Enhancement of wastewater treatment using novel laser-made Ti/SnO_2-Sb anodes with improved electrocatalytic properties

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Abstract

In this study, a novel Ti/SnO_2-Sb anode, improved using a laser heating manufacturing procedure, was applied in wastewater treatment. For comparison purposes, similar anodes were manufactured using the conventional furnace heating procedure. Electrochemical characterizations in the background electrolyte confirmed that the novel material has improved electric conductivity, as compared to the furnace-made one and, hence, it may lead to much lower operating costs in real applications. The electrocatalytic properties of the novel anode in comparison with the conventional were evaluated using a standard and well-known reaction: the phenol oxidation. Different operational conditions were evaluated. Concentrations of phenol were monitored by HPLC and analysis of organic matter by TOC analyzer. The best condition of phenol removal was associated with a relatively low energy consumption of 0.80 kWh $(gTOC)^{-1}$ and specific electrical energy consumption of 0.81 kWh m^{-3} $order^{-1}$. Interestingly, the phenol is not completely removed after 60 min of treatment using the furnace-made anode under the same operating conditions in which was fully depleted with the new electrode. Moreover, chlorinated by-products remained in the final solution with the conventional electrode and were exhausted with the novel one. Finally, after an extensive comparison with literature about the oxidation of phenol, the Ti/SnO_2-Sb produced by laser-manufacturing procedure presented the best phenol removal as compared with both non-active and active anodes.

Keywords: MMO anode; water treatment; electrochemical treatment; phenol.

1. Introduction

Electrochemical oxidation (EO) stands out as a promising alternative for wastewater treatment, due to its attractive advantages, such as versatility, ease of operation, and being environmentally friendly. In this technology, the oxidation of recalcitrant or bio-refractory pollutants can occur following two routes: direct electron transfer or indirect mediated oxidation in the bulk solution (Radjenovic and Sedlak, 2015; Moreira et al., 2017). In the direct oxidation, the pollutant can be oxidized directly on the anode surface. Sometimes, oxidation via hydroxyl radicals ($^{\bullet}OH$) electrogenerated by the electrolysis of the water is also considered as direct (although it is a mediated process) because both the electron transfer mechanisms and the oxidation via hydroxyl radicals cannot be distinguished in bulk electrolysis. In the hydroxyl radical's mechanism, the combustion of the organics to CO_2 and H_2O is favored with an extremely low generation of intermediates. On the other hand, in other indirect oxidation mechanisms, the pollutants are oxidized by the electrogenerated oxidative species, and in this route, the conversion of organics into more oxidized intermediates is favored before reaching mineralization (Marselli et al., 2003).

The efficiency of EO depends on many factors. Among them, it is worth mentioning the catalytic anode material (Wu et al., 2014; Martínez-Huitle et al., 2015). Ti/SnO_2-Sb anodes are among the most studied non-active anodes, due to its low cost and high overpotential for the oxygen evolution reaction, which leads to excellent performance in the oxidation of organic compounds, associated to the generation of weakly bonded (physisorbed) hydroxyl radicals ($^{\bullet}OH$) (Rao and Venkatarangaiah, 2014; Wu et al., 2014). However, the practical application of these anodes is mainly hindered by its shorter service lifetime (Sun et al., 2015). In this sense, studies have been developed in the direction of improving the service life of Ti/SnO_2-Sb anodes, and many inputs have been evaluated, such as the addition of

dopants (Xu et al., 2012; Sun et al., 2015) or the modification of the calcination temperature (Lei et al., 2018) and heating rate (Da Silva et al., 2018).

In recent previous work, Ti/SnO_2-Sb anodes synthesized using CO_2 laser heating were found to be five-fold more stable than conventional anode made by conventional heating in furnaces (Santos et al., 2020). The main advantages of this novel technique of fabrication are the fast heating and cooling rate (Santos et al., 2019), which do not also reduce costs but mainly improves the electrochemical properties of this material, turning it competitive for the oxidation of organic compounds.

In this context, phenol appears as a standard reaction to evaluate the performance of novel materials or processes in wastewater treatment, because of the well-known reactivity towards oxidants generated during electrolysis. Moreover, its simple and representative structure makes phenol one of the most significant model pollutants in water research (Ahmed et al., 2010; Villegas et al., 2016; Brillas and Garcia-Segura, 2019; Jun et al., 2019; Ribeiro et al., 2019). It is reported that in using active anodes, treatment of phenol, or phenolic compounds leads to the deposition of adhesive polymeric by-products, which are responsible for the decrease in the electrode activity and, sometimes, in the deactivation of the catalytic surface (Iniesta et al., 2001). Opposite, with non-active electrodes, the complete mineralization can be reached, as there are no heteroatoms in this model compound.

In the present work, it is evaluated the performance in the electrochemical oxidation of an improved Ti/SnO_2-Sb anode, using phenol as a model compound to be degraded electrochemically. As explained before, the oxidation mechanisms of this aromatic pollutant are well-known, and there are many papers in the literature reporting electrochemical oxidation of phenol, which are going to be used for comparison purposes. The performance of this novel anode is going to be compared to that of the conventional furnace-made anode.

Various conditions were applied, and the mechanisms under which hydroxyl and chlorine radicals attack are compared.

2. Experimental section

2.1 Chemicals

Phenol (99.5 %) from Sigma Aldrich®, sodium sulfate (99.0%, Vetec®), and sodium chloride (99.0%, Neon®) were used to compose the electrolytic solutions. The initial pH was adjusted using solutions of 1.0 M H_2SO_4 (95–97%, Emsure®) or 0.5 M NaOH (97%, Vetec®). Immediately after aliquots were withdrawn, $NaHSO_3$ ($SO_2 \geq 58.5\%$, Dinâmica®) solution in the same proportion of the chloride was added to quench the oxidants presents in the solution. All solutions were prepared using ultrapure water (Gehaka MS 2000 system).

