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ORIGINAL PAPER

Electrochemical degradation of glyphosate formulations at DSA® anodes in chloride medium: an AOX formation study

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Abstract The electrochemical degradation of different glyphosate herbicide formulations on RuO_2 and IrO_2 DSA® electrodes is investigated. Parameters that could influence the formation of organochloride compounds during electrolysis are studied. The effects of chloride concentration, electrodic composition, current density, and electrolysis time are reported. The influence of the oxide composition on herbicide degradation seems to be almost insignificant; however, there is a straight relationship between anode composition and organic halides formation. Commercial herbicide formulations have lower degradation rates and lead to the formation of a larger quantities of organochloride compounds. In high chloride concentrations, there is a significant increase in organic mineralization, and the relationship between chloride concentration and organic halides formation is direct. Only in low chloride medium investigated the organochloride concentration obtained was below the limit values allowed in Brazil. The determination of organic halides absorbable (AOX) during electrolysis increases significantly with the applied current. Even during long-term electrolysis, a large amount of organochloride compounds is formed.

Keywords Electrochemical degradation · Glyphosate · AOX · DSA® electrodes · Roundup®

1 Introduction

In recent years, the effects of several organic pollutants on the environment have been studied and discussed in different scientific areas. The development of agricultural techniques has significantly increased the use of pesticides. Moreover, agrochemicals have increased environmental concern, mainly because of their adverse effects on soil and aquatic microorganisms [1]. Glyphosate [*N*-(phosphonomethyl) glycine] is a highly effective broad-spectrum, post-emergence, and non-selective herbicide that is widely employed in agriculture worldwide [2]. Glyphosate herbicide is highly soluble in water (12 g L^{-1} at 25 °C), and it is used in more than 30 crops to control a wide variety of annual weeds, mainly in sugarcane and soybean plantations. The main reason for the widespread use of this chemical worldwide is its relative low toxicity to human and animals. However, one of its main metabolites, aminomethylphosphonic acid (AMPA), displays relatively high toxicity.

Glyphosate is commercialized as an isopropylamine salt. Even though glyphosate commercial formulations are considered to have low toxicity, there are evidences of noxious effects on the environment after its prolonged use, mainly because of the resistance gained by the annual weeds. Moreover, some components of the commercial formulations are more toxic and persistent than the active ingredient. The commercial formulations contain surfactants based on ethylamine which is significantly more dangerous than glyphosate itself and very toxic for invertebrates and fish [2]. The half-life of the commercial formulations is relatively long, about 7–70 days [3]. According to resolution 375 of CONAMA (National Brazilian Environmental Council), the maximum value allowed for glyphosate in sweet water is 0.280 mg L^{-1}.

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The US Environmental Protection Agency also classifies glyphosate as “extremely persistent.”

Among the various treatment techniques available, electrochemical processes are always claimed to be an attractive alternative to the oxidation of organic pollutants. The main advantage of the electrochemical treatment is its versatility, easy operation, and lower cost [4]. Metallic oxide electrodes containing RuO_2 and IrO_2 have been widely used in environmental electrochemistry because of their mechanical resistance, inexpensiveness, and successful scale-up in the electrochemical industry. Besides leading to chloro-alkali production, dimensionally stable anode (DSA®) electrodes are also a good alternative to the oxidation of various organic compounds [5]. In this investigation, we propose some materials that have been prepared and characterized by our group in recent years [6–10]. From the wide range of investigated materials and compositions, we have chosen the ones which displayed the best performance concerning life stability, catalytic activity, cost, and easiness of preparation.

Although the electrochemical mineralization of organics can occur by a direct mechanism (Eqs. 1 and 2), the efficiency of this process is very low due to competition with the oxygen evolution reaction (OER, Eq. 3) [11].

