



Electrochemical oxidation of synthetic tannery wastewater in chloride-free aqueous media

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ABSTRACT

The electrochemical treatment of a synthetic tannery wastewater, prepared with several compounds used by finishing tanneries, was studied in chloride-free media. Boron-doped diamond (Si/BDD), antimony-doped tin dioxide (Ti/SnO₂-Sb), and iridium-antimony-doped tin dioxide (Ti/SnO₂-Sb-Ir) were evaluated as anode. The influence of pH and current density on the treatment was assessed by means of the parameters used to measure the level of organic contaminants in the wastewater; i.e., total phenols, chemical oxygen demand (COD), total organic carbon (TOC), and absorbance. Results showed that faster decrease in these parameters occurred when the Si/BDD anode was used. Good results were obtained with the Ti/SnO₂-Sb anode, but its complete deactivation was reached after 4 h of electrolysis at 25 mA cm⁻², indicating that the service life of this electrode is short. The Ti/SnO₂-Sb-Ir anode is chemically and electrochemically more stable than the Ti/SnO₂-Sb anode, but it is not suitable for the electrochemical treatment under the studied conditions. No significant changes were observed for electrolyses performed at different pH conditions with Si/BDD, and this electrode led to almost complete mineralization after 4 h of electrolysis at 100 mA cm⁻². The increase in current density resulted in faster wastewater oxidation, with lower current efficiency and higher energy consumption. Si/BDD proved to be the best electroodic material for the direct electrooxidation of tannery wastewaters.

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1. Introduction

The electrochemical oxidation of both real and synthetic tannery wastewaters using dimensionally stable anodes (DSA[®]) has been previously studied [1,2]. In these works, the effect of several parameters, such as electroodic composition, current density, and supporting electrolyte type and concentration, on the efficiency of the process has been evaluated. Electrolyses carried out using chloride as supporting electrolyte resulted in more efficient degradations than those carried out in the presence of sulfate [1,2]. The higher the chloride concentration, the faster the removal of phenolic compounds, colour, total organic carbon (TOC), and chemical oxygen demand (COD) from the wastewater [2].

DSA[®] electrodes display low overpotential for both chlorine and oxygen evolution reactions [3]. Chlorine can be electrogenerated with good yields on DSA[®]-type electrodes containing iridium and tin [4]. In aqueous solution, chlorine disproportionates into hypochlorous acid/hypochlorite, and the relative concentration of each of these species depends mainly on the pH [2,4]. Active chlorine species (Cl₂, HClO, and ClO⁻) are powerful oxidants

that efficiently degrade organic compounds in the region close to the anode surface (boundary layer) and/or in the bulk of the electrolyte [5]. The indirect electrooxidation mediated by active chlorine species electrochemically generated on DSA[®] electrodes has proven to be efficient for the degradation of organic contaminants, but the main disadvantage of this process is the production of organochloride compounds [6–8]. On the other hand, the oxygen evolution reaction is favored when electrolyses are carried out on DSA[®]-type anodes in the presence of sulfate as supporting electrolyte, competing with the direct oxidation of organic compounds [1,2]. Thus, the electrochemical degradation of organic compounds on these anodes is more selective and less efficient in the presence of sulfate than in the presence of chloride.

Contrary to DSA[®] electrodes, boron-doped diamond (BDD) and antimony-doped tin dioxide (SnO₂-Sb) display high overpotential for the oxygen evolution reaction, so they are suitable for the direct electrooxidation of organic contaminants *via* HO[•] radicals produced from water oxidation on the electrode [9]. These radicals are able to promote the complete mineralization of organic compounds. Electrooxidation *via* HO[•] radicals is usually referred as direct because their lifetime is very short (<1 μs), so the oxidation takes place at the electrode boundary layer or very close to it, even when these radicals are weakly adsorbed on the electrode (*quasi* free radicals) [10–12].

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It has been reported that tannery wastewaters usually present high chloride concentrations in their compositions ($1500\text{--}28,000\text{ mg L}^{-1}$) [13,14]. Indeed, large amounts of NaCl are used to inhibit bacterial growth in the hides and skins after their removal from animal bodies [15]. NaCl can also be used as an auxiliary reactant in the chrome tanning step [15,16]. In other words, NaCl is used only in some steps of leather processing, and high chloride concentrations are only found in wastewaters of tanneries that carry out these steps. NaCl is not usually employed by finishing tanneries, which transform wet-blue leather (chrome-tanned leather) into finished leather. When chloride is present in the wastewaters of this kind of tannery, it is detected in low concentrations [1]. In this case, it is probable that chloride remains from previous stages of the tanning process.

The electrochemical treatment is efficient in the presence of high chloride concentrations [2], but it can also exhibit good performance in the absence of chloride if an anodic material with high overpotential for oxygen evolution reaction is used. Under this condition, the electrooxidation of organic compounds occurs *via* hydroxyl radical, which is more reactive than the active chlorine species. Moreover, the electrochemical treatment of tannery wastewaters in the absence of chloride avoids the formation of persistent and potentially toxic organochloride byproducts.

In the present work, the direct electrooxidation of a synthetic wastewater prepared with substances used by finishing tanneries was investigated. The effects of the electrodic material, pH, and current density were evaluated.

