Electrochemical oxidation of Methyl Red using Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and Ti/Pt anodes

Marcela G. Tavares [a], Lozele V.A. da Silva [a], Aline M. Sales Solano [b], Josealdo Tonholo [a],
Carlos A. Martínez-Huitle [b], Carmem L.P.S. Zanta [a],*

[a] *Instituto de Química e Biotecnologia da Universidade Federal de Alagoas, CEP 57072-970, Maceió-Al, Brazil*
[b] *Universidade Federal do Rio Grande do Norte, Centro de Ciências Exatas e da Terra, Instituto de Química, Lagoa Nova, CEP 59078-970, Natal, RN, Brazil*

HIGHLIGHTS

▶ The direct and indirect oxidations of dye using Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and Ti/Pt anodes were studied.
▶ The mechanism of direct and indirect electro-oxidation of Methyl Red was discussed.
▶ It was studied the oxidation of dye by active chlorine electrogenerated.
▶ It was available the influence of electrodic material in intermediated of Methyl Red oxidation.

ARTICLE INFO

ABSTRACT

The present study was motivated by a report by Martínez-Huitle et al. in 2005, on the electrochemical oxidation of oxalic acid at a Pt anode in the presence of halide ions in alkaline medium. Addition of halide salts increased the mineralization rate in the order: control < NaCl < NaBr < NaF. Therefore, in this work, the direct and indirect oxidations of an organic model substrate (Methyl Red, MR) using Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and Ti/Pt anodes were investigated. Galvanostatic electrolyses of dye solutions led to complete decoloration and total organic carbon (TOC) removal at different operating conditions (current density (j) and temperature). The influence of these parameters was examined, in order to compare the effect of active chlorine and addition of different NaCl concentrations to the dyes solutions during the mediated electrochemical oxidation of MR. Byproducts generated during the direct and indirect MR electrochemical oxidation were identified on the basis of GC–MS results. Chlorinated compounds were produced during mediated electrochemical oxidation, but these were completely eliminated in the final of the process; confirming that this treatment processes can be a suitable alternative for depuration effluents. The findings presented herein are described and discussed in the light of the existing literature data.

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1. Introduction

Synthetic dyes have been extensively employed in many technological fields. Due to their large-scale production and countless applications, synthetic dyes can cause considerable environmental pollution and pose serious health risks [1].

A broad range of techniques for the removal of dyes from wastewaters exist. Indeed, methods such as chemical precipitation, chemical oxidation, and chemical adsorption with subsequent biological treatment have been developed [2]. Electrochemical processes have been recently proposed as an innovative alternative for the treatment of effluents containing dyes [3], because electrochemical technologies offer advantages such as versatility, environmental compatibility, and potential cost-effectiveness [4–7]. Indeed, the feasibility of electrochemical conversion/destruction of organic substrates present in wastewaters has long attracted a lot of attention. Several scientific groups have applied this technique, particularly direct and indirect (mediated) oxidation, to aqueous solutions, which culminated in decoloration and dyes degradation [3]. As for indirect oxidation, where the main reaction stages take place in the solution bulk because of production of reactive oxidizing species on the anodic surface, a specially interesting case is that of active-chlorine mediation, which has been dealt with in a number of papers and whose practical applications have been described in several reviews [5–7]. A wide variety of electrode materials have been suggested, such as dimensionally stable anodes, noble metals (e.g., platinum), carbon-based anodes, PbO$_2$, and boron-doped diamond (BDD), and different removal organic matter efficiencies have been achieved.

The applicability of electrochemical technologies to the treatment of dyes solutions with dimensionally stable anode (DSA)-type electrodes has been extensively investigated [3]. For instance, the Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ anode has been utilized for degradation of

* Corresponding author. Tel./fax: +55 82 3214 1372.
  E-mail address: clp@qui.ufal.br (C.L.P.S. Zanta).

Reactive Red [8], Direct Red [9], Direct Black [9], Acid Violet 1 [10], and Reactive Blue 19 [11], whereas Ti-supported Pt has been employed in the electrochemical oxidation of azo dyes such as Methylene Blue [12]. The influence of pH, dye content, temperature, supporting electrolyte, cathode material, current density, and anode potential was evaluated for both anodes, in order to optimize the degradation conditions [3]. However, few papers have compared the color removal and TOC reduction of some azo and disperse dyes with active chlorine produced at DSA-type anodes and reported the by-products formed during this process.

In the present work Methyl Red (MR) was selected as a model dye because it belongs to the group of azo dyes, the largest among the synthetic colorants (60–70%), and is widely used in textile dyeing and paper printing [13]. MR destruction has already been studied by other authors [14–16]. Indeed, Panizza and Cerisola [14] have treated 225 mg dm^{-3} COD solutions of Methyl Red in 0.5 M Na_2SO_4 with different anodes using the flow cell system, and these authors demonstrated strong dependence of the comparative COD removal on the anode material, which decreased in the order Si/BDD > Ti/PbO_2 > Pt > $Ti/Ti_{0.50}Ru_{0.45}Sn_{0.05}O_2$. Zhou et al. [15,16] have analyzed the electro-Fenton process in 100 cm^3 Methyl Red solutions by means of the three-electrode Pt/graphite–PTFE cell arrangement, using electrodes with 1 cm^2 area. They concluded that the best performance was achieved by employing 0.1 M Na_2SO_4, 0.2 mM Fe^{2+}, pH 3.0, and E_{cat} = −0.55 V vs. SCE. Under these optimum conditions, a solution with 20 mg dm^{-3} of the dye became colorless in 20 min, whereas at a higher dye concentration, namely 100 mg dm^{-3}, only 74% color removal was attained within the same time period. However, additional results are still necessary, in order to ascertain the relative electrocatalytic activity of the large variety of DSA-type electrodes available for active chlorine-mediated MR electro-oxidation. This is because no attempts to degrade or eliminate MR from aqueous solutions by indirect oxidation have been published yet.

Therefore, herein we report on the catalytic activities of two anode materials, namely $Ti/Ru_{0.3}Ti_{0.7}O_2$ and Ti/Pt, on the direct and indirect electrochemical oxidation of dyes solutions containing MR, using bulk electrolysis; and centering of attention on the by-products formed and energy consumption. The utilization of the electrochemical technology is proposed as an alternative for dyes removal from effluents, in order to eliminate their strong color and mitigate their ecotoxicological consequences for the aquatic environment.