2.2 Preparation of the electrodes

The Ti/SnO_2-Sb anodes were prepared by thermal decomposition of polymeric precursors (also known as the Pechini method) using CO_2 laser heating (GEM-100 L – Coherent). In order to obtain the precursors' solutions, $SnCl_2$ (99.99%), $SbCl_3$ (99.99%), anhydrous citric acid (99%), and ethylene glycol (99.8%) were used, all purchased from Sigma-Aldrich®. First, the titanium plates were pre-treated, as previously reported (Da Silva et al., 2018). Then, the metallic precursors were dissolved in the citric acid (CA) and ethylene glycol (EG) at 90 °C, according to the molar ratio 10:6:1 (EG/CA/metal molar ratio), where the Sn/Sb molar ratio for the coating preparation was 0.94/0.06. After spreading the obtained precursor solution over both sides of the titanium plates, the thermal treatment was conducted. For the laser heating, the strategy was to increase the power density 0.01 W/mm^2 reaching a power density of 0.3 W/mm^2, allowing the temperature reach to 600 °C almost instantaneously, which was

kept constant for 15 min and then cooled immediately to room temperature (Santos et al., 2020).

For comparison, Ti/SnO_2-Sb anodes were produced using the furnace exclusively, under the same conditions. The loading amount of coating was controlled at ~1.2 mg cm^{-2}, which required four brush-pyrolysis stages for both calcination processes. It is essential to point out that for the laser-made anode, the first layer was calcined using the furnace, and the remaining three layers were calcined by laser heating only.

2.3 Electrochemical Characterization

Cyclic voltammetry (CV) measurements were obtained from applying 50 mV s^{-1}, varying from 0.0 to 2.0 V. Studies with electrochemical impedance spectroscopy (EIS) were carried out covering the frequency range from 0.1 Hz – 10 kHz with a logarithmic distribution of 10 frequencies per decade using an AC sine signal amplitude of 5 mV. Potential applied for EIS was considered as the potential regions of the onset of the oxygen evolution reaction (OER) for each anode. Both characterizations were carried out in supporting electrolyte containing 0.1 M Na_2SO_4 in the presence or absence of the phenol (50 mg L^{-1}). The service lifetime tests were performed in the 0.1 M Na_2SO_4 background solution at an applied current density of 200 mA cm^{-2}. The anodes were considered deactivated when the measured potential reached a value of 10.0 V.

2.4 Electrolysis

The degradations were carried out in a one-compartment electrochemical cell using a Pt plate as the counter electrode. As anodes plates of 10 cm^2 of Ti/SnO_2-Sb obtained by the novel laser radiation (Santos et al., 2020) and the traditional thermal decomposition using a furnace

(Pechini method) were used. A volume of 0.15 L aqueous solution containing phenol was treated. The investigated variables were the concentration of the NaCl (0.0–0.07 M) in the supporting electrolyte (Na_2SO_4 0.1 M), the cell potential (6–10 V), the pH of the bulk solution (2–10) and the initial concentration of phenol (10–100 mg L^{-1}). The pH values were monitored throughout reaction time (60 min).

2.5 Analytical procedures

Samples were collected at given times of reaction and analyzed in an HPLC (Shimadzu 20A LC system with a UV detector). A Phenomenex reversed-phase C18 column was used as the stationary phase (150 mm × 4.6 mm, 5 μm particle size) and a mixture of 70 % acetonitrile and 30 % ultrapure water as mobile phase at a flow rate of 1 mL min^{-1}. The sample injection was 20 μL, and the detection wavelength was 270 nm.

The energy consumption (EC, in (kWh (g TOC)$^{-1}$) was obtained according to the Eq. (1), where E_{cell} is the cell potential (V), I is the current intensity applied (A), t is the electrolysis time (s), V is the volume of treated solution (L), and Δ(TOC) is the variation in the TOC removal (Garcia-Segura and Brillas, 2016).

$$EC = \frac{E_{cell} \times I \times t}{V \times \Delta(TOC)} \quad (1)$$

The specific electrical energy (E_{EO}) was used as figure-of-merit for comparison purposes with other advanced oxidation processes, in terms of cost-efficiency. The E_{EO} is defined as the electrical energy (kWh) required to reduce the concentration of pollutants by one order of magnitude (i.e., by 90%) in 1 m^3 of water and can be calculated from Eq. (2) for batch operation mode. In this equation, E_{cell} is cell potential (V), I is the average applied current density (A), and *t* is the electrolysis time (h) (Bolton et al., 2001; Garcia-Segura and

Brillas, 2016; Lanzarini-Lopes et al., 2017). This expression can be simplified, assuming first-order kinetics, according to Eq. (3), because of log (C_0/C_f) = 0.4343 k_1t, where t (min), k_1 is the pseudo-first-order constant (min^{-1}). And 38.4 × 10^{-4} is a conversion factor (1 h / 60 min / 0.4343) (Bolton et al., 2001).

$$E_{EO}\ (KW\ h\ m^{-3}\ order^{-1}) = \frac{E_{cell} \times I \times t}{V \times log\ (C_0/C_f)} \quad (2)$$

$$E_{EO}\ (KW\ h\ m^{-3}\ order^{-1}) = \frac{38.4 \times 10^{-4} \times E_{cell} \times I}{V \times k_1} \quad (3)$$

Mineralization current efficiency (MCE) was calculated according to Eq. (4), where n is the number of electron transfers in the oxidation of phenol (n=28), F is the Faraday's constant (96.485 C mol^{-1}), V is the solution volume (L), $\Delta(TOC)_{exp}$ is the experimental solution TOC decay (mg L^{-1}), n is the number of electrons consumed per phenol molecule (28 mol), m is the number of carbon atoms of phenol (m=6), I is the applied current (A), and t is the electrolysis time in h, and 4.32 × 10^7 is a conversion factor for units consistency (3600 s h^{-1} × 12,000 mg mol^{-1}) (Lanzarini-Lopes et al., 2017).

$$MCE = \frac{n\ F\ V\ (\Delta TOC)}{4.32 \times 107\ m\ I\ t}\ F\ V \quad (4)$$

3. Results and discussion

3.1 In situ characterization of the anode

CV and EIS are useful techniques for the investigation of reactions that occurs at the electrode/solution interface. Here, the Ti/SnO_2-Sb anode produced either using a conventional furnace, as well as the alternative laser heating, was characterized by CV and EIS in the

presence and absence of phenol in the background supporting electrolyte containing Na_2SO_4 (Fig. 1).

