

Electrochemical treatment of tannery wastewater using DSA[®] electrodes

Carla Regina Costa^a, Clarice M.R. Botta^b,
Evaldo L.G. Espindola^b, Paulo Olivi^{a,*}

^a Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo,
CEP 14049-901 Ribeirão Preto, SP, Brazil

^b Núcleo de Estudos em Ecossistemas Aquáticos, Centro de Recursos Hídricos e Ecologia Aplicada,
Escola de Engenharia de São Carlos, Universidade de São Paulo, CP 292, CEP 13560-970 São Carlos, SP, Brazil

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Abstract

In this work we studied the electrochemical treatment of a tannery wastewater using dimensionally stable anodes (DSA[®]) containing tin, iridium, ruthenium, and titanium. The electrodes were prepared by thermal decomposition of the polymeric precursors. The electrolyses were performed under galvanostatic conditions, at room temperature. Effects of the oxide composition, current density, and effluent conductivity were investigated, and the current efficiency was calculated as a function of the time for the performed electrolyses. Results showed that all the studied electrodes led to a decrease in the content of both total phenolic compounds and total organic carbon (TOC), as well as lower absorbance in the UV–vis region. Toxicity tests using *Daphnia similis* demonstrated that the electrochemical treatment reduced the wastewater toxicity. The use of DSA[®] type electrodes in the electrochemical treatment of tannery wastewater proved to be useful since it can promote a decrease in total phenolic compounds, TOC, absorbance, and toxicity.

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1. Introduction

The tanning of animal skins aims at transforming them into stable and imputrescible products known as leather [1,2]. In this process, the skins undergo a chemical treatment for which a large number of organic and inorganic compounds like natural and/or synthetic tannins (polyphenolic compounds), surfactants, sulfonated oils, dyes, biocides, acrylic resins, organic acids, as well as ammonium, chromium(III), chloride, and sulfide salts are employed [3–6].

The transformation of skins into leather involves three main stages [4,7]: (a) the beamhouse, which cleans and eliminates the substances that will not compose the leather; (b) the tanning, which is the stage when pretreated skins are transformed into leather; and (c) the finishing, which complements the main tan-

ning and confers leather some desired physical and mechanical properties such as uniform color, tensile strength, impermeability, softness, elasticity, as well as its definitive presentation and aspect.

Tanneries are normally classified according to the stages involved in skin processing [4], i.e., (a) integrated tannery, which is able to perform all the operations on going from raw leather (fresh or cured skin) to finished leather; (b) wet-blue tannery: which processes raw leather until the chrome-tanned leather called wet-blue is achieved; (c) half-finishing tannery, which uses the wet-blue leather as raw material and transforms it into half-finishing leather, also known as crust; and (d) finishing tannery, which transforms crust leather into finished leather. Tanneries that process wet-blue leather until the finished leather is achieved also belong to the latter category.

The leather industry is a major producer of wastewaters and solid wastes containing potential water and soil contaminants [8,9]. Considering the large amount and variety of chemical agents used in skin processing, the wastewaters generated by

* Corresponding author. Tel.: +55 1636023869; fax: +55 1636024838.
E-mail address: olivip@ffclrp.usp.br (P. Olivi).

tanneries are very complex. Therefore, the development of treatment methods for these effluents is extremely necessary.

The main wastewater treatment processes are the primary treatment and the biological treatment. In the primary treatment process, also known as coagulation process, a coagulating agent is added to the wastewater. Aluminum salts such as $\text{Al}_2(\text{SO}_4)_3$ and AlCl_3 are generally used as coagulating agents. In solution, the aluminum ion hydrolyzes and generates some ionic monomeric species like $\text{Al}(\text{OH})_4^-$, $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_3^{2+}$, polymeric species like $\text{Al}_3\text{O}_4(\text{OH})_{24}^{7+}$, as well as $\text{Al}(\text{OH})_3$. The interaction of these species with the wastewater contaminants leads to the aggregation of colloidal particles that sediment later [10,11]. The sedimented portion, called primary sludge, is then separated from the clear effluent. Although this process is efficient to remove wastewater contaminants, it is a simple physico-chemical process of phase transference. Sludges resulting from this treatment are placed into industrial deposits and they can cause soil, ground and underground water contamination by contaminant leaching.

Contrary to the primary treatment, the biological process used in wastewater treatment promotes oxidation of the organic contaminants. However, the capacity of some microorganisms to degrade some of the contaminants is limited, which does not allow the complete removal of these compounds by a conventional biological process. For instance, some groups of tannins have complex structures, which are not easily degraded by microorganisms in either aerobic or anaerobic environments [12,13]. Moreover, variations in pH values, effluent composition, as well as contaminant type, structure and concentration may inhibit the functioning of an established biological system, thus paralyzing the microorganism metabolism [14]. Other limitations of the biological process include the long time needed for the effluent to reach the required standards and the low color removal efficiency [14,15]. Tannery wastewater treatment by the biological process may still be difficult because of the presence of broad spectrum biocides used in the leather industry to prevent fungal attack [16].

Due to the limitations of the primary and biological wastewater treatment processes, alternative processes have been pursued. Amongst them, electrochemical processes have been proposed and they have received increasing attention in the last years [12,17–19]. Compared to traditional methods, electrochemical processes offer [17,20]: (a) versatility, since they may be used to treat liquid and solid waste by direct and indirect organic compound oxidation, metal reduction and electrodeposition, not to mention the electrocoagulation and electroflotation processes; (b) automation, since the current and the potential are parameters that are easily acquired and controlled, facilitating the automation of the treatment process; and (c) environmental compatibility, since electrochemical processes are mediated by electron exchange with the electrode surface, dismissing the need for the addition of other chemical agents.

Oxide electrodes may be used in the electrochemical treatment of wastewaters containing high concentrations of potentially polluting species, and they can promote the oxidation of their organic constituents. An attractive and viable alternative is to employ dimensionally stable anodes (DSA[®]), because they

present high catalytic activity, high stability to anodic corrosion, and excellent mechanical stability [21–23]. These electrodes consist basically of a metallic support, frequently titanium, on which an electrically conductive oxide layer is deposited. In these electrodes, oxidation can occur by direct electron exchange between the contaminant and the electrode surface, or by indirect in situ electrogeneration of catalytic species with high oxidizing power, such as H_2O_2 , O_3 and Cl_2 , which are able to promote contaminant oxidation [14,17]. DSA[®] electrodes have shown to be efficient for the oxidation of various organic compounds such as pesticides [24], dyes [23,25], phenol [26] and formaldehyde [27].

The conductive layer of DSA[®] electrodes is generally formed by a mixture of active and inert metal oxides. The active oxides act as electrocatalysts, while the inert oxides modulate the electrochemical properties of the active components, providing high catalytic activity and higher lifetime [28,29]. In this work, we used IrO_2 and RuO_2 as electrocatalysts and SnO_2 and TiO_2 as modulator agents. TiO_2 was chosen because it is able to promote mechanical stability [22]. Besides, the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode is generally used as a standard DSA[®] in literature [30], which allows comparison with other electrochemical materials. SnO_2 was chosen because, in general, doped SnO_2 exhibits low resistivity, good stability, high overpotential for the oxygen evolution reaction (OER), and efficient phenol removal [31]. SnO_2 electrodes are also able to promote complete organic compound oxidation and it has been reported that antimony-doped SnO_2 electrodes behave as a metal-like material [32]. For these reasons, antimony-doped SnO_2 is a promising electrochemical material for organic compound removal from industrial wastewaters.

