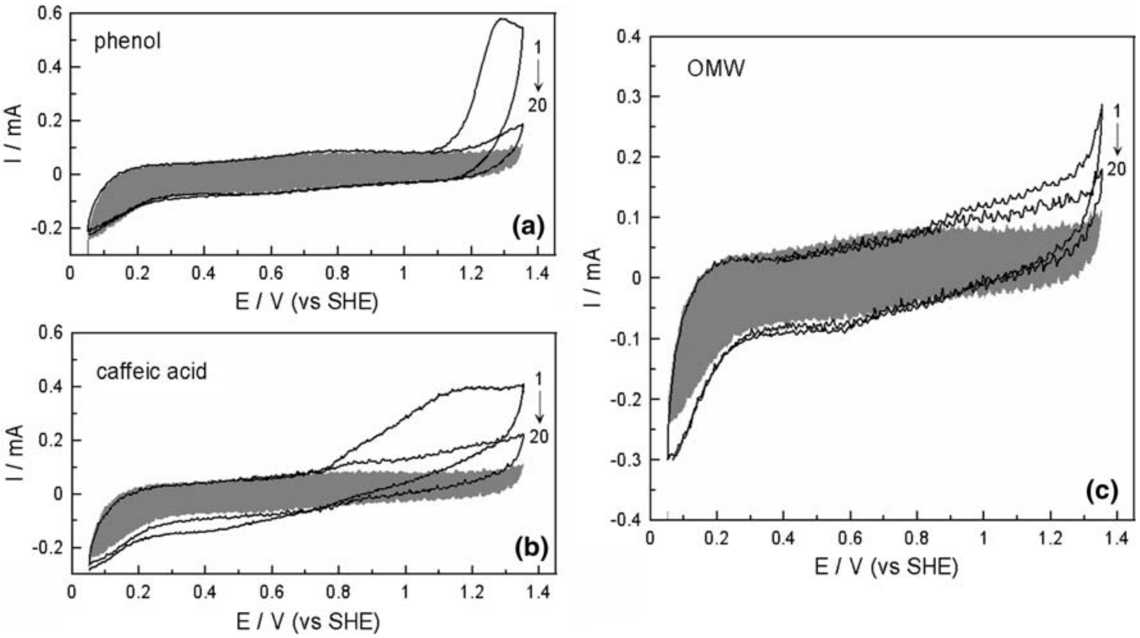

Fig. 1 Cyclic voltammograms over Ti/RuO_2 anode using 1 M $HClO_4$ electrolyte **a** with 3 mM phenol; **b** with 3 mM caffeic acid; **c** with OMW at 1,220 mg L^{-1} COD. *Shaded voltammograms* correspond to 1 M $HClO_4$ electrolyte without organics. Scan rate = 50 mV s^{-1}; $T = 30$ °C; potential window = 0.05–1.34 V versus SHE

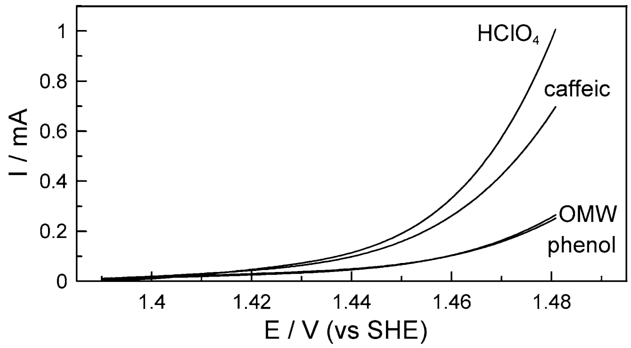

Fig. 2 Cyclic voltammograms over Ti/RuO_2 anode using 1 M $HClO_4$ electrolyte with 3 mM phenol, 3 mM caffeic acid, or OMW at 1,220 mg L^{-1} COD. Scan rate = 10 mV s^{-1}; $T = 30$ °C; potential window = 1.39–1.48 V versus SHE

organic compounds. A similar behavior was observed using Ti/IrO_2 [1]. Although one would expect to see several oxidation and reduction peaks due to the redox reactions of the 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.