The voltammograms recorded exhibited typical profiles (Fig. 1a,b) in which no change in current occurred in the region between 0.0 and 1.6 V *vs.* Ag/AgCl, but a current increase related to the oxygen evolution reaction (OER) appears at potentials higher than 1.6 V *vs.* Ag/AgCl. Moreover, these voltammograms revealed that the presence of phenol increased the anodic charge potentials. On the other hand, results from Nyquist plots (Fig. 1c,d) recorded at the onset potential of the oxygen evolution reaction show the formation of one well-developed semicircle in the medium to low-frequency range (0.1–10^4 Hz). This behavior agrees with previous studies (Liu et al., 2000; Ding et al., 2010; Santos et al., 2019). The wider semicircle in the presence of phenol shows the increase in the resistivity, which can be explained by the adsorption of the pollutant species onto the anode surface, which is consistent with CV results.

Similarly, some authors have reported, for other anode materials, that this increase in the semicircle diameter in EIS spectra may be associated with the presence of 4-chlorophenol or phenol (Karimi-Maleh et al., 2014; Keivani et al., 2017). Also, from EIS results, the diameter of the semicircles for the anode prepared by laser radiation is more than 4 times lower than those observed for the conventional furnace anodes, which indicate a lower charge transfer resistance and suggests a more active surface. Regarding service lifetime tests performed in the background solution (Fig. 1e), the superiority in the stability of the laser-manufactured anode is confirmed by the durability increased 9-fold, at a high applied current density of 200 mA cm^{-2}.

3.2 Phenol removal and mineralization

3.2.1 Influence of the supporting electrolyte concentration

Phenol electrochemical degradation in aqueous solution was performed in different supporting electrolytes (0.1 M Na_2SO_4 with the addition of NaCl in the range 0.0–0.07 M). The starting conditions were fixed to be 8 V of potential applied, pH 6, and phenol concentration of 50 mg L^{-1}. Profiles of phenol decay as a function of the electrolysis time (Fig. 2a) showed that the pollutant removal in the absence of NaCl (i.e., 0.1 M Na_2SO_4) reached 45.5% after 60 min of electrolysis. However, in the presence of NaCl, the total removal of the pollutant is achieved in less than 20 min. This behavior indicates that phenol degradation depends on the nature of the electrolyte and that it could be occurring by both direct and mediated oxidation. It has been proposed that hydroxyl radicals formed by water oxidation ($H_2O \rightarrow {}^{\bullet}OH + H^+ + e^-$) can contribute to the oxidation of the organics. On the one hand, as Ti/SnO_2-Sb are classified as non-active anodes (Rao and Venkatarangaiah, 2014; Wu et al., 2014; Comninellis, 1994), the hydroxyl radicals (M($^{\bullet}$OH)) generated during water oxidation are expected to be the main oxidizing species produced and can be responsible for the phenol removal in sulfate media. On the other hand, in the presence of chloride ions, a significant contribution of indirect oxidation is expected because of the presence of strong chlorine oxidizing species generated during electrolysis, which explains the faster complete removal of the contaminant. Primarily chlorine can be disproportionated into hypochlorous acid (HClO), which in turn can be deprotonated and produce hypochlorite anion (ClO^-), according to the Equations (5)–(8) (da Silva et al., 2018; Machado et al., 2018).

$$2Cl^- \rightleftarrows Cl_{2(el)} + 2e^- \quad (5)$$

$$Cl_{2(el)} \rightleftarrows Cl_{2(sol)} \quad (6)$$

$$Cl_{2(sol)} + H_2O \rightarrow HClO + Cl^- + H^+ \quad (7)$$

$$HClO \rightleftarrows H^+ + ClO^- \quad (8)$$

222 The results observed in the present study agree with those from Loloi and coworkers
223 (Loloi et al., 2016), who showed that electrolysis (40 mA cm^{-2}) using a Ti/SnO_2-Sb_2O_4 anode
224 with a supporting electrolyte containing chloride ions (0.25 M), the phenol (100 mg L^{-1}) was
225 removed entirely in 1 h, whereas 98.5 % of phenol was removed after 10 h of electrolysis in
226 Na_2SO_4 (0.25 M). In another study, Santos et al. (2011) observed that 90% of phenol was
227 removed after 60 min of electrolysis at 10 mA cm^{-2} from an initial concentration of 100 mg
228 L^{-1} in NaCl 0.34 M as the supporting electrolyte (Santos et al., 2011). Comparing to our data,
229 the Ti/SnO_2-Sb anode here studied is much more efficient than the binary oxide (Ti/SnO_2-
230 Sb_2O_4) reported by Loloi et al. (Loloi et al., 2016) and the Ti/SnO_2-Sb reported by Santos et
231 al. (2011) (Santos et al., 2011).
232 From Fig. 2b, it can be pointed out that organic carbon removal is affected by the
233 presence of chlorides. The higher TOC removal is seen for 0.03 M NaCl, and further increase,
234 above this limit, causes a decrease of the organic carbon removal. Similarly, Montanaro and
235 Pettrucci (Montanaro and Petrucci, 2009) found a negative effect of sodium chloride addition
236 for values above 0.01 M in the TOC removal of remazol brilliant blue reactive. They showed
237 that when NaCl addition changed from 0.01 to 0.025 M in Na_2SO_4 solution, the time to
238 achieve complete mineralization increased from 240 min to 360 min, while the further
239 increase to 0.05 M NaCl in Na_2SO_4 solution, decreased the TOC abatement to 90% for 360
240 min. This behavior was explained by the different reaction mechanisms promoted in the
241 presence of higher concentrations of chlorides. In this view, it was demonstrated the
242 importance of determining the optimum concentration of chloride (Montanaro and Petrucci,
243 2009). Other authors also suggested an optimum concentration of NaCl for the removal of
244 sulfamethazine (El-Ghenymy et al., 2013), picloram (Coledam et al., 2018) and tebuthiuron
245 (Montes et al., 2017) in electrochemical oxidation based processes, because of the more

recalcitrant by-products that are favored at higher concentration of NaCl, which may cause the reduction in the TOC removal.

