

Electrochemical oxidation of 4-chlorophenol and its by-products using Ti/Ru_{0.3}M_{0.7}O₂ (M = Ti or Sn) anodes: preparation route versus degradation efficiency

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Abstract The electrochemical degradation of 4-chlorophenol and its main by-products was investigated in acid medium using binary oxides electrodes of nominal composition Ti/Ru_{0.3}Ti_{0.7}O₂ and Ti/Ru_{0.3}Sn_{0.7}O₂ prepared by thermal decomposition through two different routes: inorganic precursors dissolved in isopropanol and polymeric precursors (PPM). The aim of this study was to investigate the influence of both the composition and preparation methodology of these electrodes in the electrooxidation of the organic pollutants 4-chlorophenol and its by-products. Electrolyses were carried out using a filter press-type flow cell and monitored by high performance liquid chromatography (HPLC), total organic carbon (TOC), and chloride analyses. Besides CO₂, the by-products formed in the reactions were 1,4-benzoquinone, 4-chlorocatechol, and hydroquinone, as well as oxalic, maleic, malic, malonic, and succinic acids. The electrocatalytic efficiency with respect to the degradation of by-products was evaluated through the electrooxidation of 1,4-benzoquinone and oxalic acid (OA).

The anodes investigated in this work are very promising for the degradation of pollutants because of their excellent efficiency concerning the consumption of 4-chlorophenol and its by-products, although the mineralization of the starting material is not complete. The cleavage of the aromatic ring occurs preferentially in the case of electrodes prepared by decomposition of

inorganic precursors due to their larger electrochemically active area and electrocatalytic activity for oxygen evolution reaction (OER). However, OA oxidation is favored on Ti/Ru_{0.3}Sn_{0.7}O₂ prepared through decomposition of PPM.

Keywords Ruthenium oxide · Tin oxide · Electrochemical degradation · 4-Chlorophenol · Benzoquinone

1 Introduction

Intense industrial activity is responsible for the considerably high levels of organochlorinated pollutants detected in industrial effluents. Organic compounds such as 4-chlorophenol (4-CP) and its by-products have raised attention due to their toxicity and bioaccumulation in animals and humans (liposolubility), not to mention their carcinogenicity [1, 2].

Chlorophenolic compounds are very resistant to conventional biological treatment of industrial wastewater. Therefore, alternative methods have been employed in degradation of these pollutants such as adsorption and electrosorption at high-area C-felt electrodes [3], chemical oxidation [4], advanced oxidation processes [5, 6], and electrochemical oxidation [7]. In particular, the electrochemical degradation has been shown to be promising because this process is environmentally compatible, versatile, safe, selective and of easy automation [8]. However, the complete mineralization and the reduction from the toxicity of the solutions are still the main challenges.

It is well established that DSA[®]-type oxides electrodes are a good alternative for the electrochemical

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degradation of toxic effluents and many investigations have been carried out for different purposes [2, 9–16]. In contrast with more expensive materials such as anodes based on diamond layers, these traditional anodes have been largely applied to the treatment of industrial effluents due to their low cost, easy manufacture and good lifetime [17].

In view of the fact that anode materials for the electrochemical oxidation of organic species has been thoroughly investigated in the literature, the goal of the present work is to investigate the use of low-cost anode materials that achieve good CO₂ conversion yields, or that at least lead to a Total Organic Carbon (TOC) amount that is environmentally acceptable. Oxidation of 4-CP, benzoquinone (BQ) and oxalic acid (OA) has been used as a representative model system for the electrochemical cleavage.

The degradation of these organic compounds was investigated by applying Ti/Ru_{0.3}M_{0.7}O₂ (M = Ti or Sn) anodes. As proposed previously, SnO₂, a non-active oxide, increases the electrode lifetime compared to RuO₂-TiO₂ anodes [18]. The influence of the preparation method was also investigated using surface-coated layers prepared by the thermal decomposition technique from two different routes: the standard method (SM) [19], and the polymeric precursor method based on the Pechini–Adams method [18, 20, 21]. The latter method furnished more robust electrodes with lifetimes at least 5 times higher than those prepared by SM using HCl as solvent [18].

2 Experimental

2.1 Preparation of electrodes

Electrodes of nominal composition Ti/Ru_{0.3}Ti_{0.7}O₂ and Ti/Ru_{0.3}Sn_{0.7}O₂ were prepared via thermal decomposition (400 °C) using two different routes: decomposition of precursor salts [19] dissolved in isopropanol (standard method—SM/ISO) and decomposition of polymeric precursors (PPM) [20]. The PPM were prepared by mixing citric acid (Merck) with ethylene glycol (Merck) at 65 °C. After total citric acid dissolution, the temperature was raised to 90–95 °C. Tin citrate, prepared as described elsewhere [22], titanium isopropoxide (Acros), or RuCl₃·nH₂O (Aldrich) were then added to the solution. The metal: citric acid:ethylene glycol molar ratio used to prepare the respective resins was: Ru = 1:3:10, Ti = 1:4:16, and Sn = 1:3:10. The inorganic precursors used in the SM/ISO RuCl₃·nH₂O (Aldrich), TiCl₄ (Aldrich), and

SnCl₂·2H₂O (Merck) were individually dissolved in isopropanol (Merck) to give ~0.2 mol L⁻¹ solutions.