DSA[®] electrodes can be prepared by thermal decomposition of polymeric precursors, also known as the Pechini method [33]. This method is based on the ability of certain hydroxycarboxylic acids, such as citric acid, to form chelates with various metallic cations [33,34]. Firstly, the complexation of the organic acid with the metallic cation takes place. These chelates undergo polyesterification when heated in the presence of a polyhydroxyl alcohol such as ethylene glycol [34–36]. After heating, a polymeric resin containing uniformly distributed metallic cations strongly bound to the carboxylic groups is obtained [33,35]. This polymeric matrix can be deposited on a substrate and then thermally decomposed at elevated temperatures to form the desired oxide [35]. The Pechini method offers advantages such as low cost, good composition homogeneity, and high purity [35–37]. Moreover, some works have reported that Ti/RuO_2 and Ti/IrO_2 electrodes prepared by this method have longer lifetime and higher electrochemical active area than those prepared by traditional methods [21].

In this work we present the results obtained from the electrochemical treatment of tannery wastewater using dimensionally stable anodes prepared by the Pechini method. The evaluated parameters were total organic carbon (TOC), total phenolic compounds, UV–vis spectrum, chromium(VI) concentration, and acute toxicity for *Daphnia similis*. Effects of the oxide composition, current density, and effluent conductivity were also evaluated.

2. Experimental

2.1. Tannery wastewater characterization

The tannery wastewater submitted to electrochemical treatment was collected from the equalization tank of a finishing tannery that had processed wet-blue leather until finished leather was achieved. This wastewater was characterized using the following parameters: TOC, total phenolic compounds, UV–vis spectrum between 200 and 800 nm, total chromium, chromium(VI), chloride, conductivity, and pH. Acute toxicity bioassays with *D. similis* were also performed.

TOC was analyzed using a Shimadzu TOC-V_{CPN}. Total phenolic compounds were measured by the Folin-Ciocalteu method [38], and Cr(VI) was analyzed by the diphenylcarbazide method [38] using a Hewlett-Packard model 8452A spectrophotometer. UV–vis spectra were recorded using a Varian model Cary 50 Conc spectrophotometer. Total chromium was determined by atomic absorption using a Shimadzu model AA-680 flame spectrometer and a hollow cathode lamp for chromium (Hamamatsu Photonics K.K.) operating at 357.9 nm with a slit of 0.5 nm. Chloride was measured by potentiometric titration with a AgNO₃ 0.1 mol L⁻¹ solution using a combined-silver wire indicator electrode coupled to a Minipa model 207 pH meter/potentiometer. Conductivity was determined by an Orion model 105A+ conductivity meter purchased from the Thermo Electron Corporation and the pH was measured with a pH electrode coupled to a Qualxtron model 8010 pH meter.

Toxicity bioassays with *D. similis* were performed to determine the wastewater median effective concentration that could immobilize 50% of the organisms within 48 h (EC₅₀) [39]. These bioassays were performed in 30 mL test vessels. For the initial tannery wastewater, the bioassays were performed in four repeated experiments per concentration. For this, 10 mL of the test solutions and five organisms (6 h < age < 24 h) were used in each vessel. The test concentrations were 5.00, 2.50, 1.25, 0.63, and 0.32% and the samples were diluted with ground water with hardness of 40–48 mg L⁻¹ as CaCO₃ and pH of 7.0–7.6 (dilution water). After 48 h of incubation at 23 ± 1 °C, the immobile organism percentage was recorded. The result is expressed as EC₅₀ and it was statistically estimated by the trimmed Spearman-Kärber method [40].

2.2. Preparation and characterization of the oxide films

Electrodes with compositions Ti/Ir_{0.01}Sn_{0.99}O₂, Ti/Ir_{0.10}Sn_{0.90}O₂, Ti/Ru_{0.10}Sn_{0.90}O₂, Ti/Ru_{0.30}Ti_{0.70}O₂, Ti/Ir_{0.15}Ru_{0.15}Sn_{0.70}O₂, and Ti/Ir_{0.30}Ti_{0.30}Sn_{0.40}O₂ were prepared by the Pechini method [33]. The tin, iridium, ruthenium, and titanium precursor solutions were prepared using the following metal precursors: tin citrate, prepared according to a method described elsewhere [41]; IrCl₃·3H₂O (Acros); RuCl₃·*n*H₂O (Aldrich); and titanium isopropoxide (Acros). Iridium and ruthenium chlorides had been previously dissolved in a HCl (Vetec) 1:1 (v:v) solution, so that a 0.1 mol L⁻¹ concentration would be achieved. The polymeric precursor solutions were prepared by dissolution of citric acid (Merck) in ethylene glycol (Mallinckrodt), at

65 °C. After total dissolution of the citric acid, the temperature was raised to 90 °C, and the metal precursor was added. The metal: citric acid: ethylene glycol molar ratio was 1:3:10, in the case of the tin, iridium and ruthenium solutions, and 1:4:16 for the titanium solution [21,28]. Each mixture was then kept under vigorous magnetic stirring for about 3 h.

The prepared precursor solutions were standardized by gravimetric analysis. For this, 1 g of each solution was precisely weighed in a crucible and burned at 650 °C for 4 h under air atmosphere. This procedure was performed three times for each precursor solution. The products obtained after the burning (SnO₂, RuO₂, IrO₂, and TiO₂) were weighed and the concentrations of the precursor solutions were determined.

Antimony was added to the tin precursor solution in a 2.0% mol ratio in relation to tin. For this, Sb₂O₃ (Riedel-de Haën) and some drops of concentrated HNO₃ were added to the precursor solution, which was then heated at a temperature of 60 °C until complete dissolution of Sb₂O₃ was achieved.

The tin, iridium, ruthenium, and titanium precursor solutions were mixed in order to obtain the desired molar ratios in the oxide mixtures (nominal compositions). The oxide films were prepared on titanium supports with 0.15 mm thickness. They consist of a plate with dimensions 1 cm × 1 cm and a stem of 3 cm length (Fig. 1a). These supports were pretreated by steel sphere blasting and chemical processes (immersion in boiling water for 30 min, ultrasonication in isopropanol for 30 min, immersion in boiling HCl 20% solution for 5 min, and immersion in boiling oxalic acid 10% solution for 20 min). After pretreatment, the precursor solution mixtures were spread on both sides of the titanium plates (electrode total geometric area = 2 cm²) with the help of a brush. The supports were then heated in an air furnace at 120–130 °C for 5 min and burned at 450 °C for 5 min under oxygen flow (5 L min⁻¹). These steps were repeated until a mass corresponding to a nominal thickness of 2 μm was reached (typically 10 applications). The electrodes were then burned for 1 h at the same temperature and oxygen flow.

After the burning, the stems of the supports were polished to remove the TiO₂ layer formed in the burning process. An electrical contact was established between the titanium support stem and a copper wire. The assembly was placed in a glass

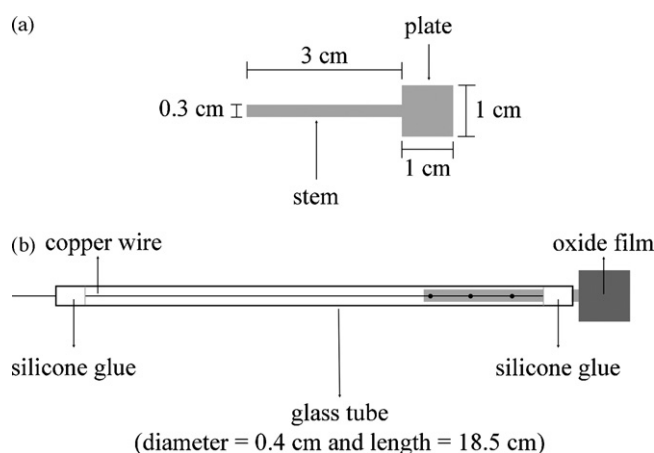


Fig. 1. Scheme of (a) the titanium support and (b) the final mounted electrode.

tube that was sealed with a silicone glue in order to prevent the solution from entering the tube during the experiments. Fig. 1b shows a scheme of the final electrode mounting.