Cyclic voltammetry experiments were also carried out at 1.39–1.48 V versus SHE potential window (oxygen evolution regime) as high current densities are usually employed to oxidize organic molecules. Steady state (after 10 scans) anodic current density curves are shown in Fig. 2 for phenol, caffeic acid, OMW, and 1 M $HClO_4$ (without organics). In all cases, the potential where oxygen evolution takes place increases with the presence of organic compounds in the solution. This significant increase in the anodic overpotential has also been observed with "active" electrodes and organic molecules such as maleic and acetic acids [17]. This shift is more pronounced for phenol and OMW (where various organic compounds are present), while caffeic acid has only a small effect on the overpotential. Similar results regarding the potential where oxygen evolution occurs were obtained for caffeic acid and OMW oxidation over Ti/IrO_2 [1]; noticeably, phenol exhibited a totally different behavior since its oxidation over Ti/IrO_2 led to reduced potential for oxygen evolution. 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. Both of them led to rapid anode deactivation on repeated scans, similar to their behavior with Ti/IrO_2 [1].

3.2 Bulk electrolysis of OMW

3.2.1 Effect of operating conditions on COD and TOC removal

The effect of changing current density on the electrochemical oxidation of OMW at 1,220 mg L^{-1} COD_0 ($TOC_0 = 600$ mg L^{-1}) as a function of treatment time is shown in Fig. 3. It is obvious that OMW oxidation is more efficient at increased current densities reaching 52% COD and 38% TOC removal after 5 h at 50 mA cm^{-2}, with the respective values being 34 and 30% at 30 mA cm^{-2}. To assess the oxidizability of the effluent, the run at 50 mA cm^{-2} was prolonged at 24 h yielding 71% COD and 67% TOC reduction. Interestingly, COD appears to increase or remain unchanged during the early stages of reaction and this is more pronounced at 15 mA cm^{-2}. This phenomenon may be due to oxidative polymerization of certain OMW constituents like phenols and tannins, which would result in COD increase in the effluent as has also been observed by other researchers [7, 13], as well as dissolution of unfiltered solids upon electrochemical oxidation, thus releasing organic matter in the liquid phase as has also been reported by Kotta et al. [24]. Nonetheless, such dissolution is not expected to contribute substantially to the increased concentrations since most of the solids had already been removed from the effluent by means of filtration. Figure 3 also shows the extent of COD and TOC removal at different current densities as a function of the applied charge rather than time. As clearly seen, TOC removal increases with increasing applied charge but it does not depend on the current density, i.e., applying a fixed charge to achieve a certain TOC reduction, one may operate either at low currents and long treatment times or vice versa. Conversely, COD removal seems to increase with increasing both the applied charge and current. This may be due to the fact that changes in COD are associated with a complex network of pathways involving polymerization, depolymerization, partial oxidation, and total oxidation reactions of a composite mixture of organics of diverse susceptibility to electrochemical oxidation. On the other hand, a decrease in TOC corresponds to liquid phase organic carbon being totally oxidized to carbon dioxide and water, while other chemical transformations do not affect its value. Moreover, total oxidation typically proceeds through the formation of oxygenated intermediates that are eventually converted to mineral end-products. This is consistent with the fact that TOC removal is always lower than COD removal (see Figs. 3, 4).

The effect of initial organic loading on the electrochemical oxidation of OMW at 50 mA cm^{-2} is shown in