The precursor mixtures were applied on both sides of the pre-treated Ti-support by brushing [23], and the solvent was evaporated by a hot air flow (80 °C). In the case of the SM/ISO electrodes, the coatings were calcinated at 400 °C for 5 min under O₂-flux (5 dm³ min⁻¹). As for the PPM electrodes, they were initially heated in a furnace at 120 °C for 5 min to polymerize the coating, and then calcinated at 400 °C for 5 min under O₂-flux (5 dm³ min⁻¹). Averages of 7–10 applications were required to obtain the desired oxide thickness (2 μm), corresponding to ≈1.0–1.3 mg cm⁻². The coatings were finally annealed at 400 °C for 1 h under O₂-flux (5 dm³ min⁻¹). Duplicate samples were prepared for each electrode composition. Details of the electrode final mounting are described elsewhere [24].

2.2 Chemicals

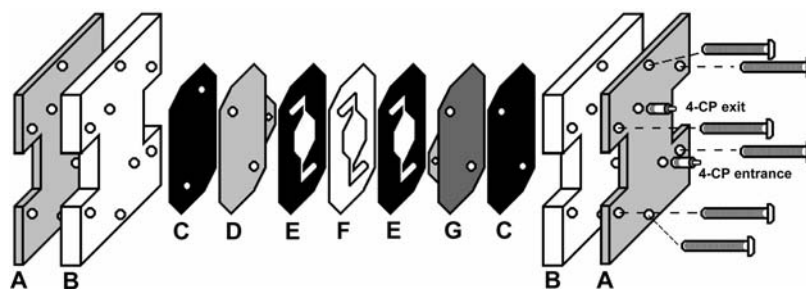
The following chemicals were used in this work: 4-CP (Riedel-de-Häen); 1,4-benzoquinone (BQ) (Fluka); hydroquinone (HQ) (Baker); catechol (Acros); phenol (Aldrich); 2,4-dichlorophenol (Acros); 4-chlorocatechol (4-CC) (Acros); maleic (Baker), malic (Fluka), malonic (Acros), oxalic (Merck), fumaric (Carlo Erba), formic (Merck), acetic (Merck), succinic (Aldrich), tartaric (Mallinkrodt), glycolic (Mallinkrodt) and sulfuric (Merck) acids; NaOH (Acros-50% w/v aqueous solution); sodium carbonate (Merck), and methanol (Aldrich-HPLC grade). Milli-Q quality (Millipore, 18 MΩ cm) water was also employed.

2.3 Voltammetric characterization and electrolyses

Cyclic voltammograms were obtained using a EG&G PARC 273A potentiostat/galvanostat controlled by the M270 software in a one-compartment cell (50 mL) with five entrances: (i and ii) two 15 cm spiral platinized platinum wires as counter electrodes; (iii) one reference electrode (SCE); (iv) one working electrode (A = 1 cm²) and (v) N₂-flux.

Galvanostatic electrolyses (i = 100 mA cm⁻²) were carried out using a Ecochemie Autolab potentiostat/galvanostat (PGSTAT 30) coupled to a current booster (BRTS10A), both monitored by a microcomputer. The 4-CP solution (100 mL, 5 mmol L⁻¹ in 0.5 mol L⁻¹ H₂SO₄) was circulated in a filter press-type homemade cell (Fig. 1) using a Cole-Parmer peristaltic pump coupled to a Masterflex[®] rotation controller. The flow of the organic compounds solutions was maintained constant at 6.0 mL min⁻¹ throughout the electrolysis (6 h). A Ti/Ru_{0.3}M_{0.7}O₂ flat plate electrode (A = 14 cm²) was used

Fig. 1 Sketch of the filter press-type flow cell: (A) stainless steel plate, (B) Teflon® plate, (C) rubber to sealing, (D) stainless steel counter electrode, (E) rubber extender, (F) Teflon® extender, and (G) working electrode



as the working electrode and a stainless steel plate was employed as the counter electrode. Freshly prepared anodes were submitted to a chronopotentiometric program (100 mA cm^{-2} for 1 h) to promote the total activation of the oxide coatings.

