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Article

Electrochemical Degradation of Reactive Dyes at Different DSA® Compositions

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Este trabalho investiga a oxidação eletroquímica dos corantes azul reativo 4 (RB-4) e laranja reativo 16 (RO-16) utilizando ânodos dimensionalmente estáveis de RuO_2. As eletrólises foram realizadas sob controle galvanostático em função do eletrólito de suporte e composição do material eletródico. As eletrólises feitas na presença ou ausência de NaCl foram capazes de remover totalmente a coloração da solução; no entanto, um aumento significativo da combustão do corante somente foi obtido para na presença de cloreto (valores de 80% de remoção de carbono foram atingido). Concentrações elevadas de cloreto não implicaram em aumento significativo de remoção da cor ou mineralização. A composição do óxido influência na destruição do corante (com ou sem cloreto), observa-se que $Ti/Ru_{0.30}Ti_{0.70}O_2$ é o material mais ativo para oxidação dos compostos investigados. A reação de desprendimento de oxigênio é uma reação paralela limitante em ambos os eletrólitos de suporte investigados, NaCl e Na_2SO_4, e a competição com a oxidação do composto orgânico ainda é um obstáculo. A análise da formação de compostos organoclorados (AOX) revela que existe um pequeno consumo das espécies formadas nos primeiros minutos de eletrólise, a composição $Ti/(RuO_2)_{0.70}(Ta_2O_5)_{0.30}$ é a composição com melhores características para emprego no tratamento ambientais. Tanto a composição como o eletrólito afetam a formação de compostos indesejáveis.

This paper investigates the electrochemical oxidation of the reactive dyes reactive blue 4 (RB-4) and reactive orange 16 (RO-16) on RuO_2 dimensionally stable anode (DSA®) electrodes. Electrolysis was achieved under galvanostatic control as a function of supporting electrolyte and electrode composition. The electrolyses, performed in either the presence or absence of NaCl, were able to promote efficient color removal; moreover, at low chloride concentration (0.01 mol L^{-1}), total color removal was obtained after just 10 min of electrolysis, and a significant increase in total dye combustion was achieved for all the studied anodes in chloride medium (reaching *ca.* 80% - chemical oxygen demand - COD removal). No significant enhancement in dye color removal or mineralization was observed upon increasing chloride concentration. The influence of oxide composition on dye elimination seems to be significant in both media (with or without chloride), being $Ti/Ru_{0.30}Ti_{0.70}O_2$, the most active material for organic compound oxidation. The oxygen evolution reaction (OER) was shown to be a limiting reaction in both supporting electrolytes; *i.e.*, NaCl and Na_2SO_4, and its competition with organic compound oxidation remained an obstacle. The adsorbable organo halogens (AOX) formation study revealed that there is slight consumption of the undesirable species formed within the first minutes of the electrolysis, being $Ti/(RuO_2)_{0.70}(Ta_2O_5)_{0.30}$ the most environmentally friendly composition. Both anode composition and chloride concentration affect the formation of these undesirable compounds.

Keywords: reactive dyes, electrochemical oxidation, DSA® electrodes, wastewater, AOX

Introduction

In recent years, the effects of many organic pollutants on the environment have been investigated and discussed in different scientific areas. Remediation of water contaminated with toxic organic compounds such as dyes, herbicides, pesticides, pharmaceuticals, detergents, and many other highly toxic compounds has been the subject of many investigations.[1-5] Various research teams worldwide are currently seeking for alternative methods of the degradation of these toxic organic compounds.[6] Despite the economic advantages of conventional methods

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such as chemical and biological treatment, they are no longer able to convert many compounds into their non-toxic form. Some approaches to the treatment of toxic organic materials, to remove or convert these pollutants into biodegradable compounds, are available. Electrochemical, ozonation, electro and photo-Fenton, photocatalysis, and heterogeneous photocatalysis are some of the processes that have been frequently proposed for the treatment of organic pollutants by many researchers in the recent literature.[7-12]

