

Electrochemical Degradation of Diuron in Chloride Medium using DSA® Based Anodes

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Este trabalho apresenta um estudo da degradação do herbicida diuron utilizando os anodos $\text{Ti/Ru}_x\text{Ti}_{(1-x)}\text{O}_2$ e $\text{Ti/Ir}_x\text{Ti}_{(1-x)}\text{O}_2$ ($x = 0,3, 0,5$ e $0,7$). A investigação da degradação foi conduzida na presença e na ausência de cloreto. O estudo da remoção do herbicida em função da densidade de corrente na ausência de cloreto rendeu remoções de 41 e 49% de demanda química de oxigênio (COD) e remoções de 10 e 14% de carbono orgânico total (TOC) a 100 mA cm^{-2} , respectivamente. Mantendo-se o tempo de eletrólise constante (4 h), a composição do anodo $\text{Ti/Ru}_{0,7}\text{Ti}_{0,3}\text{O}_2$ foi determinada como a mais ativa para remoção do diuron e seu subproduto. O valor de remoção máximo atingido após 4 h foi 58%. A adição de cloreto dobrou a taxa de remoção, e obteve-se 100% de remoção de COD para $\text{Ti/Ru}_{0,3}\text{Ti}_{0,7}\text{O}_2$. A análise por cromatografia líquida de alto rendimento (HPLC) confirmou a remoção total do herbicida em meio de cloreto e indicou a formação de subprodutos de degradação. Os subprodutos gerados são apresentados em função da densidade de corrente aplicada e da composição do anodo. Os anodos baseados em Ir promoveram a oxidação de maneira mais branda e forneceram mais subprodutos em meio aquoso.

This work presents a study of the electrochemical degradation of the herbicide diuron using $\text{Ti/Ru}_x\text{Ti}_{(1-x)}\text{O}_2$ and $\text{Ti/Ir}_x\text{Ti}_{(1-x)}\text{O}_2$ ($x = 0.3, 0.5$ and 0.7) anodes. The investigation of the degradation was conducted in the presence and in the absence of chloride. The study of the herbicide removal as a function of the current density in the absence of chloride yielded 41 and 49% COD (chemical oxygen demand) removals and 10 and 14% TOC (total organic carbon) removal at 100 mA cm^{-2} , respectively. By keeping the electrolysis time constant (4 h), $\text{Ti/Ru}_{0,7}\text{Ti}_{0,3}\text{O}_2$ anode composition was determined as the most active for removal of diuron and its byproduct. The maximum removal value achieved after 4 h was 58%. Addition of chloride doubled the removal ratio, and 100% COD removal was obtained for $\text{Ti/Ru}_{0,3}\text{Ti}_{0,7}\text{O}_2$. High-performance liquid chromatography (HPLC) analysis confirmed the total removal of the herbicide in chloride medium and indicated the formation of byproducts. The generated byproducts presented as function of the applied current density and the anode composition. Ir-based anodes promoted milder oxidation and furnished more byproducts in aqueous medium.

Keywords: diuron herbicide, electrochemical oxidation, DSA® electrodes, electrolysis, wastewater

Introduction

The search for new approaches for better degradation of toxic and persistent organic compounds remains a challenge to be faced by many research teams worldwide.¹⁻³ Pesticides (herbicides), dyes and medicines, among others, are generally a matter of concern for many environmental regulatory agencies. When accumulated in the environment, either in the soil or water, these organic compounds can cause damage to our fauna and flora. Because of the high toxicity and the large amount of pesticides being

used for the control of many types of pests worldwide, much attention has been given to the determination and degradation of well-known insecticides, herbicides and fungicides.⁴⁻⁶ In this context, the degradation of herbicides employed in the control of weeds that grow together with the target plant culture, such as sugarcane and soy bean, among others, has raised the interest of some research groups, including ours.⁷⁻⁹

Diuron [3-(3,4-dichlorophenyl)-1,1-dimethyl urea] is one of the herbicides that is most commonly utilized for the control of the growth of undesirable species. Because it is chemically stable and belongs to the class of phenylurea herbicides, this chemical has been used for over 40 years,

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even though it is considered to be highly toxic and persistent.¹⁰ Diuron is widely used in agriculture and is also utilized as a large spectrum herbicide in urban and industrial areas in many parts of the world. Its action mechanism regarding weed control generally involves blockage of the electron transport in photosystem II, thereby inhibiting photosynthesis.¹¹