2.4 Product analysis

Three parameters were measured to evaluate the efficiency of the electrochemical treatment: remaining concentration of 4-CP coupled with the evaluation of the total amount of by-products formed throughout the electrolysis, as determined by high performance liquid chromatography (HPLC); TOC present in the solution; and total amount of chloride ions by means of an ion-selective electrode (Analion/CL-651).

Chromatographic analyses were performed on a Shimadzu instrument containing the following modules: an SCL-10A VP controlling system, an LC-10AT VP isocratic pump, a CTO-10AS VP oven, as well as an SPD-10A VP UV-detector and an RID-10A refraction index detector coupled in series. The aromatic by-products and 4-CP were analyzed using a Nucleosil C18 (Merck) column. To analyze the polar oxidation by-products (carboxylic acids), the solution was filtered in C18 cartridges (Alltech), freshly activated with ethanol, so that an aromatic-free solution could be injected into the Aminex HPX-87H column. Table 1 shows the best performance condition established for HPLC detection as a function of the analyzed compound. Organic compounds were determined by comparison of their retention times with those obtained for pure reference products under the same analytical conditions.

Table 1 HPLC experimental settings

	Aromatic compounds	Non-aromatic compounds	Carbonate
Column	C18 CLC-ODS(M) Shimadzu	HPX-87H Bio-Rad	HPX-87H Bio-Rad
$T_{\text{oven}}/^{\circ}\text{C}$	40	35	35
Eluent	Methanol:Water 60:40 (v/v)	H_2SO_4 3.3 mmol L^{-1}	H_2SO_4 3.3 mmol L^{-1}
Flow/ $(\text{cm}^3 \text{ min}^{-1})$	0.8	0.6	0.4
Detector	UV- $\lambda = 254 \text{ nm}$	UV- $\lambda = 210 \text{ nm}$	RID

The CO_2 formed during the electrolysis was collected by means of a trap cell containing 1.0 mol L^{-1} NaOH (4 mL). Carbonate formed was quantitatively analyzed using Na_2CO_3 (Merck) as reference.

All the results presented in this paper are an average of two or more experiments.

3 Results and discussion

3.1 Voltammetric characterization in the presence of 4-CP

The preliminary stage of this research consisted in selecting a suitable electrode material and the medium where the highest rate of 4-CP electrocatalytic degradation would occur. This was accomplished by preparing $\text{RuO}_2\text{-TiO}_2$ and $\text{RuO}_2\text{-SnO}_2$ electrodes via SM/ISO and PPM and investigating their activity in basic and acid medium. In basic medium, the electrodes underwent fast deactivation with decrease in the anodic current after a few cycles. Electrode surface poisoning was a result of the growth of adherent polymeric film or of the production of stable by-products that are not easily oxidized under the mild electrochemical conditions [25, 26]. This is frequently observed for anodes under low oxidizing medium [12, 13]. Thus, the acid medium was chosen for further investigation of 4-CP oxidation.

The voltammetric behavior observed for the electrodes investigated in this work is typical of thermally prepared oxide coatings, and has already been described elsewhere [18, 27]. The electrochemically active area of the electrode, which is a measure of the

number of active sites on the anode material, was estimated by integrating the anodic charge (q_a) in the voltammetric curves, in the double layer domain ($\Delta E = 0.1\text{--}1.0$ V vs. SCE) [28]. Table 2 shows anodic charge values as a function of both the electrode nominal composition and preparation methodology.

When TiO_2 is replaced with SnO_2 , it can be observed that the preparation route promotes great changes during the thermal treatment. For instance, in the case of the SM/ISO route, a considerable increase in the active area is observed when SnO_2 is introduced. On the other hand, SnO_2 decreases the q_a -values in the case of PPM electrodes. However, when we compare the $\text{RuO}_2\text{-TiO}_2$ electrodes, they display almost the same electrochemical area for both methodologies investigated. This result indicates that changes in the preparation methodology promote more changes in the number of active sites for the $\text{RuO}_2\text{-SnO}_2$ composition than for the $\text{RuO}_2\text{-TiO}_2$ one.

Figure 2 shows the curve of i vs. E in 0.5 mol L^{-1} H_2SO_4 in the presence of 4-CP (1 mmol L^{-1}) for all the electrodes investigated in this work. Voltammograms display a well-defined oxidation peak located at $0.9\text{--}1.0$ V vs. SCE. By comparing Fig. 2A and B, it can be concluded that the substitution of TiO_2 for SnO_2 does not promote any changes in the overpotential of the 4-CP oxidation. However, fixing the composition and comparing the electrode preparation route, a shift of ~ 100 mV toward less positive potentials is observed for PPM-electrodes, which indicates that under mild oxidation conditions the polymeric precursor route promotes a more active surface. There is still an ongoing dispute as to which material is better under given conditions. Therefore, further investigation on the morphology and composition and their correlation with structure and reactivity is necessary. To clarify this matter, the use of a technique such as X-ray Photoelectron Spectroscopy might determine whether there are changes in the electronic environments.