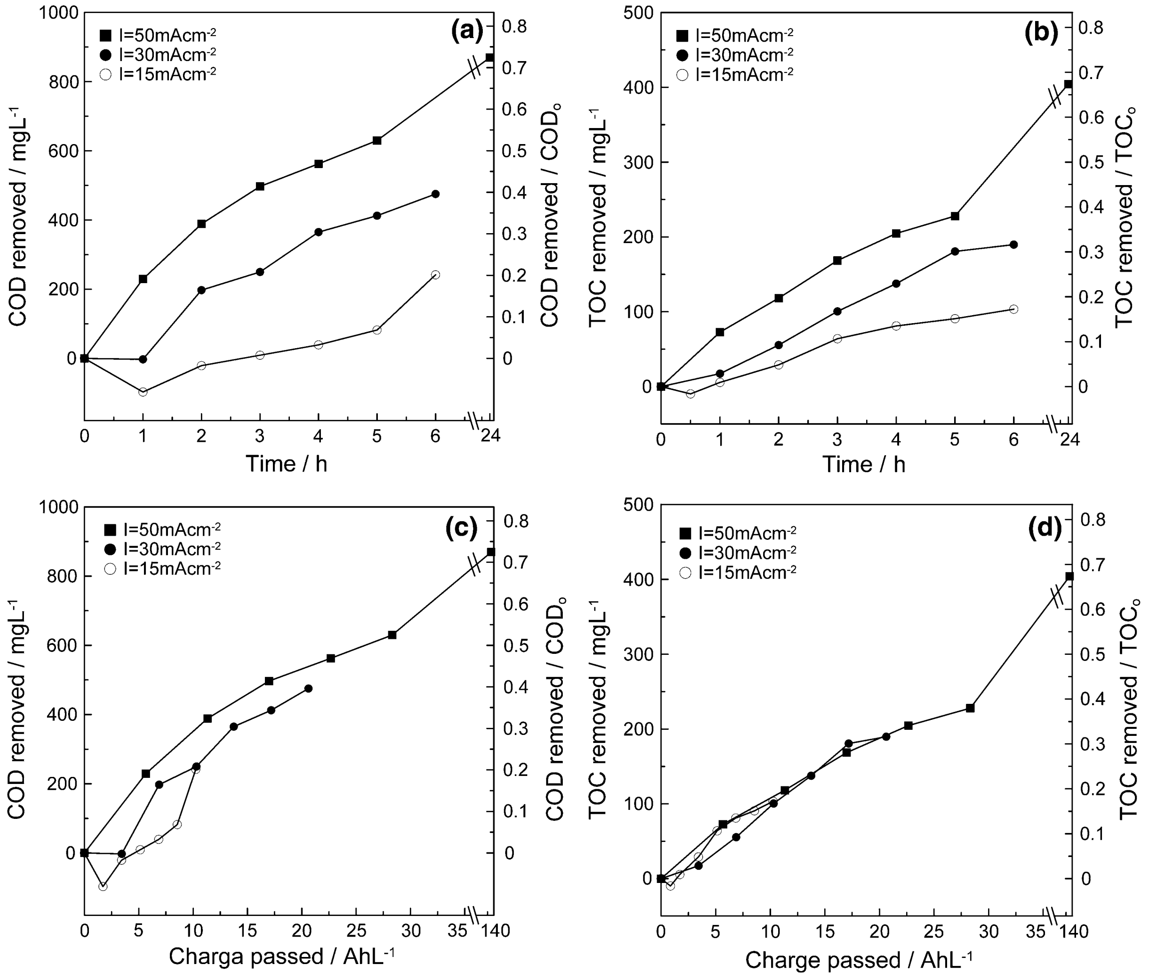

Fig. 3 Effect of current density on the electrochemical oxidation of OMW at 1,220 mg L^{-1} COD_0 as a function of treatment time (**a** and **b**) and applied charge (**c** and **d**)

Fig. 4. Treatment for 5 h results in 52, 44, and 45% COD removal at 1,220, 550, and 300 mg L^{-1} COD_0, respectively, with the corresponding values for TOC removal being 38, 31, and 38%. Interestingly, COD and TOC conversion is almost constant regardless the initial organic loading and this is also the case at different treatment times (e.g., COD and TOC conversion is 36 ± 5 and 24 ± 4%, respectively, after 3 h at 50 mA cm^{-2}). This is a good indication of the apparent reaction rate order with respect to COD or TOC concentration. If the reaction was zero-order, an increase in initial COD would result in a similar conversion decrease; conversely and for first-order kinetics, conversion would remain constant for runs performed at different initial COD values. At the conditions in question, the apparent reaction rate of OMW oxidation is near first-order.