Nowadays, there are many techniques being developed for the treatment of wastewater. The most frequently investigated are photochemical, fenton, photo-fenton, electrochemical, photoelectrochemical and biological processes, among others.¹²⁻¹⁵ Although advancements have been made during the past years in terms of treatment efficiency and convenience, the existing methodologies also have limitations. The choice of a proper treatment technique will generally depend on economic factors, as well as on the controllability, reliability and efficacy of the method, not to mention the type of chemical that must be treated.¹⁶ Biological techniques are more often employed for the treatment of industrial waste, because they are less expensive and easy to operate. However, their kinetics is slow and their action is limited to compounds of low toxicity and to low concentrations of contaminants. Advanced oxidation processes (AOPs) have also been widely tested for the decontamination of water containing organic pollutants. Several studies using these processes have been published, and different possibilities and alternatives for better degradation of hazardous compounds have been presented.^{17,18} Although each process provides a different medium in terms of reactivity, they are all characterized by the production of hydroxyl radicals ($\bullet\text{OH}$), which are able to oxidize and mineralize organic molecules, thus resulting in less oxidizable compounds, CO_2 and inorganic ions.¹⁹

In this context, our research team has concentrated efforts on the development of electrochemical processes using DSA® anodes for the oxidation of several classes of organic hazardous compounds, such as herbicides, phenolic compounds and dyes. Indeed, our group has shown that good degradation yields can be obtained from electrochemical treatment.^{7,8,20,21} Electrochemical processes appear as an attractive alternative for the treatment of wastewater containing organic pollutants due to their versatility, facile operation, effectiveness, low cost and ability to generate different reactive species on the electrode surface (O_3 , $\bullet\text{OH}$, H_2O_2 and O_2). The choice of the material to be applied in the electrochemical process is always a critical step once it involves consideration of the cost, and convenience of the preparation method, besides examination of the potential of the technique for the scaling-up to large reactors, with a view to applying in industrial treatment plants. The tridimensional DSA®-type anodes

are traditionally used in many industrial electrochemical processes, such as the chlorine/soda process. DSA® electrodes are usually prepared by casting a mixture of metal oxides onto a titanium support. Several methods for the preparation of oxide electrodes have been reported, but the thermal decomposition of chlorides (traditional method) and the thermal decomposition of polymeric precursor (Pechini method) are generally employed.²²⁻²⁴ The traditional method is accomplished via deposition of inorganic salt precursor layers, usually in the form of chlorides, dissolved in hydrochloric acid and water 1:1 solution, followed by heat treatment ranging from 400 to 550 °C in order to obtain the desired metal oxide loading. The main difference between the traditional and the Pechini method is that the latter involves the formation of a polymer before the calcination process, so that the metal atoms are trapped within the resulting polymeric matrix, thereby hindering evaporation and consequent loss of the atoms.²⁵

Among the different electrode compositions that have been investigated to date, metallic oxides containing RuO_2 and IrO_2 have been widely utilized in environmental electrochemistry because of their mechanical strength, relatively low cost and successful scaling-up for industrial electrochemistry. In addition to these features, the association of ruthenium oxide with titanium oxides promotes excellent mechanical stability to the material,^{26,27} and their high catalytic activity often makes them an interesting choice for application in water electrolysis, chlorine production, organic synthesis and oxygen reduction.²⁸⁻³⁰

The literature brings some degradation studies that use diuron herbicide as a model molecule. An interesting approach has been demonstrated by Oturan *et al.*,³¹ which showed the degradation route of this herbicide under fenton, electron-fenton and photo-fenton processes. These authors obtained a quasi-complete mineralization under these treatments. There are also reports on diuron degradation by biological processes,³² and by association between biological and photo-Fenton process.³³ Also, some good results have been obtained with the photocatalytic process.³⁴ Furthermore, the combination of the photo-Fenton treatment with the biological process has furnished satisfactory data concerning the mineralization of this herbicide in industrial wastewater.³³ Nevertheless, despite the good oxidation rates that have been reported, the mineralization rate of this compound must be improved.

In this sense, the present work aims at evaluating the electrooxidation of the herbicide diuron using $\text{Ti}/\text{Ir}_x\text{Ti}_{(1-x)}\text{O}_2$ and $\text{Ti}/\text{Ru}_x\text{Ti}_{(1-x)}\text{O}_2$ ($x = 0.3, 0.5$ and 0.7), with a view to the total degradation of this compound or formation of more oxidable products, in the absence and in the presence of chloride.