In this context, the electrochemical processes are always claimed to be an attractive alternative to the degradation of organic pollutants. Versatility, easy operation, relatively lower cost, and no production of sludge during the treatment are some of the major advantages of the electrochemical approach. Mainly because of their mechanical resistance, inexpensiveness, and successful scale-up in the electrochemical industry, metallic oxide electrodes containing RuO_2 have been widely employed in environmental electrochemistry.[13] Besides leading to chloride-alkali production, DSA® electrodes are also a good alternative for the oxidation of various organic compounds.[14] In this work, we propose the use of some electrode materials that have been previously prepared and characterized in our laboratory.[15,16] From the wide range of investigated materials and compositions, we have chosen some of the oxide materials with the best performance concerning life stability, catalytic activity, cost, and ease of preparation. These are important issues concerning the choice of the best material to be applied, as it will later be shown that the milder activity of DSA® electrodes compared with more active materials such as boron doped diamond (BDD), toward organic compound degradation, can be overcome by choosing the right electrolyte conditions. When the proper conditions are achieved, the fact that oxide electrodes cost 10% of the value of BDD becomes an important advantage in large routine application.

The electrochemical mineralization of organic compounds may occur directly at anodes through generation of physically adsorbed hydroxyl radicals. The mechanism proposed for this reaction, which involves discharge of water molecules at the metal oxide surface, is well discussed elsewhere.[17] Because of the need for more powerful oxidizing conditions, electrochemical remediation frequently seeks the electrogeneration of highly oxidizing species such as Cl_2 and O_3. This can be obtained by changing the electrode material (SnO_2, PbO_2, boron-doped diamond) or the supporting electrolyte (chloride medium).

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. In recent years, electrolysis in chloride medium has appeared as a good alternative for electrochemical treatment. Some promising results concerning toxic organic compound degradation in this medium can be found in the literature.[3,18-20] In the case of electrolysis performed in both the presence and absence of chloride, the oxygen evolution reaction (OER, which is an undesirable side reaction responsible for diminishing the current efficiency of the organic compound oxidation in the electrochemical process) takes place.[21] For this reason, the search for better electrode materials in which the OER can be diminished is still desirable.

When electrolysis is performed in chloride medium, the formation of an organochlorine compound (RCl) during the treatment is very likely. This kind of material displays high lipophilicity, so interactions with enzymes that promote biotransformation, for instance, may take place. In addition, RCl compounds display different genotoxicity effects, which vary depending on the generated chemical structure. Some papers have also shown that RCl compounds are responsible for different carcinogenic and mutagenic effects.[22] These facts make determination of these compounds during electrolysis mandatory, mainly when an alternative route involving wastewater degradation in chloride medium is proposed. The formation of RCl in chloride medium has not received much attention over the past years. Nowadays, only a few papers investigating the influence of experimental parameters on RCl formation can be found in the literature.[18,19,23-25]

The large use of dyes by textile, paper, and plastic manufacture, among other industries, has raised significant environmental concern, mainly because these chemicals have adverse effects that are responsible for a lot of environmental damage when they are accumulated in the environment. Even at very low concentrations, dyes can result in wastewater with very strong coloration, thereby reducing the occurrence of photosynthetic processes, which directly affects all the aquatic system when these pollutants are discharged into rivers and ponds.[26,27] Azo dyes are among the various reactive dyes most commonly employed in dyeing processes; however, the highly colored and poorly biodegradable dye wastes display carcinogenic and mutagenic potential mainly because of the presence of the azo species.[28,29] In this context, diverse anodic materials have been utilized for the electrooxidation of several dyes under different conditions.[6,2,30,31] In this study, the electrochemical oxidation of the largely employed RB-4 (C.I. 61205) and RO-16 (C.I. 17757) is proposed (Figure 1). RB4 is an anthraquinone-based chlorotriazine dye mainly used in the cellulosic and textile industries. RO16, also known as remazol orange brilliant 3, contains both an azo chromophore and a sulfate ethyl sulfone reactive group.