Oxide film surface morphology was analyzed by scanning electron microscopy (SEM) using a Zeiss EVO 50 microscope. Voltammetric characterization of the electrodes was performed using an Autolab PGSTAT30 potentiostat/galvanostat coupled to a microcomputer. The cyclic voltammograms were recorded at a 50 mV s^{-1} scan rate, between 0.40 and 1.60 V vs. reversible hydrogen electrode (RHE), in a H_2SO_4 (Merck) 0.5 mol L^{-1} solution. This solution was deaerated prior to experiments by nitrogen bubbling. A 250 mL electrochemical cell was used for the voltammetric characterization. It consisted of one main central compartment for the working electrode (DSA[®]) containing an entrance for the deaeration system, and three side-compartments separated from the main compartment by coarse glass frits. One compartment contained a Luggin capillary for the reference electrode (saturated calomel electrode—SCE). The two other side-compartments, placed parallel to each other, contained the counter electrodes (spiraled platinized platinum wires). Cyclic voltammograms were also recorded in the tannery wastewater for each prepared oxide composition, using the same electrochemical cell and conditions described above.

2.3. Tannery wastewater electrochemical treatment

The tannery wastewater electrochemical treatments were performed in a 50 mL one-compartment cell, at room temperature (ca. 25°C) and under magnetic stirring, using the potentiostat/galvanostat described in Section 2.2. The prepared oxide electrodes were used as working electrodes. An RHE electrode was used as reference, and two spiraled platinized platinum wires were used as counter electrodes. The electrodes were placed in the cell in an arrangement similar to the one presented by Malpass et al. [24].

Electrolyses were performed under galvanostatic conditions at a 20 mA cm^{-2} current density, for 1, 3, and 5 h. The following parameters were evaluated after the electrolyses: TOC, total phenolic compounds, UV–vis spectra, and chromium(VI). Electrolyses at 50 and 100 mA cm^{-2} were also performed with the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode. Electrolyses at 100 mA cm^{-2} using a $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode were also performed in the presence of Na_2SO_4 0.1 mol L^{-1} to evaluate the influence of wastewater conductivity.

2.4. Effect of the electrochemical treatment on the tannery wastewater toxicity

Acute toxicity bioassays with *D. similis* were performed for the wastewaters obtained after 5 h of electrochemical treatment with the following electrodes and current densities: $\text{Ti/Ir}_{0.15}\text{Ru}_{0.15}\text{Sn}_{0.70}\text{O}_2$ electrode at 20 mA cm^{-2} , $\text{Ti/Ir}_{0.30}\text{Ti}_{0.30}\text{Sn}_{0.40}\text{O}_2$ electrode at 20 mA cm^{-2} , and $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode at 20, 50 and 100 mA cm^{-2} . The bioassays were performed in three repeated experiments per concentration and the procedure was the same as the one described in Section 2.1. In order to eliminate Cr(VI) and

the remaining active chlorine that could influence the test results, we added $24 \mu\text{L}$ of Na_2SO_3 (J.T. Baker) 1.0 mol L^{-1} solution per mL of treated wastewater. The amount of Na_2SO_3 was calculated considering that Cr(III) and Cl^- were totally oxidized to Cr(VI) and active chlorine, respectively. Since in all electrolyses Cr(III) was not totally oxidized to Cr(VI), we considered that a Na_2SO_3 excess was added. A Na_2SO_3 control solution was prepared in dilution water ($24 \mu\text{L}$ of Na_2SO_3 1.0 mol L^{-1} solution per mL of dilution water) and it was submitted to the toxicity bioassays. For this, it was diluted at the same concentrations of the wastewater samples, i.e., 5.00, 2.50, 1.25, 0.63, and 0.32%. The results were expressed as the percentage of immobile *D. similis* at a given concentration.

3. Results and discussion

3.1. Tannery wastewater characterization

Table 1 shows the results of the characterization of the wastewater obtained from a finishing tannery. The wastewater contains mainly organic compounds, used in large quantities in these tanneries. Parameters such as TOC, total phenolic compounds, absorbance, and toxicity were evaluated. The wastewater also contained chromium and chloride. The presence of chromium was expected since it is often used by finishing tanneries, while chloride ions probably remain from the first stages of the tanning process. Although the wastewater contained chromium, Cr(VI) is not detected, indicating that chromium is in the oxidation state III, which is the state that it is generally used by tanneries.

The wastewater color observed in the visible region is mainly due to the presence of dyes. The wastewater also contained suspended solids, which was confirmed by the differences observed between the visible region absorbance values obtained with the filtered and non-filtered wastewater. The wastewater also absorbed in the UV region due to the presence of compounds containing conjugated double bonds, such as aromatic compounds.

The tannery wastewater has an EC_{50} value of 2.25% for *D. similis*. The lower the value of EC_{50} , the more toxic is the efflu-

Table 1
Characteristics of the tannery wastewater

Parameter	Value
TOC (mg L^{-1})	1005.0
Total phenolic compounds (mg L^{-1})	47.3
Absorbance 440 nm—non-filtered wastewater	0.742
Absorbance 440 nm—filtered wastewater	0.323
Absorbance 600 nm—non-filtered wastewater	0.433
Absorbance 600 nm—filtered wastewater	0.165
Absorbance 228 nm—wastewater diluted 50 times	1.343
EC_{50} <i>Daphnia similis</i> —48 h (%)	2.25
Total chromium (mg L^{-1})	49.8
Chromium VI (mg L^{-1})	n.d.
Chloride (mg L^{-1})	787.0
Conductivity (mS cm^{-1})	6.1
pH	4.0

n.d.: Not detected.

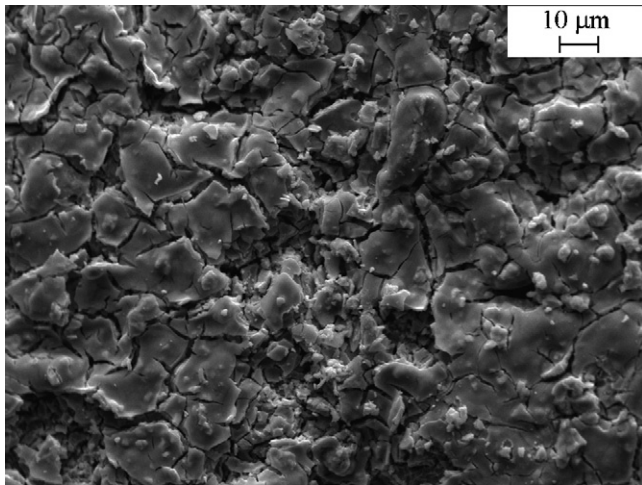


Fig. 2. SEM micrograph of the Ti/Ru_{0.10}Sn_{0.90}O₂ film (magnification 2000×).

ent, which indicates that the analyzed effluent is highly toxic for this organism.

3.2. Electrode characterization and tannery wastewater electrochemical treatment

Fig. 2 shows SEM micrograph of the Ti/Ru_{0.10}Sn_{0.90}O₂ electrode, whose morphology is similar to those of the other electrodes used in this work. This film has homogenous morphology with a “cracked mud” aspect, which is typical of oxide films obtained by thermal decomposition [42]. This kind of morphology confers high surface area to electrodes.

Fig. 3 shows the cyclic voltammograms recorded for the Ti/Ru_{0.10}Sn_{0.90}O₂ electrode in H₂SO₄ 0.5 mol L⁻¹ solution and in the tannery wastewater. All the electrodes display the expected voltammetric profile in H₂SO₄ solution. For this solution, the anodic peak observed at ca. 1.15 V (vs. RHE) is attributed to the Ru(III)/Ru(IV) transition, and the cathodic peak at ca. 1.12 V is attributed to the reverse process. A fast current increase is observed from 1.45 V (vs. RHE) in H₂SO₄ solution, due to the

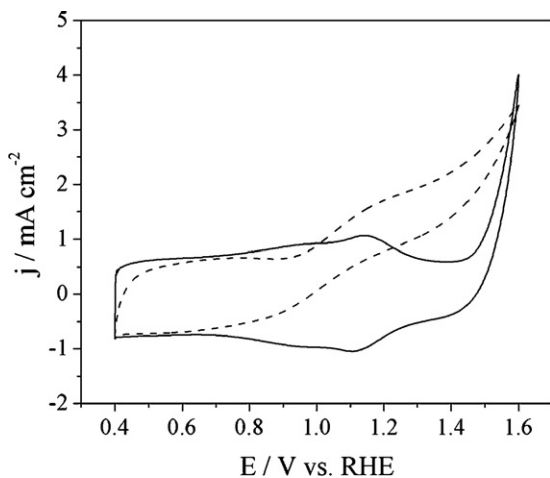


Fig. 3. Cyclic voltammograms recorded with the Ti/Ru_{0.10}Sn_{0.90}O₂ electrode at a 50 mV s⁻¹ scan rate in: (—) H₂SO₄ 0.5 mol L⁻¹ solution, (---) the tannery wastewater.