Experimental

Chemicals

Except for the commercial suspension solution of diuron, which was kindly provided by Nortox SA, all the reagents were of analytical grade and were used without further purification. The support electrolyte was Na_2SO_4 (Synth), and the ionic strength was kept constant at 1.5 mol L^{-1} in all the experiments in both the presence and absence of chloride (1000 mg L^{-1}). H_2SO_4 and NaOH were employed for adjustment of the pH of the solutions to 3.0. Solutions were prepared with high-purity water from a Milli-Q system (Millipore Industry $18 \text{ m}\Omega \text{ cm}^{-1}$), and pH measurements were carried out with a pH electrode coupled to a Qualxtron pH meter model 8010.

Preparation of the electrodes and electrochemical tests

The choice of electrode nominal composition was based on the most suitable composition as previously described by one of us.³⁵ Therefore, it was used a longer-lasting material (Ir-based anodes) and a good active catalyst for organic compound oxidation (Ru-based anodes). Electrodes of nominal composition $\text{Ti}/\text{Ir}_x\text{Ti}_{(1-x)}\text{O}_2$ and $\text{Ti}/\text{Ru}_x\text{Ti}_{(1-x)}\text{O}_2$ ($x = 0.3, 0.5, \text{ and } 0.7$) were prepared from appropriate mol ratios by thermal decomposition of polymeric precursors at $450 \text{ }^\circ\text{C}$. Energy dispersive X-ray (EDX) analysis using a Leica microscope Zeiss LEO 440 model TEM coupled to an Oxford 7060 model analyzer was used to determine the composition of the electrodes.

The polymeric solution was prepared by mixing citric acid (CA) (Merck) in ethylene glycol (EG) (Merck) at $65 \text{ }^\circ\text{C}$. After total dissolution, the temperature was raised to $90 \text{ }^\circ\text{C}$, and titanium isopropoxide (TI) (Hulls) as well as $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (Aldrich) or an appropriate amount of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (Aldrich) solution were dissolved in HCl (Merck) ($1:1 \text{ v v}^{-1}$). The CA/EG/metal molar ratios were 4:16:1 for titanium and 3:3:1 for ruthenium and iridium resins. Appropriate resins were prepared in order to obtain the desired nominal electrode composition.

The mixture of polymeric precursors was applied onto both sides of a pre-treated titanium support of 1 cm^2 (total exposed area of 2 cm^2) by brushing, followed by calcination. Details concerning the preparation and the physical and electrochemical characterization are discussed elsewhere.^{25,35}

The electrochemical measurements were conducted in an open system, using a three-compartment electrolytic cell consisting of a main body (60 mL solution), and two smaller compartments containing the counter electrodes,

which were isolated from the main body by coarse glass frits (see supplementary material). Two spiraled platinum wires (15 cm), placed parallel to each other, were used as counter electrodes. All the potentials are referred to the saturated calomel electrode (SCE). The electrolyses were conducted in the galvanostatic mode applying 25, 50 and 100 mA cm^{-2} , representing 360, 720 and 1440 C, respectively, under magnetic stirring, using the Potentiostat/Galvanostat Solartron 1480 multistate model at $25 \pm 1 \text{ }^\circ\text{C}$.

Analyses

After the electrolysis, the analytical control for the total degradation of the herbicide and the possible byproducts was followed by: total organic carbon (TOC) (Shimadzu TOC-VCPN), chemical oxygen demand (COD) (Reactor Hach; Hach DR 2800 spectrophotometer) and high performance liquid chromatography (HPLC) data (apparatus from Shimadzu containing a UV-Vis detector, the products were separated in a C_{18} Shim-pack CLC-ODS column). Spectrophotometric detection of diuron was performed at 254 nm , using a Varian model Cary 50 Conc spectrophotometer. All the results are based on the measurement of triplicate samples.

Results and Discussion

Optimization of the conditions employed during electrolysis

EDX analyses of the prepared electrodes showed the following experimental compositions: $\text{Ru}_{0.18}\text{Ti}_{0.82}\text{O}_2$, $\text{Ru}_{0.29}\text{Ti}_{0.71}\text{O}_2$ and $\text{Ru}_{0.49}\text{Ti}_{0.51}\text{O}_2$ for ruthenium electrodes and $\text{Ir}_{0.21}\text{Ti}_{0.79}\text{O}_2$, $\text{Ir}_{0.40}\text{Ti}_{0.60}\text{O}_2$ and $\text{Ir}_{0.60}\text{Ti}_{0.40}\text{O}_2$ for iridium ones.