Plots of removal of phenol in electrolytes containing different concentrations of NaCl revealed a linear relationship between reaction time and the natural logarithm of the variation of the pollutant concentration, which means that phenol abatement follows pseudo-first-order kinetics. The rate constant (k) was obtained from the slope of Eq. (9). Where C_0 and C are the initial and final concentrations (in mg L^{-1}) of phenol, respectively, and k (min^{-1}) represents the first-order rate constant, and t is time (min).

$$\ln \frac{C_0}{C} = k \cdot t \qquad (9)$$

The values of k (min^{-1}) for the phenol removal and percentage of TOC removed according to electrolyte concentration are summarized in Table 1. The energy consumption per mass of TOC removed, as well as the specific electrical energy are critical factors in determining the feasibility of the electrochemical removal of organics from wastewaters. The values of EC and E_{EO} determined for different concentrations of the electrolyte are shown in Table 1. The addition of NaCl reduces the energy consumption gradually reaching a minimum value of 0.55 kWh (g TOC)$^{-1}$ and 0.67 kWh m^{-3} $order^{-1}$ when 0.07 M NaCl is added. This observation can be explained in terms of the improved conductivity of the solution, as pointed out by Malpass et al. (2012). However, both phenol and TOC removals are faster with the addition of 0.03 M NaCl, and because of this higher rate, this electrolyte was employed in all further experiments. Finally, the highest mineralization current efficiency found was 58.35%, which supports this condition as the more suitable for the subsequent experiments.

Table 1. Observed kinetic constants for phenol removal, energy consumption per unit of TOC removed, and energy consumption for the electrochemical oxidation of phenol under different conditions.

Parameter	Phenol Removal t_{10min} (%)	k (min^{-1})	R^2	TOC Removal (%)	EC ($kWh(gTOC)^{-1}$)	E_{EO} ($kWh\ m^{-3}\ order^{-1}$)	MCE (%)
[NaCl] (M)[a]							
0	12.75	0.012	0.99	20.9	2.09	47.76	14.34
0.01	84.0	0.208	0.93	22.5	2.32	3.29	18.20
0.03	100	0.592	0.91	52.9	0.80	0.81	58.35
0.05	100	0.555	0.92	45.8	0.75	0.76	24.70
0.07	99.7	0.422	0.85	39.4	0.55	0.67	13.04
pH[b]							
2	99.7	0.627	0.86	50.0	2.01	1.60	61.20
10	99.6	0.563	0.969	38.0	1.52	1.77	34.18
E (V) [c]							
6	35.6	0.041	0.96	4.00	1.02	1.31	1.00
10	95.8	0.316	0.98	34.0	0.51	0.72	13.2
$[Phenol_0]$[d] ($mg\ L^{-1}$)							
10	99.4	0.509	0.99	55.0	0.71	0.21	7.90
100	52.9	0.086	0.98	20.0	0.93	5.67	13.2

Electrolysis conditions: [a] $[Phenol_0]$ = 50 $mg\ L^{-1}$; pH = 6; E = 8 V; [b] [NaCl] = 0.03 M; E = 8 V; $[Phenol_0]$ = 50 $mg\ L^{-1}$; [c] [NaCl] = 0.03 M; pH = 6; $[Phenol_0]$ = 50 $mg\ L^{-1}$; [d] [NaCl] = 0.03 M; pH = 6; E = 8 V.

a. 2 Influence of initial pH

Investigation of the role of initial pH has been carried out in a range of pH values from acid to alkaline conditions. It is known that the speciation of chlorine depends on the pH, as well as its oxidation capacity. For instance, at acid pH, the hypochlorous acid is the primary species, and it has a higher oxidation capability than the hypochlorite, which is the most important species in the alkaline medium (Wu et al., 2014). Fig. 3a shows that phenol decay is not significantly affected by increasing the pH. Regarding TOC removal (Fig. 3b), the effect is less critical, changing from pH 2 to 6, where similar removals are seen; however, an increase to pH 10 provokes a reduction of 30% in the TOC removal.

The acid medium slightly favored the degradation due to the prevalence of the hypochlorous acid (Equation 10), with higher oxidative capacity than the hypochlorite species (Equation 11) (Wu et al., 2014).

$$HOCl + organics \rightarrow Cl^- + by\text{-}products \quad (10)$$

$$2OCl^- + organics \rightarrow 2Cl^- + by\text{-}products \quad (11)$$

As shown in Table 1, the value of k for phenol removal is quite close, varying from 0.627 min^{-1} (at pH 2) to 0.563 min^{-1} (pH 10), showing only slight improvement in the sequence: pH 2 > pH 6 > pH 10. It is important to highlight the good applicability of this anode at a wide pH range for the removal of phenol. Regarding the E_{EO}, the lowest value was found at an initial pH of 6 and a slight decrease for pH 2 and 10, which confirms that in the conditions studied, the pH is not of great influence. Therefore, from this point, the pH value was maintained as 6 since no initial adjustment is needed.

3.2.3 Influence of the potential applied

Another critical parameter in electrochemical degradation is the potential, which in turn affects the applied current density. As a general trend, at low potential values, only soft oxidation occurs when the electrochemical oxidation is not kinetically limited by mass transport, while an increase in the cell potential increases the removal of pollutants. The higher generation of oxidative species can explain this behavior. However, under mass-transport limitations, the increase in the potential can favor parasitic reactions (i.e., the OER), which must be avoided in wastewater treatment, since they result in a loss in energy and reduces the current efficiency (Martínez-Huitle et al., 2015). In order to evaluate the effect of this parameter, the electrolysis experiments were carried out with applied potential in the range 6 to 10 V (Fig. 3c). When comparing profile decays from 6 to 8 V, the phenol removal increases substantially, resulting in a maximum TOC removal (Fig. 3d). However, an increase up to 10 V prioritizes parallel reactions, probably due to the competition between the reaction of the oxygen evolution reaction and the chlorine formation, leading to a lower TOC removal.