2. Experimental

2.1. Chemicals and dye solution

Ultrapure water was obtained by a Simplicity purification system. Chemicals were of the highest commercially available purity grade and were used without further treatment. H_2SO_4 and NaCl were purchased from Fluka. The dyestuff solution was prepared by dissolving the textile dye (MR = 100 mg dm^{-3}) in distilled wastewater containing 0.25 M H_2SO_4.

2.2. Electro-oxidation experiments

Bulk oxidations were performed in an undivided electrochemical cell whose reaction compartment had a capacity of 0.4 L (Fig. 1). The MR oxidation experiments were conducted under galvanostatic conditions using a power supply MINIPA MPL-3305. Ti-supported Pt anode and $Ti/Ru_{0.3}Ti_{0.7}O_2$ were supplied by Industrie De Nora S.p.A. (Milan, Italy) and (Sorocaba/SP, Brazil), respectively. Ti/Pt or $Ti/Ru_{0.3}Ti_{0.7}O_2$ was employed as anode, and two titanium plates were utilized as cathodes. The electrodes were square and
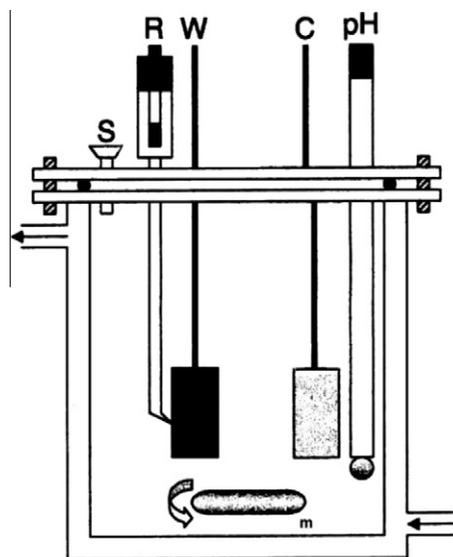

Fig. 1. Diagram of the one-compartment electrochemical cell used for studying anodic oxidation of MR: C, counter, R, reference, and W, working electrodes, respectively; pH electrode; S, sample holder; and m, magnetic stirrer.

each of them had a geometric area of 24 cm^2; and with a separation of 1.5 cm between them. Electrochemical oxidation experiments were accomplished at 25 °C, to assess the role of applied current density (20, 40, and 60 mA cm^{-2}). Furthermore, the temperature effect was investigated by carrying out experiments in the 25–60 °C range and applying a current density of 60 mA cm^{-2}. In the case of the mediated oxidation process, experiments were performed by varying the NaCl concentration in solution (0.0, 0.2, 0.4, and 0.8 g in 0.4 L of solution containing MR dye), at 400 rpm agitation rate and 60 mA cm^{-2} current density.

Concerning the Ti/Pt anode, the electrochemical analyses were conducted on an Autolab 302N (CH, Instruments). Quasi-steady polarization curves were obtained at a scan rate of 0.5 mV s^{-1} and 0.45 mV potential step, in solutions with different NaCl concentrations, using H_2SO_4 to further increase electrolyte conductivity. Potential values were referred against a double-walled, saturated calomel electrode (SCE), with an intermediate saturated $NaNO_3$ solution. A small Ti/Pt plate with a real surface area of about 4.7 mm^2 was used for quasi-steady polarization curve measurements, as determined by evaluation of hydrogen accommodation [17].

2.3. Analytical methods

Color removal was monitored by measuring the reduction in absorbance with the aid of a UV 1800 Shimadzu spectrophotometer. The relative absorbance parameter was employed, in order to express color decay: Relative absorbance = ABS_t/ABS_0, where ABS_t corresponds to the absorbance of each dye at time t and ABS_0 is the dye's initial absorbance, at the maximum visible wavelength (λ_{max}) of the dye solution. TOC measurements were accomplished on a Shimadzu model TOC analyzer. The energy consumption per volume of treated effluent was estimated and expressed in kW h m^{-3}. The cell voltage during the electrolysis was taken for calculation of the energy consumption, as follows:

$$\text{Energy consumption} = \left(\frac{V \times A \times t}{V_s}\right) \quad (1)$$

where t is the time of electrolysis (h); V (volts) and A (amperes) are the cell voltage and the electrolysis current, respectively; and V_s is the sample volume (m^{-3}).

3. Results and discussion

3.1. Color removal

The MR visible spectrum (data not shown) displays maximum absorption peaks in the visible light range, in accordance with the color of MR solutions. So color removal was measured at 517.5 nm by means of a UV/Vis spectrophotometer. Color decay was confirmed by the reduction in the absorbance band at 517.5 nm as a function of time during the galvanostatic electrolysis of MR solutions containing 100 mg dm^{-3} MR, by applying 40 mA cm^{-2} of current density and using Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and Ti/Pt anodes. For both Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and Ti/Pt anode materials, the intensity of the visible band diminished continuously until it disappeared after about 300 and 150 min of electrolysis, respectively, leading to complete solution decoloration. The absorbance changes were reasonably rapid, indicating that during the first treatment stages there are mechanisms involving dye oxidation to other more simple organics [15]. Oxidation of this complex molecule can result in formation of many intermediates by elimination of chromophore groups (chromophore group cleavage) prior to production of aliphatic carboxylic acids and carbon dioxide. This outcome is in agreement with data reported by other authors for the anodic oxidation of dyes [12,14,18,19].

3.2. Influence of applied current density

Fig. 2 presents the influence of applied current density (20, 40, and 60 mA cm^{-2}) on color decay as a function of time for the Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and Ti/Pt electrodes. Complete color removal was achieved for the MR solution (100 mg dm^{-3}) in all cases. However, the decoloration time and color removal rate depended mainly on the applied current density and on the nature of the material (Fig. 2). Whilst the decoloration time decreased when the applied current density was raised, the elimination rate increased substantially. Although complete color removal was obtained for both anodes, the color removal rate was faster for the Ti/Pt electrode. This behavior suggests that dye oxidation depends on the nature of the anode material, and that it could be carried out by both direct

electro-oxidation and mediated oxidation (hydroxyl radicals) [18,19]. It has been proposed that ·OH radicals formed by water oxidation (Eq. (2)) can be either electrochemically oxidized to dioxygen (Eq. (3)) or contribute to complete oxidation of the organic compounds, in this case, the dye (Eq. (4)):

$$H_2O \rightarrow {\cdot}OH + H^+ + e \tag{2}$$

$${\cdot}OH \rightarrow \frac{1}{2}O_2 + H^+ + e \tag{3}$$

$$dyes \xrightarrow{\cdot OH} CO_2 + H_2O \tag{4}$$

However, adsorption of dyes and byproducts on the anode electrode surface plays an important role in the electrochemical oxidation process.

Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and Ti/Pt materials are classified as active anodes [5,6]. The electrochemical and chemical reactivity of heterogeneous hydroxyl radicals (M(·OH)) produced during water oxidation (Eq. (2)) depends on the nature of the electrode material. The surface of active anodes strongly interacts with ·OH, and a so-called higher oxide or superoxide (MO) may be formed. This may occur when higher oxidation states are available for a metal oxide anode, above the standard potential for oxygen evolution ($E°$ = 1.23 V vs. SH E). The redox couple MO/M acts as a mediator in the oxidation of organics, which competes with the side reaction of oxygen evolution (Eq. (3)) via chemical decomposition of the higher oxide species. Next, electrochemical conversion is achieved, thereby transforming MR into other oxidized compounds, the byproducts. The latter are oxidized, usually to carboxylic acids, until their complete oxidation (CO$_2$ and H$_2$O) is attained. This behavior increases the electrolysis time, as already indicated by other authors [12,14,18–20].

TOC measurements confirmed the assumptions above. Slower MR electro-oxidation at the Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ electrode was observed, as shown in Fig. 3. Lower TOC decay values (ranging from 10% to 35%) were achieved at all j values (Fig. 3). This behavior is due to the fact that metal cations in the oxide lattice may reach higher oxidation states under anodic polarization, which is followed by stabilization of the adsorbed OH radicals, thereby favoring oxygen
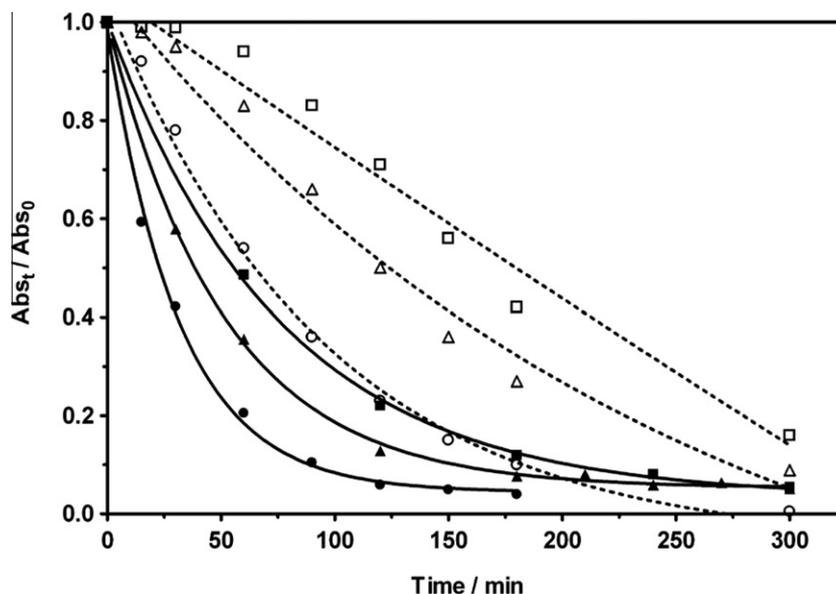

Fig. 2. Influence of applied current density on color removal, as a function of time, during direct MR oxidation at Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ (dashed lines) and Ti/Pt (continuous lines) anodes. Operating conditions: [MR]$_0$ = 100 mg dm^{-3}, Electrolyte = 0.25 M H$_2$SO$_4$, Temperature = 25 °C, and different applied current densities: (square) 20 mA cm^{-2}; (triangle) 40 mA cm^{-2}, and (circle) 60 mA cm^{-2}.
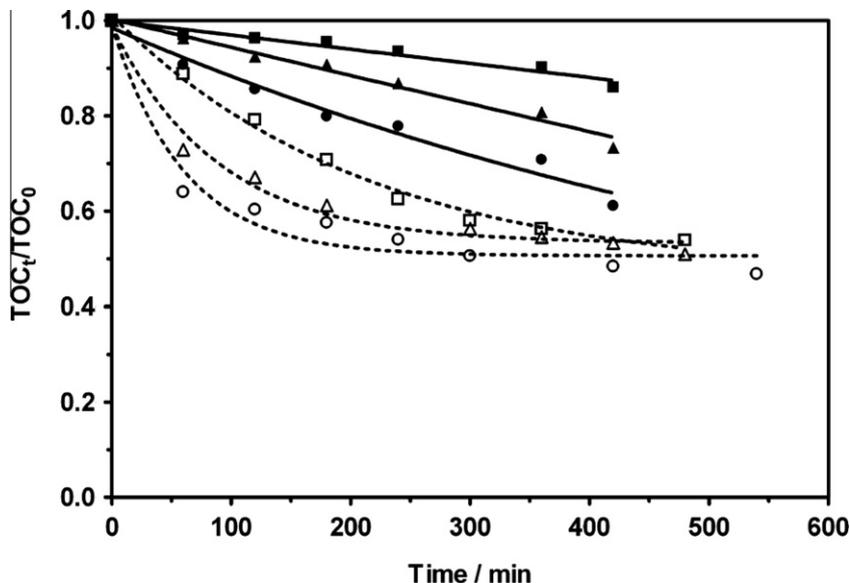
Fig. 3. Influence of current density on TOC_t/TOC_0 removal, as a function of time, during MR anodic oxidation at $Ti/Ru_{0.3}Ti_{0.7}O_2$ (continuous lines) and Ti/Pt (dashed lines) anodes. Operating conditions: $[MR]_0 = 100$ mg dm^{-3}, Electrolyte = 0.25 M H$_2$SO$_4$, Temperature = 25 °C, and different applied current densities: (square) 20 mA cm^{-2}; (triangle) 40 mA cm^{-2}, and (circle) 60 mA cm^{-2}.

evolution at the expense of the electrochemical incineration reaction. Simultaneously, poor adsorption of the dye compound and byproducts can reduce the rate of direct oxidation, which is based on electron transfer between the electrode surface and the adsorbed substrates, as proposed by several authors for (DSA)-type electrodes [4–6,12,19].

