Int. J. Electrochem. Sci., 10 **(2015)** 7840 - 7853

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Effectiveness of Ti/RuO_2 and $Ti/RuIrCo(40\%:40\%:20\%)O_x$ Anodes for Electrochemical Tretament of Paper Industry Wastewater

Teresa Zayas[1,2,*], *Mario Picazo*[1], *Ulises Morales*[3], *Eduardo Torres*[1,2], *Leonardo Salgado*[3]

[1]Posgrado en Ciencias Ambientales, Benemérita Universidad Autónoma de Puebla, P.O. Box 1613, C.P. 72000 Puebla, México
[2]Centro de Química del Instituto de Ciencias, Benemérita Universidad Autónoma de Puebla, P.O. Box 1613, C.P. 72000 Puebla, México
[3]Depto. de Química, Universidad Autónoma Metropolitana Iztapalapa, A.P. 55-534, C.P. 09340 México D.F., MEXICO
[*]E-mail: tzayasp@hotmail.com

Received: 18 April 2015 / *Accepted:* 30 May 2015 / *Published:* 28 July 2015

The electrochemical oxidation of paper industry wastewater was studied using two types of dimensionally stable anodes: Ti/RuO_2 and $Ti/RuIrCo(40\%:40\%:20\%)O_x$. The electrodes were characterized using SEM micrography and EDS spectroscopy. The local mapping analysis was performed on $Ti/RuIrCo(40\%:40\%:20\%)O_x$. The presence of Ir and Co significantly modified the surface morphology of Ti/RuO_2. The oxidation process was analyzed as a function of the electrolysis time at a constant cell potential in the absence or presence of an electrolyte (NaCl) and at an initial pH of 6.2. The effectiveness with which the two anodes electrochemically oxidized the wastewater was evaluated by measuring the removal of the chemical oxygen demand (COD), color, and total polyphenols, and using UV-Vis spectroscopy. The results revealed that both anodes reduced the COD, color, and polyphenols; however, the ability to remove organic matter depended on the nature of the electrode material, the presence or absence of NaCl, and the electrolysis time. In the absence of NaCl, the effectiveness of the Ti/RuO_2 electrode exceeded that of $Ti/RuIrCo(40\%:40\%:20\%)O_x$ for the removal of COD, color, and polyphenols. The presence of NaCl was a determining factor in the process of electrochemical oxidation. In the presence of NaCl, both anodes increased their capacities for removing the COD, color, and polyphenols; however, the anode $Ti/RuIrCo(40\%:40\%:20\%)O_x$ was more effective than the anode Ti/RuO_2 in reducing the COD. The UV-Vis spectrum suggested the formation of hypochlorite ions (ClO^-) during the electrolysis process, indicating that the electrochemical oxidation proceeded via an indirect mechanism with the participation of hypochlorite ions. The Ti/RuO_2 electrode modified with Ir and Co favored an indirect mechanism involving hypochlorite ions.

Keywords: Electrooxidation; Ti/RuO_2; $Ti/RuIrCo(40\%:40\%:20\%)O_x$; Anodes; Wastewater