The values of the pseudo-first-order rate constants for the removal of phenol at different potential applied are shown in Table 1. The value of *k* for 8 V is included in the study of the influence of NaCl concentration in the electrolyte. Therefore, the *k* value for the 0.03 M NaCl is the best condition among studied applied potential range (6–10 V) in [$NaCl_0$]: 0.03 M. Also, the potential applied of 8 V (0.03 M NaCl) was determined as optimal for maximum oxidation and TOC removal in the shortest time and with the lowest expenses of energy. Under these conditions, an E_{EO} value of 0.8 kW h m^{-3} $order^{-1}$ is required to degrade phenol entirely and to remove 52.9% of organic load. This value is much lower when compared to other AOPs to remove phenol from aqueous solutions. Thus, in the O_3-UV-TiO_2 (Suzuki et al., 2015), UV–H_2O_2 (Primo et al., 2007), US–H_2O_2–CuO (Drijvers et al., 1999), the E_{EO} values were 28.1, 130.51, 335.92 kW h m^{-3} $order^{-1}$, respectively.

3.2.4 Influence of initial concentration of phenol

The initial pollutant concentration can affect the performance of the process, so defining the optimal treatable contaminant range is of interest. Initial concentrations in the range of 10–100 mg L^{-1} of phenol were treated at 8 V, in an electrolyte containing 0.03 M NaCl at an initial pH 6. As shown in Fig. 4, the Ti/SnO_2-Sb electrode is efficient at removing phenol at the studied concentrations, with complete phenol removal being observed within 30 min for the highest concentration (100 mg L^{-1}). As expected, and shown in Table 1, the increase in initial phenol concentration produces a decrease in the phenol removal percentage attained after the same electric charge passed and also affects the mineralization (only 20 % mineralization was observed for the highest concentration while for 10 and 50 mg L^{-1} more than 50.0 % of initial concentration is mineralized). This behavior points out that electric charge passes should be adjusted to the organic load of the waste.

On the other hand, when comparing specific electrical energy, the values are quite close, ranging from 1.40 to 1.74 kWh m^{-3} $order^{-1}$, for 10 and 100 mg L^{-1} respectively, which means that the process is limited by mass transfer of the pollutant towards the electrode surface (Tahar and Savall, 1998).

3.3 Final products

At this point, the electrolyses using the conventional anode of Ti/SnO_2-Sb manufactured in a conventional furnace were carried out with the purpose of understanding and compare mechanisms with relation to the laser-made anode. In this scenario, Fig. 5 shows the HPLC chromatograms of the samples in the presence and absence of chlorides for the EO process carried out using the conventional Ti/SnO_2-Sb anode (Fig. 5a,b) and the laser-made anode (Fig. 5c,d). It can be observed the peak related to phenol at a retention time of 5.1 min. Besides, many by-products appearing in the chromatograms were identified based on the

352 literature and using standards of the main by-products. As a result, five of the seven aromatics
353 by-products peaks were identified in the C-18 column, namely hydroquinone, benzoquinone,
354 2- and 4- chlorophenol, and 2,4 dichlorophenol.

355 The identified by-products, structure, and appearance as a function of the time of
356 electrolysis in chloride medium for both anodes are shown in Table SM-1.

357 It is recognized that various oxidative species, such as Cl, hypochlorous
358 acid/hypochlorite (Malpass et al., 2012; Sirés et al., 2014), and •OH radicals (Neto and De
359 Andrade, 2009), are generated during electrolysis in supporting electrolytes containing NaCl
360 and Na_2SO_4, and therefore, different routes may be involved in the degradative process. The
361 reaction mechanism for the electrochemical oxidation of this model organic in Na_2SO_4
362 medium is in agreement with the literature in which the oxidation of phenol on a SnO_2-based
363 anode initially involves •OH radicals as the primary oxidant (Li et al., 2005; Enache and
364 Oliveira-Brett, 2011). Results from HPLC shows that during electrolysis only appears a band
365 with overlapped peaks between 2.8 and 3.3 min retention time (Fig. 5), which corresponding
366 with standard solutions of hydroquinone and benzoquinone, but the presence of other peaks of
367 low intensity may suggest the formation of catechol and resorcinol at lower concentrations
368 (Oliveira et al., 2007). From further analysis, it is worth noting that other aromatic by-
369 products overlapped the absorbance peak of phenol and can be clearly noted an increase in the
370 absorption band around 240 nm (Fig. SM-1), which has been ascribed to the intermediate
371 formation of quinonic compounds. This observation agrees with those from HPLC analysis.
372 Then, first, a reaction mechanism for the EO in Na_2SO_4 media with the Ti/SnO_2-Sb anode
373 used in this work is proposed (Fig. SM-2a) and is in good agreement with the literature in that
374 oxidation reaction involves •OH employing SnO_2-based anodes (Li et al., 2005). In these
375 pathways, first occurs the formation of quinonic by-products (such as hydroquinone and
376 benzoquinone) and in minor proportion probably resorcinol, catechol, followed by the

cleavage of the aromatic ring leads to a mixture of carboxylic acids to finally CO_2 (Li et al., 2005; Xu et al., 2012; Loloi et al., 2016).

On the other hand, when chloride ions are present, the proposed route (Fig. SM-2b) shows possible mechanisms that involve the addition of $Cl^{\bullet}$ along with $^{\bullet}OH$ to the phenol molecule. The aromatic ring could suffer attack by active chlorine present in the medium to yield, 2- and 4-chlorophenol, with retention times of 6.3 and 6.7 minutes, respectively, formed mainly as early intermediates, being the 2-chlorophenol formed in higher proportion (Fig. SM-3). These two compounds were followed by the chromatographic area (Fig. SM-3). Further addition of chlorine to both compounds led to the formation of 2,4 dichlorophenol. Furthermore, other peaks of low intensity are speculated to be probably 2,4,6 trichlorophenol at 9.3 minutes of retention time. The chlorinated by-products are totally removed within 60 min of treatment in the Na_2SO_4 0.1 M and with the addition of 0.03 M of NaCl in the supporting electrolyte. On the contrary, for the conventional anode, the removal of phenol is slower (k = 0.0973; R^2:0.93) (Fig. SM-4), and due to this, the chlorinated by-products are not entirely removed after 60 min of electrolysis.