The first stage of this investigation consisted in finding the optimal conditions for the electrooxidation of the herbicide diuron. To this end, several experiments were carried out by applying different current densities and using freshly-prepared electrodes. The concentration employed for the commercial diuron formulation was 50 mg L^{-1} (which was the maximum solubility achieved in the investigated support electrolyte), corresponding to approximately 22 mg L^{-1} of TOC and $80 \text{ mg O}_2 \text{ L}^{-1}$ COD. The TOC and COD values were experimentally obtained at least in triplicate. The correlation between COD and TOC may vary depending on the quality of the wastewater and the presence of recalcitrant compounds, so it is noteworthy to report both data.

Figure 1 depicts the representative percentage of organic matter removal (COD and TOC) after 4 h of electrolysis as a function of the applied current using the electrode composition $\text{Ti}/\text{Ru}_{0.29}\text{Ti}_{0.71}\text{O}_2$. According to the obtained

results, there was only a slight increase in the organic matter removal upon elevation of the applied current density. In fact, the COD removal percentage ranged from 41 ± 3 to $49 \pm 4\%$, whereas the TOC removal varied from 10 ± 0.5 to $14 \pm 0.7\%$, ongoing from the applied charges (360-1440 C). On the basis of this degradation behavior, two situations can clearly be delineated. Firstly, the TOC/COD removal indicates a small ability of the electrochemical technique in terms of total organic matter removal. Secondly, the mass transfer seems to limit the achievement of higher percentage removal of diuron under the studied experimental conditions.

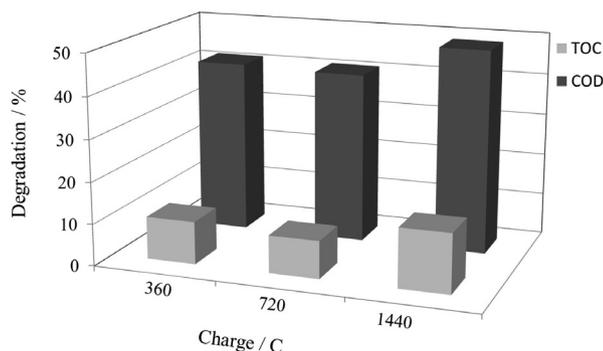


Figure 1. Percentages of COD and TOC degradations as a function of the applied charge for $\text{Ti/Ru}_{0.29}\text{Ti}_{0.71}\text{O}_2$ in 50 mg L^{-1} diuron solution containing Na_2SO_4 , $\mu = 1.5 \text{ mol L}^{-1}$, $\text{pH} = 3$.

Keeping the current density at the level in which the highest degradation was obtained which represents 1440 C, electrolyses were performed as a function of the electrode composition. Figure 2 illustrates the typical behavior achieved for the degradation of diuron at the various electrodes investigated herein, at lower metal composition, both electrodes have similar degradation rate, nevertheless at the higher catalyst percentages, Ru-based electrodes furnished higher degradation rates. In fact, the best Ru electrode composition ($\text{Ti/Ru}_{0.49}\text{Ti}_{0.51}\text{O}_2$) furnished degradation rates of 25 ± 1.25 and $58 \pm 5\%$ for TOC and COD, respectively, whereas the most efficient Ir-electrode composition ($\text{Ti/Ir}_{0.21}\text{Ti}_{0.79}\text{O}_2$) gave just 18 ± 0.9 and $38 \pm 1.9\%$ of TOC and COD removal, respectively. Among the different compositions tested in this work, the results obtained with the Ru electrodes confirmed that the composition with the lower amount of Ti, i.e., the higher catalysts content, provided a slight increase in the oxidation performance. These results are similar to previously reported data.^{7,8,20}

The low overpotential for the oxygen evolution reaction (OER), an undesirable side reaction that is responsible for decreased electrochemical degradation efficiency since it consumes large part of the current applied during the