Despite its good dyeing properties, it is highly resistant to conventional treatment methodologies.[32]

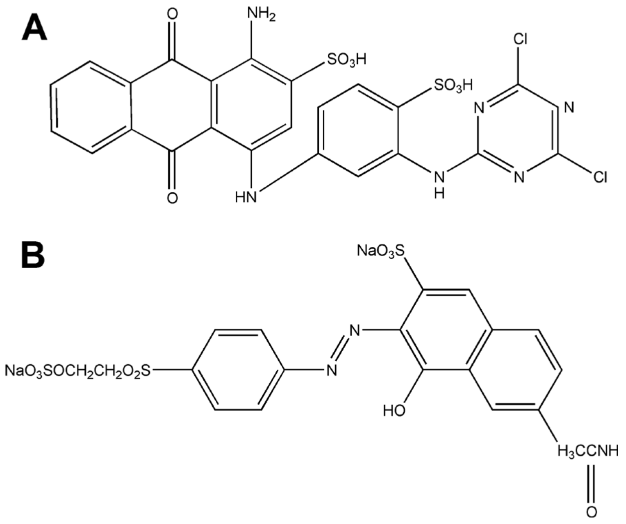

Figure 1. Chemical structure of the reactive dyes RB-4 (A) and RO-16 (B).

The present work thus investigates the performance of a set of RuO_2-based electrodes with respect to the electrooxidation of the aforementioned dyes. The influence of different electrolysis parameters such as supporting electrolyte, current density, and anode composition has been examined. The formation of adsorbable organo halogens (AOX) during the treatment has also been evaluated.

Experimental

Electrolytic system and electrodes

The working anodes were 2 cm^2 large and were prepared by thermal decomposition. The precursor mixtures were applied onto both sides of the pre-treated Ti support by brushing, as described in previous works.[15,16] The following nominal compositions were tested: $Ti/(RuO_2)_{0.70}(Ta_2O_5)_{0.30}$, $Ti/Ru_{0.30}Ti_{0.70}O_2$, and $Ti/Ru_{0.30}Sn_{0.70}O_2$. Details about the preparation, methodologies, and the physical and electrochemical characterization of these anodes are given elsewhere.[15,16] 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 a main body (50 mL solution) and two smaller compartments containing the counter electrodes, which were isolated from the main body by coarse glass frits. The electrolyses experiments were accomplished 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 carried out at 25 ± 1 °C.

Reagents

Both RB-4 and RO-16 dyes were purchased from Sigma-Aldrich and used as received. All the other chemicals were analytical reagent grade and were utilized without further purification. In all the experiments, the ionic strength was kept constant ($\mu = 1.5$) by adjusting the Na_2SO_4 and NaCl concentrations. Solutions were prepared with high-purity water from a Millipore Milli-Q system.

Analyses

The efficiency of the electrolytic process was evaluated by monitoring the dye decolorization at the maximum absorption wavelengths of 596 nm for RB-4, and 493 and 388 nm for RO-16 with a Varian model Cary 50 Conc spectrophotometer. Total combustion of the samples was followed by chemical oxygen demand (COD, for electrolysis performed in chloride medium) and total organic carbon (TOC, for electrolysis performed in Na_2SO_4 medium). The chemical oxygen demand (COD) was analyzed by the closed reflux colorimetric method using a reactor and a DR2800 spectrophotometer (Hach, USA).[33]

Total organic carbon (TOC) in solutions was determined with a Shimadzu TOC-V_{CPN} Total Organic Analyzer. AOX analyses were performed using a multi X 2000 model instrument (Analytika Jena, Germany). Before the analyses, residual chlorine and hypochlorite were removed by addition of a proper amount of sodium sulfite. Briefly, the measurement involved the adsorption of organochlorine on activated carbon, mineralization of organically-bound halogen by combustion at 950 °C, and determination of chloride by micro-coulometric titration. The detection limit was 0.01 mg L^{-1}. All the results are based on the measurement of triplicate samples.

The determination of the instantaneous current efficiency (ICE) during electrochemical oxidation was carried out by considering that two parallel reactions take place during electrochemical incineration (organic compound oxidation and OER). Therefore, the ICE is defined as the current fraction used for organic compound degradation. The ICE was determined by considering the COD values of the wastewater before and after the electrolysis, using the relation:

$$ICE = \frac{FV}{8I} \frac{[(COD)_t - (COD)_{t+\Delta t}]}{\Delta t} \qquad (1)$$

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 $(COD)_t$ and $(COD)_{t + \Delta t}$ are the chemical oxygen demand (g O_2 m^{-3}) at time t and t + Δt (s), respectively.