Also, further analysis from UV/Vis spectra of the samples treated using the laser-made Ti/SnO_2-Sb anode suggests that aromatic compounds are entirely removed. Since no band can be detected after 60 min of reaction (Fig. SM-2b), the remaining peaks at around 3 minutes can be related to carboxylic acid formed that were observed to appear at this retention time (here we remind that at the end of the treatment, in the UV/Vis spectra, the peaks corresponding to quinonic compounds are completely decreased) (Fig. SM-2b). Since this optimized condition presented more than 50 % of TOC removed, this can be easily correlated with carboxylic acids formed. Few authors have proposed the degradation of phenol in the NaCl medium for non-active anodes. For example, a recent study by Zhang et al., (2016) reported the role of the concentration of chlorides in the removal of 50 mg L^{-1} of phenol in a

single reactor in batch mode using BDD anodes. They also found there is no apparent improvement in increasing the NaCl concentration (above 0.05 M NaCl) (Zhang et al., 2016).

3.4 Comparison of the EO between laser-made Ti/SnO_2-Sb and the literature

Plenty of studies have employed different electrode materials for phenol removal, as previously stated, due to relevance as a model pollutant, structure, and potential hazardous effect (Xu et al., 2012; Sun et al., 2015). In the view to have an in-depth comparison of our data with the literature, here we provide a review on the performance of different SnO_2-based anodes (doped or not) prepared by different techniques that were reported until now in terms of better results obtained towards the removal of phenol (Table 1).

The study of electrochemical oxidation to remove phenolic compounds started in the seventies when Nilson et al. (1973) (Nilsson et al., 1973), Mieluch et al. (1975) (Mieluch et al., 1975), and Dabrowski et al. (1976) (Dabrowski et al., 1976) tried this technology for the treatment of wastewaters. Later, the use of electrochemical oxidation for the destruction of phenol in a pilot plant scale was reported in the eighties by De Sucre and Watkinson (De Sucre and Watkinson, 1981), Chettiar and Watkinson (Chettiar and Watkinson, 1983), and Sharifan and Kirk (Sharifian and Kirk, 1986). They used synthetic wastewater solutions containing phenol. Low reaction rates and low efficiencies were the main drawbacks for commercial employment of electrochemical oxidation (the percentages of phenol removed ranged in 53–70%, depending on the operational conditions). One reason for the low reaction rate found was the electrode fouling by some organic polymeric compounds. Phenol is well known for its ability to foul electrodes since it may form polymerization products during electrochemical oxidation (Gattrell and Kirk, 1990; Panizza et al., 2002; Yang et al., 2013).

In the nineties, Kotz et al. (1991) (Kötz et al., 1991) and Stucki et al. (1991) (Stucki et al., 1991) in sequenced papers have proposed the use of SnO_2 anode doped with Sb as an

alternative candidate for the wastewater treatment. The rate of phenol removal was about 5 times higher for Ti/SnO_2-Sb than the Pt or PbO_2 anode.

After, Comninellis and Pulgarin (1993) used phenol oxidation as a model reaction for the abatement of organics on Ti/SnO_2-Sb anodes (Comninellis and Pulgarin, 1993). A 90% removal of 2000 mg L^{-1} of phenol was obtained after 6.25 h at 50 mA cm^{-2}. In 1994, Comninellis (1994) proposed the mechanisms for the electrochemical oxidation (or combustion) of organics using different anode materials (Pt, Ti/IrO_2, Ti/SnO_2-Sb), where phenol was used as a model pollutant: while SnO_2-Sb anode favored combustion of pollutant, the IrO_2, and Pt anodes favored selective oxidation (Comninellis, 1994). Then, Comninellis and Nerini (1995) studied the oxidation of phenol with Ti/SnO_2-Sb and Ti/IrO_2 anodes in the presence of 0.085 M NaCl. They found a key role of the electrogenerated ClO^- in the oxidation of organics close to the anode or into the bulk solution. Phenol was removed after 8 h using both anodes regardless of the NaCl concentration. When the Ti/IrO_2 is used the primary oxidation mechanism is mediated by the ClO^-, and when the Ti/SnO_2-Sb anode is used the attack by an additional amount of the hydroxyl radicals remained more critical, and thus the rate of TOC removal at this anode was much higher than that of Ti/IrO_2 (Comninellis and Nerini, 1995).

Li and coworkers reported similar results for the oxidation of phenol at Ti/SnO_2-Sb, Ti/RuO_2, and Pt anodes in 0.25 M Na_2SO_4. The Ti/SnO_2-Sb showed better performance removing phenol after 5 h at the Ti/SnO_2-Sb, which was attributed to the higher generation of hydroxyl radicals. The primary intermediates identified for this anode were hydroquinone and benzoquinone that were further converted into carboxylic acids (Li et al., 2005).

In recent years, doping with another element has been reported to improve the performance of the SnO_2-Sb anode. For example, Yang et al. (2012) examined the doping effects of metals on SnO_2-Sb anodes for the removal of phenol. The authors found an

enhancement by doping with Ni by a factor up to 14, in terms of phenol degradation at around 22.2 mA cm^{-2} in 0.1 M Na_2SO_4 (Yang et al., 2012). Regarding SnO_2-Sb doped with molybdenum (Mo), Lian et al. (2015) reported an improvement in the electrocatalytic activity of the anodes in the electrochemical oxidation of phenol. The insertion of 1% of Mo presented a more compact structure and longer service lifetime (36.6% higher than the Ti/SnO_2-Sb). Moreover, higher electrocatalytic activity for removal of phenol (100 mg L^{-1}) in 0.25 M Na_2SO_4 was observed with the use of the Ti/SnO_2-Sb-Mo(1%). Electrolysis performed at 10 mA cm^{-2} for 3.5 h resulted in 99.6% of removal of phenol and removal of organic load in 82.67% de TOC (Liang et al., 2015). Sun et al. (2015), showed that Ti/SnO_2-Sb doped with Ni-Nd could remove 100 % of phenol after 2 h, while for the Ti/SnO_2-Sb anode, 4 h was required (Sun et al., 2015). Berenguer et al. (2016) studied the activity of the Ti/SnO_2-$Sb_{(13-x)}$-Pt-$Ru_{(x)}$ (x = 0, 3.25, and 9.75%) toward phenol oxidation in alkaline medium and found that the Ti/SnO_2-Sb-Pt anode presented improved catalytic activity but low stability. The insertion of low quantities of Ru (3.25–9.75%) improved the stability, but decreased the electroactivity: at best conditions, about 85% removal efficiency is attained at 100 mA cm^{-2} and 24 h of treatment for the Ti/SnO_2-$Sb_{(9.75)}$-Pt-$Ru_{(3.25)}$. However, the authors have considered consumption and stability and stated that the cost-effectiveness of this anode makes it suitable for phenol removal in alkaline media (Sun et al., 2015; Berenguer et al., 2016).