$$MO_x + H_2O \rightarrow MO_x(^{\bullet}OH) + H^+ + e^- \tag{1}$$

$$R + MO_x(^{\bullet}OH) \rightarrow CO_2 + \text{inorganic ions} + MO_x + H^+ + e^- \tag{2}$$

$$MO_x(^{\bullet}OH) \rightarrow MO_x + {}^1\!/_2O_2 + H^+ + e^- \tag{3}$$

Knowing that electrochemical remediation calls for more powerful oxidizing conditions, one can work in chloride media to maximize the performance of the organic compound oxidation at DSA® anodes. NaCl is one of the most attractive media in the field of indirect oxidation owing to its straightforward impact on electrochemical technology. Oxide electrodes such as DSA® anodes are very active for Cl_2 evolution. As described elsewhere, the mechanism of chlorine evolution reaction (ClER) proceeds as follows [12]:

$$2Cl^- \leftrightarrows Cl_{2(el)} + 2e^- \tag{4}$$

$$Cl_{2(el)} \leftrightarrows Cl_{2(sol)} \tag{5}$$

The subsequent reaction of $Cl_{2(sol)}$ in solution results in the formation of reactive species, such as hypochlorous acid (HClO) and hypochlorite (ClO^-), responsible for promoting faster organic compound degradation:

$$Cl_{2(sol)} + H_2O \rightarrow HClO + Cl^- + H^+ \tag{6}$$

$$HClO \leftrightarrows H^+ + ClO^- \tag{7}$$

When someone performs electrolysis in chloride medium, he/she must be aware of the possibility of organochloride compound (RCl) formation, which would increase the lipophilicity of the organic compound, thereby favoring interactions with enzymes and promoting biotransformation, for example. In addition, RCl compounds present different genotoxicity effects which vary with the generated chemical structure. Some articles have also shown that RCl compounds are responsible for different carcinogenic and mutagenic effects [13]. These facts make the determination and evaluation of these compounds during electrolysis extremely urgent, mainly when they are proposed as an alternative route to degrading wastewater.

The formation of organochloride compounds during electrolysis in chloride medium has not received much attention. Only a few reports have investigated the influence of experimental parameters on the formation of organochlorine compounds [14–16]. This study aims to determine the influence of organic halides absorbable onto active carbon (AOX). Our approach consisted in investigating the effects of chloride concentration, electrodic composition, current density, as well as studying AOX degradation as a function of electrolysis time.

2 Experimental

2.1 Anodes and electrochemical cell

The following nominal compositions were proposed for this work: $Ti/(RuO_2)_{0.70}(Ta_2O_5)_{0.30}$, $Ti/Ru_{0.30}Ti_{0.70}O_2$, $Ti/Ru_{0.30}Sn_{0.70}O_2$, $Ti/Ru_{0.30}Pb_{0.70}O_2$, and $Ti/Ir_{0.30}Sn_{0.70}O_2$. The working anodes were 2-cm^2 large, and they were prepared by thermal decomposition. The precursor mixtures were applied on both sides of the pre-treated Ti support by brushing, as described in previous works; details about the preparation, methodologies, and the physical and electrochemical characterization of these anodes are given elsewhere [6–10]. Two spiraled platinized platinum wires (15 cm), placed parallel to each other, were used as counter electrodes. All potentials are referred to the saturated calomel electrode (SCE).

The electrochemical measurements were conducted in an open system, using a three-compartment electrolytic cell consisting of (1) a main body (50 mL of solution), and (2) two smaller compartments containing the counter electrodes, which were isolated from the main body by coarse glass frits. The electrolyses experiments were conducted in the galvanostatic mode, under magnetic stirring. Electrochemical experiments, cyclic voltammetry and galvanostatic electrolyses, were performed using a potentiostat/galvanostat Autolab, mode SPGSTAT30. All experiments were performed at 25 ± 1 °C.

2.2 Reagents

The oxidation of three different samples was investigated in this study. Two glyphosate commercial formulations, namely, herbicide 1, used in large-scale agricultural activity (Roundup®, from Monsanto Company) and herbicide 2, a sample used in gardening service (Orium® from Dominus Química LTDA) as well as a standard solution (secondary standard 95.5%, gently provided by Fersol Indústria e Comércio LTDA), named herbicide 3, were employed.

Activated charcoal was provided by Analytik Jena AG. All the other chemicals were analytical reagent grade and were used without further purification. In all experiments, the ionic strength [17] was kept constant ($\mu = 1.5$ mol dm^{-3}) by adjusting the Na_2SO_4 and NaCl concentrations. Solutions were prepared with high-purity water from a Millipore Milli-Q system.

2.3 Analyses

Spectrophotometric detection of glyphosate was performed at 243 nm after derivatization, as discussed elsewhere [18]. Details of this analysis are given in a previous study [19]. The total combustion of the samples was followed by chemical oxygen demand (COD) after electrolysis. UV–vis spectra were recorded using a Varian model Cary 50 Conc spectrophotometer. All results are based on the measurement of triplicate samples.