Results and Discussion

Voltammetric characterization and electrolyses as a function of the anode composition

In an attempt to determine the oxidation potential window of the reactive dyes, cyclic voltammograms were performed for all the electrode compositions in both the absence and presence of the organic compound dye. The voltammetric behavior observed for different electrode compositions in Na_2SO_4 is typical of thermally prepared RuO_2 oxide coatings. Moreover, all the voltammograms displayed the onset of OER at potentials higher than 1.0 V *vs.* SCE, while a slight shift in the onset of OER was observed for the different anode compositions.[15,16] Figure 2 shows the representative cyclic voltammograms obtained in either the absence or presence of the organic compounds. None of the tested dyes were electroactive in the investigated potential window, since the onset of their oxidation was hindered by OER. This situation illustrates the main difficulty inherent to the electrochemical degradation of organic compounds, which shows it is important to take the side reaction into account.

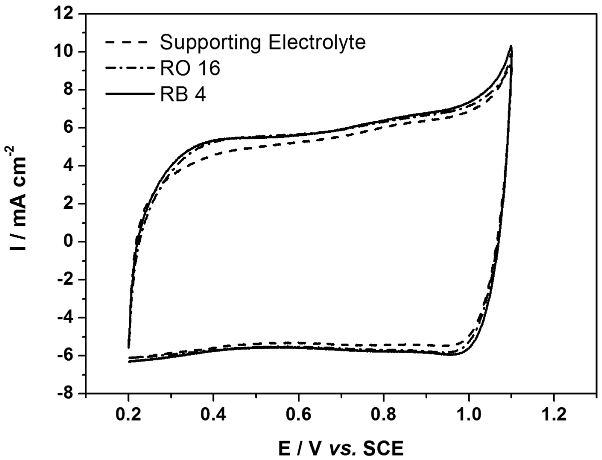

Figure 2. Representative cyclic voltammograms as a function of different reactive dyes at the $Ti/(RuO_2)_{0.70}(Ta_2O_5)_{0.30}$ electrode. ν = 50 mV s^{-1}, μ = 1.5 mol L^{-1}, supporting electrolyte = Na_2SO_4, $[dyes]_{initial}$ = 100 mg L^{-1}, pH = 3.

The first stage of this investigation consisted in selecting a suitable electrode material that would lead to the highest rate of reactive dye degradation. Oxidation of RB-4 and RO-16 was investigated for all the anode compositions as a function of electrolysis time, while the current density was kept at 50 mA cm^{-2} and the dye concentration was maintained at 100 mg L^{-1} in Na_2SO_4 medium. The decolorization results are expressed as percentage of color removal (color removal = $A_0 - A_t / A_0 \times 100$, where A_0 and A_t are the absorbances of the wastewater before and after electrolysis, respectively).

After just a few min of electrolysis, the visual color of the solutions containing the dyes changed from the respective dye color to pale yellow. Figure 3 contains the representative decolorization profile of the reactive dyes at the maximum absorption wavelengths as a function of electrolysis time. For both dyes investigated here, 50% color removal was observed after 60 min of reaction; after 90 min of treatment, all the absorbance bands had disappeared and total color removal had been obtained for all the anode materials. It can also be observed that RB-4 color removal was more pronounced compared to that achieved for the azo compound (RO-16). After 40 min of electrolysis, 90% color removal had been obtained for RB-4 against only 30% color removal for RO-16. The complex chemical structure of the investigated dyes makes the exact attributions of the bands in the UV-Vis spectra difficult. However, the decreased absorbance values observed at 387, 492, and 596 nm, probably related to the naphthalene ring, and the azo and anthraquinone groups, respectively, is due to the break in the conjugated system of the dyes.[34,35] Besides the more efficient RB-4 decolorization data, Figure 3 reveals that there is a slight difference in the decrease of the RO-16 bands; *i.e.*, the results indicate that the electrochemical degradation of the azo group is easier compared to naphthalene ring oxidation.

An examination of the decolorization profile as a function of the electrode material showed that this parameter had no significant influence on the degradation; *i.e.*, color removal data during the evaluated electrolysis time was similar for all the tested anode compositions.