Regarding active anodes, a comparison is also included in Table 2. Compared to the non-active anode here produced, none of the active anodes was capable of removing the pollutant in less than 60 min, even in the presence of chloride ions. It means that the anode proposed in this work is much better not only as compared with non-active anodes but also of active anodes. For example, Santos et al. (2010) found that after 30 min of electrolysis at 10 mA cm^{-2}, 100 mg L^{-1} of phenol in 20 g L^{-1} of NaCl, was almost fully removed using Ti/RuO_2 anode (Santos et al., 2010). Another study showed that mixed-metal oxides of Ti/SnO_2–

RuO_2–IrO_2, Ta_2O_5–IrO_2, and RhO_2–IrO_2 were successfully applied to removal of phenol (47 mg L^{-1}) up to 99–99.3 % after 8 h of electrolysis in the electrolyte containing 0.010 g L^{-1} KCl (Makgae et al., 2008).

Table 2. Comparison of the performance of SnO_2-Sb based anodes for the oxidation of phenol in aqueous medium under the best operational conditions.

Preparation method	Experimental method	Best phenol removal	Reference
	Non-active anodes		
Ti/SnO_2-Sb — 600ºC Pechini method (laser heating)	t = 1 h P_{cell} = 8V C_0 = 50 mg L^{-1} v = 200 mL Electrolyte = 0.1 M Na_2SO_4 + 30 M NaCl Anodic area = 10 cm^2	100% decay after 10 min 52.9% TOC decay K = 0.592 (R^2:)	This work
Ti/SnO_2-Sb — 600ºC Conventional Pechini method	t = 1 h P_{cell} = 8V C_0 = 50 mg L^{-1} v = 200 mL Electrolyte = 0.1 M Na_2SO_4 + 0.03 M NaCl Anodic area = 10 cm^2	100% decay after 60 min 8.8% TOC decay k = 0.0973 (R^2:0.93)	This work
Ti/SnO_2-Sb-Ni-Nd — 550ºC sol-gel method	t = 4 h j = 10 mA cm^{-2} C_0 = 50 mg L^{-1} v = 60 mL Electrolyte = 0.05 M Na_2SO_4 Anodic area = 8 cm^2	100% decay before 2 h 90.8% TOC decay after 4 h	(Sun et al., 2015)
SnO_2-Sb — 550ºC Pechini Method	t = 2.5 h j = 30 mA cm^{-2} C_0 = 500 mg L^{-1} v = 100 mL Electrolyte = 0.1 M Na_2SO_4	60.2% COD 83.6% decay k = 0.018 min^{-1}	(Xu et al., 2012)
SnO_2-Sb — 600 ºC Pechini method	t = 60 min j = 10 mA cm^{-2} C_0 = 100 mg L^{-1} v = 200 mL Electrolyte = 0.34 M NaCl Anodic area = 27 cm^2	90% decay	(Santos et al., 2011)
Ti/SnO_2-Sb — 400 ºC electrodeposition	t = 50 min j = 20 mA cm^{-2} / P_{cell} = 4.6 V C_0 = 490 mg L^{-1} v = 80 mL Electrolyte = 0.25 M Na_2SO_4	100% TOC decay after 16 h 100% decay after 5h	(Li et al., 2005)

	Anodic area = 6 cm²		
Ti/SnO_2-Sb-Mo — 600 ºC dip-coating	t = 3.5 h j = 10 mA cm^{-2} C_0 = 100 mg L^{-1} v = 400 mL Electrolyte = 0.25 M Na_2SO_4 Anodic area = 2 cm²	99.62% decay 82.67% TOC decay	(Liang et al., 2015)
SnO_2-Sb-Ni	t = 0.02 L j = 22.2 mA cm^{-2} C_0 = 7.5 g L^{-1} v = 200 mL Electrolyte = 0.1 M Na_2SO_4 Anodic area = 4.5 cm^{-2}	100% decay after 20 min k = 0.03 min^{-1}	(Yang et al., 2012)
Ti/SnO_2-Sb_2O_4 — 450ºC electrodeposition and dip-coating	t = 3 h P_{cell} = 2 V C_0 = 20 mg L^{-1} v = 100 mL Electrolyte = not informed Anodic area = 7 cm² 250 W – high pressure mercury lamp (λ = 365 nm)	85% TOC removal after 3 h 100% decay after 2 h	(Yan et al., 2009)
Ti/ SnO_2-Sb — 600ºC ultrasonic spray pyrolysis	t = not informed j = 10 mA cm^{-2} COD_0 = 1174 mg L^{-1} v = not informed Electrolyte = 1500 mg L^{-1} Na_2SO_4 Anodic area = 7.7 cm^{-2}	97% DOC removal after a charge loading of 7 Ah L^{-1}	(Yao, 2011)
Ti/SnO_2-Sb_2O_3-Nb_2O_5/PbO_2 — 480ºC thermal decomposition/electrochemical deposition	t = 2 h j = 20 mA cm^{-2} C_0 = 500 mg L^{-1} v = 50 mL Electrolyte = 21.3 g L^{-1} NaCl Anodic area = 5.5 cm²	97.2% decay	(Yang et al., 2009)
	Active anodes		
Ti/RuO_2 - commercial®	t = 360 min j = 10 mA cm^{-2} C_0 = 100 mg L^{-1} v = 0.25 L Electrolyte = 20 g L^{-1} NaCl Anodic area = 27 cm²	99.6% decay	(Santos et al., 2010)
Ti/IrO_2-Ta_2O_5 or Ti/SnO_2-RuO_2-IrO_2 or Ti/RhO_2-IrO_2 Sol-gel method	t = 8 h E = 1.5 V C_0 = 47 mg L^{-1} v = 50 mL Electrolyte = 0.01 g L^{-1} KCl Anodic area = 1 cm²	99 – 99.3% decay	(Makgae et al., 2008)
Ti/RuO_2 - commercial®	t = 180 min j = 119 mA cm^{-2} C_0 = 100 mg L^{-1} v = 1 L	100% COD decay 100% decay	(Fajardo et al., 2017a)