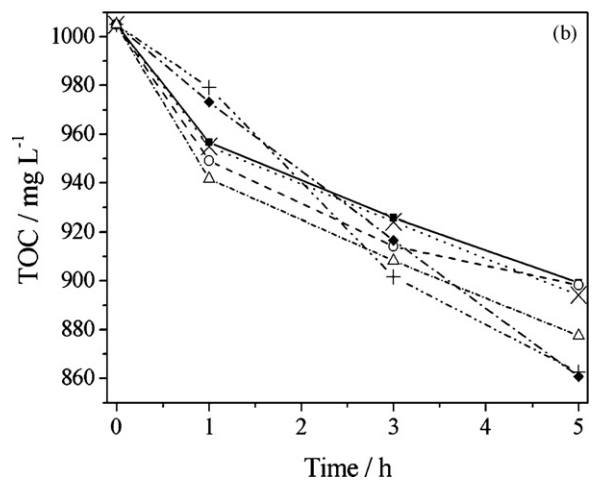
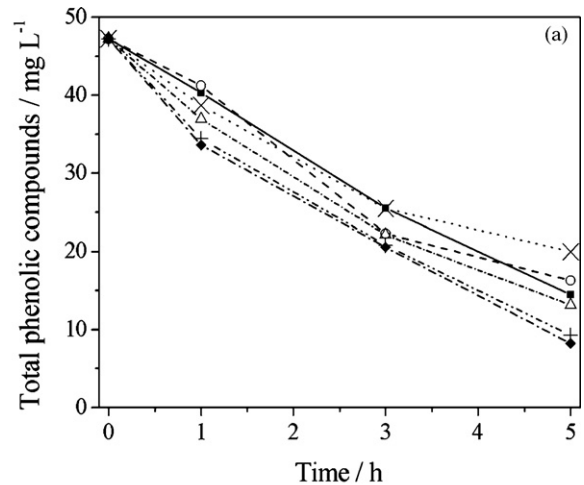


Fig. 4. Decay of (a) the total phenolic compound concentration and (b) TOC as a function of electrolysis time for the experiments performed at 20 mA cm⁻² with the following electrodes: (■) Ti/Ir_{0.01}Sn_{0.99}O₂, (○) Ti/Ir_{0.10}Sn_{0.90}O₂, (×) Ti/Ru_{0.10}Sn_{0.90}O₂, (◆) Ti/Ru_{0.30}Ti_{0.70}O₂, (+) Ti/Ir_{0.15}Ru_{0.15}Sn_{0.70}O₂, and (△) Ti/Ir_{0.30}Ti_{0.30}Sn_{0.40}O₂.

oxygen evolution reaction. The voltammetric profile observed for all the electrodes used in this work agrees with literature data regarding both the redox transitions involving iridium and ruthenium and the potentials associated with OER [42,43]. For the cyclic voltammogram of the Ti/Ru_{0.10}Sn_{0.90}O₂ electrode recorded in the tannery wastewater, there is an oxidation process around 1.20 V, which may be attributed to the wastewater constituents, since this process is not observed in the absence of the wastewater. A similar behavior is observed for the other electrodes; only the potentials in which the process occurs and the obtained current values are different.

Electrolyses at a 20 mA cm⁻² current density were performed for all the electrodes. The results show that all the electrodes are able to decrease the content of phenolic compounds in the wastewater. Fig. 4a shows the amount of total phenolic compounds at different electrolysis times. The Ti/Ru_{0.30}Ti_{0.70}O₂ and Ti/Ir_{0.15}Ru_{0.15}Sn_{0.70}O₂ electrodes are the most efficient for phenol oxidation. For these electrodes the phenol removals are 82.6 and 80.4% respectively, after 5 h of electrolysis.

The electrodes are not so efficient for TOC removal (Fig. 4b) as for total phenolic compound removal. After 5 h of electrolysis at 20 mA cm^{-2} , the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ and $\text{Ti/Ir}_{0.15}\text{Ru}_{0.15}\text{Sn}_{0.70}\text{O}_2$ electrodes, which were the most efficient for phenol oxidation, were also the most efficient for TOC removal. For these electrodes, the TOC removals after 5 h are 14.3 and 14.2%, respectively. The decrease in TOC is associated with the complete oxidation of organic contaminants into carbon dioxide and water, i.e., contaminant mineralization.

The color removal was spectrophotometrically evaluated in the visible region (from 400 to 800 nm). Fig. 5a shows the visible region spectra obtained along the electrolysis when the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode was used at 20 mA cm^{-2} . Similar spectra were obtained for the other electrodes. In order to compare the performance of the six electrodes with respect to color removal, we plotted absorbance values obtained at 440 nm (Fig. 5b) and 600 nm (Fig. 5c) vs. electrolysis time. The $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode is superior to the others when the absorbance at 440 nm is evaluated. The absorbance decreases at 600 nm, but it does not differ significantly when different electrodes are considered. At 440 nm, this difference is slightly larger.

We also recorded spectra of the wastewater diluted 50 times in the ultraviolet spectral region (from 200 to 400 nm) to evaluate the oxidation of organic compounds containing conjugated double bonds. These compounds absorb in the UV region due to $\pi \rightarrow \pi^*$ transitions [44]. Fig. 6a shows the UV spectra obtained for the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode at 20 mA cm^{-2} . Fig. 6b shows the absorbance values at 228 nm vs. electrolysis time. The wavelength 228 nm was chosen due to the presence of a band in this spectral region. Another band can be observed at 279 nm; however, at this wavelength, a similar absorbance value is obtained for all the electrodes. The $\text{Ti/Ir}_{0.15}\text{Ru}_{0.15}\text{Sn}_{0.70}\text{O}_2$ electrode is the best for the degradation of organic compounds when the absorbance at 228 nm is evaluated.

Results of the electrolysis carried out at 20 mA cm^{-2} show that the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ and $\text{Ti/Ir}_{0.15}\text{Ru}_{0.15}\text{Sn}_{0.70}\text{O}_2$ electrodes were the most efficient for phenol and TOC removal. The $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode was the most efficient for color removal at 440 nm, and the $\text{Ti/Ir}_{0.15}\text{Ru}_{0.15}\text{Sn}_{0.70}\text{O}_2$ electrode was the best for degradation of organic compounds with unsaturated bonds.

The $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode was also used in the electrochemical treatment of the tannery wastewater at higher current densities, i.e., 50 and 100 mA cm^{-2} . Fig. 7 shows the total phenolic compound and TOC values as a function of the electrolysis time. After 1 and 3 h of electrolysis, higher current densities result in higher phenol removals, but after 5 h, there is not a significant difference between the current densities. Phenol removals are 82.6% at 20 mA cm^{-2} , 78.5% at 50 mA cm^{-2} , and 83.9% at 100 mA cm^{-2} , after 5 h of electrolysis. On the other hand, higher TOC removals are obtained at higher current densities in all the time ranges. After 5 h of electrolysis, the TOC removals are 14.3, 31.3, and 40.5% at 20, 50, and 100 mA cm^{-2} , respectively.