Besides the degradation profile based on color removal, mineralization of the dyes (followed by TOC before and after treatment) as a function of the electrode material was also performed. A slight influence of the electrode material on the mineralization rate could be observed. After 120 min of RO-16 electrolysis, 38, 28, and 20% mineralization was obtained with the $Ti/Ru_{0.30}Ti_{0.70}O_2$, $Ti/Ru_{0.30}Sn_{0.70}O_2$, and $Ti/(RuO_2)_{0.70}(Ta_2O_5)_{0.30}$ anode compositions, respectively. RB-4 mineralization results were quite similar, reaching 32, 27, and 22% mineralization for the $Ti/Ru_{0.30}Ti_{0.70}O_2$, $Ti/Ru_{0.30}Sn_{0.70}O_2$, and $Ti/(RuO_2)_{0.70}(Ta_2O_5)_{0.30}$ compositions, respectively. The ICE data under these electrolysis conditions were also very low. The values varied from 3 to the highest value of only 6%. In other words, independent

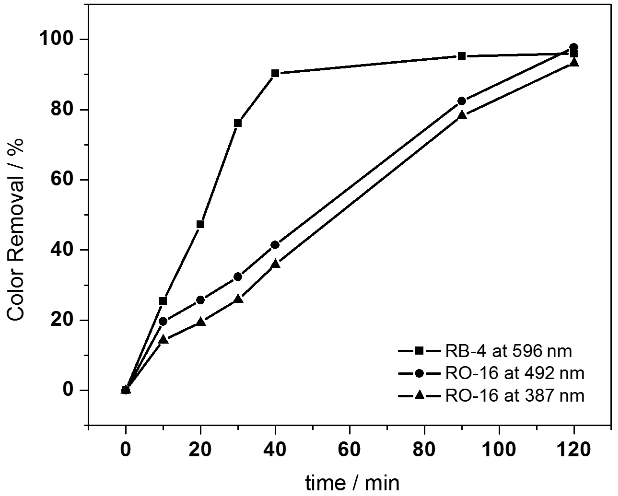

Figure 3. Representative reactive decolorization profile of the dyes at the maximum absorptions wavelengths as a function of time at the Ti/$Ru_{0.30}Sn_{0.70}O_2$ electrode. i = 50 mA cm^{-2}, $[dyes]_{initial}$ = 100 mg L^{-1}, t = 120 min, Na_2SO_4 $\mu = 1.5$, pH = 3.

of the employed electrode material, more than 90% of the electron flow was being lost to OER.

Assays as a function of the applied current density were also performed; however, even under very drastic electrolysis conditions (> 100 mA cm^{-2}) the achieved mineralization values were not significantly enhanced and the results were meaningless. This behavior indicates that OER seems to be the limiting step and is responsible for lowering the process efficiency in detriment of the organic compound oxidation. These results also indicate that, for a better degradation rate to be achieved, the electrochemical processes should be carried out under milder electrolysis conditions, which also promotes much lower energy consumption during the treatment.

Although the electrochemical process in Na_2SO_4 medium was quite efficient for color removal, the dyes total combustion results showed that this process is not effective for organic compound mineralization. The low mineralization rates obtained for the evaluated electrodes can be understood by the general mechanism of organic compound oxidation.[36] Dyes oxidation is in continuous competition with OER on the anode side, which diminishes the rate of organic compound oxidation. As discussed elsewhere, the oxidation power of the anode is directly related to the overpotential for oxygen evolution. In DSA®-like electrodes, hydroxyl radicals bind firmly to the surface, occasionally leading to the indirect oxidation of organics *via* formation/decomposition of a higher valence state oxide.[37] The results as a function of the anode composition showed that the Ti/$Ru_{0.30}Ti_{0.70}O_2$ electrode led to a higher degradation rate, probably due to its higher overpotential for OER. Similar results for both mineralization values and current efficiency in this electrolysis medium at Ti/$Ru_{0.30}Ti_{0.70}O_2$ were found in the case of