In the case of Ti/Pt anodes (Fig. 3) TOC decreased up to 50%, thus attesting for the oxidation of organic pollutants (MR and byproducts) present in the dye solution by the electrogenerated oxidizing species (Eq. (2)). Increment in the current resulted in enhanced oxidation rate, but charge consumption also augmented due to increased oxygen evolution. The Ti/Pt anode furnished higher % of TOC removal at 20, 40, and 60 mA cm^{-2} current density, as compared to the $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrode (Fig. 3). This is probably because electrocatalytically active sites allowed for more efficient MR anodic oxidation at Ti/Pt compared to the $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode. This performance has been clearly confirmed by Panizza and Cerisola [14] upon treatment of 225 mg dm^{-3} COD solutions of MR in 0.5 M Na$_2$SO$_4$ with different anodes (lead oxide, pure platinum metal, Ti–Ru–Sn ternary oxide, and diamond electrodes), using the flow cell at 500 mA, which corresponds to anode potentials in the O$_2$ evolution region). This study [14] demonstrated the strong dependence of the comparative COD removal on anode material, which decreased in the order Si/BDD > Ti/PbO$_2$ > Pt > Ti/Ti$_{0.50}$Ru$_{0.45}$Sn$_{0.05}$O$_2$.

Even though the TOC removal obtained at Ti/Pt electrodes was higher than that achieved at the $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode (Fig. 3), namely about 50%, it was not satisfactory for industrial applications. The low TOC depletion (at the final electrolysis times, see Fig. 3), the rapid decrease in the reaction rate, and the consequent low value of current efficiency could be attributed to the growth of an adherent passivating film on the anode surface, which poisoned the electrode. Additionally, accumulation of oxidation intermediates, mainly aliphatic acids, which are quite stable against further attack at these electrodes, may account for these observations [14,20,21]. All this evidence gives supplementary support to the hypothesis that the role of concomitant oxygen evolution becomes decisive when low concentrations of organic depolarizer are attained. This boosts the efficiency of the parasitic reaction (experiments are carried out at constant *j*), thus modifying the Ti/Pt

electrode surface and diminishing its activity toward MR oxidation, which in turn promotes concomitant oxygen evolution [1].

3.3. Temperature effect

Fig. 4 corresponds to the influence of temperature on color and TOC decay (inset) as a function of time upon application of 60 mA cm^{-2} current density. Total color removal was achieved with both the $Ti/Ru_{0.3}Ti_{0.7}O_2$ and Ti/Pt anode materials. It seems that temperature has a significant impact on the kinetics of MR electrochemical oxidation, because the color removal rate was considerably enhanced upon rising temperature (from 25 to 40 or 60 °C), as shown in Fig. 4. An elevation in temperature from 25 to 60 °C reduced the electrolysis time required for total color removal from 150 to 60 min in the case of the Ti/Pt anode (Fig. 4, continuous lines). However, decoloration times required at 25 °C, 40 °C, and 60 °C for the $Ti/Ru_{0.3}Ti_{0.7}O_2$ material were modestly lower in comparison to the Ti/Pt anode (Fig. 4, dashed lines).

Temperature changes had slight influence on the electro-oxidation with hydroxyl radicals. This can be explained by the increment in the chemical reactions rates, in agreement with results reported by other authors [12,14,18,19]. In fact, TOC decayed more quickly during the initial stages of the oxidation process, increasing the efficiency from 50% to 70% for the Ti/Pt electrode, depending on the employed temperature (Fig. 4 inset, continuous lines). As can be seen in Fig. 4, incomplete TOC removal was attained at the $Ti/Ru_{0.3}Ti_{0.7}O_2$ material, and these figures were lower than those obtained at Ti/Pt. This is because the side reaction of oxygen evolution is favored at higher temperatures. Nevertheless, TOC decay values achieved at 40 and 60 °C were higher (45% and 52% of TOC removal, respectively) than that obtained at 25 °C (38% of TOC removal).

3.4. Kinetic and activation energy analysis

To study the kinetics of the overall reaction involved in the disappearance of MR and intermediates by direct electrochemical oxidation, was considered the decay of TOC under different temperatures. Results given in Fig. 4 were further analyzed using kinetic equations related to different reaction orders. Good linear
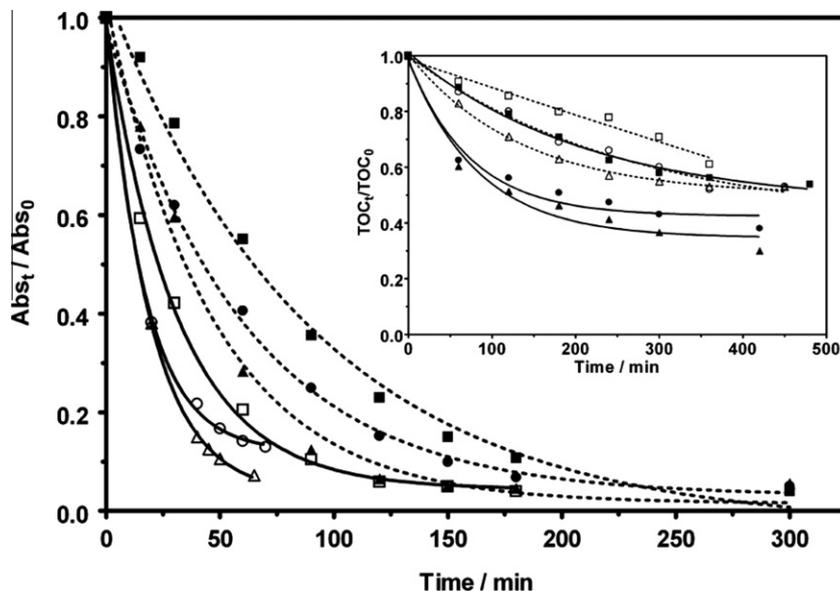
Fig. 4. Influence of temperature on color and TOC removal (inset), as a function of time, during MR anodic oxidation at Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ (dashed lines) and Ti/Pt (continuous lines) anodes. Operating conditions: [MR]$_0$ = 100 mg dm^{-3}, Electrolyte = 0.25 M H$_2$SO$_4$, j = 60 mA cm^{-2}, and different temperatures: (square) 25 °C; (circle) 40 °C, and (triangle) 60 °C.

plots were only obtained, for Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ electrode, when the TOC concentration decays were fitted to a pseudo-first-order reaction (ln(TOC$_0$/TOC$_t$) vs. time). As can be seen in Fig. 5, this behavior was found for all temperatures for Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ electrode up to 300 min, giving a pseudo-rate constant (k) of 1.07×10^{-3} min^{-1} (r^2 = 0.99) for 25 °C, 1.69×10^{-3} min^{-1} (r^2 = 0.99) for 40 °C and 2.33×10^{-3} min^{-1} (r^2 = 0.99) for 60 °C. This suggests that the reaction rate increase when an increase in the temperature is attained, and also that, the concentration of all oxidizing species (·OH) depends on temperature used. However, these figures suggest that the ·OHs are consumed to favor oxygen evolution.