1. INTRODUCTION

Wastewater from the paper industry presents an environmental pollution problem because the high quantity of water used in the process, 76–227 m^3 per ton of product, results in large amounts of wastewater with a high organic load [1]. Several pollutants have been identified in the effluents produced at different stages of papermaking. These pollutants are present in the form of chlorinated compounds, suspended solids, fatty acids, tannins, resin acids, lignin and its derivatives, and organic sulfur compounds [2]. Xenobiotic compounds formed during the process of pulping and paper making (chlorinated lignins, resin acids, phenols, dioxins, and furans) can induce genetic changes in exposed organisms [3,4]. To reduce the adverse effects of the paper industry wastewater on the environment, it is necessary to identify efficient wastewater treatments prior to discharge into the water bodies. The main treatment that is applied to pulp and paper mill effluent consists of an initial clarification step (sedimentation or flotation), followed by a secondary biological treatment (anaerobic or aerobic) [1]. Although such treatments have been used to reduce organic content, they fail to remove the diverse recalcitrant organic compounds that resist biological degradation and, hence, remain present in the effluent [5]. In recent decades, the studies of the treatment of paper industry wastewater have gained interest given the need to reduce adverse environmental effects. A variety of studies have examined treatments based on biological processes (aerobic, anaerobic, algal, fungal biomass) or physicochemical approaches (coagulation–flocculation, ozonation, photocatalysis, electrochemistry) [1,6-12]. The electrochemical oxidation of organic matter has provided favorable results in the treatment of wastewater from different industries [13-16]. In the paper industry, this process has been applied using graphite [17], lead anodes [10], or dimensionally stable anode-type electrodes (DSA): $Ti/TiO_2/RuO_2$ [18], $Ti/Co/SnO_2$-Sb_2O_5 [19], $Ti/Ru_{0.3}Ti_{0.7}O_2$ [20], or $Ti/RuPb(40\%)O_x$ [21]. These electrode materials can reduce the COD, color, and polyphenols from the paper industry wastewater. The effectiveness of the electrochemical oxidation process applied to organic matter depends essentially on the electrocatalytic activity of the electrode material that constitutes the anode; therefore, the appropriate selection of the anode can increase the removal of organic matter with a high efficiency [22]. Dos Santos *et al.* [15] showed that the electrochemical oxidation of phenol and its byproducts at an Ti/RuO_2 anode resulted in rapid break-down in the presence of chloride ions. They suggested that the Ti/RuO_2 anodes could be used for the treatment of effluents containing phenols in a chloride environment. Studies of anodes based on Ru, Ir, or Co electrodes have revealed high activities and a high resistance to corrosion [23-25]. Considering the importance of the anode composition on the electrochemical oxidation process, we compared the effectiveness of the oxidation processes in paper industry wastewater treatment using two types of dimensionally stable anodes with compositions based on Ru oxide or Ru-Ir-Co oxides supported on Ti. These electrodes were represented as electrode 1 (E1), for Ti/RuO_2, and electrode 2 (E2), for Ti/RuIrCo (40%: 40%: 20%) O_x. The effectiveness of the anodes in removing organic matter from paper industry wastewater revealed that RuO_2 displayed unique electrocatalytic properties in the presence of Ir and Co. The effectiveness of the electrochemical treatment of wastewater using both anodes was evaluated by measuring the removal COD, color, and polyphenols, and by using UV-Vis spectroscopy.

2. EXPERIMENTAL

2.1. Characteristics of the paper industry wastewater

The wastewater samples used in this study were obtained from a paper production plant (México), and stored at 4°C. The wastewater was characterized for COD, conductivity, color, turbidity, pH, total dissolved solids, chloride and polyphenols. The data are listed in Table 1.

Table 1. Characteristic measures of the raw paper industry wastewater.

Parameters	Values
COD (mg O_2/L)	2585
Conductivity (mS cm^{-1})	2.9
Color (m^{-1})	101.2
Turbidity (NTU)	486
pH	6.2
TDS (g/L)	2.1
Chloride concentration (mg/L)	80
Total polyphenols (mg/L)	48

2.2. Reagents

Sodium chloride (Merck AR) was used as the support electrolyte. Folin-Ciocalteau reagent (a mixture of phosphomolybdic and phosphotungstic acids; Merck AR) was used to measure the total polyphenol concentrations. Spectroquant® COD Cell Test (a mixture of potassium dichromate, mercury sulfate, silver sulfate and sulfuric acid; Merck, Germany) with different sensitivity ranges were used to determination the chemical oxygen demand (COD).