AOX analyses were performed using a multi X 2000 Analyzer (Analytika Jena, Germany). Before the analysis, residual chlorine and hypochlorite were removed by the addition of a proper amount of sodium sulfite. Briefly, the measurement involved adsorption of the organochlorine on activated carbon, mineralization of the organically bound halogen by combustion at 950 °C, and determination of chloride by microcoulometric titration. The detection limit was 0.01 mg L^{-1}.

ICP-MS analyses were performed using an ELAN DRC-II Perkin Elmer Sciex.

3 Results and discussion

3.1 Characterization of the herbicide formulations and voltammetric investigation

Table 1 Characteristics of the different herbicides formulations

Herbicide	Initial COD (mg O_2 L^{-1})	Initial TOC (mg L^{-1})	Initial AOX (mg L^{-1})
Herbicide 1	1,179	450	0.32
Herbicide 2	1,014	388	0.17
Herbicide 3	586	223	n.d.

Table 1 presents some initial parameters for the different herbicides (1,000 mg L^{-1}) investigated in this study. Organic compound loading in the various herbicide formulations is different due the presence of adjuvants besides the active ingredient in commercial formulations. The so-called “inert compounds” are in their majority carriers, wetting agents, antifreezes, and other compounds employed to facilitate handling and application. Most of them are surfactants that increase the spreading and the penetration power. Interestingly, the organochloride compounds were found in the commercial formulations before electrolysis. The quantities of AOX found in these formulations were much lower than the limit value allowed by the CONAMA agency (National Brazilian Environmental Council). However, this data may be considered relevant, especially when one takes the huge amount of herbicides employed worldwide into account. In the case of herbicide 3, organochloride compounds are not detected (n.d.), since this is our reference standard sample.

In an attempt to determine the oxidation potential of the herbicide formulations, cyclic voltammograms were performed for all the electrode compositions in both the absence and presence of herbicide formulations. Figure 1 shows representative cyclic voltammograms obtained in the absence and in the presence of the organic compounds for the investigated DSA® electrodes. None of the tested herbicides are electroactive in the potential window of the investigated oxide anodes. Their oxidation is hindered by the OER which appears as the main difficulty inherent to electrochemical organic compound degradation.

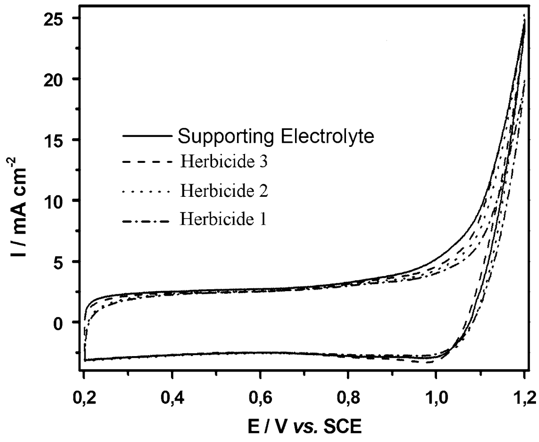

Fig. 1 Representative cyclic voltammograms as a function of different herbicide formulations at $Ti/Ru_{0.3}Sn_{0.7}O_2$ electrode. $\nu = 50$ mV s^{-1}, $\mu = 1.5$ mol dm^{-3}, supporting electrolyte = Na_2SO_4, pH = 3

3.2 Degradation as a function of the chloride concentration

In order to investigate the influence of the initial chloride ion concentration on the indirect oxidation of glyphosate formulations, via chlorine generation, the Ti/$Ir_{0.30}Sn_{0.70}O_2$ anode was employed in the electrolyses of the different herbicides (1,000 mg L^{-1}) for 4 h. The initial pH of the solution was 3 and no further adjustment was performed during the electrolysis; however, the current density was kept constant at 50 mA cm^{-2}. The effect of the initial chloride concentration on the degradation rate was investigated over the range 200–2,700 mg L^{-1}; the maximum yield of chloride employed here was based on a previous investigation carried in our laboratory, which showed that the removal efficiency decreases for chloride concentrations higher than 3,000 mg L^{-1}. Also, it was borne in mind that the formation of other species is favored at high current density and high chloride concentration [19].