Whereas, when the TOC decay for Ti/Pt was analyzed and fitted for the profile of pseudo-first-order reaction (ln(TOC$_0$/TOC$_t$) vs. time), it does not follow a straight line well. And it is found that the profile of (1/TOC$_t$ − 1/TOC$_0$) as a function of time finely follows a straight line with the correlative coefficients (r^2) of

0.99, compared with the r^2 of 0.94 for the profile of ln(TOC$_0$/TOC$_t$) with time, as reported in Table 1. Thus, it is accepted that TOC decay for Ti/Pt anode in this study should follow apparent second-order kinetics. This behavior indicates that the process depends on oxidizing species (·OH) concentration and organic matter in solution; and at the same time, it may be depends on adsorption steps on anode surface, being limited by an increase on the temperature.

Finally, the reaction rate constants (k) and temperatures were plotted to estimate the apparent activation energy for both anodes, as illustrated for Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ electrode in the inset of Fig. 5, and reported in Table 1. On the other hand, the process activation energy indicates that the electrochemical oxidation process for Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ requires more energy in order to favor the TOC elimination than that required for Ti/Pt anode, confirming the assumptions reported in Sections 3.2 and 3.3.
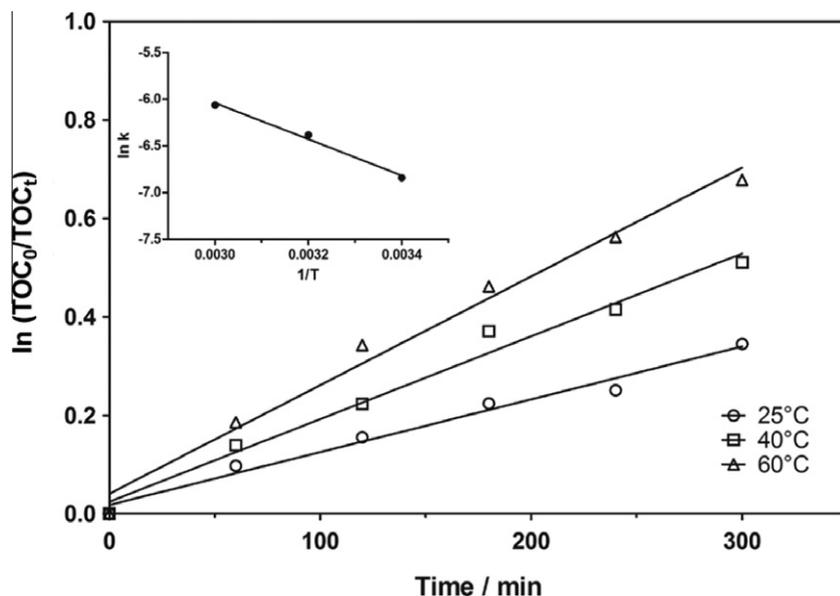

Fig. 5. Kinetic analysis for the pseudo-first-order reaction of TOC decay related to the trials of Fig. 4, for Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ anode.

Table 1
Reaction rate constant (k), correlative coefficient (R^2) and process activation energy for order kinetics of TOC decay for each anode material.

|	Reaction order	Rate constants (k)			Process activation energy
Temperatures (°C)		25	40	60	
Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$	Pseudo-first-order reaction	1.07×10^{-3} min^{-1} ($r^2 = 0.99$)	1.69×10^{-3} min^{-1} ($r^2 = 0.99$)	2.33×10^{-3} min^{-1} ($r^2 = 0.99$)	3298 kJ mol C/L
Ti/Pt	Pseudo-first-order reaction	1.85×10^{-3} min^{-1} ($r^2 = 0.99$)	2.72×10^{-3} min^{-1} ($r^2 = 0.97$)	3.21×10^{-3} min^{-1} ($r^2 = 0.95$)	–
	Apparent second-order	5.05×10^{-5} (mg L)$^{-1}$ min^{-1} ($r^2 = 0.99$)	9.06×10^{-5} (mg L)$^{-1}$ min^{-1} ($r^2 = 0.99$)	1.22×10^{-4} (mg L)$^{-1}$ min^{-1} ($r^2 = 0.99$)	57.6 kJ mol C/L
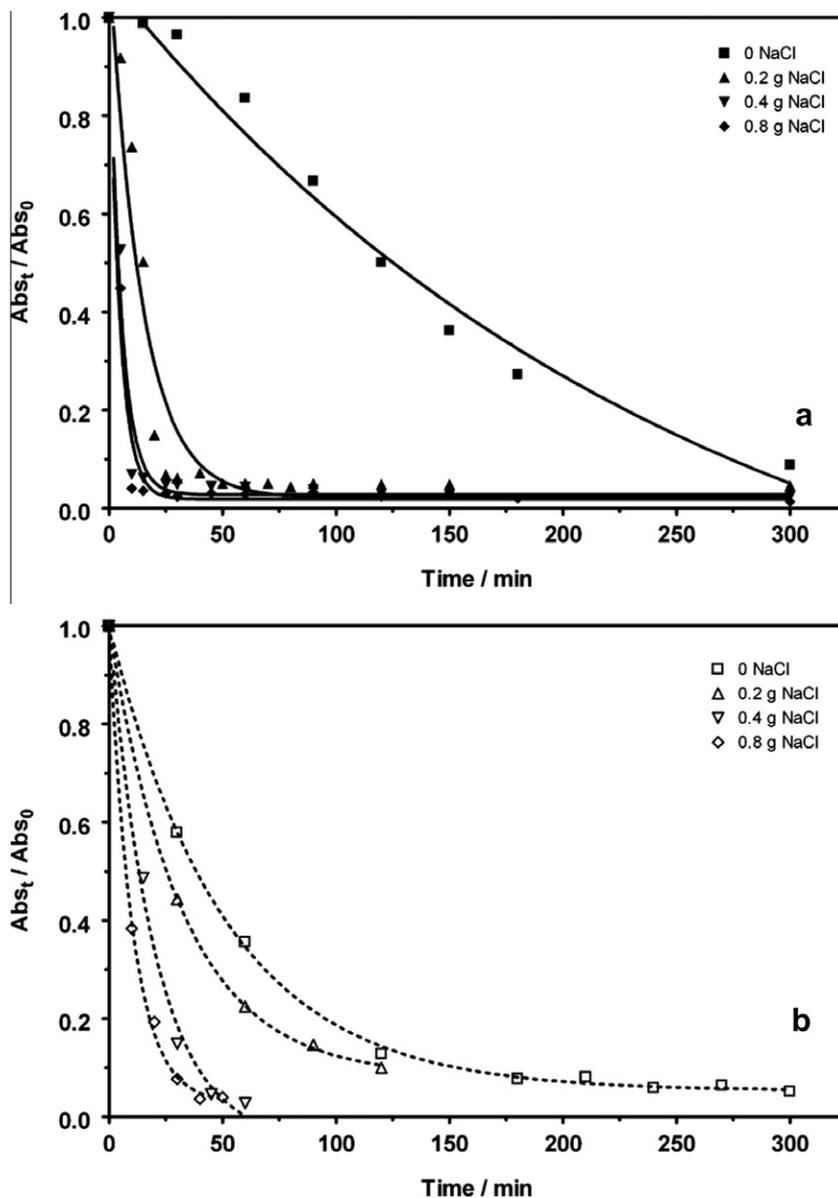
Fig. 6. Influence of NaCl concentration in solution on color removal, as a function of time, during indirect MR oxidation at (a) Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and (b) Ti/Pt anodes. Operating conditions: [MR]$_0$ = 100 mg dm^{-3}, Electrolyte = 0.25 M H$_2$SO$_4$, j = 40 mA cm^{-2}, Temperature = 25 °C, and different NaCl concentrations.