For all the investigated electrodes the 4-CP oxidation peak decreases after successive cycles. Polymerization of 4-chlorophenol is a possible cause of the

electrode deactivation. As shown before, the rate of electrode passivation is pH-dependent and occurs at lower range in acid medium [25, 26, 29]. In order to renew the electrode surface, the anode was removed to a cell containing the supporting electrolyte and submitted to a chronopotentiometric program ($i = 100\text{ mA cm}^{-2}$ for 20 min); details can be found elsewhere [16]. Although electrode passivation was observed, bulk electrolysis performed under drastic conditions, such as higher overpotential with simultaneous oxygen evolution reaction (OER), is effective in degrading the aromatic pollutants.

3.2 Efficiency of the 4-CP electrolyses

Figure 3 shows the 4-CP degradation profile when the current density is maintained at 100 mA cm^{-2} using a constant flux (6.0 mL min^{-1}) and room temperature. At the end of the electrolysis the influence of the composition or preparation method is less significant, showing that 98–99% of the starting material has been oxidized. Meanwhile, the influence of the electrode composition and preparation method in the degradation rate is observed during the first hours of electrolysis. The percentage of 4-CP removal is 65%, 56%, 51%, and 36% for SM/ISO-Sn, PPM-Ti, SM/ISO-Ti, and PPM-Sn, respectively, for the first 2 h of electrolysis. A small advantage for 4-CP removal can be observed when the SM/ISO-Sn electrode is compared with the other investigated electrode materials.

The kinetic studies were carried out by plotting $\ln([4\text{-CP}]_t/[4\text{-CP}]_0)$ vs. electrolysis time. To remain in the linear domain, slope evaluation was performed between 0 and 2 h for the results displayed in Fig. 3. An excellent linearity, showing regression coefficients above 0.99 for each slope assessment, was observed for all the investigated electrodes, indicating that the 4-CP electrochemical degradation presents pseudo-first order reaction kinetics. The kinetic constant for 4-CP degradation ($k_{4\text{-CP}}$) was taken as $k = k_{4\text{-CP}} A V^{-1}$, where A (m^2) is the geometric area of the anode, V (m^3) is the volume of the 4-CP solution and k is the

Table 2 Anodic charge (q_a) and kinetics results obtained for a set of mixed ruthenium oxides electrodes for 4-CP, BQ, and OA degradation in acid medium (0.5 mol L^{-1} H_2SO_4)

Nominal composition	Preparation method	$^a q_a/\text{mC}$	$^b i^0/\text{mA cm}^{-2}$	$k_{4\text{-CP}}/10^{-4}\text{ m s}^{-1}$	$k_{\text{BQ}}/10^{-4}\text{ m s}^{-1}$	$k_{\text{OA}}/10^{-4}\text{ m s}^{-1}$
Ti/Ru _{0.3} Ti _{0.7} O ₂	SM/ISO	33.4	1.8	6.8	7.7	4.8
Ti/Ru _{0.3} Ti _{0.7} O ₂	PPM	34.4	15.0	7.3	6.7	1.7
Ti/Ru _{0.3} Sn _{0.7} O ₂	SM/ISO	82.0	5.9	10.1	4.9	3.9
Ti/Ru _{0.3} Sn _{0.7} O ₂	PPM	19.6	11.6	4.5	4.5	3.8

^a Data obtained by integration of the anodic region in the 4-CP absence between 0.1 and 1.0 V vs. SCE