Electrolysis in NaCl medium

A possibility of increasing the degradation performance using DSA® electrodes are to investigate the use of NaCl as supporting electrolyte. The advantage of accomplishing the electrochemical processes in this medium is the possible formation of different powerful oxidizing species during the treatment, such as chlorine radical, hypochlorous acid ($HClO^-$), and hypochlorite ion (ClO^-). The chlorine evolution reaction (ClER) and subsequent formation of oxidizing species in solution proceed as follows.[20]

$$2Cl^- \rightleftharpoons Cl_{2(el)} + 2e^- \qquad (1)$$
$$Cl_{2(el)} \rightleftharpoons Cl_{2(sol)} \qquad (2)$$
$$Cl_{2(sol)} + H_2O \rightarrow HClO + Cl^- + H^+ \qquad (3)$$
$$HClO \rightleftharpoons H^+ + ClO^- \qquad (4)$$

In order to investigate the influence of the initial concentration of chloride ion on the indirect oxidation of the dyes *via* chlorine generation, the electrolysis was conducted by varying the chloride concentration from 0.01 to 0.1 mol L^{-1}. The assay was carried out for 120 min at 50 mA cm^{-2} as a function of the anode composition. The results of color removal in chloride medium showed that the decolorization power increased compared to the data obtained in Na_2SO_4 medium for all the investigated anodes. For both dyes, total color removal was obtained after just 10 min of electrolysis even in the lowest chloride concentration (0.01 mol L^{-1}). There was no significant enhancement in the color removal rate with increasing chloride concentration, indicating that the maximum color removal rate is related to the oxidation of the chromophore group.

Mineralization of the dyes in chloride medium was also evaluated. Figure 4 displays the representative degradation profile in both supporting electrolytes as a function of the anode composition. Results of dyes total combustion in chloride medium revealed significant performance gain compared to the data obtained in Na_2SO_4 medium. COD removal values increased from about 30 to 80%. The mineralization results also showed that Ti/$Ru_{0.30}Ti_{0.70}O_2$ composition leads to the highest dyes degradation in chloride medium. As in the case of the results found in the absence of chloride, this data can be understood on the basis of OER overpotential. In the same way that Ti/$Ru_{0.30}Ti_{0.70}O_2$ displayed the highest overpotential for the undesirable reaction (OER) in Na_2SO_4 medium, this behavior in chloride medium should also favor the production of powerful oxidizing chloride species, thereby enhancing the degradation power. Likewise, the lower degradation performance obtained for the $Ti/Ru_{0.30}Sn_{0.70}O_2$ and $Ti/(RuO_2)_{0.70}(Ta_2O_5)_{0.30}$ compositions in both conditions can be explained by considering their lower OER overpotential compared to the more efficient material. Despite the good mineralization rates, ICE data obtained in chloride medium were still very low; for all the investigated compositions, the efficiency reached no more than 10% after treatment, indicating that OER plays an important role in the case of both supporting electrolytes evaluated in this work.

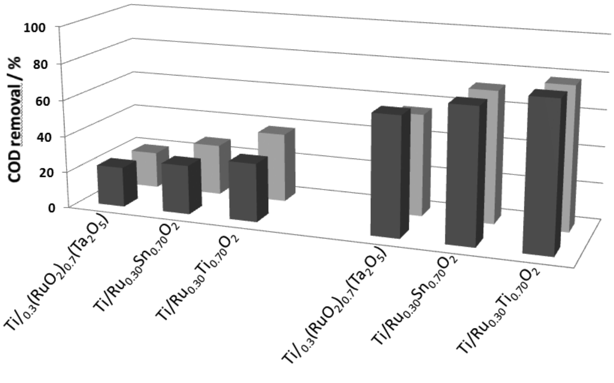

Figure 4. Representative degradation profile of the dyes in Na_2SO_4 medium (left side) and 0.01 Cl^- (right side) as a function of the anode composition. ■ = RB-4, ▨ = RO-16. i = 50 mA cm^{-2}, $[dyes]_{initial}$ = 100 mg L^{-1}, t = 120 min, μ = 1.5, pH = 3.

Analogously to the behavior found for decolorization data, a little gain (less than 5%) was observed for COD removal in higher chloride concentration. For the most active anode material, $Ti/Ru_{0.30}Ti_{0.70}O_2$, a mineralization performance varying from 78 and 80% at 0.01 mol L^{-1} to 82 and 86% at 0.1 mol L^{-1} for RB-4 and RO-16 were respectively achieved.