3.5. Electro-oxidation with active chlorine

Due to the lower direct oxidation performances obtained at both Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and Ti/Pt anodes, new electrochemical conditions were chosen for a study of the behavior of these materials in mediated oxidation. The behavior of mediated MR decoloration was investigated by applying a 40 mA cm^{-2} current density in the presence of 0.2, 0.4, or 0.8 g NaCl in 0.4 L synthetic dye solution, using the Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and Ti/Pt anodes. As illustrated in Fig. 6a and b, the electrochemical decoloration of MR at both electrocatalytic

materials was significantly accelerated in the presence of the halide salt in solution. Interestingly, the mediated process did not depend on the applied current density, but it varied as a function of the NaCl concentration in solution. Furthermore, Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ furnished higher decoloration rate and efficiency compared to Ti/Pt anode.

It is well-known that electrolysis of chloride aqueous solutions in an undivided cell involves the direct oxidation of the chloride ion at the anode, to yield soluble chlorine:

$$2Cl^- \rightarrow Cl_{2(aq)} + 2e^- \tag{5}$$

There is concomitant reduction of water at the cathode, which affords hydroxide ion and hydrogen gas. If the local concentration of dissolved chlorine exceeds its solubility, then supersaturation culminates in the formation of chlorine gas bubbles. Because the electrogenerated chlorine diffuses away from the anode, it can react with chloride ions, to produce the trichloride ion:

$$Cl_{2(aq)} + Cl^- \leftrightarrow Cl_3^- \tag{6}$$

Alternatively, chlorine is rapidly hydrolyzed, with its consequent disproportionation into hypochlorous acid and chloride ion:

$$Cl_{2(aq)} + H_2O \leftrightarrow HClO + Cl^- + H^+ \tag{7}$$
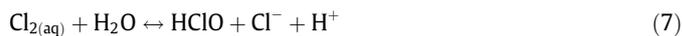
In the bulk solution, this acid is in equilibrium with the hypochlorite ion (pK_a = 7.55), as follows:

$$HClO \leftrightarrow ClO^- + H^+ \tag{8}$$

A very low concentration of Cl$_3^-$ is formed up to pH ca. 4, while the predominant species is Cl$_{2(aq)}$ until pH near 3, HClO in the pH range 3–8, and ClO$^-$ for pH > 8. The mediated oxidation of dyes with these species is thus expected to be faster in acidic conditions compared to alkaline medium owing to the higher standard potential of Cl$_{2(aq)}$ ($E°$ = 1.36 V vs. SHE) and HClO ($E°$ = 1.49 V vs. SHE) as compared to ClO$^-$ ($E°$ = 0.89 V vs. SHE). Therefore, a pH value around 1 was employed in this work. Also, the possibility of chlorate formation under their operating conditions could be considered, according to the reaction:
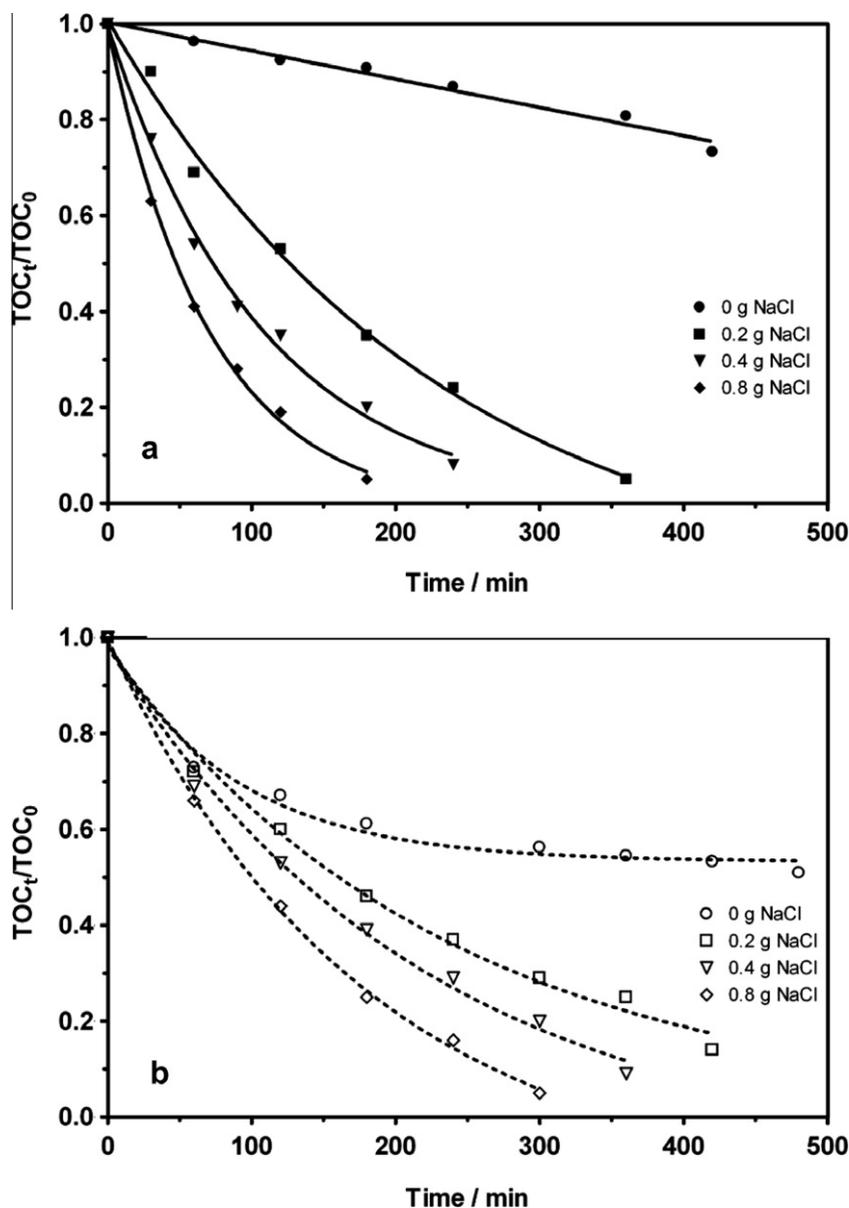