In an attempt to enhance treatment efficiency, it was decided to modify effluent conductivity through the addition of various salts and the results are shown in Fig. 5. Addition of 5 mM NaCl enhances substantially COD removal, which becomes 31% after 5 h at 15 mA cm^{-2} and 1,220 mg L^{-1} COD_0, while the respective value without salt is only 7%. A four-fold increase in NaCl concentration results in 54% COD removal, thus underlying the important role of chlorine in electrochemical processes. 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 compounds. At acidic conditions, free chlorine is expected to be the dominant oxidizing agent in the solution [11], thus explaining increased removal rates. Moreover, chlorohydroxyl radicals can be formed on the anode surface, which can also oxidize the organic compounds [6, 11–13, 25]. Addition of 1.67 mM $FeCl_3$ (this concentration was chosen to match the chlorine content of 5 mM NaCl) results in 39% COD removal after 5 h at 15 mA cm^{-2}, which is slightly better than that at 5 mM NaCl. This improvement can be attributed to the catalytic role of iron that may facilitate the oxidative degradation of

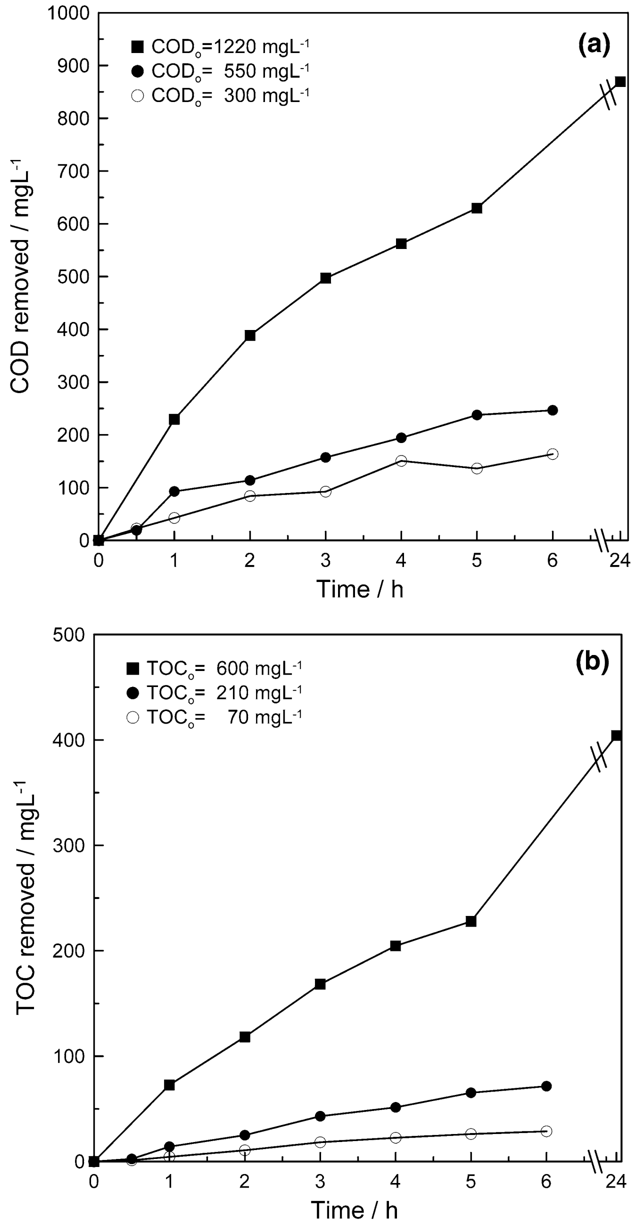

Fig. 4 Effect of initial organic loading on the electrochemical oxidation of OMW at 50 mA cm^{-2}

various organic compounds in the reaction mixture [25]. In further runs, Na_2SO_4 was employed as the supporting electrolyte at 5 or 20 mM; its performance is inferior compared to that of Cl-containing salts, which again highlights the beneficial role of chlorine, but still better than that without salt. It is well documented [26] that at sufficiently high current densities and electrode overpotentials for oxygen evolution, Na_2SO_4 yields $SO_4^{-}/S_2O_8^{2-}$ (peroxodisulfate) and H_2O_2, which can promote bulk electrochemical oxidation. Similar findings regarding the effect of various salts on performance were obtained for TOC removal (data not shown).