2. Experimental

2.1. Preparation and characterization of the synthetic tannery wastewater

All chemicals used in the preparation of the synthetic wastewater were supplied by a finishing tannery located in Brazil and were used as received. The preparation of the wastewater was based on some tanning formulas used by that tannery. The following reagent concentrations were used: (a) natural and synthetic tannins: 293.6 mg L^{-1} acácia extract (Seta Natur N), 4.5 mg L^{-1} castanheiro extract (Mark), 4.5 mg L^{-1} quebracho extract (Mark), 370.4 mg L^{-1} Tancurt D-920 (Tanquímica), 417.1 mg L^{-1} Tanicor PSL-BR (Clariant); (b) dyes: 8.3 mg L^{-1} acid black 210 dye Preto Duacouro MK (A Chemical), 0.5 mg L^{-1} acid brown 97 dye Castanho Duacouro MFR (A Chemical), 2.9 mg L^{-1} acid brown 161 dye Castanho Duacouro NGB (A Chemical), 0.6 mg L^{-1} acid brown 434 dye Castanho Duacouro RL (A Chemical), 0.5 mg L^{-1} acid brown dye mixture Beije Duacouro MN (A Chemical), 0.5 mg L^{-1} non-registered black dye Preto Dermacarbon AF (Clariant), 0.8 mg L^{-1} non-registered black dye Preto Duacouro BA (A Chemical), 0.06 mg L^{-1} non-registered gray dye Cinza Sellasolido CLL (TFL); (c) oils: 478.1 mg L^{-1} Derminol Licker AS-1-BR (Clariant), 62.5 mg L^{-1} Derminol Licker L-198 (Clariant), 49.8 mg L^{-1} Dissogras CTE (Dissoltex), 84.5 mg L^{-1} Sedaflor STF (Cognis); (d) acrylic resin: 432.8 mg L^{-1} Leukotan 1084 (Corium Química); (e) surfactant: 12.5 mg L^{-1} Miltopan DBE SPP-20 (Cognis); (f) microbiocide: 9.9 mg L^{-1} Busan 1086 (Buckman); (g) organic acid: 468.9 mg L^{-1} formic acid (Base Química); (h) salts: 195.0 mg L^{-1} sodium formate (Oxiquim), 30.9 mg L^{-1} sodium bicarbonate (Bicarbonato); (i) compounds based on naphthalene: 3.8 mg L^{-1} product resulting from the condensation of naphthalene and phenolic compounds Basyntan LB-2 (BASF), 92.7 mg L^{-1} product based on sodium sulfonated naphthalene Tancurt NA-85 (Tanquímica); (j) other products: 92.4 mg L^{-1} product based on melanin, urea and formaldehyde Relugan D (BASF), 98.7 mg L^{-1} product based on aromatic sulfonic acids and dicarboxylic aliphatic acids Sellasol NG (TFL), 108.7 mg L^{-1} humectant agent RSU 100

Table 1

Initial characteristics of the synthetic tannery wastewater.

Parameter	Value
Total phenols (mg L^{-1})	73 ± 2
COD (mg L^{-1})	2370 ± 30
TOC (mg L^{-1})	756 ± 6
Absorbance 228 nm (wastewater diluted 100 times)	1.01 ± 0.01
Colour Hazen (Hz)	1240 ± 70
Initial pH	2.4 ± 0.1

(Dissoltex). $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ *p.a.* provided by Merck was added to the wastewater, resulting in a concentration of 0.10 mol L^{-1} .

Total phenols were measured by the 2-hydrazono-3-methylbenzothiazoline (MBTH) method [17] using Spectroquant[®] phenol cell tests (Merck) and a Spectroquant[®] Nova 60 spectrophotometer (Merck). TOC was determined using a Shimadzu TOC-V_{CPN} analyzer. COD was analyzed by the closed reflux colorimetric method [18] using Spectroquant[®] COD cell tests (Merck), a Stuart Scientific block heater, and the same spectrophotometer used for phenol analysis. Colour Hazen was measured by the platinum–cobalt standard method [18] using the Spectroquant[®] spectrophotometer described above. In colour analyses, the turbidity correction was performed by the spectrophotometer itself. UV spectra were recorded in the 200–400 nm range using a Helios Gamma single-beam spectrophotometer purchased from Thermo Electron Corporation. pH measurements were performed with a Crison model 52-01 PI1000 pH electrode coupled with a Basic 20 Crison pH meter.

Table 1 shows the results obtained from the characterization of the synthetic tannery wastewater. Each parameter was analyzed at least eight times, so each result is expressed as an average and its respective absolute mean deviation.

2.2. Electrode preparation and electrolysis conditions

Electrolyses of the synthetic tannery wastewater were carried out in a one-compartment filter-press flow cell, under galvanostatic conditions for 4 or 5 h, using a Blausonic DC power supply. The system setup is shown in Fig. 1. Si/BDD, Ti/SnO₂–Sb, and Ti/SnO₂–Sb–Ir electrodes were employed as anode and a stainless steel plate was used as cathode. Anode and cathode had a geometric area of 20 cm^2 , and the inter-electrode gap was about 1.4 cm. An Ag/AgCl/KCl sat. electrode was used as reference. The wastewater was stored in a thermo-regulated glass reservoir, which was maintained at a temperature of $30 \pm 3\text{ }^\circ\text{C}$. From a 250 mL reservoir, the wastewater was circulated inside the electrolytic cell by a centrifugal pump at a 90 L h^{-1} flow rate. During the electrolyses, samples were collected every 1 h and submitted to all the analyses described in Section 2.1.