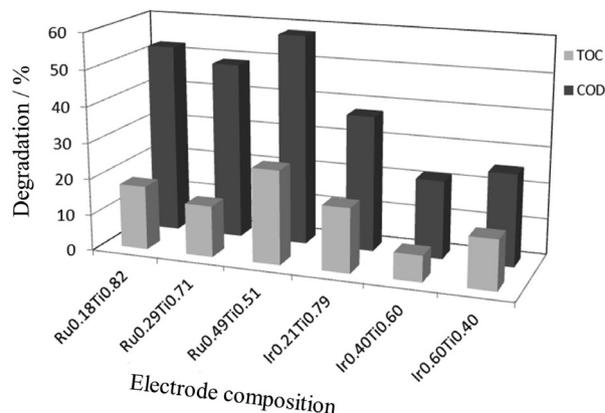


Figure 2. Percentages of COD and TOC removals at 100 mA cm^{-2} using different electrode compositions in 50 mg L^{-1} diuron solution containing Na_2SO_4 , $\mu = 1.5 \text{ mol L}^{-1}$, $\text{pH} = 3$.

treatment accounts for the low TOC/COD removal attained with both anode compositions. Ruthenium based anodes are referred to have higher activity towards OER than iridium based anodes.^{36,37} The better performance observed for this material can be due to many RuO_2 oxidation states which can improve the total organic compound oxidation.

The degradation rates were investigated applying 25 mA cm^{-2} at a fixed catalyst composition of ruthenium and iridium oxides ($\text{Ti/M}_{0.2}\text{Ti}_{0.8}\text{O}_2$, $\text{M} = \text{Ir}$ and Ru). Figure 3 shows the behavior of the electrolysis. The kinetic data obtained indicated that the rate constant is independent of the catalyst investigated and the measurement technique. The following values were obtained for ruthenium and iridium catalyst, respectively: TOC data ($k = 2.89 \times 10^{-5}$ and $1.0 \times 10^{-5} \text{ s}^{-1}$) COD data (4.6×10^{-5} and $4.8 \times 10^{-5} \text{ s}^{-1}$).

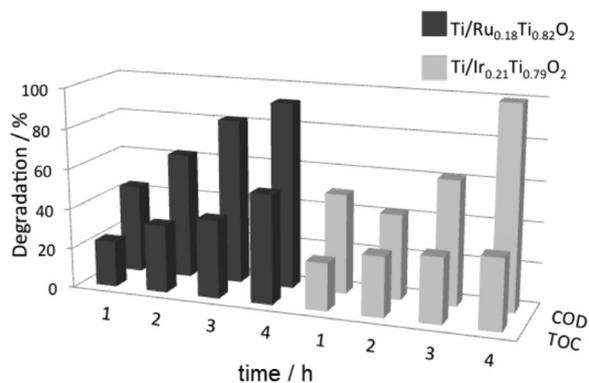


Figure 3. COD and TOC removals for 50 mg L^{-1} diuron solution in function of time at 25 mA cm^{-2} using $\text{Ti/M}_{0.2}\text{Ti}_{0.8}\text{O}_2$ ($\text{M} = \text{Ir}$ and Ru). Na_2SO_4 , $\mu = 1.5 \text{ mol L}^{-1}$, $\text{pH} = 3$.

Because almost 50% of the organic carbon still remained in the solution without being mineralized, it is very important to find out which other species might also

be formed during the electrolysis. In the particular case of diuron, both UV-Vis and HPLC assays conducted after the electrolysis indicated the formation of undesirable byproducts for all the investigated electrode compositions. Figure 4 shows a representative UV-Vis spectra of 50 ppm diuron solutions before and after electrolysis ($i = 100 \text{ mA cm}^{-2}$, Ti/Ru_{0.29}Ti_{0.71}O₂). The spectra recorded after the electrolysis displayed a slightly decreased peak in the UV region of the spectrum (254 nm), which was accompanied by the enhancement of the shoulder at 288 nm. These features suggest the formation of byproducts. The chromatographic analyses obtained for the 50 ppm diuron solution before electrolysis at 100 mA cm^{-2} display only the single peak relative to the herbicide diuron, after 4 h of electrolysis. There is evidence that partial oxidation of the herbicide occurred since the well-defined peak of diuron diminished to 42% as compared to the peak registered for the freshly prepared herbicide solution. Furthermore, four new peaks were detected, independent of the investigated electrode. These new peaks can be directly related to some of the common byproducts of diuron oxidation.³⁸ The chromatographic data thus confirmed the previous results presented in Figures 2 and 3, and also corroborated with spectroscopic data, indicating that approximately 25% of the herbicides was converted to intermediate products after 4 h of electrolysis, and that 15% CO₂ was formed.