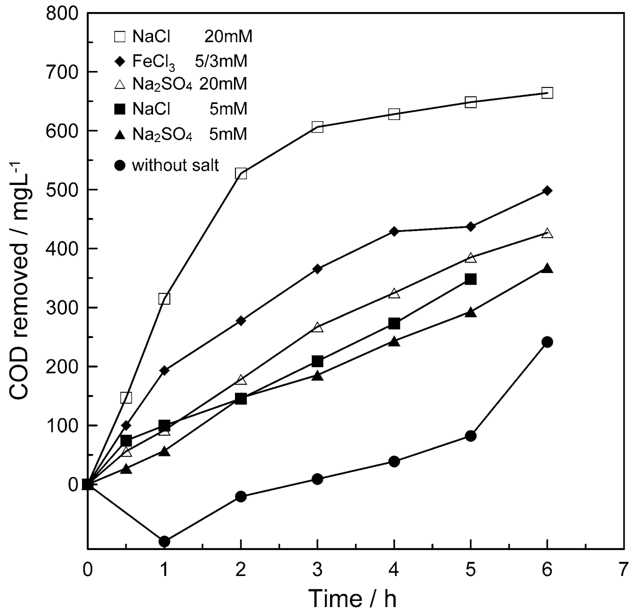

Fig. 5 Effect of various salts (NaCl, $FeCl_3$, or Na_2SO_4) on the electrochemical oxidation of OMW at 15 mA cm^{-2} and 1,220 mg L^{-1} COD_0

Table 1 Efficiency of partial oxidation for COD removal, ε, at various treatment conditions

Current density (mA cm^{-2})	COD_0 (mg L^{-1})	Salt	Partial oxidation efficiency at 1 h	Partial oxidation efficiency at 5 h
30	1,220	None	ND	0.11
50	1,220	None	0.35	0.26
50	550	None	0.35	0.21
50	300	None	0.54	0.17
15	1,220	5 mM NaCl	0.31	0.06
15	1,220	1.67 mM $FeCl_3$	0.68	0.34

ND not determined

Table 1 shows the relative contribution of total and partial oxidation reactions for the electrochemical treatment of OMW at various conditions. The efficiency of partial oxidation, ε, reaches a value of 0 when only total oxidation occurs and 1 for the ideal case that only partial oxidation occurs. At the conditions in question, OMW degradation predominantly occurs via total oxidation reactions (i.e., ε is generally less than 0.5) and this is more pronounced at prolonged treatments.

3.2.2 *Removal of TPh and decolorization*

Figure 6 shows changes in TPh concentration as a function of current density and treatment time during the

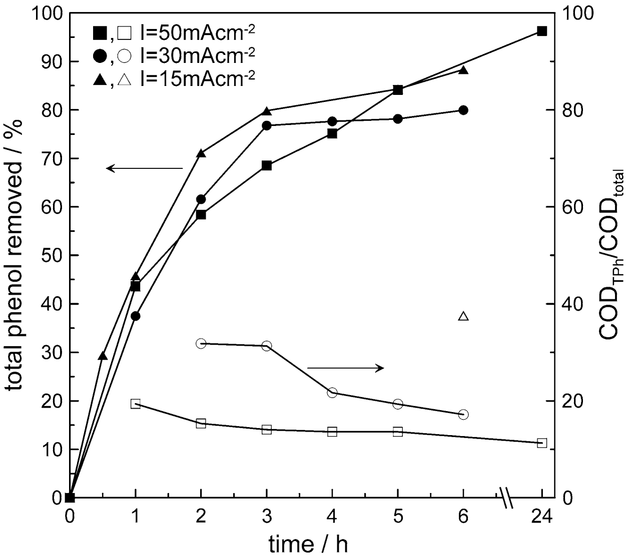

Fig. 6 Changes in TPh concentration as a function of current density and treatment time during the electrochemical oxidation of OMW at 1,220 mg L^{-1} COD_0