Figure 2 shows the glyphosate and COD removal at different sodium chloride concentrations. High degradation values are found even at a very low NaCl concentration (220 mg L^{-1}), and increasing initial chloride ion concentrations lead to a significant increase in the rate of glyphosate removal and organic mineralization. After 4 h of electrolysis, complete glyphosate removal is obtained for all the formulations in chloride medium (2,662 mg L^{-1}). COD removal reaches 81%, 86%, and 91% for herbicides 2, 1, and 3, respectively. Figure 2 also reveals that the commercial formulations are more persistent compared with the standard herbicide, and the sample used in gardening is the most difficult to degrade. We can infer that the "inert" compounds present in the commercial formulations are responsible for this behavior. A difference in the COD values and glyphosate removal is also observed. This could be related to the formation of less oxidizable species or organochloride compounds. In order to investigate this possibility, AOX analysis as a function of the chloride concentration was performed at the end of the electrolysis (Fig. 3). AOX concentration values ranged from 1.4 to 5.5 mg L^{-1} for herbicide 1, 0.8–4.7 mg L^{-1} for herbicide 2, and 0.15–1.5 mg L^{-1} for herbicide 3. Considering that the starting material concentration is very high (1,000 mg L^{-1}), the R–Cl values are still too small to explain the difference in the degradation profile depicted in Fig. 2. In conclusion, formation of less oxidizable species, such as AMPA and *n*-methylglycine (sarcosine), should explain the behavior seen in Fig. 2 [20].

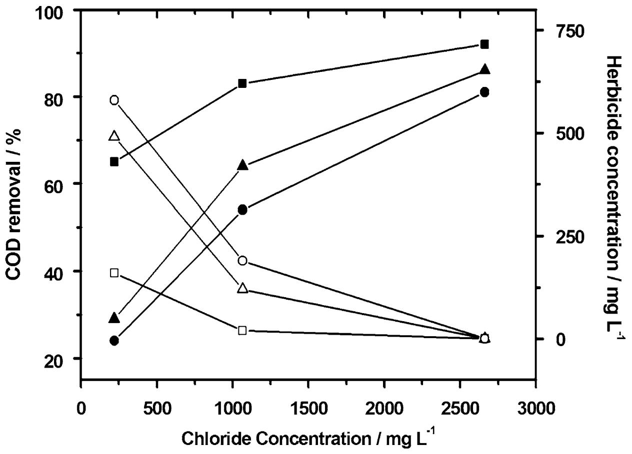

Fig. 2 COD and glyphosate removal as a function of chloride concentration at Ti/$Ir_{0.30}Sn_{0.70}O_2$; $i = 50$ mA cm^{-2}, $t = 4$ h. *Filled square*, *open square* = herbicide 3; *filled triangle*, *open triangle* = herbicide 1; *filled circle*, *open circle* = herbicide 2. Open symbol (herbicide concentration), close symbol (COD removal)

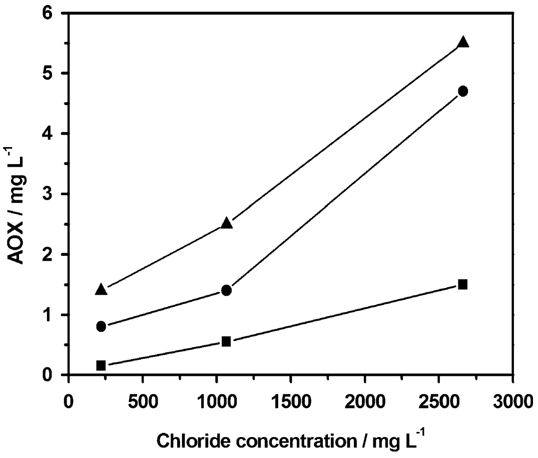

Fig. 3 Formation of AOX as a function of the chloride concentration for the different samples used at Ti/$Ir_{0.30}Sn_{0.70}O_2$; $t = 4$ h, $i = 50$ mA cm^{-2}. *Filled square* = herbicide 3; *filled circle* = herbicide 2; and *filled triangle* = herbicide 1

Figure 3 clearly shows a direct relationship between chloride concentration and AOX formation; a higher formation of organochloride compounds in commercial formulations is also observed. Differences in adjuvant compounds between different commercial formulations should explain the larger amount of AOX in the case of the herbicide 1. However, it is noteworthy that only at the lowest tested chloride concentration is AOX detected below the allowed limit values in Brazil (1 mg L^{-1}). Therefore, one should be aware of the presence of inert carriers in the electrolyte as well as the amount of chloride in the supporting electrolyte. This evidence supports that many factors must be accounted for before a degradation route is proposed, as will be shown in the next section. The most efficient material for the oxidation of hazardous compound may produce undesirable byproducts.