Na_2SO_4 was added to the tannery wastewater to verify the influence of the wastewater conductivity. Addition of this salt

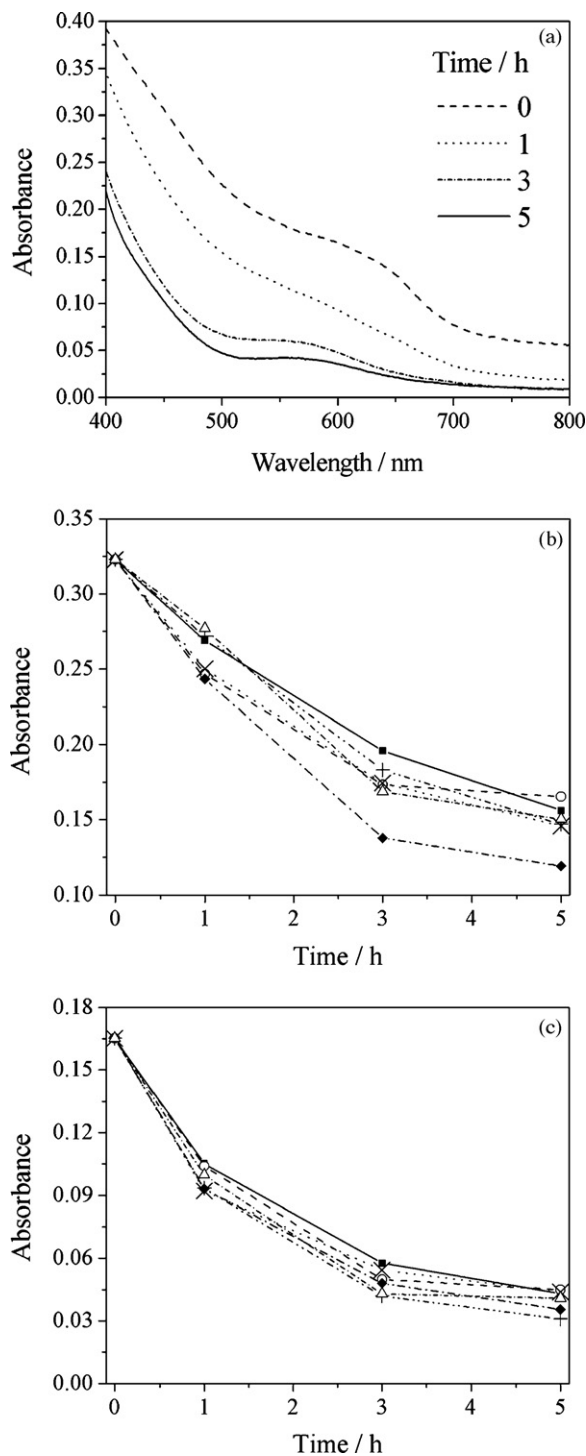


Fig. 5. (a) Visible spectra of the tannery wastewater as a function of electrolysis time, for the experiments performed at 20 mA cm^{-2} with the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode. Absorbance at (b) 440 nm and (c) 600 nm as a function of electrolysis time for the experiments performed at 20 mA cm^{-2} with the following electrodes: (■) $\text{Ti/Ir}_{0.01}\text{Sn}_{0.99}\text{O}_2$, (○) $\text{Ti/Ir}_{0.10}\text{Sn}_{0.90}\text{O}_2$, (×) $\text{Ti/Ru}_{0.10}\text{Sn}_{0.90}\text{O}_2$, (◆) $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$, (+) $\text{Ti/Ir}_{0.15}\text{Ru}_{0.15}\text{Sn}_{0.70}\text{O}_2$, and (△) $\text{Ti/Ir}_{0.30}\text{Ti}_{0.30}\text{Sn}_{0.40}\text{O}_2$.

increases the conductivity from 6.1 to 20.3 mS cm^{-1} . The electrochemical treatment of the wastewater in the presence of Na_2SO_4 using the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode at 100 mA cm^{-2} results in a phenol removal of 81.7% (Fig. 7a) and a TOC removal

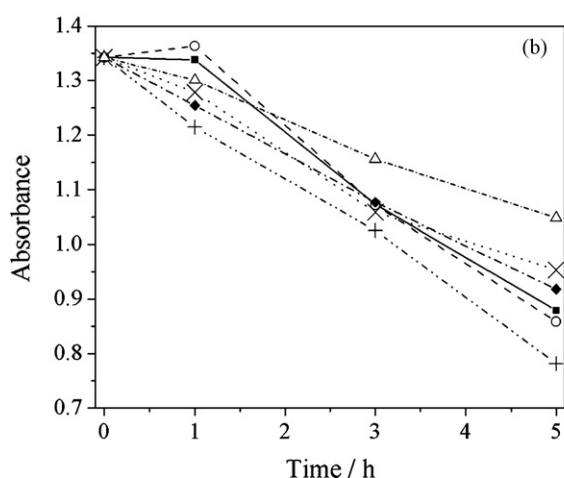
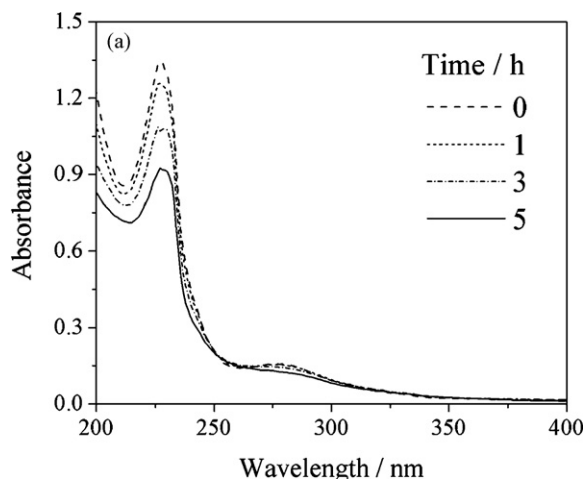


Fig. 6. (a) UV spectra of the tannery wastewater diluted 50 times as a function of electrolysis time for the experiments performed at 20 mA cm^{-2} with the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode. (b) Absorbance at 228 nm as a function of electrolysis time for the experiments performed at 20 mA cm^{-2} with the following electrodes: (■) $\text{Ti/Ir}_{0.01}\text{Sn}_{0.99}\text{O}_2$, (○) $\text{Ti/Ir}_{0.10}\text{Sn}_{0.90}\text{O}_2$, (×) $\text{Ti/Ru}_{0.10}\text{Sn}_{0.90}\text{O}_2$, (◆) $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$, (+) $\text{Ti/Ir}_{0.15}\text{Ru}_{0.15}\text{Sn}_{0.70}\text{O}_2$, and (△) $\text{Ti/Ir}_{0.30}\text{Ti}_{0.30}\text{Sn}_{0.40}\text{O}_2$.

of 25.7% (Fig. 7b), after 5h. Phenol removal at 100 mA cm^{-2} in the presence of Na_2SO_4 is similar to that obtained at 50 mA cm^{-2} , in the absence of the salt. The decrease in TOC at 100 mA cm^{-2} in the presence of Na_2SO_4 is lower than those obtained at 50 and 100 mA cm^{-2} in the absence of the salt, but higher than that achieved at 20 mA cm^{-2} .