The Si/BDD electrode was provided and synthesized by Adamant Technologies (Switzerland), while the Ti/SnO₂–Sb, and Ti/SnO₂–Sb–Ir electrodes were prepared by the thermal decomposition of precursor salts on titanium supports. The following salts were used as precursors for the preparation of Ti/SnO₂–Sb and Ti/SnO₂–Sb–Ir electrodes: $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (Aldrich), SbCl_3 (Fluka), and $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ (Aldrich). A precursor solution containing 10% $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 1% SbCl_3 in ethanol and a precursor solution containing 1% $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ in ethanol were prepared. Only the first solution was used for preparation of the Ti/SnO₂–Sb electrode, while both precursor solutions were mixed for preparation of the Ti/SnO₂–Sb–Ir electrode, in order to obtain an oxide with nominal Sn/Ir molar ratio of 9:1.

The titanium supports (plates) were previously treated 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

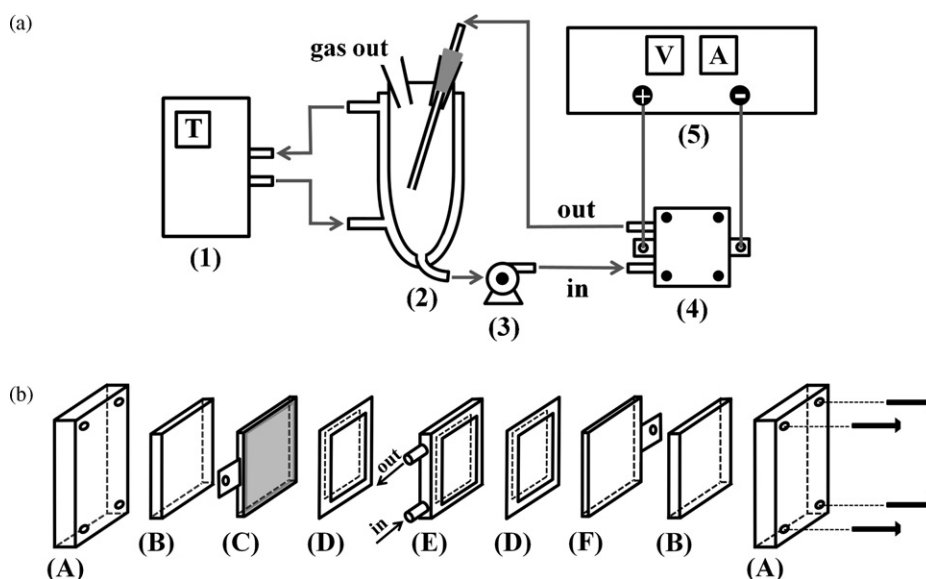


Fig. 1. (a) Schematic representation of the system used for the electrochemical treatment of the synthetic tannery wastewater: (1) thermostatic bath, (2) thermo-regulated glass reservoir, (3) centrifugal pump, (4) electrochemical cell (front view), and (5) power supply. (b) Sketch of the one-compartment filter-press flow cell (side view): (A) steel plates, (B) silicone gaskets, (C) anode, (D) silicone sealing spacers with 20 cm² opening, (E) plastic spacer with 20 cm² opening and two canals for wastewater in and out in the cell, and (F) cathode.

oxalic acid 10% solution for 1 h). After these treatments, the supports were washed with water and dried. Next, the precursor solutions were spread on one of the sides of the titanium plates with the aid of a brush. The supports were then heated in a furnace at 70 °C for 5 min and burned at 400 °C for 10 min. These steps were repeated until a mass loading of 1 mg cm⁻² was achieved. The electrodes were then burned for 1 h at 550 °C.

In order to evaluate the influence of the electroodic material, pH, and current density on the electrochemical treatment of the synthetic tannery wastewater in the presence of 0.10 mol L⁻¹ Na₂SO₄, electrolyses were performed under the following conditions: (a) Si/BDD, pH 2.4, and 25 mA cm⁻²; (b) Ti/SnO₂-Sb, pH 2.4, and 25 mA cm⁻²; (c) Ti/SnO₂-Sb-Ir, pH 2.4, and 25 mA cm⁻²; (d) Si/BDD, pH 7.3, and 25 mA cm⁻²; (e) Si/BDD, pH 12.0, and 25 mA cm⁻²; (f) Si/BDD, pH 2.4, and 50 mA cm⁻²; and (g) Si/BDD, pH 2.4, and 100 mA cm⁻². For the electrolyses performed at pH 7.3 and 12.0, these values were initially adjusted with 1.0 mol L⁻¹ NaOH (Merck) solution.