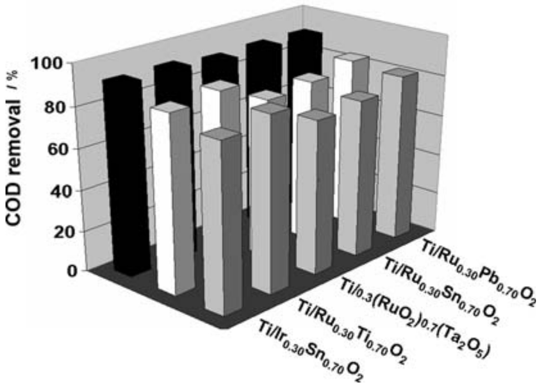

Fig. 4 COD removal for the different herbicides as a function of the electrode composition; $[Cl^-] = 2662$ mg L^{-1}, $t = 4$ h, $i = 50$ mA cm^{-2}. *Filled square* = herbicide 3; *open square* = herbicide 1; ▨ = herbicide 2

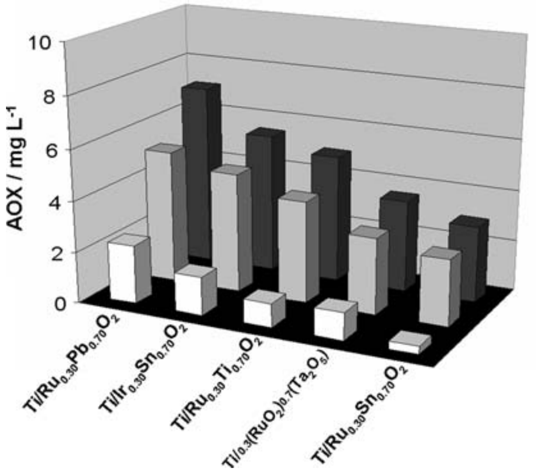

Fig. 5 Formation of AOX for the different herbicides as a function of the electrode composition, $[Cl^-] = 2{,}662$ mg L^{-1}, $t = 4$ h, $i = 50$ mA cm^{-2}. *Open square* = herbicide 3; ▨ = herbicide 2; and *filled square* = herbicide 1

3.3 Degradation as a function of the electrode composition

In order to investigate the influence of the electrode material on organic compound degradation in Cl medium, electrolyses were performed for the Ti/$(RuO_2)_{0.70}(Ta_2O_5)_{0.30}$, Ti/$Ru_{0.30}Ti_{0.70}O_2$, Ti/$Ru_{0.30}Sn_{0.70}O_2$, Ti/$Ru_{0.30}Pb_{0.70}O_2$, and Ti/$Ir_{0.30}Sn_{0.70}O_2$ electrodes at a fixed concentration of active ingredient (1,000 mg L^{-1}). The chloride concentration (2,662 mg L^{-1}) and the current density (50 mA cm^{-2}) were also kept constant for 4 h. Figure 4 shows that all the investigated electrode compositions have similar efficiency concerning herbicide degradation. Good mineralization rates (COD removal) are obtained in all cases, reaching approximately 80%, 85%, and 90% for herbicides 2, 1, and 3, respectively.

Nevertheless, AOX analysis reveals some interesting behavior related to anode composition and RCl yields. Figure 5 shows that Ti/$Ru_{0.30}Sn_{0.70}O_2$ leads to the lowest AOX values. Considering that all the investigated electrodes result in almost the same COD removal, Ti/$Ru_{0.30}Sn_{0.70}O_2$ is the most environmentally friendly composition. Probably, the more intrinsic efficient compositions (Ti/$Ru_{0.30}Pb_{0.70}O_2$) in terms of chlorine production, and consequently active chloride species, favor the formation of undesirable organic byproducts [19].