2.3. Electrodes

RuO_2-coated titanium (Ti/RuO_2) and RuIrCo(40%:40%:20%)O_x-coated titanium (Ti/RuIrCo(40%:40%:20%)O_x) electrodes were used as the anodes, and a PtPd(10%)O_x-coated titanium (Ti/ PtPd(10%)O_x) electrode was used as the cathode in all cases. These electrodes were prepared in our laboratory and were dimensionally stable anode (DSA)-type electrodes. A titanium mesh (ASTM grade 2) was used to support the oxide layers. The mesh was prepared by thermally decomposing of the precursors in an alcoholic solution and was applied by brushing onto the metallic support. The elemental content in the film (Ru, Ir, and Co) corresponded to the nominal molar percent composition of the precursor solution. The solvent was evaporated at a low temperature (100°C) and the electrode was annealed for 1 h at 450°C to form the metallic oxide phase. The electrode mesh area was 41.25 cm^2 (7.5 cm x 5.5 cm). For practical purposes, the anodes were labeled as follows: E1 for the Ti/RuO_2 anode and E2 for the Ti/RuIrCo(40%:40%:20%)O_x anode. The electrodes were characterized using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) using a JEOL JSM-7600F instrument operated at a voltage of 15 keV.

2.4. Electrochemical methodology

The electrochemical oxidation process was performed in an electrochemical cell with a capacity of 150 mL and a sample volume of 100 mL. The parallel electrodes (anode and cathode) were placed vertically with a separation distance of 3 mm. Raw wastewater samples (100 mL) were subjected to electrolysis. The operation conditions were the cell potential difference (6 V), concentration of the support electrolyte (NaCl: 5.0 g/L), pH of the solution (6.2) and electrolysis time as variable. The potential difference was applied from an external power source (DS-304M, Zurich), and the current and voltage were measured using a conventional multimeter.

2.5. Analytical control

The effects of the electrochemical treatment were analyzed based on the physicochemical parameters, including the COD, color, and polyphenol content, as well as the UV–Vis spectra. pH measurements were obtained using a Conductronic PC 18 pH meter. The COD and color were monitored using a spectrophotometer (SQ118, Merck). Sample digestion was performed in a TR 300 Thermoreaktor (Merck) over 2 hours at 148°C. The UV-Vis spectra were obtained from the samples using a Perkin–Elmer Lambda 20 spectrometer. The total polyphenol content was determined using the Folin–Ciocalteau colorimetric reaction [26].

3. RESULTS AND DISCUSSION

3.1. SEM and EDS analysis of the Ti/RuO$_2$ and Ti/RuIrCo(40%:40%:20%)O$_x$ electrodes

Figure 1 shows (a) an SEM micrograph and (b) the EDS spectrum of the RuO$_2$-coated titanium electrode prepared by thermal decomposition. The SEM image (Fig. 1.a) shows the cracked Ti surface, which is common to DSA-type electrodes as a result of sintering processes [27, 28]. The EDS spectra (Fig. 1.b) confirmed the presence of Ru and Ti in the RuO$_2$ surface layer applied to the Ti substrate.

Figure 2 shows (a) an SEM micrograph, (b) the local mapping analysis, and (c) the EDS spectrum of the RuIrCo (40%:40%:20%) electrode. The oxide-coated titanium electrode was prepared using the conventional thermal decomposition route. The surface of the Ti/RuIrCo(40%:40%:20%)O$_x$ electrode was rough, heterogeneous, and cracked (Fig. 2.a). Apparently, the surface morphology of the Ti/RuIrCo(40%:40%:20%)O$_x$ differed from that of Ti/RuO$_2$. The EDX spectra (Fig. 2.c) confirmed the presence of Ru, Ir, Co, and Ti, and a local mapping analysis of the film components revealed the surface distribution of Ru, Ir, and Co, as shown in Fig. 2.b.