2.3. Calculations

The apparent rate constants for the removal of phenolic compounds (k_{phenols}), TOC (k_{TOC}), and absorbance at 228 nm ($k_{\text{Abs-228nm}}$) from the synthetic tannery wastewater were calculated according to Eq. (1), assuming a first-order kinetics.

$$\ln \frac{X}{X_0} = -kt \quad (1)$$

In each case, X and X_0 are the concentration of phenolic compounds, the TOC content, and the 228 nm absorbance value at times t and 0, respectively. During the electrolyses, samples were collected every 1 h and submitted to all the analyses described in Section 2.1. After 5 h of electrolysis, the volume reduction caused by sampling was close to 15%. In order to correct this volume change, the method described by Choo et al. for first-order reactions was employed [19].

The current efficiency (CE) for the electrochemical mineralization of the synthetic tannery wastewater was calculated according

to Eq. (2) [1]:

$$CE = 2.67FV \frac{(\text{TOC})_0 - (\text{TOC})_t}{8I\Delta t} \quad (2)$$

In the previous equation, $(\text{TOC})_0$ 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 C mol⁻¹); and V is the electrolyte volume (L).

The energy consumption (EC) for the electrochemical treatment was calculated in kWh per g of removed TOC, according to Eq. (3).

$$EC = \frac{Ult}{1000V[(\text{TOC})_0 - (\text{TOC})_t]} \quad (3)$$

In the previous equation, U is the average cell voltage during electrolysis (V), I is the current applied during electrolysis (A), t is the electrolysis time (h), V is the wastewater volume (m³), and $(\text{TOC})_0$ and $(\text{TOC})_t$ are the total organic carbon (g m⁻³) at times 0 and t (h).

3. Results and discussion

Fig. 2 shows the variation in [phenols]/[phenols]₀, COD/COD₀, and TOC/TOC₀ as a function of time during the electrochemical treatment of the synthetic tannery wastewater at 25 mA cm⁻², on the different anodic materials and in different pH conditions. Si/BDD is the most efficient electrode for removal of total phenols, COD, and TOC, followed by the Ti/SnO₂-Sb electrode. The different anodic performances can be explained by considering two types of anodic surface behaviors: active and non-active [11,20]. In both cases, the first step of the electrooxidation mechanism is the discharge of water molecules on the active sites at the anode surface (M), to form hydroxyl radicals (Eq. (4)). Ti/SnO₂-Sb-Ir displays an active behavior. In this case, hydroxyl radicals are strongly adsorbed on the anode and are able to transfer oxygen to it, generating the so-called higher oxide (Eq. (5)). Higher oxides (MO) can oxidize organic compounds (R), but the oxidation is partial and selective (Eq. (6)). Moreover, higher oxides can chemically decompose to molecular oxygen (Eq. (7)), hindering the oxidation of organic compounds. On the other hand, Si/BDD and Ti/SnO₂-Sb display a non-active behavior. This indicates that these electrodes act only as sink for

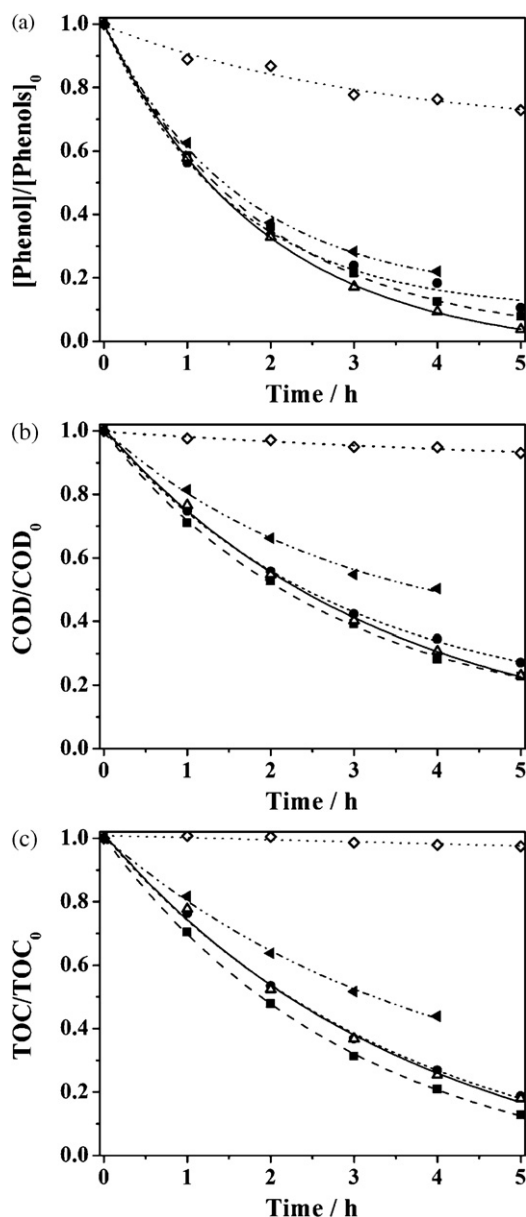
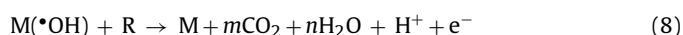
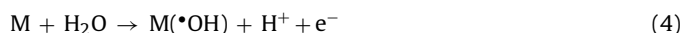