Fig. 8a displays the absorbance values obtained at 440 and 600 nm as a function of electrolysis time for the experiments performed at different current densities using the same electroodic composition. The electrolyses performed at 50 and 100 mA cm^{-2} resulted in higher decrease in the absorbance values at 600 nm than that obtained at 20 mA cm^{-2} . However, at 440 nm, an increase in absorbance values is observed after 5 and 3 h of electrolysis at 50 and 100 mA cm^{-2} respectively, but this behavior is not observed for the electrolyses performed at 20 mA cm^{-2} . This increase in absorbance values at 440 nm can be explained by the presence of chromium in the wastewater. Cr(III) displays an absorbance maximum at 600 nm, while Cr(VI) strongly absorbs in the region of 400 nm [38]. The

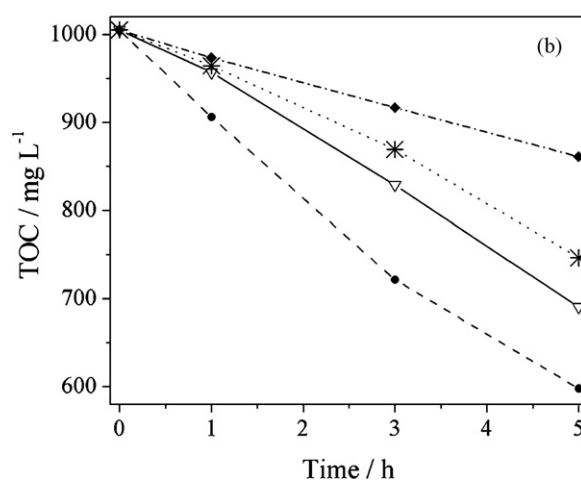
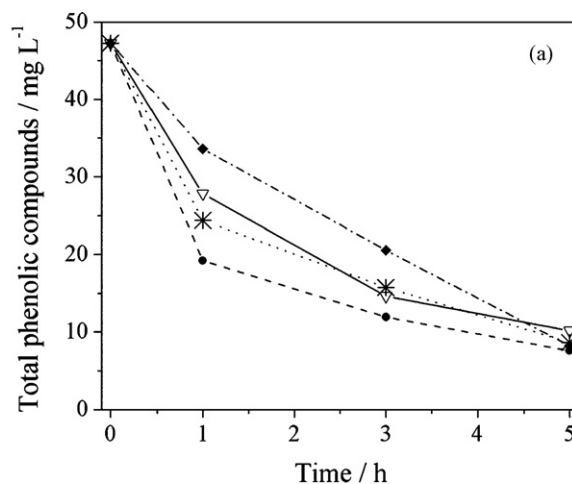


Fig. 7. Decay of (a) the total phenolic compound concentration and (b) TOC as a function of electrolysis time for the experiments performed with the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode at the following current densities: (◆) 20 mA cm^{-2} , (▽) 50 mA cm^{-2} , (●) 100 mA cm^{-2} , and (*) 100 mA cm^{-2} , in the presence of $\text{Na}_2\text{SO}_4 0.1 \text{ mol L}^{-1}$.

increase in the absorbance values at 440 nm with a concomitant decrease in the absorbance values at 600 nm indicate that Cr(III) is being oxidized to Cr(VI) along the electrochemical process at higher current densities. In order to confirm this hypothesis, Cr(VI) analyses were performed. The results are shown in Table 2.

Cr(VI) is not detected for the electrolysis carried out at 20 mA cm^{-2} , except when the $\text{Ti/Ir}_{0.01}\text{Sn}_{0.99}\text{O}_2$ and $\text{Ti/Ir}_{0.10}\text{Sn}_{0.90}\text{O}_2$ electrodes are used. Although the Cr(III)/Cr(VI) oxidation does not take place during electrolysis with the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode at 20 mA cm^{-2} , Cr(VI) is detected in the electrolyses at 50 and 100 mA cm^{-2} . In the presence of Na_2SO_4 , Cr(VI) is also detected. The Cr(VI) concentration in the presence of the salt as a function of electrolysis time at 100 mA cm^{-2} is lower than that obtained in the electrolysis performed under the same condition, in the absence of the salt. However, in the wastewater containing Na_2SO_4 , Cr(VI) is detected after 1 h of electrolysis, while in the electrolysis in the absence of the salt, it is detected only after 3 h of electrolysis.

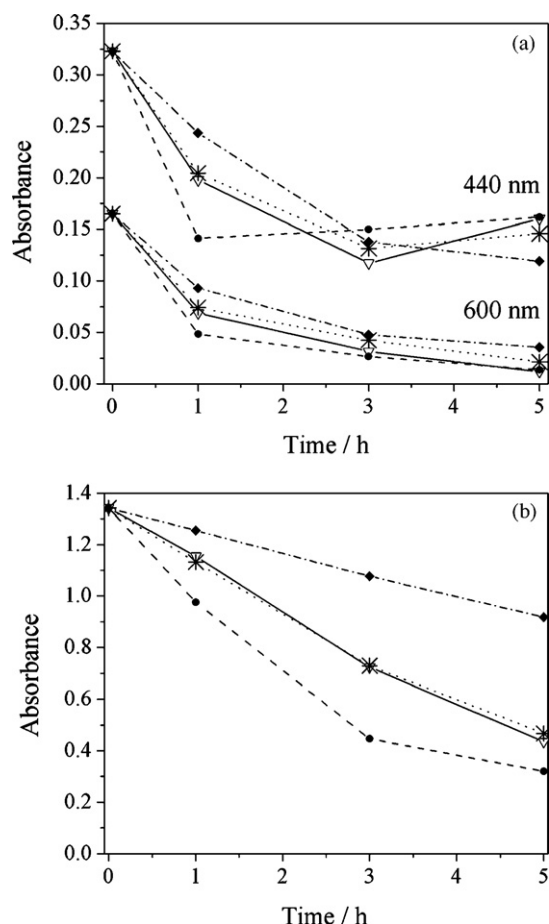


Fig. 8. Absorbance at (a) 440 and 600 nm and at (b) 228 nm as a function of electrolysis time for the experiments performed using the Ti/Ru_{0.30}Ti_{0.70}O₂ electrode at the following current densities: (◆) 20 mA cm⁻², (▽) 50 mA cm⁻², (●) 100 mA cm⁻², and (*) 100 mA cm⁻², in the presence of Na₂SO₄ 0.1 mol L⁻¹.

Fig. 8b shows the absorbance values at 228 nm as a function of electrolysis time, for the experiments performed with the Ti/Ru_{0.30}Ti_{0.70}O₂ electrode at different current densities. Higher compound degradations are obtained at higher current densities. Compound degradation at 100 mA cm⁻² in the presence of Na₂SO₄ is similar to that obtained at 50 mA cm⁻² in the absence of the salt.

Table 2
Cr(VI) concentration during electrolyses

Electrolysis conditions	Cr(VI) (mg L ⁻¹)		
	1 h	3 h	5 h
Ti/Ir _{0.01} Sn _{0.99} O ₂ at 20 mA cm ⁻²	n.d.	n.d.	3.9
Ti/Ir _{0.10} Sn _{0.90} O ₂ at 20 mA cm ⁻²	n.d.	5.8	9.3
Ti/Ru _{0.10} Sn _{0.90} O ₂ at 20 mA cm ⁻²	n.d.	n.d.	n.d.
Ti/Ir _{0.15} Ru _{0.15} Sn _{0.70} O ₂ at 20 mA cm ⁻²	n.d.	n.d.	n.d.
Ti/Ir _{0.30} Ti _{0.30} Sn _{0.40} O ₂ at 20 mA cm ⁻²	n.d.	n.d.	n.d.
Ti/Ru _{0.30} Ti _{0.70} O ₂ at 20 mA cm ⁻²	n.d.	n.d.	n.d.
Ti/Ru _{0.30} Ti _{0.70} O ₂ at 50 mA cm ⁻²	n.d.	0.4	16.8
Ti/Ru _{0.30} Ti _{0.70} O ₂ at 100 mA cm ⁻²	n.d.	15.6	25.1
Ti/Ru _{0.30} Ti _{0.70} O ₂ at 100 mA cm ^{-2a}	0.1	2.0	17.8

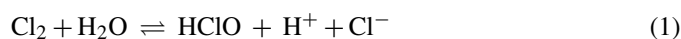
n.d.: Not detected.

^a In the presence of Na₂SO₄ 0.1 mol L⁻¹.

The oxidation of the organic constituents of the tannery wastewater, confirmed by the decrease in the values of total phenolic compounds, TOC, and absorbance, can be attributed to two different processes. The first is the direct oxidation of wastewater components by the metal oxide or HO• radicals available at the electrode surface. The second is the indirect oxidation of the wastewater components by oxidizing agents formed in parallel reactions, as is the case of ClO⁻, which is formed from Cl⁻ oxidation [45].