^b Data obtained in $E = 1.2$ V vs. SCE

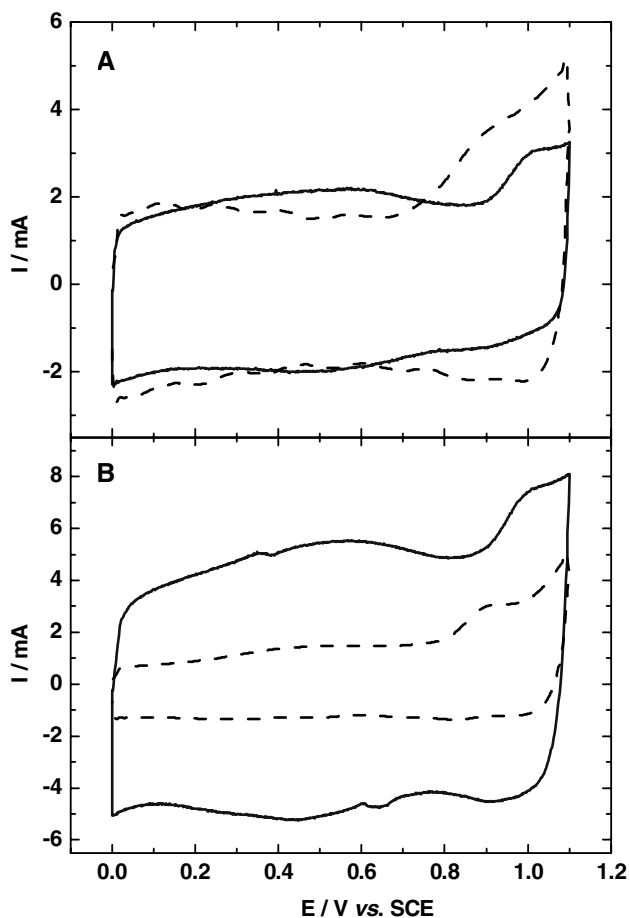


Fig. 2 Representative 4-CP (1 mmol L^{-1}) cyclic voltammograms as a function of both anode composition **(A)** $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and **(B)** $\text{Ti/Ru}_{0.3}\text{Sn}_{0.7}\text{O}_2$, and preparation method (—) SM/ISO-anodes and (---) PPM-anodes. $v = 50 \text{ mV s}^{-1}$, $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$

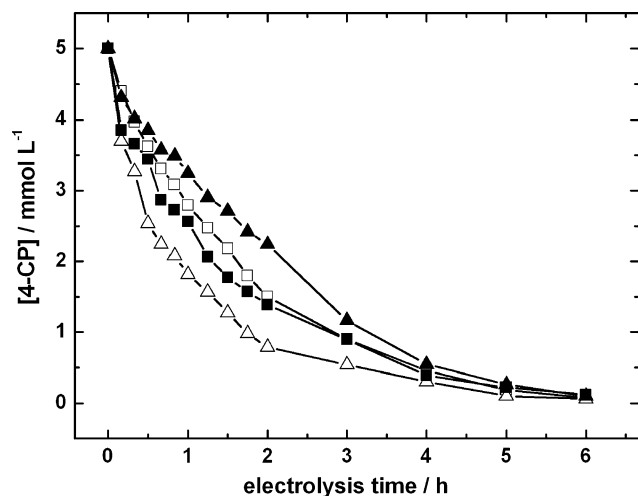


Fig. 3 4-CP concentration profile during electrolysis on different electrode materials: (■, □) $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ and (▲, Δ) $\text{Ti/Ru}_{0.3}\text{Sn}_{0.7}\text{O}_2$; open symbols stand for SM/ISO-anodes and closed ones for PPM-anodes. $A = 14 \text{ cm}^2$, $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, $[\text{4-CP}]_0 = 5 \text{ mmol L}^{-1}$, $i = 100 \text{ mA cm}^{-2}$

pseudo-first-order rate constant. Table 2 presents the results for 4-CP oxidation kinetics as a function of the anode nominal composition and preparation methodology. Analysis of this table confirms the previously shown results; i.e., under the applied current (100 mA cm^{-2}) the changes in the catalytic efficiency observed at the voltammetric domain are less pronounced and all the investigated materials are good for 4-CP degradation. However, the anode material containing the largest active area (SM/ISO-Sn) leads to the highest consumption of 4-CP, which is in agreement with the higher number of electroactive sites available for the oxidation of this pollutant. Once we have demonstrated that changes in the preparation methodology influence the number of active sites on the anode, this efficiency can also be controlled.

Figure 4 shows the concentration of 4-CP and CO_2 obtained at the end of the electrolysis (6 h) for the SM/ISO-Sn electrode as a function of current density. Comparison between these two parameters clearly shows that an increase in the current density increases the oxidation performance. In fact, at 100 mA cm^{-2} , 4-CP is totally removed. Total combustion of the formed by-products also increases with the increase in current density; however, these values are still low under the investigated time window (6 h).

Table 3 presents the percentage of removed TOC and recovered CO_2 at the end of 4-CP electrolysis as a function of both the anode nominal composition and preparation methodology. TOC measurements indicated that 35–50% of the carbon was mineralized after 6 h of reaction. The extent of degradation obtained from HPLC analysis (CO_2 recovered) is 10–30% lower