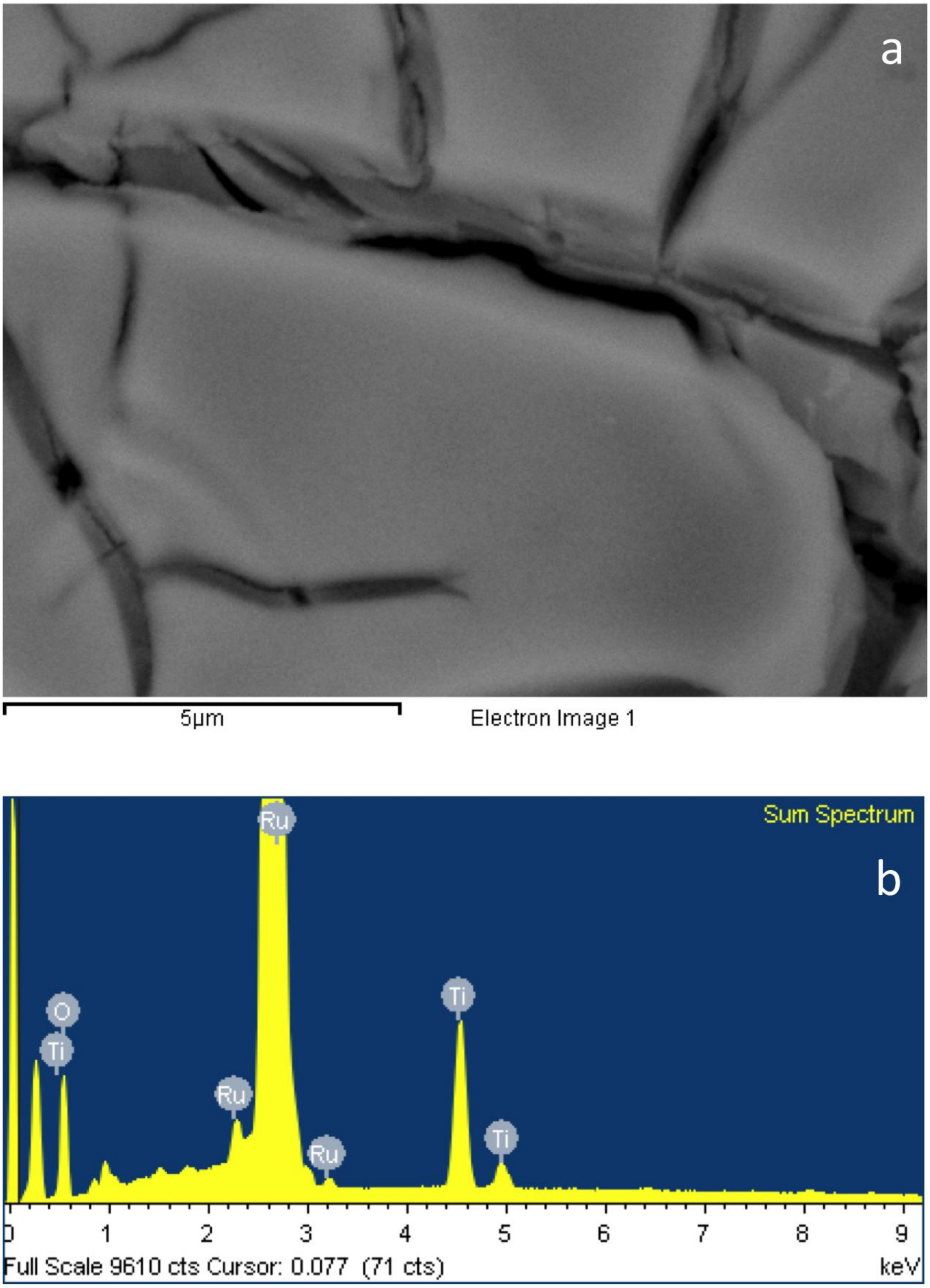

Figure 1. (a) SEM micrographs and (b) EDS spectrum of the Ti/RuO_2 electrodes prepared via a conventional thermal decomposition route.