Effective contaminant degradation is based on the direct electrochemical process and depends mainly on the reaction with HO• radicals at the electrode surface [18]. These radicals are powerful oxidizing agents, they are non-specific, and they can promote organic contaminant mineralization [12].

DSA[®] electrodes have high electrocatalytic activity with respect to chlorine evolution because of the surface redox reactions that take place at transition metal oxides, which act as active sites for the adsorption of chlorine atoms [19]. The chlorine formed at the electrode undergoes a dismutation reaction in solution (Eq. (1)), to form hypochlorous acid and hypochlorite ion, depending on the solution pH (Eq. (2)) [12]. Chlorine, hypochlorous acid, and hypochlorite ions are strong oxidizing agents. These solution species are referred to as active chlorine [12].



Although active chlorine can act as a mediator in wastewater treatment, it is not able to completely oxidize organic compounds to water and carbon dioxide [18]. Besides, reactions between these species and organic compounds can produce organochloride compounds [46]. In fact, the formation of chlorinated compounds was observed during the electrochemical oxidation of phenol using a DSA[®] electrode in the presence of chloride [47]. Although reactions between active chlorine and organic compounds can result in the formation of organochlorides, which are mostly lipophilic, persistent and toxic in aquatic environments, it is estimated that only a low percentage of the applied chlorine ends up in the form of chlorinated organic products [46].

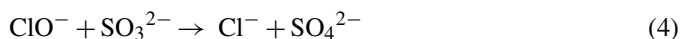
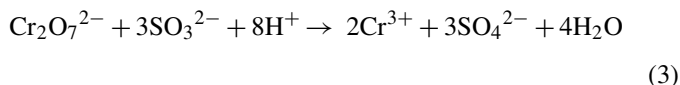
The results obtained in this work indicate that the degradation of tannery wastewater contaminants occurs by both the direct and indirect processes. The decrease in TOC values along the treatment process gives evidence that the direct process takes place, while the characteristic strong odor of active chlorine during the electrolysis gives evidence of the indirect process.

The addition of Na₂SO₄ to the tannery wastewater results in lower organic species oxidation at 100 mA cm⁻² if compared to the electrolyses performed at the same current density, but in the absence of the electrolyte. Since the current densities in the two cases are the same, the electrode potential when the wastewater treatment is performed in the presence of Na₂SO₄ is lower due to the higher wastewater conductivity. This lower potential inhibits the wastewater organic compound mineralization, and the presence of SO₄²⁻ ions in the wastewater makes Cl⁻ oxidation more difficult, thus hindering contaminant oxidation by the

indirect process. Although active chlorine species are not able to completely oxidize the contaminants into water and carbon dioxide, it is probable that the products formed in these reactions are more easily mineralized.

RuO_2 and IrO_2 are known to be active electrocatalysts for chlorine evolution, being RuO_2 more active than IrO_2 [48]. In the case of the electrolyses at 20 mA cm^{-2} , only the electrodes containing iridium and tin were able to oxidize Cr(III). This can be explained by the competition between Cl^- and Cr(III) oxidation at lower current densities, which is not observed with the electrodes containing iridium and ruthenium or only ruthenium as electrocatalysts. The $\text{Ti}/\text{Ir}_{0.30}\text{Ti}_{0.30}\text{Sn}_{0.40}\text{O}_2$ electrode is not able to oxidize Cr(III) to Cr(VI) at 20 mA cm^{-2} indicating that a higher iridium amount and/or the presence of titanium in the electrodes may have inhibited Cr(III) oxidation at a lower current density. On the other hand, the Cr(III)/Cr(VI) oxidation also depends on the current density, if we remember that Cr(VI) was not detected in the electrolyses using the $\text{Ti}/\text{Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode at 20 mA cm^{-2} , but it was detected when the electrolyses were performed at higher current densities. The presence of Na_2SO_4 probably facilitates Cr(III) oxidation, since Cr(VI) is detected after 1 h of electrolysis at 100 mA cm^{-2} . However, since the resulting electrode potential is lower than that obtained in the absence of sulfate, after 3 and 5 h, the Cr(VI) concentration in the wastewater containing Na_2SO_4 is lower than that detected in the wastewater that did not contain any added sulfate.

The Cr(III)/Cr(VI) oxidation is a disadvantage of the electrochemical treatment of tannery wastewater using DSA[®] electrodes, since Cr(VI) is more toxic than Cr(III). However, this drawback can be easily overcome by means of a reducing agent, which is able to reduce Cr(VI) to Cr(III). Sodium sulfite (Na_2SO_3) and its analogs sodium bisulfite (NaHSO_3) and sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) are the best reducing agents in this case because, besides promoting Cr(VI) reduction and producing sulfate as byproduct (Eq. (3)) [49], they are also used in tanneries during skin processing [4]. At the end of the process, Cr(III) can be precipitated as $\text{Cr}(\text{OH})_3$ using Na_2CO_3 [47]. Besides promoting Cr(VI) reduction, Na_2SO_3 can also reduce the remaining active chlorine species (Eq. (4)).



Apart from promoting the direct and indirect oxidation of wastewater contaminants, the electrochemical process can also lead to contaminant aggregation by electroflotation, thanks to hydrogen and oxygen gases generated from water electrolysis in a parallel process [17,45]. It is possible that this process occurred during the wastewater electrochemical treatment since the formation of some suspended solids was observed.

3.3. Toxicity bioassays with *D. similis*

Fig. 9a shows the results of the toxicity bioassays performed for the tannery wastewaters obtained after 5 h of electrochemical

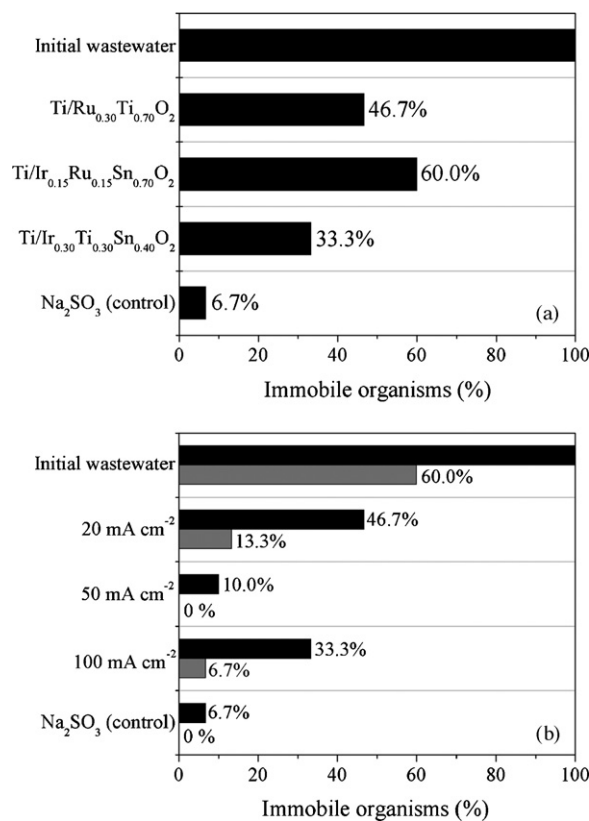


Fig. 9. Immobile *Daphnia similis* percentage obtained placing the organisms for 48 h in (■) 5.00% and (▒) 2.50% solutions prepared from tannery wastewater, before and after electrochemical treatments (a) with DSA[®] electrodes at 20 mA cm^{-2} for 5 h and (b) with $\text{Ti}/\text{Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode at 20, 50 and 100 mA cm^{-2} for 5 h.

treatment with the $\text{Ti}/\text{Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$, $\text{Ti}/\text{Ir}_{0.15}\text{Ru}_{0.15}\text{Sn}_{0.70}\text{O}_2$, and $\text{Ti}/\text{Ir}_{0.30}\text{Ti}_{0.30}\text{Sn}_{0.40}\text{O}_2$ electrodes at 20 mA cm^{-2} . In these conditions all wastewaters obtained after the electrochemical treatment exhibit lower toxicity than the initial tannery wastewater. The toxicity of the Na_2SO_3 control solution diluted in the same concentrations of the wastewater samples is insignificant compared to the wastewater samples. This result shows that the toxicity bioassays are not affected by the presence of Na_2SO_3 , since the concentration of this salt in the treated wastewaters is lower than that in the control solution. Besides, this suggests that Na_2SO_3 is a good reducing agent for use in the toxicity bioassays with *D. similis*, and it may be used as a complementary step of the electrochemical treatment of tannery wastewaters to reduce Cr(VI) and the remaining active chlorine, which are potentially toxic species.