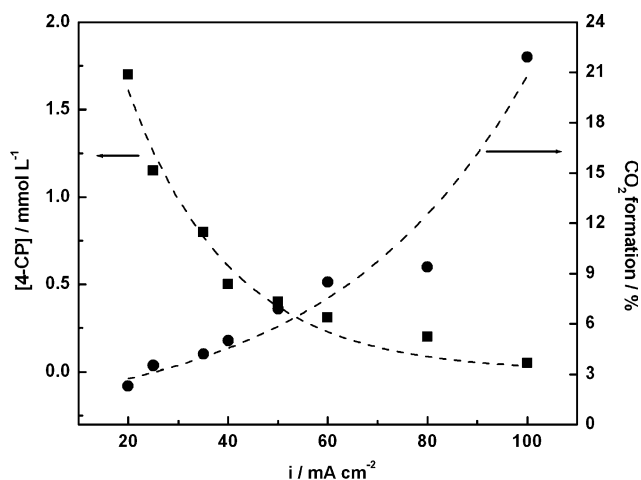


Fig. 4 4-CP concentration (■) and CO_2 formation percentage (●) profile as a function of the current density applied to $\text{Ti/Ru}_{0.3}\text{Sn}_{0.7}\text{O}_2$ anode prepared through SM/ISO. $A = 14 \text{ cm}^2$, $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, $[\text{4-CP}]_0 = 5 \text{ mmol L}^{-1}$, $i = 100 \text{ mA cm}^{-2}$

Table 3 Removed TOC, CO₂ and chloride ions in the solution at the end of the electrolysis (6 h) (supporting electrolyte = 0.5 mol L⁻¹ H₂SO₄, [4-CP]₀ = 5 mmol L⁻¹, i = 100 mA cm⁻², A = 14 cm²)

Anode	Preparation method	Removed TOC (%)	Produced CO ₂ (%)	Cl ⁻ (%)
Ti/Ru _{0.3} Ti _{0.7} O ₂	SM/ISO	52	27	27
Ti/Ru _{0.3} Ti _{0.7} O ₂	PPM	45	14	14
Ti/Ru _{0.3} Sn _{0.7} O ₂	SM/ISO	36	22	21
Ti/Ru _{0.3} Sn _{0.7} O ₂	PPM	40	31	10

TOC in the initial 4-CP solution corresponds to 360.3 mg L⁻¹

if compared with the TOC measurements. The difference between the measurements can be explained by CO₂ leakage from the flow cell system. Moreover, the formation of an adherent film on the anode surface or on the glass wall cannot be dismissed [25, 26, 30, 31].

The low recovery of chloride ions obtained in the solution at the end of the electrolysis (<30%) can be attributed to chlorine/hypochlorite electrogeneration on the anode surface [32, 33].

3.3 By-product analysis

HPLC analyses were performed to identify and monitor both the aromatic and non-aromatic products formed during the 4-CP degradation. The aromatic portion contained BQ, HQ, 4-CC, and a dimer (m/z = 288), as well as the starting material. HQ was formed by reduction of BQ on the cathode side. This hypothesis was confirmed by conducting the electrolysis in a divided cell, to prevent access of BQ to the cathode. Under this condition, HQ was not detected in any of the compartments.

The degradation of a desired toxic compound can lead to by-products that are as toxic as the starting pollutant [34, 35]. The concentration of the main aromatic products; i.e., BQ, HQ and 4-CC throughout the electrolysis are shown in Fig. 5. The OA yields after ring-opening were also monitored. The reaction profile for all by-products shows an increase at the beginning of electrolysis, followed by their subsequent consumption. In contrast with what was observed for the starting material at the end of the electrolysis the final concentration of by-products depended on the electrode material and its preparation route. SM/ISO-anodes were more efficient at oxidizing the aromatic portion than the PPM-ones.

The aromatic by-products formed in the electrolyses were further oxidized at the anode, giving mainly aliphatic acids and CO₂. The main detected aliphatic by-products were oxalic, maleic, malic, malonic and succinic acids. Again, an interesting selectivity was observed concerning the electrode preparation route. SM/ISO-electrodes led to higher yields of aliphatic

compounds if compared with the PPM-ones. This selectivity can be explained considering the higher selectivity of SM/ISO electrodes for the oxidation of aromatic compounds.

Since the concentration of these by-products depend on how fast they are generated from the degradation of 4-CP, and because these parameters change when the composition and preparation route are changed, we evaluated the efficiency of the electrode material at performing electrolyses starting with BQ and OA as representative degradation by-products. The observed rate constants are shown in Table 2. This analysis explains the role of the electrode material on the degradation of 4-CP. For BQ degradation, SM/ISO electrodes were more efficient. For the same preparation methodology it was observed that TiO₂-based anodes are better at oxidizing the aromatic by-products than the SnO₂ ones. In fact, Figure 6 shows that all BQ was removed at the SM/ISO-TiO₂ anode at the end of the electrolysis. The explanation for such behavior can be found in the generally accepted electrochemical oxidation mechanism of organic compounds involved