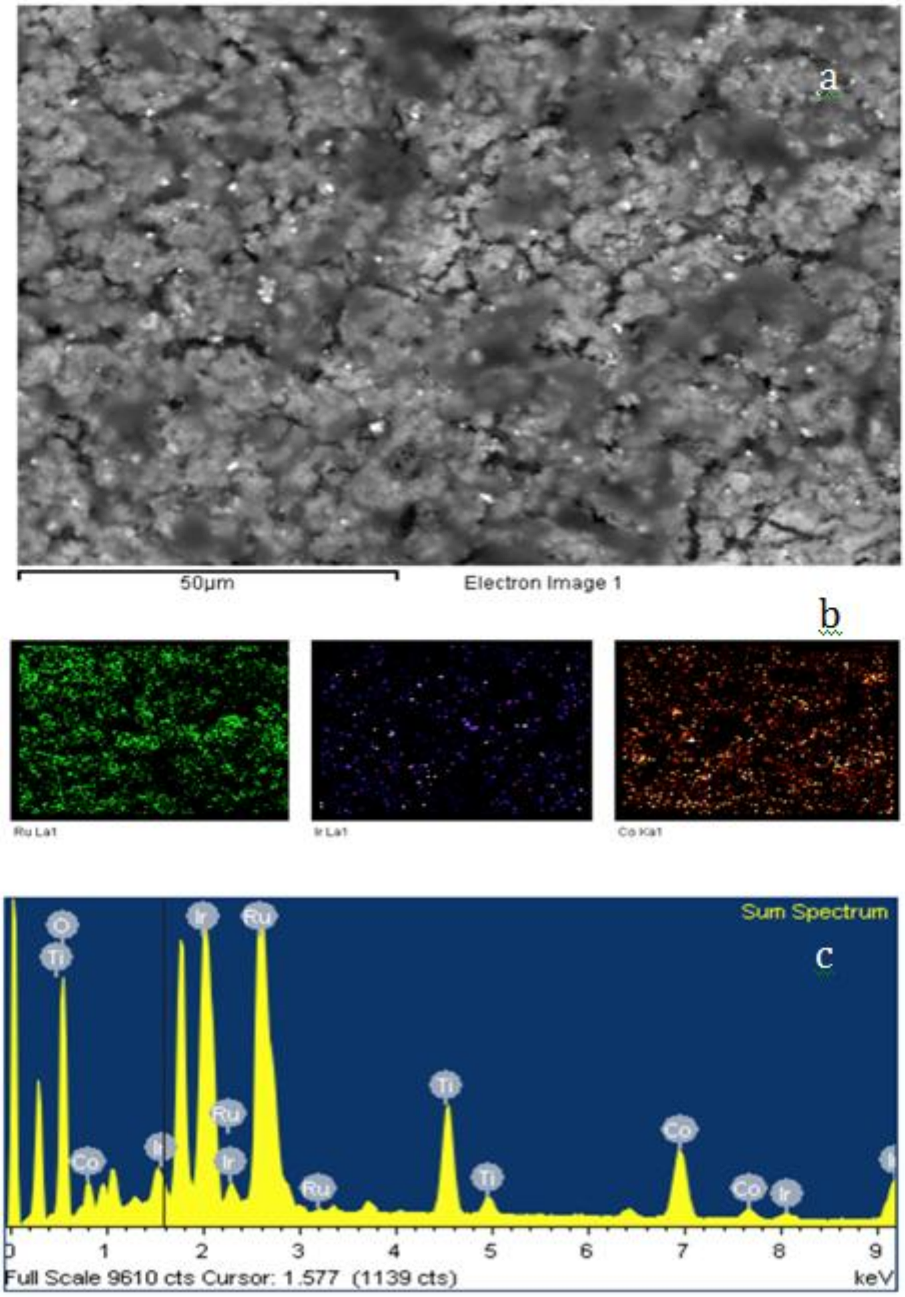

Figure 2. (a) SEM micrographs, (b) local mapping analysis, and (c) EDS spectrum of the Ti/RuIrCo(40%:40%:20%)O_x electrode prepared using conventional thermal decomposition methods.

3.2. Electrochemical oxidation of wastewater from the paper industry using the anodes E1 and E2, without added NaCl.

Raw wastewater samples, to which the support electrolyte (NaCl) had not been added, were subjected to electrochemical oxidation in the presence of each anode (E1 and E2), under application of a constant potential difference (6 V), and the samples were monitored as a function of the electrolysis time. The COD, color, polyphenol removal, and pH are plotted over the electrolysis time, as shown in Figs. 3.a–3.d, respectively, for each anode used (E1 and E2). The COD removal percentage (Fig. 3a), color (Fig. 3b), and polyphenol removal (Fig. 3c) followed similar trends in the presence of each anode.