It is evident that it is not easy to mimic the conditions likely to be encountered in a real dye wastewater (normally a very complex mixture), and this was not the aim of this work. Most of the time, the oxidation of a dye with a specific structure does not usually enable one to extend the results for other dyes; however, from the similar degradation profile obtained for both anthraquinone and azo dyes, one can infer that electrochemical oxidation can be effective for a wide range of organic compounds. As stated, the gap in degradation values of both reactive dyes is not so prominent. Even when one compares the results of this study with the electrochemical oxidation of different organic compounds (disregarding the peculiarities of each work), such as herbicides, the mineralization behavior is not so different.[3,18] The results from dyes oxidation has shown that, besides being quite efficient as a remediation method in chloride medium, this investigation suggests that the electrochemical process requires low chloride concentration for the achievement of higher degradation rates. This is a very interesting result concerning environmental issues, since undesirable species can also be formed during the treatment when chloride is introduced in the electrolyte medium (see discussion below).

AOX formation study

Despite being a good oxidizing medium, the use of NaCl as supporting electrolyte may lead to the formation of organochlorine compounds (RCl) during the electrolysis, which is a major disadvantage. To evaluate the formation of this undesirable species, AOX analysis during the treatment was performed in all the electrolyses. Figure 5 depicts the AOX formation profile as a function of the anode composition after treatment. The $Ti/Ru_{0.30}Ti_{0.70}O_2$ and $Ti/Ru_{0.30}Sn_{0.70}O_2$ composition was the most active electrode for chloride evolution, favoring increased organic compound oxidation. The results also indicated that this composition favors the formation of organochloride species. Likewise, the less active anode for chloride evolution ($Ti/(RuO_2)_{0.70}(Ta_2O_5)_{0.30}$) also led to lower AOX quantities.

This kind of situation turns out to be quite common in electrochemical degradation studies, since several experimental factors affect the process as a whole. In a future choice of material to be applied in wastewater treatment, the catalytic efficiency, the lifetime of the material, and the amount of toxic compounds formed during the process must be carefully evaluated, so that a more suitable composition can be chosen. In this sense, it must be emphasized that although the composition $Ti/(RuO_2)_{0.70}(Ta_2O_5)_{0.30}$ displayed the lowest degradation values for the organic material (in the considered period), the low amount of AOX formed after treatment, added to the fact that this material has a significantly longer lifetime compared to the other compositions, makes this composition extremely advantageous for a future large-scale application.[16] So it can also be inferred that anode compositions based on Ru and Ta oxides seem to be potentially environmentally friendly.

The formation of persistent organochloride compounds during the electrolysis has already been investigated elsewhere. Some papers have indicated that once the R–Cl compound is formed, it is quickly consumed before the end of the electrolysis;[23] however, a different degradation profile has been described recently, where continuous increase[18] and almost constant AOX formation during the electrolysis was observed.[38] Our results as a function of the electrolysis time revealed that there is a slight formation of the AOX

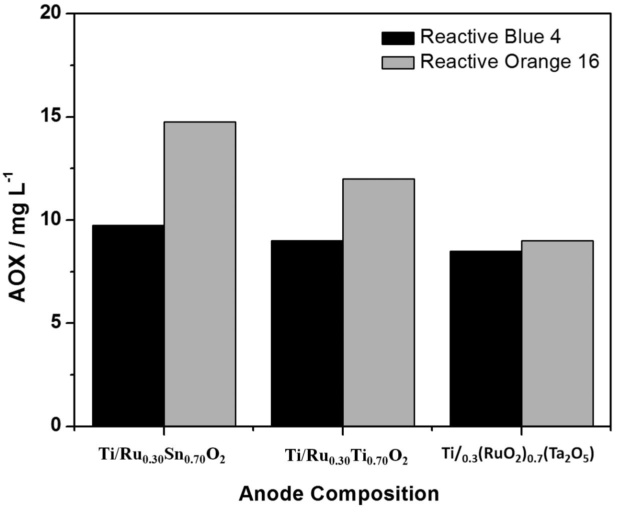

Figure 5. AOX formation in function of the anode composition. [Cl$^-$] = 0.01 mol L^{-1}, [dyes]$_{initial}$ = 100 mg L^{-1}, i = 50 mA cm^{-2}, t = 120 min, μ = 1.5, pH = 3.