Since lead was employed in one of the anode compositions (Ti/$Ru_{0.30}Pb_{0.70}O_2$), it is very important to verify whether there is any lead dissolution due to its corrosion during electrolysis. To this end, the supporting electrolyte was analyzed by ICP-MS, and the lead concentration found for the first electrolysis of the fresh-prepared anode in the supporting electrolyte solution was very low (12 μg L^{-1}). Moreover, we observed, by following the electrode charge, that there was not a continuous dissolution of the electrode during all the electrode experiments. The observed lead dissolution is very small compared with the initially deposited electroactive oxide (≈3.8 mg) [21], showing that the preparation methodology seems to be environmentally feasible.

A very interesting way to obtain more clues about the efficiency of each tested material is to study the instantaneous current efficiency (ICE) during the different electrolyses. The determination of ICE during electrochemical oxidation was accomplished considering that two parallel reactions (organic compound oxidation and OER) take place during electrochemical incineration. ICE is defined as the current fraction used for the organic compound oxidation; the efficiency is calculated considering the COD values of the wastewater before and after electrolysis, using the relation:

$$\mathrm{ICE} = \frac{FV}{8I}\,\frac{\left[(\mathrm{COD})_t - (\mathrm{COD})_{t+\Delta t}\right]}{\Delta t}, \tag{8}$$

where F is the Faraday constant (C mol^{-1}), V is the volume of the electrolyte (m^3), I is the applied current (A), and $(\mathrm{COD})_t$ and $(\mathrm{COD})_{t+\Delta t}$ are the chemical oxygen demand (g O_2 m^{-3}) at time t and $t + \Delta t$ (s), respectively.

Figure 6 shows the ICE profile as a function of the anode composition. The ICE data in these conditions are very similar for all the investigated compositions. The ICE profile reveals a higher efficiency for commercial formulations, once these herbicides exhibit higher initial COD. Figure 6 also shows that ICE values are not so high, reaching approximately 20%, 30%, and 40% for herbicides 3, 2, and 1, respectively. Considering that a current density corresponding to the anode potential in the region of water discharge was applied, the OER plays an important role in total current consumption.

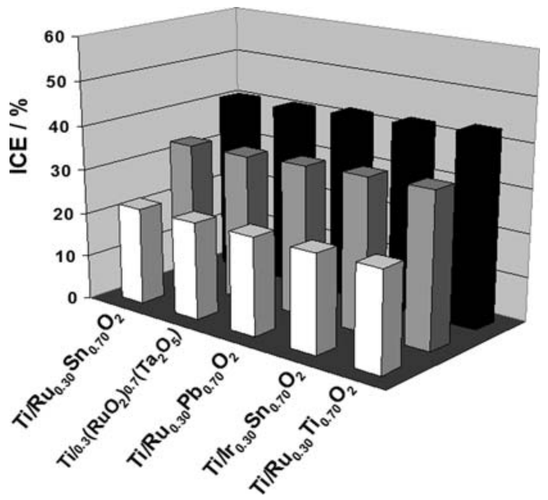

Fig. 6 ICE profile for the different herbicides as a function of the electrode composition; [Cl$^-$] = 2,662 mg L^{-1}, $t = 4$ h, $i = 50$ mA cm^{-2}. *Open square* = herbicide 3; ■ = herbicide 2; and *filled square* = herbicide 1

3.4 Current density effects

Figure 7 shows the effect of current density on the oxidation of different herbicide formulations at the Ti/Ir$_{0.30}$Sn$_{0.70}$O$_2$ electrode in chloride medium (2,662 mg L^{-1}) for 4 h. The increase in current density provides higher ClO$^-$ production; therefore, an increase in the oxidation of all the investigated herbicides should be expected. The behavior observed in Fig. 7 clearly shows that the different organic compound loadings lead to different oxidation behavior. Considering glyphosate and COD removal data for herbicide 3, an increase in current density provides a mild increase in the oxidation performance. For this sample, mineralization is virtually complete (90% COD removal) at low current density values ($I \geq 30$ mA cm^{-2}). Commercial formulations lead to a steadier increase in the oxidation rate with current density, and they are more resistant to oxidation, because at low current density, COD removal is much lower compared with values obtained from the standard sample values. Only at higher current density is total glyphosate removal obtained.