	pH_0 = 3.4 Electrolyte = 10 mg L^{-1} NaCl Anodic area = 21.1 cm^2		
70TiO_2/30RuO_2 - thermal deposition	t = 90 min j = 20 mA cm^{-2} C_0 = 50 mg L^{-1} v = 300 mL pH_0 = 7 Electrolyte = 0.1 M Na_2SO_4 Anodic area = 100 cm^2 UV lamp = 125 W	85% decay and 70% TOC decay after 90 min	(Pelegrini et al., 2001)
Ti/IrO_2 commercial®	t = 180 min j = 119 mA cm^{-2} C_0 = 100 mg L^{-1} v = 1000 mL pH = 3.4 Electrolyte = 10 mg L^{-1} NaCl Anodic area = 21.1 cm^2	100% decay phenolic content 84.8% COD decay	(Fajardo et al., 2017b)
70TiO_2/30RuO_2 commercial®	t = 300 min j = 100 mA cm^{-2} C_0 = 100 mg L^{-1} v = 500 mL pH = 4 flow rate = 120 L h^{-1} Electrolyte = 0.5 M of Na_2SO_4 and H_2SO_4 Anodic area = 21.6 cm^2	90% decay after 2 h	(Pelegrino et al., 2002)
Ti/Ni_xO_y-RuO_2-SnO_2-Sb_2O_5 - thermal decomposition	t = 60 min j = 70 mA cm^{-2} C_0 = 300 mg L^{-1} v = 1000 mL pH = 2 Electrolyte = 4 g L^{-1} NaCl Anodic area = about 40 cm^2	73.6% COD decay	(Saxena and Ruparelia, 2018)

Finally, from the above comparison, it can be highlighted that the anode produced in this research is very promising, and it has confirmed an outstanding performance, previously suggested in our previous paper (Santos et al., 2020). The proposed mechanisms of oxidation in different conditions described here will be useful to compare the performance of EAOP through figures of merit in order to evaluate the operating performance as well as associated energy costs.

Conclusions

From this work, the following conclusions can be drawn:

- The Ti/SnO_2-Sb laser-made anode presented improved electrocatalytic properties and easier charge transfer in the tested electrolytes, comparing favorably with conventional electrodes of the same composition and allowing better treatment results than other competing anode materials.
- The best conditions for the electrochemical oxidation of phenol using the novel Ti/SnO_2-Sb anode were achieved in this work using 0.030 M NaCl, 8 V of applied potential, and pH 6. These conditions led to the highest percentage of TOC removal, which was associated with relatively low energy consumption. Compared with a conventional furnace-made anode, the kinetics for phenol removal was 6.1 faster.
- The increase of applied potential to 10 V does not improve degradation efficiency. It is explained in terms of the promotion of side reactions favored at the anode surface. Also, a further increase in NaCl in the electrolyte increases (> 0.03 M) does not alter the pollutant removal kinetics significantly but reduces the TOC removal, which was related to the accumulation of more refractory organochlorinated.
- Chlorinated by-products were identified, and cleavage of the aromatic ring by hydroxyl and/or chlorine radicals led to the formation of carboxylic acids and complete removal of aromatics under the electrolytic conditions employed was observed only for the laser-made anode.
- The results presented here demonstrated the efficiency of the electrochemical oxidation using a laser-made Ti/SnO_2-Sb for wastewater treatment, pointing out its promising features for future applications.

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Figure Captions

Fig. 1. (a) Cyclic voltammograms for the Ti/SnO_2-Sb anode produced using a conventional furnace and (b) using alternative laser heating recorded at 50 mV s^{-1} and (c) Nyquist plots for the Ti/SnO_2-Sb anode produced using a conventional furnace and (d) using alternative laser heating recorded at 1.7 V *vs.* Ag/AgCl and (e) service lifetime of anodes in the 0.1 M Na_2SO_4 background electrolyte.

Fig. 2. (a) Influence of supporting electrolyte on the removal of phenol as a function of electrolysis time and (b) TOC removal after 60 min of treatment in the Na_2SO_4 0.1 M and with the addition of distinct concentration of NaCl in the supporting electrolyte. Conditions: [$Phenol_0$]: 50 mg L^{-1}; pH: 6; applied voltage: 8 V. Inset: Pseudo-first-order kinetics for the removal of phenol.

Fig. 3. (a) Phenol removal as a function of the electrolysis time, varying pH values at a fixed applied potential of 8 V and (b) corresponding TOC removal after 60 min of treatment of potential applied; (c) Phenol removal as a function of the electrolysis time, varying the different potential applied at fixed pH: 6 and (d) corresponding TOC removal after 60 min of the treatment. [$Phenol_0$]: 50 mg L^{-1}; Electrolyte: 0.03 M NaCl + 0.1 M Na_2SO_4

Fig. 4. (a) Phenol removal as a function of electrolysis time and initial phenol concentration and (b) TOC removal during the treatment in the 0.30 M NaCl + 0.1 M Na_2SO_4 varying the potential applied. Conditions: pH: 6, E: 8 V.

Fig. 5. HPLC chromatograms analyzed using a reversed-phase C18 column, UV detection at 254 nm as a function of electrolysis time during the treatment in the Na_2SO_4 0.1 M using conventional (a) and laser-made anode (c) and in Na_2SO_4 0.1 M with the addition of 0.03 M of NaCl using conventional (b) and laser-made anode (d). Conditions: [$Phenol_0$]: 50 mg L^{-1}, pH: 6; applied voltage: 8 V, t = 60 min.