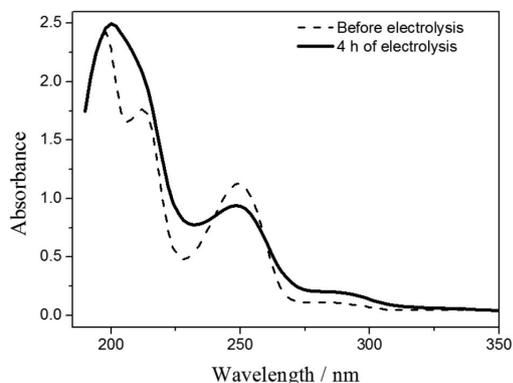


Figure 4. UV-Vis spectra before and after 4 h of electrolysis at 100 mA cm^{-2} , using the electrode composition Ti/Ru_{0.29}Ti_{0.71}O₂ in 50 mg L^{-1} diuron solution containing Na_2SO_4 , $\mu = 1.5 \text{ mol L}^{-1}$, $\text{pH} = 3$.

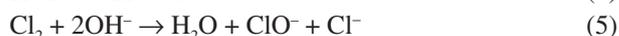
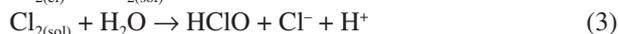
The UV-Vis and HPLC analyses evidenced that the removal of the active ingredient does not depend on the electrode material and composition because there was a 40% decrease in the amount of diuron for all the examined electrodes.

Considering the similar performance of the electrodes with respect to diuron degradation, the Ti/Ru_{0.18}Ti_{0.82}O₂ and Ti/Ir_{0.21}Ti_{0.79}O₂ compositions were selected for assessment of the effect of chlorine on the degradation rate. These

compositions were chosen for the lower amount of Ru and Ir employed during electrode preparation in order to make the electrodes economically more viable.

Electrochemical oxidation in chloride medium

Chlorine has been widely used as a decontaminant agent for aqueous effluents. For this purpose, it is directly added in the form of hypochlorite or *in situ* generated by conduction of the electrolysis under chloride medium. DSA[®]-based electrodes are highly active for chloride evolution, so they have been often employed in the chlor-alkali industry.²³ The advantage of using this type of electrode when sodium chloride is employed as the supporting electrolyte is the direct generation of many powerful oxidizing species, such as Cl₂ gas, ClO⁻ and HClO, in the bulk solution. The mechanism for the chlorine evolution reaction (CIER) in oxide electrodes ends with formation of Cl₂ gas at the anode surface producing reactive species responsible for faster organic compound degradation, as follows:²³



Sodium chloride plays an important role in the degradation of organic compounds because it can provide a media with more powerful oxidizing species during the electrolysis. These species, in turn, are able to oxidize the herbicide faster, thereby promoting increased degradation rates. Figure 5 represents the degradation behavior of diuron after 4 h of electrolysis in the presence of 1000 mg L^{-1} chloride, upon application of different charges (360, 720 and 1440 C). The analysis of Figure 5 clearly shows that the presence of chloride ions enhances the performance of the electrode for herbicide degradation. Even at low current density, chloride provides much better organic removal as compared to the electrolysis carried out in sodium sulfate. Moreover, again, it seems that the current density does not have an important part in the electrolysis efficiency, i.e., for both electrodes employed herein, the best rates of diuron degradation were obtained at low current densities. So, even at low current density, the electrodes are capable of generating sufficient amount of the oxidizing species that are responsible for better removal of organic matter. The comparison of both evaluated materials evidences that the Ru-based electrodes afford much better removal than Ir-based electrodes. In fact, $55 \pm 2.5\%$ TOC removal and almost 100% COD removal were attained after 4 h

electrolysis, with the Ti/Ru_{0.18}Ti_{0.82}O₂ material, by passing 360 C. Again, Ir-based electrodes led to lower efficiency as compared to Ru-based ones. This indicates that, besides presenting higher performance in the absence of chloride, the Ru-based electrode seems to be more active for the chloride evolution reaction, thus generating more active species during the electrolysis.