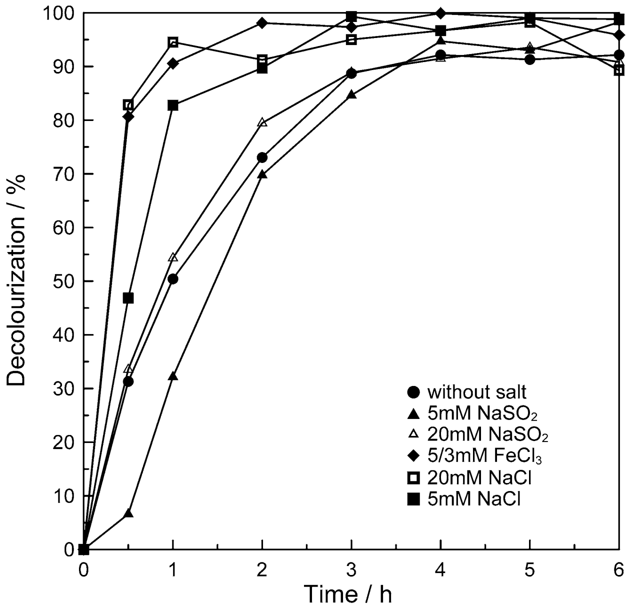

Fig. 7 Effect of various salts (NaCl, $FeCl_3$, and Na_2SO_4) on the decolorization of OMW at 15 mA cm^{-2} and 1,220 mg L^{-1} COD_0

electrochemical oxidation of OMW at 1,220 mg L^{-1} COD_0. As clearly seen, TPh conversion is as much as about 40 ± 3 and 81 ± 3% after 1 and 5 h of treatment, respectively; unlike COD and TOC removal, the applied current has little effect on the extent of TPh removal, thus implying that phenols are easily oxidized at the conditions in question. At 50 mA cm^{-2} and prolonged treatment, TPh conversion is nearly complete, i.e., 93 and 96% at 12 and 24 h, respectively. Figure 6 also shows the ratio of equivalent COD removed due to phenols (i.e., computed from the COD content of gallic acid) over the total COD removed. This ratio is generally low and, for instance, it takes values of 19 and 13% after 1 and 5 h, respectively, at 50 mA cm^{-2} and 32 and 19% after 2 and 5 h, respectively, at 30 mA cm^{-2}, thus implying that electrochemical oxidation is a non-selective process. As the reaction time proceeds, other organic compounds also undergo oxidation and this explains why the relative contribution of TPh degradation decreases. Moreover, the contribution is higher at lower current densities and this is consistent with the fact that the level of applied current has a more pronounced effect on total COD removal rather than on TPh removal. Noticeably, TPh removal is accompanied by an equally high effluent decolorization. As seen in Fig. 7, treatment at 15 mA cm^{-2} yields 50 and 91% color reduction after 1 and 5 h, respectively, while the respective values for TPh removal are 46 and 84%, thus implying that polyphenols are responsible to a great degree for the effluent's dark color [1, 13]. Figure 7 also shows the effect of various salts on decolorization; with the exception of Na_2SO_4, decolorization becomes quantitative within the first hour of treatment.