Fig. 2. Effect of the electrochemical material and pH on the electrooxidation of the synthetic tannery wastewater in $0.10 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ at 25 mA cm^{-2} : (a) $[\text{phenols}]/[\text{phenols}]_0$, (b) COD/COD_0 , and (c) TOC/TOC_0 as a function of electrolysis time. Electrolysis conditions: (\diamond) $\text{Ti}/\text{SnO}_2\text{-Sb-Ir}$ and pH 2.4, (\blacktriangle) $\text{Ti}/\text{SnO}_2\text{-Sb}$ and pH 2.4, (\blacksquare) Si/BDD and pH 2.4, (\bullet) Si/BDD and pH 7.3, and (\triangle) Si/BDD and pH 12.0.

the transfer of electrons; they undergo no transformation in their oxidation states during the oxidation process. In these cases, the oxidation of organic compounds occurs *via* hydroxyl radicals (Eq. (8)). The $\text{Ti}/\text{SnO}_2\text{-Sb}$ and Si/BDD electrodes have different adsorption properties. While hydroxyl radicals exist mainly adsorbed on the $\text{Ti}/\text{SnO}_2\text{-Sb}$ surface, due to the strong adsorption property of this material, these radicals are considered *quasi* free on the Si/BDD surface, which exhibits weak adsorption property [9,21]. Thus, the oxidation of organic compounds can occur *via* adsorbed hydroxyl radicals on $\text{Ti}/\text{SnO}_2\text{-Sb}$, but it exclusively occurs *via quasi* free hydroxyl radicals on Si/BDD [21]. The oxidizing capacity of the anodic material depends on the adsorption strength of the hydroxyl radical on the anode surface: the weaker the adsorption, the higher the chemical reactivity of the hydroxyl radical for the oxidation of organic compounds and the lower the electrochemical activity of the material for the oxygen evolution reaction [9]. Thus, Si/BDD is

expected to perform better than $\text{Ti}/\text{SnO}_2\text{-Sb}$ in the direct electrooxidation of organic compounds.



Although $\text{Ti}/\text{SnO}_2\text{-Sb}$ is less efficient than Si/BDD for the oxidation of organic compounds, it can be observed in Fig. 2 that good results are obtained when the former electrode is used in the electrochemical treatment of the synthetic wastewater, mainly with respect to the oxidation of phenolic compounds. However, the low electrochemical stability and short service life of $\text{Ti}/\text{SnO}_2\text{-Sb}$ make its industrial application unpractical. In our case, during the electrolysis carried out at 25 mA cm^{-2} using the $\text{Ti}/\text{SnO}_2\text{-Sb}$ electrode, the cell potential remained constant until 3 h of electrolysis. After this time period, the potential began to increase, and complete electrode deactivation was reached after 4 h of electrolysis. The deactivation of $\text{Ti}/\text{SnO}_2\text{-Sb}$ electrodes upon anodic polarization is mainly due to the formation of a passivating hydroxide layer in the electrode outer layer in contact with the electrolyte [22]. The introduction of a noble metal into $\text{Ti}/\text{SnO}_2\text{-Sb}$ films avoids formation of the hydroxide passivating layer, improving the stability of these electrodes [23,24]. Indeed, the addition of Ir to the $\text{Ti}/\text{SnO}_2\text{-Sb}$ electrode significantly increases its chemical and electrochemical stability, but it may result in an active electrode that is not efficient for the oxidation of organic compounds. In fact, much slower removals of total phenols, COD, and TOC are obtained with the $\text{Ti}/\text{SnO}_2\text{-Sb-Ir}$ electrode (Fig. 2).

No significant changes are observed in the electrochemical treatment efficiency using the Si/BDD anode when the initial pH of the wastewater is increased (Fig. 2). For all the studied pH conditions, the average electrode and cell potentials for the electrolyses carried out at 25 mA cm^{-2} were $2.8 \pm 0.1 \text{ V}$ versus $\text{Ag}/\text{AgCl}/\text{KCl}$ sat. electrode and $6.2 \pm 0.1 \text{ V}$, respectively. From an industrial standpoint, the fact that the oxidation process efficiency does not depend on the pH is interesting in both practical and economic terms because tannery wastewaters usually present highly variable pH. In other words, it would not be necessary to adjust the pH value before electrochemical treatment.

Fig. 3 presents the effect of the current density on the evolution of total phenols, COD, and TOC as a function of time for electrolyses performed using the Si/BDD anode at initial pH 2.4. The increase in current density leads to faster removal of all the analyzed parameters, but lower CE values are obtained at higher current densities, as discussed below.

Under all the studied electrolysis conditions, the COD and TOC curves as a function of time display similar profiles (Figs. 2 and 3). For this reason, current efficiencies were only calculated from the TOC values. Fig. 4 shows CE values as a function of time for all the electrolyses carried out at initial pH 2.4. For the electrochemical treatment of the synthetic tannery wastewater at 25 mA cm^{-2} (Fig. 4a), the CE values are 0.99 and 0.62 after 1 h of electrolysis with Si/BDD and $\text{Ti}/\text{SnO}_2\text{-Sb}$, respectively. CE decreases as a function of time, reaching values of 0.59 after 5 h and 0.48 after 4 h with the former and latter electrodes, respectively. As for the $\text{Ti}/\text{SnO}_2\text{-Sb-Ir}$ electrode, the CE values do not exceed 0.02 in the 5 h range. In this case, low CE values are obtained due to the low overpotential for the oxygen evolution reaction exhibited by the electrode. Although the $\text{Ti}/\text{SnO}_2\text{-Sb-Ir}$ electrode is not efficient for the treatment of the synthetic tannery wastewater in chloride-free media, higher CE values can be obtained in chloride-containing media [2].