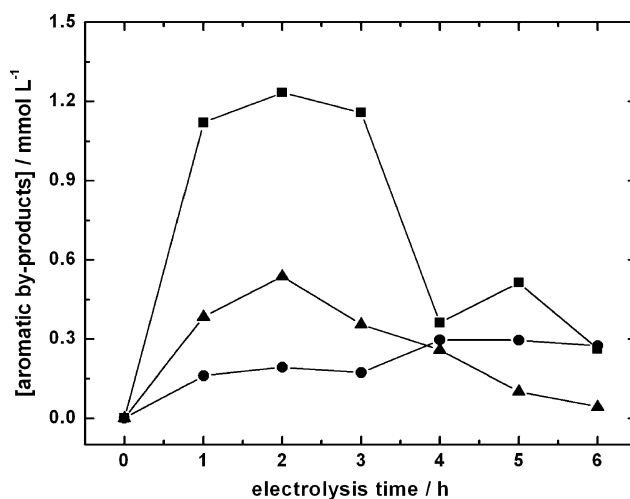


Fig. 5 Benzoquinone (■), hydroquinone (●), and 4-chlorocatechol (▲) concentration profile during electrolysis of 4-CP on Ti/Ru_{0.3}Sn_{0.7}O₂ (SM/ISO-anode). A = 14 cm², 0.5 mol L⁻¹ H₂SO₄, [4-CP]₀ = 5 mmol L⁻¹, i = 100 mA cm⁻²

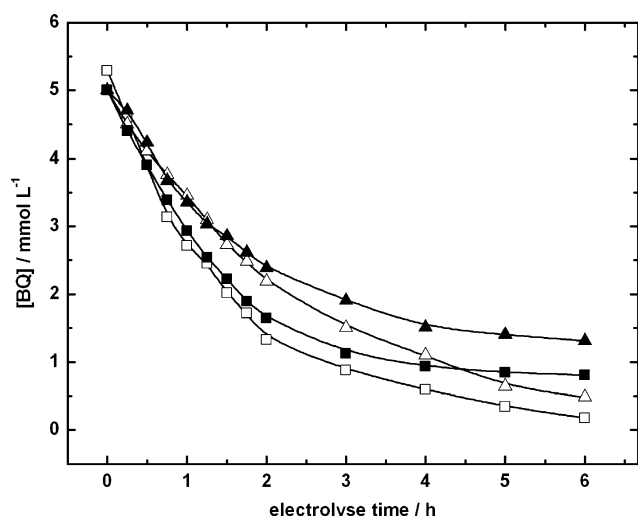


Fig. 6 BQ concentration profile during electrolysis on different electrode materials: (■, □) Ti/Ru_{0.3}Ti_{1.7}O₂ and (▲, Δ) Ti/Ru_{0.3}Sn_{0.7}O₂; open symbols stand for SM/ISO-anodes and closed ones for PPM-anodes. A = 14 cm², 0.5 mol L⁻¹ H₂SO₄, [4-CP]₀ = 5 mmol L⁻¹, i = 100 mA cm⁻²

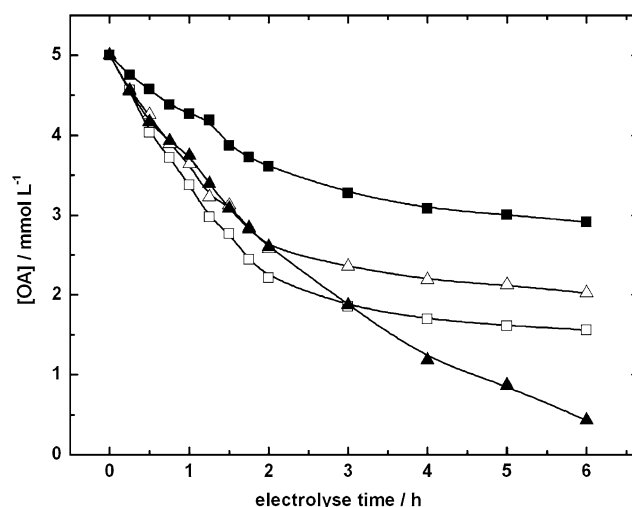


Fig. 7 OA concentration profile during electrolysis on different electrode materials: (■, □) Ti/Ru_{0.3}Ti_{1.7}O₂ and (▲, Δ) Ti/Ru_{0.3}Sn_{0.7}O₂; open symbols stand for SM/ISO-anodes and closed ones for PPM-anodes. A = 14 cm², 0.5 mol L⁻¹ H₂SO₄, [4-CP]₀ = 5 mmol L⁻¹, i = 100 mA cm⁻²