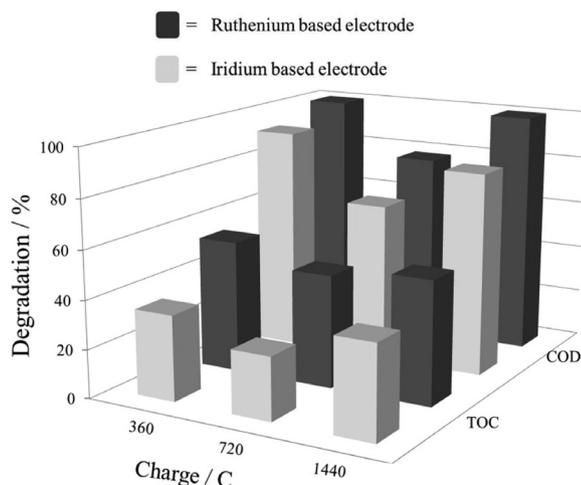


Figure 5. Percentages of COD and TOC removal as a function of the applied charge for both Ti/Ru_{0.18}Ti_{0.71}O₂ and Ti/Ir_{0.21}Ru_{0.79}O₂ in 50 mg L⁻¹ diuron solution containing Na₂SO₄ and NaCl 1000 mg L⁻¹, $\mu = 1.5$ mol L⁻¹, pH = 3.

Another interesting feature about electrode composition can be noted by analyzing Figure 6. The UV-Vis spectrum recorded after accomplishing the electrolysis in the presence of Ti/Ru_{0.18}Ti_{0.82}O₂ in chloride medium (Figure 6a) demonstrates that the peak related to the herbicide at 249 nm disappeared, indicating complete diuron removal with formation of simple molecules. As for Ti/Ir_{0.21}Ti_{0.79}O₂ anodes (Figure 6b), the spectrum displayed an intense peak

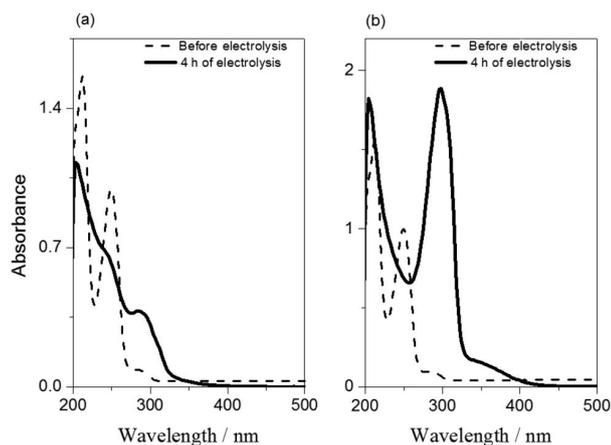


Figure 6. UV-Vis spectra before and after 4 h of electrolysis applying 360 C for both (a) Ti/Ru_{0.18}Ti_{0.82}O₂ and (b) Ti/Ir_{0.21}Ti_{0.79}O₂ in 50 mg L⁻¹ diuron solution containing Na₂SO₄ and NaCl 1000 mg L⁻¹, $\mu = 1.5$ mol L⁻¹, pH = 3.

at 300 nm, not observed before and suggests the formation of a different byproduct.

The HPLC analyses of the samples before and after the electrolysis in chloride media were conducted to investigate the possible formation of byproducts from the oxidation of diuron. After 4 h of electrolysis, the peak relative to diuron diminished, indicating that the herbicide was almost completely oxidized. Furthermore, other peaks related to the products generated from the breakdown of the diuron molecule were identified. These data are in agreement with Figure 5, which showed that $45 \pm 2.2\%$ TOC still remained in solution even under the best removal conditions.

The HPLC analysis for the chloride medium (1000 mg L⁻¹) was also performed as a function of electrode composition and charge (360, 720 and 1440 C). The examination of the data revealed that the resulting byproducts depend on electrode composition and current density.

This is an important finding since it has been observed that, while there was no significant enhancement in the total removal of organic matter, larger current densities culminate in a different byproduct profile. In other words, increased current density led to a higher amount of some of the more oxidizable species as well as to new byproducts.

Table 1 summarizes the HPLC profile obtained with both tested electrodes after 4 h of electrolysis in chloride medium. Besides the main 6 byproducts (B, D, E, F, G and H) formed under lower current density, two new byproducts (A and C) were detected at higher current densities, regardless of the electrode composition. This indicates that when higher charge is applied, new products are formed indicating the degradation of more recalcitrant byproducts can be obtained. Besides the above mentioned byproducts, a large number of new byproducts (I, J, K, L, M and N) was also detected in the case of the Ir-based electrode, also depending on the applied current. This complex behavior confirms the previous analysis showing that the oxidation at the iridium oxide electrode was milder and therefore more likely to generate a larger number of byproducts.