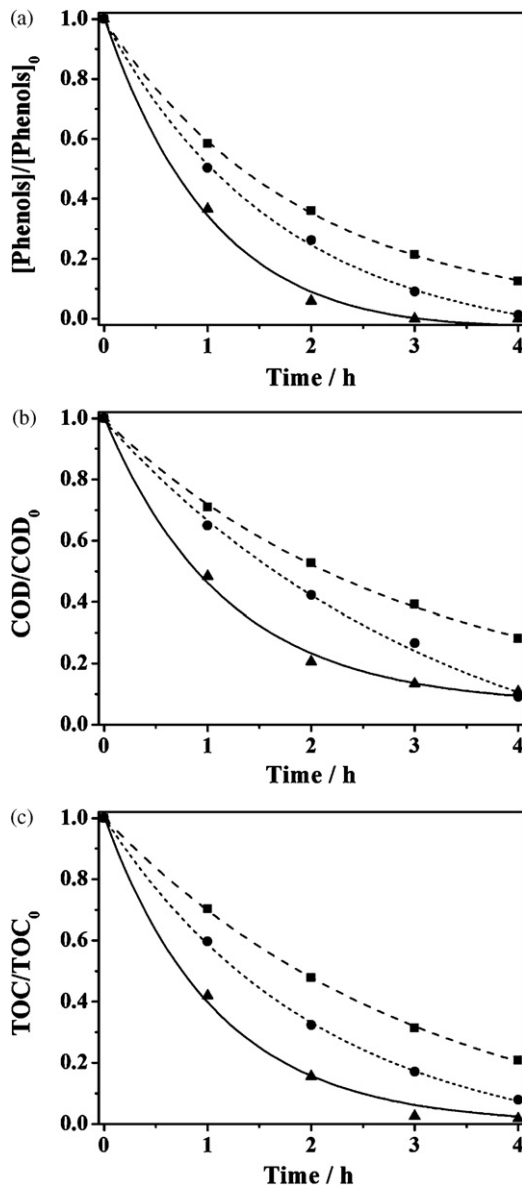


Fig. 3. Effect of the current density on the electrooxidation of the synthetic tannery wastewater in $0.10 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ ($\text{pH}=2.4$) using the BDD anode: (a) $[\text{phenols}]/[\text{phenols}]_0$, (b) COD/COD_0 , and (c) TOC/TOC_0 as a function of electrolysis time. Current densities: (■) 25 mA cm^{-2} , (●) 50 mA cm^{-2} , and (▲) 100 mA cm^{-2} .

When the current density increases, secondary anodic reactions are favored, and a decrease in CE values occurs (Fig. 4b). Besides O_2 (Eq. (9)), other species like H_2O_2 (Eq. (10)) and O_3 (Eq. (11)) can be electrogenerated on the Si/BDD electrode, mainly at high current densities [9,12,25]. H_2O_2 and O_3 are not able to efficiently oxidize many organic compounds, and the oxidation process *via* these species is only efficient when combined with UV radiation and/or Fe^{2+} because, in these cases, hydroxyl radicals are produced [26,27]. Peroxodisulfate ($\text{S}_2\text{O}_8^{2-}$) is another oxidant that can be produced on the Si/BDD anode from sulfate ions present in the supporting electrolyte (Eq. (12)) [25]. Although $\text{S}_2\text{O}_8^{2-}$ can contribute to the oxidation of organic compounds, the electrochemical production of this oxidant on BDD anodes is only efficient in the presence of high concentrations of H_2SO_4 and at high current densities [25].

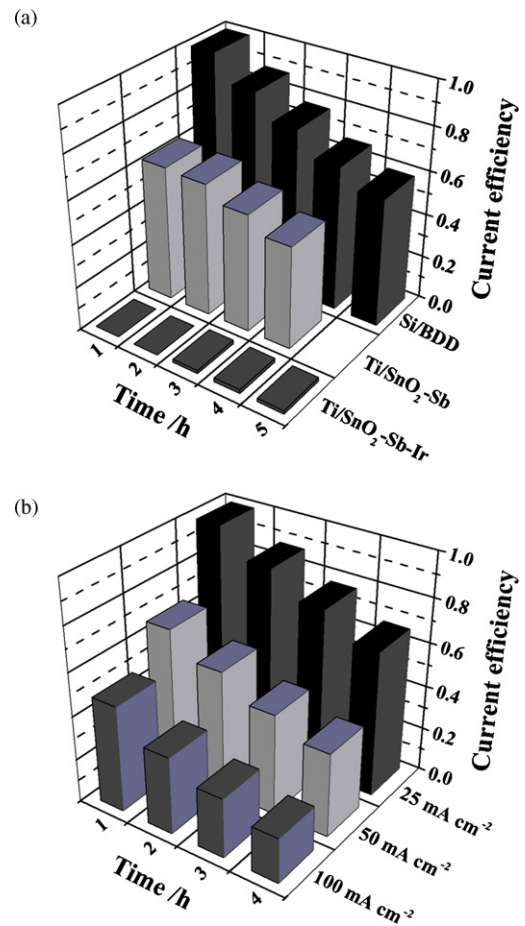
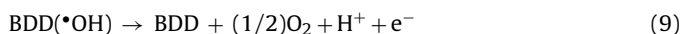
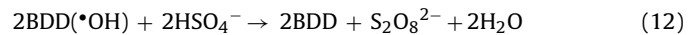
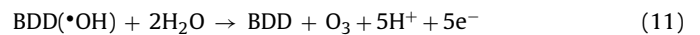


Fig. 4. Current efficiency as a function of electrolysis time: (a) for the electrolyses carried out at 25 mA cm^{-2} , $\text{pH}=2.4$, and different anodic materials and (b) for the electrolyses carried out on BDD, $\text{pH}=2.4$, and different current densities.