Fig. 7. Influence of NaCl concentration in solution on TOC removal, as a function of time, during indirect MR oxidation at (a) Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ and (b) Ti/Pt anodes. Operating conditions: [MR]$_0$ = 100 mg dm^{-3}, Electrolyte = 0.25 M H$_2$SO$_4$, j = 40 mA cm^{-2}, Temperature = 25 °C, and different NaCl concentrations.

Table 2
Energy consumption, calculated from Eq. (3), per volume of treated effluent during direct and indirect MR oxidation at $Ti/Ru_{0.3}Ti_{0.7}O_2$ and Ti/Pt electrodes for different (i) applied current densities; (ii) temperatures; and (iii) NaCl concentrations in 400 mL synthetic dye solution. $[MR]_0 = 100$ mg dm^{-3}, Electrolyte = 0.25 M H_2SO_4.

Different current densities[a]	Decoloration time (min)	Average cell voltage (V)	Energy (kW h m^{-3})
$Ti/Ru_{0.3}Ti_{0.7}O_2$ anode			
20	300	2.7	15.30
40	300	2.6	29.93
60	300	2.9	67.05
Temperature[b]			
25	300	2.9	67.05
40	250	2.8	51.56
60	220	2.7	45.38
g NaCl in 0.4 L[c]			
0	300	2.6	29.93
0,2	65	3.3	8.00
0,4	25	3.4	3.19
0,8	25	3.0	2.83
Ti/Pt anode			
20	300	3.0	26.25
40	250	3.2	46.67
60	150	4.3	56.44
Temperature[b]			
25	150	4.3	56.44
40	90	4.8	37.80
60	70	5.1	31.24
g NaCl in 0.4 L[c]			
0	250	3.2	46.67
0,2	125	5.0	36.46
0,4	60	4.7	16.45
0,8	40	4.7	10.97

[a] $T = 25\ °C$.
[b] $j = 60$ mA cm^{-2}.
[c] $j = 40$ mA cm^{-2}.

$$ClO^- + 2HOCl \rightarrow ClO_3^- + 2Cl^- + 2H^+ \tag{9}$$
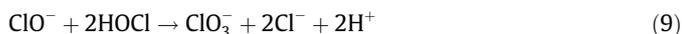
And, chlorate may contribute to indirect dye removal.

Hence, on the basis of literature results, the rates of electrode reactions are a function of the electrocatalytic activity of the anode, the chloride concentration, and the current density. As previously mentioned, these observations are in agreement with figures presented in this paper (Fig. 6). Analogous data have been reported by Bonfatti and co-workers during analysis of the Cl^--mediated glucose electro-oxidation [22], and by Panizza and Cerisola [23] for the Cl^--mediated oxidation of 2-naphthol at a Ti–Ru–Sn ternary oxide electrode. Other authors have also suggested that this behavior occurs during the oxidation of various dyes [3,5–7]. For example, Mohan et al. [24,25] studied the oxidation of Acid Brown 14 solution in 0.58 g dm^{-3} NaCl at pH 7 and they showed that such anodes yield more rapid COD decay in the order Ti/TiO_2–RuO_2–PbO_2 < Ti/TiO_2–SnO_2 < Ti/TiO_2–RuO_2, which furnished 100% decoloration efficiency and increased decontamination by 42%, 62%, and 67% at 150 min, respectively.

As already indicated by other authors [23–26], active chlorine-mediated electrochemical oxidation not only diminishes the color of dye solutions, but also reduces the amount of dissolved organic matter. Therefore, TOC decay during MR removal was monitored by applying 40 mA cm^{-2} current density in the presence of 0.2, 0.4, or 0.8 g NaCl in 0.4 L synthetic dye solution, using the $Ti/Ru_{0.3}Ti_{0.7}O_2$ and Ti/Pt anodes. The results presented in Fig. 7a and b demonstrate that TOC removal is strongly influenced by the anode material during mediated MR oxidation. Results clearly indicate that highest TOC removal efficiencies are achieved at $Ti/Ru_{0.3}Ti_{0.7}O_2$ compared to the Ti/Pt electrode (Fig 7b). Meanwhile, the TOC removal rate increased when the amount of NaCl in

solution was increased. This behavior suggests that the $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode favors the electrogeneration of larger quantities of active chlorine species compared to Ti/Pt. The $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrode yielded virtually complete TOC removal (96%) at 360 min of treatment when 0.2 g NaCl was present in the solution (Fig. 7a). Conversely, the Ti/Pt electrode required over 400 min to furnish partial TOC removal (83%) under the same experimental conditions, as shown in Fig. 7b.

A comparison between the performances of the $Ti/Ru_{0.3}Ti_{0.7}O_2$ and Ti/Pt anodes during the direct (Figs. 2 and 3) and indirect (Figs. 6 and 7) oxidation of MR dye solutions under the same operating conditions clearly evidences that the Ti/Pt anode is significantly more efficient for color and TOC removal during direct oxidation. Conversely, the $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrode is more efficient with regard to indirect oxidation with active chlorine. Although the results obtained under these experimental conditions gave evidence of different efficiencies, the behavior observed in the case of indirect oxidation was explained by considering the quasi-steady polarization curves obtained in background solutions containing 0.25 M H_2SO_4 in the absence and in the presence of different Cl^- concentrations (data not shown). In fact, the whole polarization curve shifted to more positive potentials with increasing Cl^- concentration. Consequently, the anode potentials in the region of j values applied for electrochemical incineration of organics reached values of the order of 2.0 V (vs. SCE). At these polarization levels, the population and reactivity of hydroxyl radicals adsorbed at the electrode surface and/or confined in a reaction cage around the electrode itself may lead to fast incineration of a number of organic substrates. The co-existence of oxy-chloro radicals, often assumed as being other intermediates in the chlorine evolution reaction, can but further facilitate the electrochemical mineralization processes. These results are in accord with earlier studies [1].