3.2.3 Energy consumption and post-treatment ecotoxicity

Electrochemical treatment is undoubtedly an energy-intense process and its efficiency is usually assessed in terms of ICE and/or specific energy consumption (SEC). The latter is defined as the amount of energy consumed per unit mass of organic load (e.g., COD) removed. Figure 8a shows changes in ICE as a function of time, while Fig. 8b shows SEC after 5 h of treatment at 1,220 mg L^{-1} COD_0 and various conditions. Operation at 15 mA cm^{-2} leads to low ICE (<0.05) and, consequently, high SEC (39 kW h kg^{-1} COD_{rem}). However, these values may be viewed with some caution given that COD changes at low current densities and treatment times are due to a complex reaction network (as already discussed earlier). The addition of various salts at 15 mA cm^{-2} improves drastically treatment efficiency, i.e., at 5 mM NaCl or 1.67 mM $FeCl_3$, ICE and SEC become 0.15–0.25 and 7–10 kW h kg^{-1} COD_{rem}, respectively. Operation at 30 or 50 mA cm^{-2} gives a common ICE value of 0.1, which implies that an increase in energy consumption is accompanied by a nearly equivalent increase in COD removal.

The original effluent at 1,220 mg L^{-1} COD_0 is highly ecotoxic to *V. fischeri* with EC_{50} being 10%. Following treatment at 30 mA cm^{-2} for 6 h results in a non-toxic effluent, which is consistent with 80% TPh and 40% COD reduction. Similar results were obtained during operation at 15 mA cm^{-2} and various salts; the final (i.e., after 6 h) samples are non-toxic even in the presence of chlorine and iron.

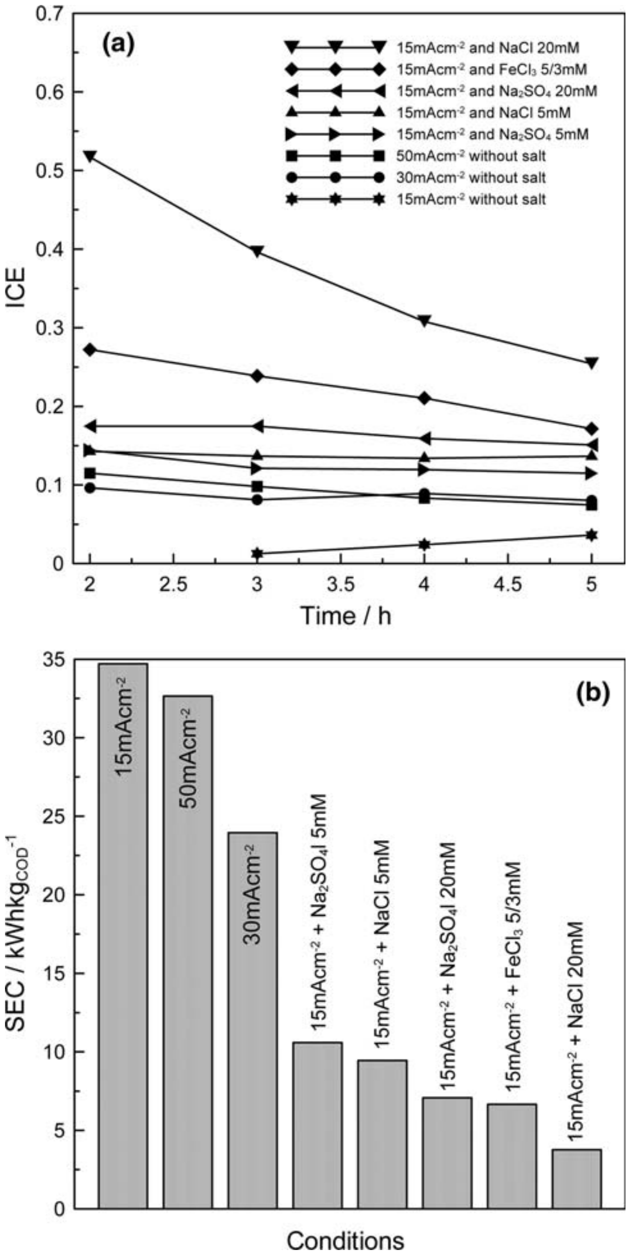

Fig. 8 Changes in **a** ICE and **b** 5 h-SEC during the electrochemical oxidation of OMW at 1,220 mg L^{-1} COD_0 and various conditions