Rate constants for the removal of total phenols, TOC, and absorbance at 228 nm are displayed in Table 2. For all the studied electrolysis conditions, the $k_{\text{phenols}}/k_{\text{TOC}}$ ratio is higher than 1, indicating that the removal of phenolic compounds is faster than the TOC removal. This occurs because the decrease in the concentration of phenols involves their oxidation to any organic byproduct like catechol, hydroquinone, or benzoquinone, while the decrease in the TOC values is related to the oxidation of the organic compounds to CO_2 and H_2O . Thus, a shorter time is necessary for the removal of phenolic compounds compared with the time demanded for complete wastewater mineralization. It is also remarkable in Table 2 that while the $k_{\text{phenols}}/k_{\text{TOC}}$ ratio varies between 1.3 and 1.9 for the electrolyses carried out with the Ti/SnO₂-Sb and Si/BDD anodes, it is equal to 7.0 for the Ti/SnO₂-Sb-Ir anode. The larger relative difference between k_{phenols} and k_{TOC} for this electrode indicates that it is more selective for the partial oxidation of phenolic compounds and less efficient for the mineralization of the byproducts derived from these compounds, as expected for an oxide anode with active behavior.

The synthetic wastewater displayed a band in the region of 228 nm similar to that obtained from a real tannery wastewater [1]. This band is mainly due to $\pi \rightarrow \pi^*$ transitions in organic compounds containing conjugated double bonds, like aromatic compounds. The absorbance at 228 nm decreases as a function of time for the several electrolysis conditions (Fig. 5a). The UV light

Table 2
Apparent rate constants for the removal of total phenols, TOC, and absorbance at 228 nm obtained from the electrochemical oxidation of the synthetic tannery wastewater in 0.10 mol L⁻¹ Na₂SO₄.

Electrolysis condition	k_{phenols} (h ⁻¹)	k_{TOC} (h ⁻¹)	$k_{\text{Abs-228nm}}$ (h ⁻¹)	$k_{\text{phenols}}/k_{\text{TOC}}$	$k_{\text{Abs-228nm}}/k_{\text{TOC}}$
Ti/SnO ₂ -Sb-Ir, 25 mA cm ⁻²	0.07 (R = 0.97)	0.01 (R = 0.99)	0.01 (R = 0.98)	7.0	1.0
Ti/SnO ₂ -Sb, 25 mA cm ⁻²	0.38 (R = 0.98)	0.20 (R = 1.00)	0.25 (R = 0.99)	1.9	1.3
Si/BDD, 25 mA cm ⁻²	0.48 (R = 1.00)	0.36 (R = 1.00)	0.35 (R = 1.00)	1.3	1.0
Si/BDD, 50 mA cm ⁻²	0.87 (R = 0.97)	0.57 (R = 1.00)	0.46 (R = 1.00)	1.5	0.8
Si/BDD, 100 mA cm ⁻²	1.28 (R = 0.99)	0.99 (R = 0.98)	0.85 (R = 0.99)	1.3	0.9

R is the correlation coefficient obtained by the linear regression from plots $\ln(X/X_0)$ versus t (Eq. (1)).

intensity absorbed by a wastewater is proportional to the concentration of UV-absorbing organic compounds present in it [18]. The $k_{\text{Abs-228nm}}/k_{\text{TOC}}$ ratio shows that there is a good correlation between the 228 nm absorbance values and the organic carbon content measured as TOC, indicating that the removal of absorbance at 228 nm reflects the mineralization progress.

Colour removal from the synthetic tannery wastewater, which can be mainly associated to the oxidation of azo dyes, was also evaluated (Fig. 5b). The curves of relative colour versus time for the electrolyses carried out at 25 mA cm⁻² with different anodic materials exhibit very different profiles. Although the Ti/SnO₂-Sb electrode is more efficient than Ti/SnO₂-Sb-Ir for oxidation and mineralization of the organic compounds present in the synthetic wastewater, the latter electrode performs better than the former in terms of colour removal. Thus, it is probable that the Ti/SnO₂-Sb-Ir electrode is also able to selectively oxidize the chromophore groups of the organic compounds that are responsible for the wastewater colour. Colour removal reaches 25.0% after 1 h of electrolysis