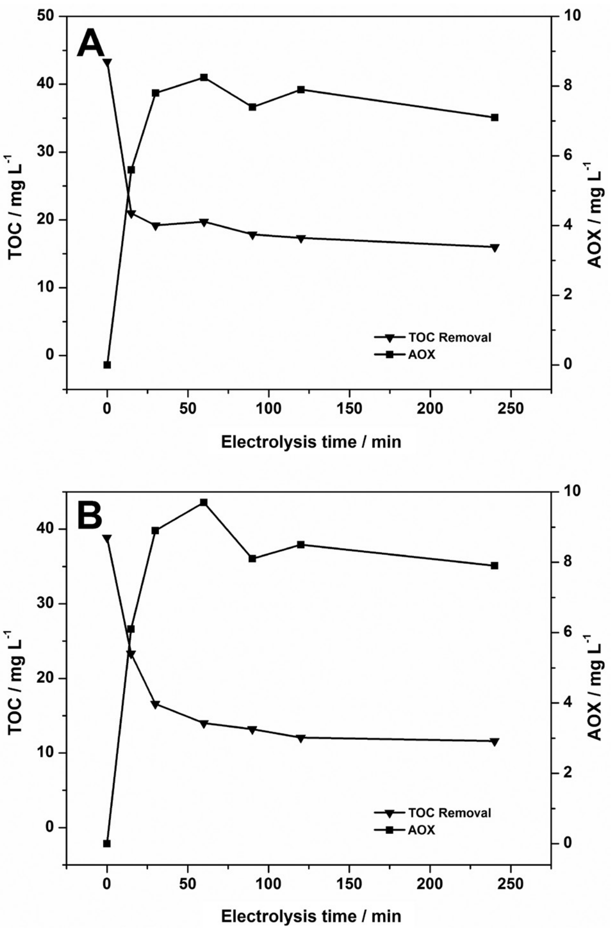

Figure 6. AOX and TOC profile obtained for the oxidation of RB-4 (A) and RO-16 (B) at Ti/Ru$_{0.30}$Ti$_{0.70}$O$_2$. [Cl$^-$] = 0.01 mol L^{-1}, [dyes]$_{initial}$ = 100 mg L^{-1}, i = 50 mA cm^{-2}, μ = 1.5, pH = 3.

species within the first minutes of the electrolytic process. However, the AOX yields keeps is kept constant, around 8 mg L^{-1}, as the TOC is continuously diminished with the progress of electrolysis. One may consider that AOX toxicity is an object of concern. This parameter should be relevant once just a few milligrams of this toxic compound make a lot of difference to the final waste when one thinks of large-scale applications. However, Figure 6 depicts an important characteristic of the dyes degradation profile, which is fast degradation within a short time period and formation of recalcitrant compounds in low yields, which need to be further investigated.

Conclusions

The electrolyses performed in both the presence and absence of NaCl promotes efficient color removal from wastewater containing RB-4 or R0-16. However, significant increase in dyes total combustion is achieved for all the studied anodes in chloride medium. The influence of the oxide composition on the elimination of the dyes seems to be significant in both media, being Ti/Ru$_{0.30}$Ti$_{0.70}$O$_2$ the most active material for organic compound oxidation. The OER has shown to be the limiting reaction in both supporting electrolytes, and the competition between the oxidation of the organic compound and the side reaction is still an obstacle. The results in both media show that for a higher ICE to be achieved, some adaptations in the process still need to be made. Cell volume and geometry, dye concentration, electrode geometry, and flow are some of the factors that must be considered for large-scale applications.

Finally, all the metallic oxide electrodes containing RuO$_2$ evaluated in this work display good performance for anodic oxidation in chloride medium under mild conditions. However, one can infer that Ti/(RuO$_2$)$_{0.70}$(Ta$_2$O$_5$)$_{0.30}$ seems to be the most environmentally friendly composition.

Acknowledgments

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