During indirect MR oxidation, a rise in NaCl concentration causes gradual displacement of the oxygen evolution reaction to more positive potentials, as compared to electrolysis carried out in the absence of a mediator. However, this effect is more evident at the $Ti/Ru_{0.3}Ti_{0.7}O_2$ anode. In other words, as shown in Fig. 7, complete MR degradation at the $Ti/Ru_{0.3}Ti_{0.7}O_2$ electrode is considerably improved in the presence of the halide salt, as compared to Ti/Pt.

3.6. Byproducts and formation of chlorinated derivatives

The mass spectra recorded during the direct oxidation of the MR by at both $Ti/Ru_{0.3}Ti_{0.7}O_2$ and Ti/Pt anode materials displayed m/z peaks at 136, 93, and 122, attributed to the formation of 4,4-N,N-dimethyl aniline, aniline, and benzoic acid. The generation of these byproducts confirms cleavage of the chromophore group, as indicated by the UV spectrophotometric analysis. The intermediate aniline undergoes further oxidation, to give nitrobenzene. Benzoic acid decarboxylation furnishes benzene. After 200 min of electrolysis, an additional m/z peak appeared at 108, ascribed to the formation of hydroquinone. In the case of Ti/Pt, the m/z peaks detected at 46, 90, and 76 after 400 min of electrolysis are due to the production of simple aliphatic carboxylic acids like formic acid and oxalic acid. These data corroborate the assumption that the low TOC depletion is due to generation of several byproducts, at both anodes, and to formation of a passivating film consisting mainly of aliphatic acids, in the case of Ti/Pt, which poisoned the anode surface and diminished the removal efficiency. This outcome is in agreement with data reported by other authors for the anodic oxidation of the MR dye by another treatment process [27].

A minor number of intermediates were detected during indirect MR oxidation at 40 mA cm^{-2} current density, in the presence of 0.2 g NaCl in 0.4 L synthetic dye solution. At the time of complete decoloration, the mass spectra presented two m/z peaks, namely

at 138 and 110, corresponding to the formation of 2-hydroxy benzoic acid and 1,4-dihydroxy benzene, regardless of the anode material. The attack of chloro-oxidizing species at the azo bond site and at the terminal *N,N*-dimethyl chain led to generation of the above mentioned intermediates. After 30 min the mass spectra exhibited two m/z peaks, more specifically at 94 and 122, assigned to production of phenol and benzoic acid. The mass spectrum recorded at 40 min of electrolysis presented two intense m/z peaks, at 78 and 112, due to benzene and chlorobenzene, respectively. The latter compound might have resulted from benzene or phenol chlorination. However, after 120 min of electrolysis GC analysis revealed no traces of organochlorinated compounds for Ti/Ru$_{0.3}$-Ti$_{0.7}$O$_2$ or Ti/Pt. It must be borne in mind that the expected formation of chlorinated derivatives from the attack of active chlorine on the organic dye calls for constant reaction monitoring, owing to the possible production of more dangerous chlorinated byproducts. In some cases, GC–MS analysis of electrolyzed solutions confirmed the evolution of these compounds during electrochemical dyes degradation [28,26], whereas in other situations they have not been identified [29]. The present data have demonstrated the applicability of this electrochemical technology for the treatment of MR dye solutions without formation of more dangerous compounds at the end of the electrochemical process.

3.7. Estimation of energy consumption

Energy and economic aspects are key points for the development of clean methodologies. Predictions, even if only indicative, about these aspects give an idea of process feasibility. Table 2 summarizes the energy consumption per volume of treated effluent at different conditions. Energy consumption seems to be proportional to the applied current density during electrolysis of MR synthetic wastewaters containing a dye concentration of 100 mg dm^{-3}. In the case of Ti/Pt, for instance, consumption increased from 26.25 to 56.44 kW h per m^3 of treated effluent when the current density was elevated from 20 to 60 mA cm^{-2}. The obtained values were higher than those achieved during electrolyses of lighter pollutants, because of the complex chemical structure of the MR dye [3]. Energy consumption values were obtained at different temperatures, and the decrease in charge requirements upon rising temperature was confirmed. On the other hand, the indirect electrochemical process seems to be more efficient when the NaCl concentration in solution is augmented. For Ti/Pt, energy consumption was 46.67 kW h m^{-3} and 10.97 kW h m^{-3} in the absence and presence of NaCl, respectively. These results highlight the excellent performance of anodic oxidation when it comes to the treatment of MR dye solutions using Ti/Pt and Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ anode materials. In terms of energy consumption, direct anodic oxidation at Ti/Pt and Ti/Ru$_{0.3}$Ti$_{0.7}$O$_2$ electrodes is not attractive for complete TOC elimination from effluents contaminated with dyes, but it can be a feasible pre-treatment process for decoloration of wastewaters containing dyestuff. It is important to remark that the textile dyeing industrial effluent frequently contains 100–150 mg dm^{-3} dissolved sodium chloride. For this reason, the indirect electrochemical process can be considered a more efficient alternative for the complete degradation of organic pollutants and color removal from textile wastewaters as compared to direct oxidation.

4. Conclusions

Our results attest for the high performance of direct or mediated electrochemical processes concerning the treatment of dye solutions. They can be considered a feasible process for the decoloration of textile wastewaters polluted with dyes. The main conclusions of this work can be summarized as follows:

(i) Anodic oxidation can be successfully used to completely remove all the color from solutions polluted with MR, considering the specific operating conditions (current density and temperature).

(ii) During galvanostatic electrolyses of MR solutions, the influence of current density and temperature, as a function of time, showed that the oxidation of the compounds generated from the anodic oxidation of the supporting electrolyte; e. g, ·OH plays an important role in the efficiency of the electrochemical process. However, adsorption of the byproducts formed during anodic oxidation is another parameter that must be considered in this process, if complete organic matter elimination is to be attained.

(iii) Larger NaCl concentrations in the dye solution enhance the color and TOC elimination rate. Thus, indirect electrochemical oxidation seems to be an efficient process for both electrocatalytic materials. Although in some cases addition of chloride ion is not practical for the remediation of wastewater due to the probable formation of organochlorinated pollutants, the ability of chloride to accelerate the electrochemical oxidation of organic pollutants is extremely interesting.

(iv) Energy consumption measured during galvanostatic electrolyses of MR dye solutions largely depends on the applied current density, but a modest influence of the temperature on energy requirements is observed.

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