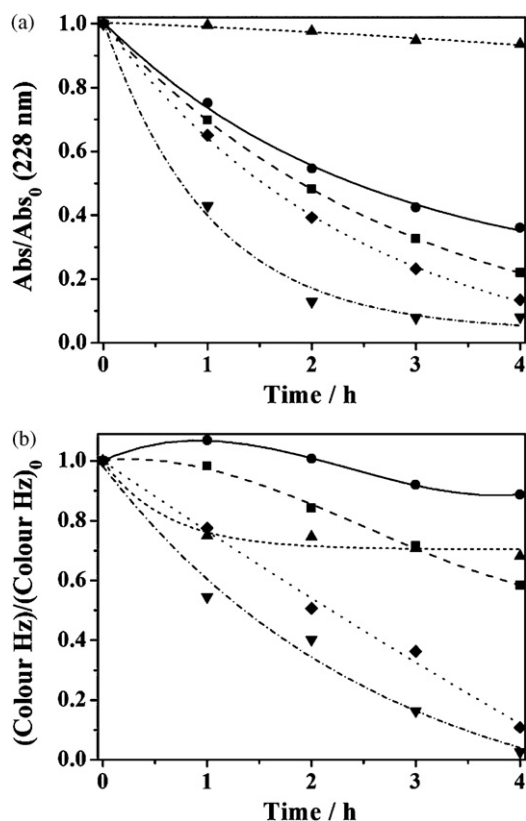


Fig. 5. Decay of the (a) relative absorbance (Abs/Abs_0) at 228 nm and (b) colour Hazen of the synthetic tannery wastewater as a function of electrolysis time for the experiments performed in 0.10 mol L⁻¹ Na₂SO₄ (pH = 2.4) and with the following electrodes and current densities: (▲) Ti/SnO₂-Sb-Ir and 25 mA cm⁻², (●) Ti/SnO₂-Sb and 25 mA cm⁻², (■) Si/BDD and 25 mA cm⁻², (◆) Si/BDD and 50 mA cm⁻², and (▼) Si/BDD and 100 mA cm⁻².

Table 3
TOC removal and energy consumption obtained after 4 h of electrochemical treatment of the synthetic tannery wastewater in 0.10 mol L⁻¹ Na₂SO₄.

Electrolysis condition	TOC removal (%)	Energy consumption per removed TOC (kWh g ⁻¹)
Ti/SnO ₂ -Sb-Ir, 25 mA cm ⁻²	2.1	2.547
Ti/SnO ₂ -Sb, 25 mA cm ⁻²	56.1	0.104
Si/BDD, 25 mA cm ⁻²	79.1	0.084
Si/BDD, 50 mA cm ⁻²	92.1	0.190
Si/BDD, 100 mA cm ⁻²	98.3	0.551

with the Ti/SnO₂-Sb-Ir anode and remains constant until 4 h. When the Si/BDD anode is used at 25 mA cm⁻², colour removal after 4 h is similar to that obtained with the Ti/SnO₂-Sb-Ir anode, but an increase in the current density leads to a faster colour removal. For the electrolysis performed with the Ti/SnO₂-Sb anode, wastewater colour increases until 1 h of electrolysis, followed by a decrease and removal of 11.3% after 4 h. In this case, the enhancement in the wastewater colour is probably related to the formation of byproducts with higher molar absorptivities in the visible region compared to their precursors. These results show that the oxidation process efficiency cannot be only based on the colour removal, since the most pronounced colour decrease is not always associated with the highest COD and/or TOC removals.

Table 3 shows TOC removal and energy consumption after 4 h of electrochemical treatment of the synthetic tannery wastewater under the different studied conditions. The Si/BDD anode is energetically more efficient than the other electrodes because it leads to faster TOC removal with lower energy consumption, although good results in terms of energy consumption are also obtained with the Ti/SnO₂-Sb anode. However, the latter anode has limited applicability because of its low stability. The Ti/SnO₂-Sb-Ir anode displays the lowest energy efficiency. The increase in current density in the case of the Si/BDD anode results in faster wastewater mineralization with higher energy consumption. Thus, the lower the current density, the slower the wastewater oxidation and mineralization (Table 2), and the lower the energy consumption (Table 3). This occurs because the Faradaic efficiency for the oxidation of organic compounds is higher at lower current densities (Fig. 4b).

4. Conclusions

The electrochemical treatment of a synthetic tannery wastewater was studied in chloride-free media. The influence of the anodic material, pH, and current density was evaluated.

The Si/BDD electrode exhibited the best performance for the removal of total phenols, COD, TOC, and absorbance at 228 nm from the wastewater, followed by the Ti/SnO₂-Sb anode. Good results were obtained with the Ti/SnO₂-Sb electrode, mainly with respect to the removal of total phenols; however, this anode presents a short service life. Wastewater oxidation was very slow in the case of the Ti/SnO₂-Sb-Ir electrode. Low current efficiency values were

obtained with the latter electrode due to its low overpotential for the oxygen evolution reaction.

The performance of the oxidation process using the Si/BDD electrode was not affected by pH. The increase in current density resulted in faster oxidation of organic compounds, but it also led to lower current efficiency and higher energy consumption.

We can conclude that Si/BDD is the best anodic material for the electrochemical treatment of tannery wastewaters containing organic compounds in chloride-free media, because it allows complete mineralization in a shorter time range and with lower energy consumption compared with other anodic materials in the same conditions. Moreover, electrooxidation in chloride-free media is more advantageous than that carried out in chloride-containing media because it avoids formation of toxic organochloride compounds.

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