The formation of organochloride compounds as a function of the applied current was also evaluated. Figure 8 shows that the commercial herbicides lead to the formation of a higher amount of organochloride compounds. As expected, an increase in the applied current causes to an increase in the amount of ClO$^-$ (Eq. 6), so the yields of AOX species are enhanced. AOX formation follows an exponential behavior in the case of commercial formulations, being herbicide 1 the formulation that produces the highest AOX concentration. For herbicide 3, formation of organochloride compounds during electrolysis increases almost linearly with the applied current, and the AOX concentration remains below the allowed values almost in all the investigated current window.

3.5 Study of degradation behavior as a function of electrolysis time

In order to investigate the degradation behavior of different glyphosate formulations as a function of time, electrolyses of all the investigated herbicides were performed at Ti/Ir$_{0.30}$Sn$_{0.70}$O$_2$ electrode in chloride medium (2,662 mg L^{-1}), applying 30 mA cm^{-2}. Figure 9 shows the behavior after long-term electrolysis. A similar behavior is obtained for all the investigated herbicides; however, commercial formulations are again more resistant to degradation (probably due to the higher initial

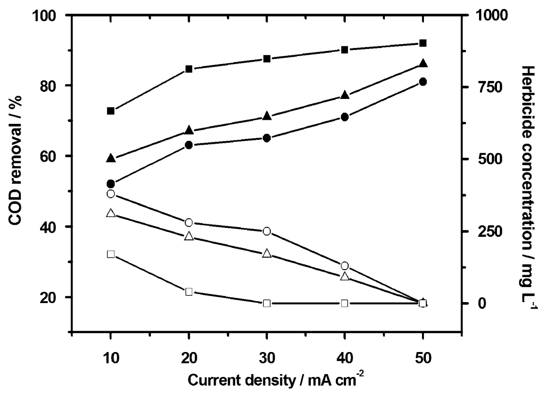

Fig. 7 COD and glyphosate removal as a function of the applied current density at Ti/Ir$_{0.30}$Sn$_{0.70}$O$_2$; [Cl$^-$] = 2,662 mg L^{-1}, $t = 4$ h. *Filled square*, *open square* = herbicide 3; *filled triangle*, *open triangle* = herbicide 1; and *filled circle*, *open circle* = herbicide 2. Open symbol (herbicide concentration), close symbol (COD removal)

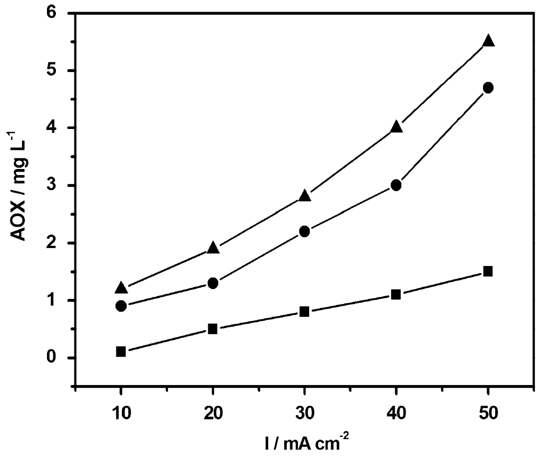

Fig. 8 Formation of AOX for the different herbicides as a function of current density at Ti/Ir$_{0.30}$Sn$_{0.70}$O$_2$, [Cl$^-$] = 2,662 mg L^{-1}, $t = 4$ h. *Filled triangle* = herbicide 1; *filled circle* = herbicide 2; and *filled square* = herbicide 3

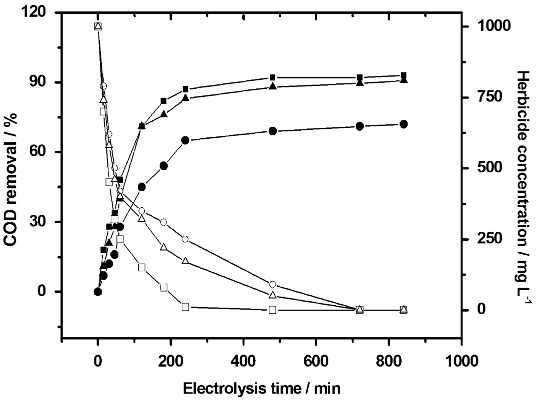

Fig. 9 COD and glyphosate removal for the different herbicides as a function of electrolysis time at Ti/$Ir_{0.30}Sn_{0.70}O_2$; $i = 30$ mA cm^{-2}, $[Cl^-] = 2{,}662$ mg L^{-1}. *Filled square*, *open square* = herbicide 3; *filled triangle*, *open triangle* = herbicide 1; and *filled circle*, *open circle* = herbicide 2. Open symbol (herbicide concentration), close symbol (COD removal)