3.3 Comparison between ruthenium and iridium oxides

Figure 9 shows a comparison of performance between Ti/RuO_2 and Ti/IrO_2 anodes for the electrochemical oxidation of OMW at about 1,200 mg L^{-1} COD_0, 50 mA cm^{-2} current density, and 80 °C temperature. (Data for Ti/IrO_2 have been adapted from our previous publication [1].) As clearly seen, ruthenium is substantially more active than iridium in terms of COD, TPh, and color removal at the conditions employed in this study. Similar results were obtained for runs with 5 mM NaCl (data not shown). The superiority of ruthenium as anode for the electrochemical oxidation of organics has recently been recognized by many research groups [27–31]. Nonetheless, one of the major problems is the stability of the oxide since upon prolonged utilization of pure RuO_2 anodes corrosion phenomena take place. The total charge of the double layer decreases with time and this is a direct indication that the active surface of the anode gradually decreases. A way to enhance RuO_2 stability, thus, overcoming the aforementioned problem, is the use of metal oxide alloys such as IrO_2/RuO_2 or TiO_2/RuO_2 [27–31]. Contrary to Ti/RuO_2 anodes, Ti/IrO_2 despite its lower activity seems to be more stable as has already been discussed elsewhere [1].

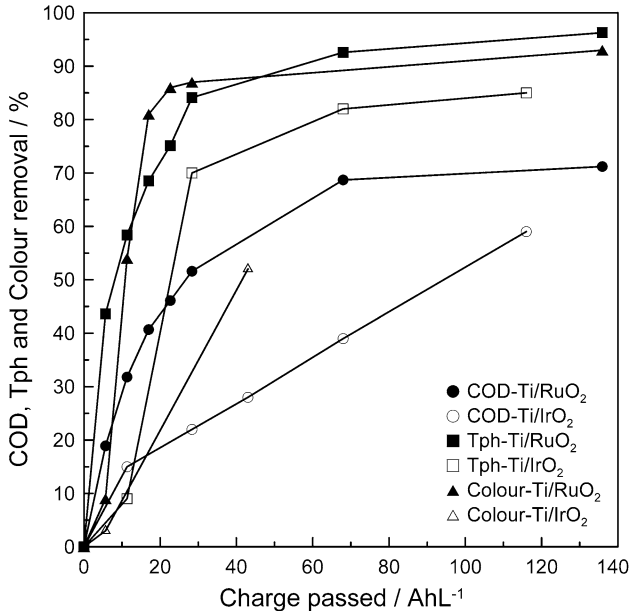

Fig. 9 Comparison of performance between Ti/RuO_2 and Ti/IrO_2 anodes for the electrochemical oxidation of OMW at about 1,300 mg L^{-1} COD_0, 50 mA cm^{-2} current density, and 80 °C temperature. (Data for Ti/IrO_2 have been adapted from reference [1].)

4 Conclusions

Dimensionally stable anodes-type electrodes like Ti/RuO_2 and Ti/IrO_2 show good activity for the treatment of agro-industrial effluents like OMW. In spite of the complex effluent composition that may compromise both activity and stability, DSA electrooxidation is capable of decreasing considerably total organic pollution and eliminating certain indices like color and ecotoxicity. In this view, electrochemical treatment may become part of an integrated process for the efficient decontamination of this type of wastes. In the present study, using Ti/RuO_2 as anodic electrode it was found that after a treatment period of 28 Ah L^{-1} at 50 mA cm^{-2} it is able to achieve quite high color and phenols removal (86 and 84%, respectively), elimination of ecotoxicity, and a satisfactory COD and TOC reduction (52 and 38%, respectively). The overall performance could be dramatically affected by the presence of various salts. For example, after the same charge passed (28 Ah L^{-1}) and using almost the one-third of the current density (15 mA cm^{-2}) it was observed an increase of the COD removal from less than 7% in a salt-free sample to 54% after addition of 20 mM NaCl.

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