Fig. 9b shows the results of the toxicity bioassays performed for the tannery wastewaters electrochemically treated with the $\text{Ti}/\text{Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode at 20, 50 and 100 mA cm^{-2} , for 5 h. The toxicity of the wastewater treated at 50 mA cm^{-2} is lower than that of the wastewater treated at 20 mA cm^{-2} . The electrolysis performed at 100 mA cm^{-2} results in a less toxic wastewater than that carried out at 20 mA cm^{-2} , but it is more toxic than that done at 50 mA cm^{-2} . Since the removals of total phenolic compounds (Fig. 7a), TOC (Fig. 7b), and organic compounds with unsaturated bonds (Fig. 8b) are higher at 100 mA cm^{-2}

than at 50 mA cm^{-2} , that Cr(VI) was reduced to Cr(III) and that active chlorine was reduced to chloride before the toxicity tests were performed, the higher toxicity of the wastewater treated at 100 mA cm^{-2} may be attributed to the probable formation of organochloride compounds, which can be favored at this current density.

3.4. Current efficiency

The current efficiency for the electrochemical oxidation processes is defined as the current fraction used for the organic compound oxidation. In the oxidation of complex samples containing several organic compounds, such as wastewaters, the current efficiency is calculated considering the values of chemical oxygen demand (COD) or TOC of the wastewater before and after the electrochemical treatment [20]. In this work, the current efficiency (CE) was calculated from the TOC values using the following relation [20,46,47]:

$$\text{CE} (\%) = 267 F V \frac{(\text{TOC})_0 - (\text{TOC})_t}{8 I \Delta t} \quad (5)$$

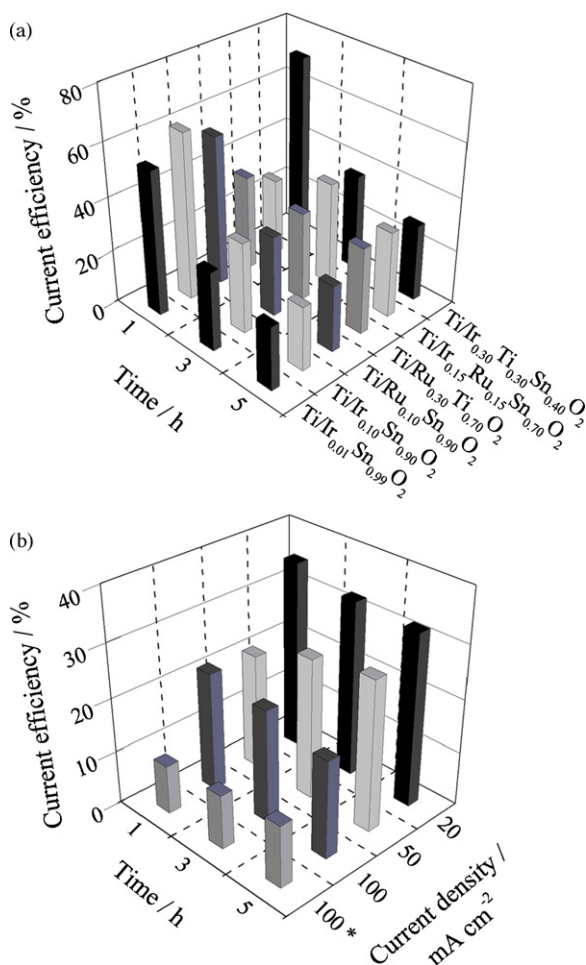


Fig. 10. Current efficiency as a function of electrolysis time: (a) for the experiments performed at 20 mA cm^{-2} and (b) for the experiments performed with the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode at 20, 50, and 100 mA cm^{-2} (electrolyses performed in the presence of Na_2SO_4).

where $(\text{TOC})_0$ and $(\text{TOC})_t$ are the total organic carbon (g L^{-1}) at times 0 and t (s), respectively; I is the current (A); F is the Faraday constant ($96,487 \text{ C mol}^{-1}$), and V is the wastewater volume (L). Fig. 10 shows the CE values as a function of electrolysis time.

Fig. 10a shows that the CE values obtained for the electrolyses performed at 20 mA cm^{-2} decrease with the electrolysis time, except for the experiments performed with the $\text{Ti/Ir}_{0.15}\text{Ru}_{0.15}\text{Sn}_{0.70}\text{O}_2$ electrode. For this electrode, the CE is 28.8% after 1 h, 38.5% after 3 h and 31.9% after 5 h. After 1 h of electrolysis, the $\text{Ti/Ir}_{0.01}\text{Sn}_{0.99}\text{O}_2$, $\text{Ti/Ir}_{0.10}\text{Sn}_{0.90}\text{O}_2$, $\text{Ti/Ru}_{0.10}\text{Sn}_{0.90}\text{O}_2$ and $\text{Ti/Ir}_{0.30}\text{Ti}_{0.30}\text{Sn}_{0.40}\text{O}_2$ electrodes present higher CE values, which indicates that in this time range, such electrodes are the most active to promote contaminant mineralization and the least active for the OER. In this time interval, the higher CE value was 70.8%, obtained from the $\text{Ti/Ir}_{0.30}\text{Ti}_{0.30}\text{Sn}_{0.40}\text{O}_2$ electrode. After 3 and 5 h, the CE values are almost similar for all electrodes.

Fig. 10b shows the CE values obtained with the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode at different current densities. At 20 and 100 mA cm^{-2} , the CE values decrease as a function of electrolysis time. At 50 mA cm^{-2} , CE is 21.6% after 1 h and reaches 28.1% after 5 h. At 100 mA cm^{-2} and in the presence of Na_2SO_4 , CE is 9.1% after 1 h and reaches 11.6% after 5 h. Higher current densities favor the OER, resulting in lower CE values. The presence of $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ results in lower CE values at 100 mA cm^{-2} than in the absence of the salt. The higher wastewater conductivity can favor the OER and make contaminant oxidation by direct and indirect processes difficult.

4. Conclusions

The electrochemical treatment of tannery wastewater was investigated under galvanostatic conditions using DSA[®] electrodes of different compositions. TOC values also decreased as a function of electrolysis time, but the reached maximum removal was only 40.5% after 5 h of electrolysis at 100 mA cm^{-2} . Although the TOC removal was not so efficient, all electrodes used in this work were able to greatly decrease the content of total phenolic compounds, the absorbance in the UV–vis region, and the wastewater toxicity. For the electrolyses performed at 20 mA cm^{-2} , the best results were obtained with the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ and $\text{Ti/Ir}_{0.15}\text{Ru}_{0.15}\text{Sn}_{0.70}\text{O}_2$ electrodes. Electrolyses performed with the $\text{Ti/Ru}_{0.30}\text{Ti}_{0.70}\text{O}_2$ electrode at 50 and 100 mA cm^{-2} resulted in better TOC removal than electrolyses performed at 20 mA cm^{-2} . However, in those conditions, Cr(III) was oxidized to Cr(VI) and lower current efficiencies were obtained. These results show that DSA[®] electrodes can be used in tannery wastewater electrochemical treatment provided that the electrode composition and the current density are conveniently chosen to avoid the oxidation of Cr(III) to Cr(VI) and the formation of more toxic compounds.

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