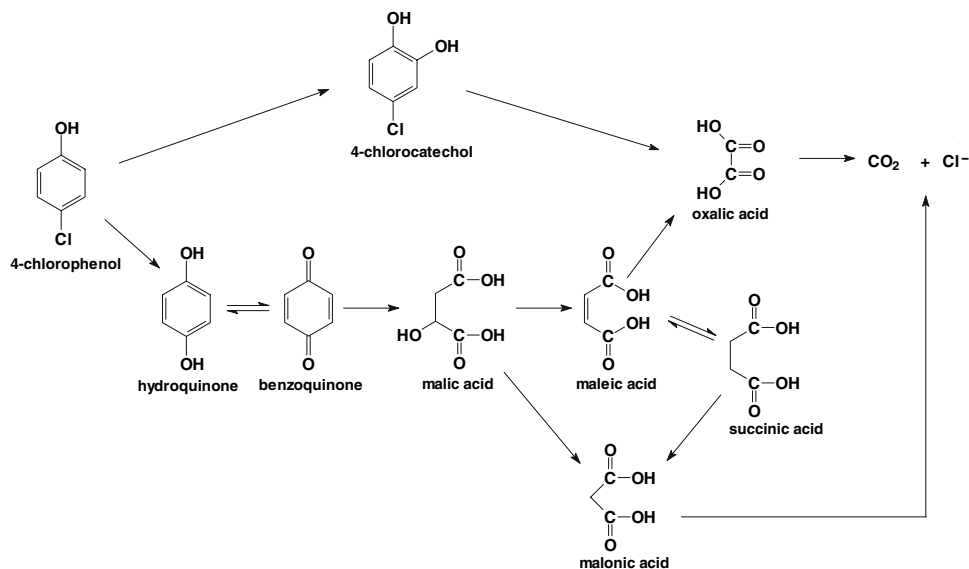
in DSA-type anodes [10]. It is well-known that SnO₂ increases the formation of adsorbed hydroxyl radicals MO_x(•OH). Meanwhile, MO_x(•OH) species can either participate in the oxidation of the organic compound or react to produce oxygen [18, 36]. This competition may hinder the catalytic gain for the organic compound oxidation. Similar results were also obtained in the oxidation of phenol [16].

In conclusion, in order to understand the global electrocatalytic efficiency for aromatic compound degradation of a certain material, it is important to measure the operational electrocatalytic performance

toward the desired reaction. The oxygen side reaction was evaluated by comparing the current densities of the oxygen evolution reaction (*i*_{OER}) in the support electrolyte solution at a fixed potential, e.g., 1.2 V/RHE OER. The *i*_{OER}-values shown in Table 2 change with the preparation route and the composition, and this can influence the global catalytic efficiency of the electrode in the degradation of the organic compound.

Figure 7 shows the oxidation of OA. In contrast to what is observed for the aromatic portion, the most efficient material for oxidation of OA is the Sn-PPM electrode. This selectivity explains why, at the end of

Fig. 8 Suggested reaction pathway for 4-CP electrochemical degradation in acid medium using mixed ruthenium derived anodes



4-CP electrolysis, a larger concentration of OA (4.4 mmol L^{-1}) for Sn-SM/ISO was obtained compared with that obtained with Sn-PPM (0.03 mmol L^{-1}).

Figure 8 presents a suggested pathway for the electrochemical degradation of 4-CP on the basis of the main products detected herein. The findings confirm the results reported by Johnson et al. [37] for 4-CP oxidation on a platinum anode covered with a metal oxide film containing a mixture of Ti, Ru, Sn, and Sb oxides and by Boye et al. [38] for 4-chlorophenoxyacetic acid oxidation at Pt.

According to the proposed mechanisms [37, 38], the first step in the electrochemical oxidation mechanism of 4-CP occurs mainly by two simultaneous routes. Route 1 leads to chlorinated aromatic by-products via 4-CP hydroxylation, and the main product obtained after ring-opening is OA [13, 37, 38]. In route 2, preferential dechlorination occurs, leading to the formation of BQ, which forms a mixture of less oxidizable aliphatic acids and small amounts of CO_2 [39]. Concerning the amount of aromatic by-products obtained at the end of the electrolysis and their concentration changes, we may infer that route 2 is preferentially followed by SM/ISO-anodes. However, OA is the ultimate carboxylic acid expected to be formed from the oxidation of longer carboxylic chain in both routes.

4 Conclusions

This research has shown a clear dependence of pollutant degradation on the preparation methodology of $\text{Ti/Ru}_{0.3}\text{M}_{0.7}\text{O}_2$ anodes. The main conclusions are:

- Although for 4-CP degradation all the investigated electrodes exhibit similar activity at the end of electrolysis, when one looks at the hazardous side-products formed the methodology used for the preparation of the anode does play an important role in the consumption of these materials. Electrodes prepared via the SM/ISO route are more active in the treatment of aromatic by-products due to their lower electrocatalytic activity for OER.
- Oxidation of OA is favored at the $\text{RuO}_2\text{-SnO}_2$ composition prepared through the PPM route.

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