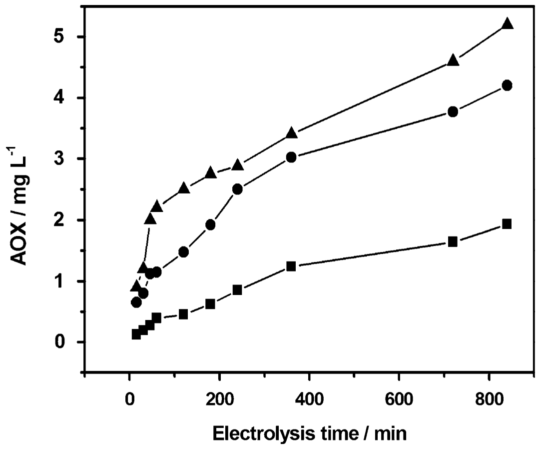

Fig. 10 Formation of AOX as a function of electrolysis time for the different samples at Ti/$Ir_{0.30}Sn_{0.70}O_2$; $[Cl^-] = 2{,}662$ mg L^{-1}, $i = 30$ mA cm^{-2}. *Filled triangle* = herbicide 1; *filled circle* = herbicide 2; and *filled square* = herbicide 3

COD and the presence of adjuvants). For herbicide 3, a saturation value is obtained after 3 h of electrolysis, as well as total glyphosate removal and 82% COD removal. The maximum COD removal is 93%. As for the commercial formulations, the sample used in gardening gives the lowest degradation rate. For these formulations, total glyphosate removal is obtained only after a long time (12 h), and the maximum COD removal is 72% and 92% for herbicides 2 and 1, respectively.

The study of organochloride compound formation as a function of electrolysis time is fundamental for the evaluation of the mechanism of AOX formation in electrochemical treatment. Although some articles have shown that once the R–Cl compound is formed, it is quickly consumed before the end of the electrolysis, giving a volcano type curve [14, 15], the results found in Fig. 10 reveal a different behavior for AOX formation. Even in long-term electrolysis (14 h), there still is a mild increase in organochloride compound formation. These results may be attributed to the lower quantity of AOX compounds formed during the electrolysis, compared with the results found elsewhere [14, 15]. Data from Fig. 10 may be understood by considering the competition between the degradation of the generated AOX and the organic compounds present in the solution. Once AOX formation is a homogeneous reaction ($ClO^- +$ Organic → RCl), this species should diffuse to the bulk solution, so that AOX oxidation should be hindered by oxidation of the starting material, which is present at a much higher concentration. In previous reports, the quantity of AOX compounds found in the beginning and in the end of the electrolysis was much higher, so that the organochloride compounds were partly consumed before the end of electrolysis. Although the formation of AOX is faster in the beginning of the electrolysis, from the results observed in Fig. 10, the quantity formed after 14 h of electrolysis is very low compared with the amount of the initial material. For this reason, an ascending behavior of AOX formation is observed for the entire investigated time window.

4 Conclusion

All the metallic oxide electrodes containing RuO_2 and IrO_2 evaluated in this study display good performance for the anodic mineralization of organic pollutants in chloride medium. The different compositions have similar efficiency concerning herbicide degradation; however, the AOX values for the different anodes reveal a straight relationship between anode composition and formation of the organochloride compounds. Higher chloride concentrations lead to a significant increase in organic mineralization. Also, there is a direct relationship between chloride concentration and AOX formation, and only in low chloride concentration is AOX detected above the limit values allowed in Brazil. Commercial herbicide formulations give lower degradation rates and leads to the formation of a larger quantity of organochloride compounds, and herbicide 1 leads to the highest AOX formation. AOX formation during electrolysis increases almost linearly with the applied current, and even in long-term electrolysis, there still is a large amount of organochloride compounds being formed.

Finally, the results of AOX formation as a function of many experimental parameters show that the formation of organochloride compounds is straightly related with factors like chloride concentration, anode material, and current density, among others. For this reason, it is very important that these parameters are carefully evaluated when an alternative treatment that allows the formation of this species in solution is proposed.

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