A very easy way to obtain more clues about the efficiency of each tested material and electrolysis condition is to determine the energy cost during the different experiments. The energy cost is defined as the energy used for the oxidation of the organic compound. The energy cost is calculated by considering the TOC values of the wastewater before and after electrolysis. The energy cost was calculated by using the equation proposed by Martínez-Huitle and Brillias:³⁹

$$\text{Energy cost (kWh g}^{-1} \text{ TOC)} = \frac{VIt}{\Delta(\text{TOC})_{\text{exp}} V_s} \quad (6)$$

Table 1. Values of peak retention times for the two investigated electrode compositions under different current densities during the oxidation of diuron in chloride medium

Peak	Retention time / min (Ru _{0.18} Ti _{0.82} O ₂)			Retention time / min (Ir _{0.21} Ti _{0.79} O ₂)		
	360 C	720 C	1440 C	360 C	720 C	1440 C
A	–	–	6.3	–	6.4	6.3
B	7.9	7.7	7.6	7.9	7.4	7.6
C	–	–	8.7	–	–	8.7
D	10.4	10.3	10.3	10.4	10.4	10.3
E	13.6	13.6	13.5	13.6	13.5	13.5
F	16.0	15.8	15.7	16.0	15.7	15.7
G	18.4	18.2	18.1	18.3	18.2	18.1
H	21.6	21.2	21.0	21.6	–	–
I	–	–	–	24.0	23.3	–
J	–	–	–	–	25.1	25.0
K	–	–	–	–	30.3	30.2
L	–	–	–	31.6	31.5	31.4
M	–	–	–	32.8	–	–
N	–	–	–	35.6	–	–

where V is the average potential of the cell (V), I is the applied current (A), t is the time during which the process is applied (h), V_s is the total volume of the electrochemical cell (L), and $\Delta(\text{TOC})_{\text{exp}}$ is the TOC decay during the treatment (g L^{-1}).

The energy cost of the ruthenium electrode (Ti/Ru_{0.18}Ti_{0.82}O₂) by passing 1440 C was 18.9 and 6.8 kWh mg⁻¹ TOC in the absence and presence of chloride, respectively, with a twofold increase in percent removal values. The same occurred in the case of the Ir-based electrode (Ti/Ir_{0.21}Ti_{0.79}O₂) with 18.5 and 9.0 kWh mg⁻¹ TOC in absence and presence of chloride. These values are very high once the cell design for large scale application was not optimized. Considering an industrial cell design, in which the small distance between anode and cathode and the high current conductivity of the solution is employed (70 mS cm⁻¹), a much better efficiency can be expected for a treatment plant.

To the best of our knowledge, there is no investigation on the electrochemical degradation of diuron employing DSA[®]-anodes. The TOC abatement shows that electrochemical treatment has potential to achieve the lower limits determined by some environmental agencies (150 mg L⁻¹).⁴⁰

Many works concerning the kinetics of chemical degradation of diuron have indicated that 33% degradation can be achieved under high temperature and extreme pH conditions.^{41,42} Other commonly investigated degradation processes are the fenton, electro-fenton and photoelectro-fenton processes. Under these conditions, total

degradation of diuron has been obtained in highly oxidizing medium (electro-fenton and photo-electro-fenton).⁴³⁻⁴⁵ An interesting feature has been reported by Polcaro *et al.*,⁴⁶ who utilized boron-doped diamond anodes under current densities of 15 and 51 mA cm⁻² and obtained complete removal of the herbicide diuron. These authors claimed no presence of intermediate products.

Conclusions

The results showed that DSA[®]-type electrodes can be potentially applied in the electrooxidation of the herbicide diuron. The studies conducted in the presence and absence of chloride demonstrated that the addition of chloride promoted a more efficient electrochemical process for the removal of COD and TOC. HPLC and UV-Vis analyses were important for assessment of the possible formation of byproducts during the oxidation of diuron. According to the chromatograms, the increase in current density led to higher amounts of some of the more oxidizable species, and some new byproducts were detected. The obtained products depended on anode composition: ruthenium-based ones gave fewer byproducts and higher degradation of the herbicide.

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Supplementary Information

Supplementary information (representative cell used) is available free of charge at <http://jbcs.sbc.org.br> as a PDF file.

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