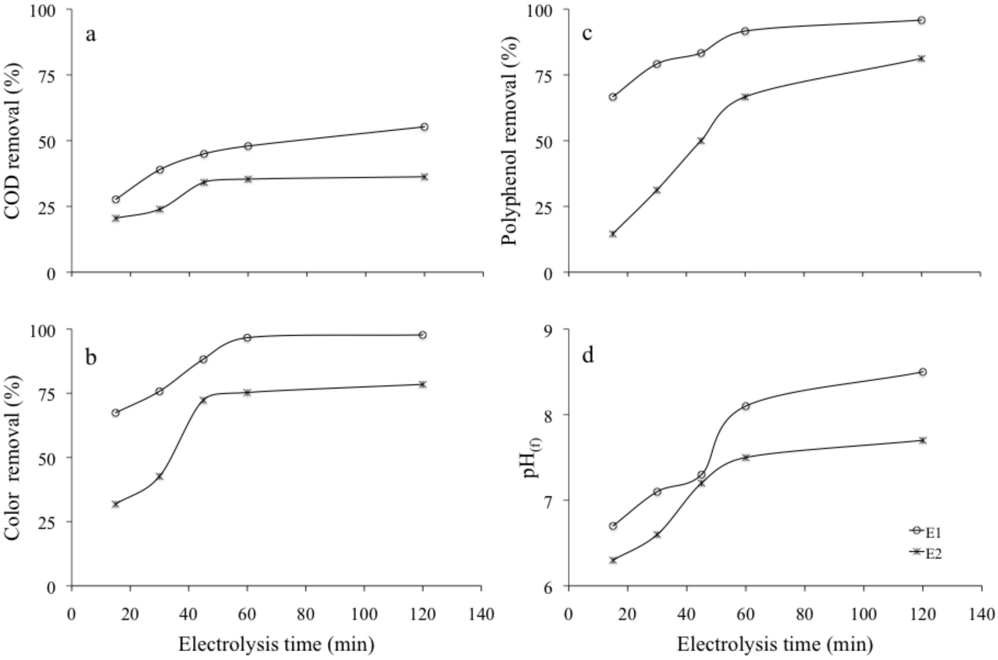

Figure 3. Percent removal of (a) COD, (b) color, and (c) polyphenols. (d) pH of the wastewater as a function of the electrolysis time. Anodes: E1 (Ti/RuO_2) and E2 (Ti/RuIrCo(40%:40%:20%)O_x). pH (initial) = 6.2, cell potential difference of 6 V, without the addition NaCl.

The removal percentage (COD, color, and polyphenol removal) increased with the electrolysis time and approached a constant maximum value; however, over the electrolysis range applied (120 min), the highest removal values measured based on the COD, color, and polyphenol measures were obtained in the presence of the E1 anode, as shown in the curves of Figs. 3.a–3.c. After a 60 min electrolysis time, the removal percentages monitored by the different parameters remained relatively constant. For example, the E1 anode yielded removal percentages based on the COD, color, and polyphenol of 49%, 96.6%, and 91.7%, respectively, whereas with the E2 anode yielded 35%, 75.3%, and 66.7%, respectively. These results suggested that under fixed electrolysis conditions, the E1 anode was more effective than the E2 anode in reducing the COD, color, and polyphenols from paper industry wastewater. Figure 3.d shows that the electrochemical oxidation of wastewater in the presence of the E1 and E2 anodes modified the initial pH of the solution. The solution pH increased with the electrolysis time, and the solution acquired a basic character. Under constant electrolysis conditions, higher pH values were obtained in the presence of the E1 anode. These results indicated that the anode composition was important to the electrochemical oxidation of wastewater, and the E1 anode, based on

Ti/RuO_2, was more efficient in reducing the COD, color, and polyphenols than the E2 anode, based on oxides of Ir, Co, and Ru.

The differences between the properties of the E1 and E2 anodes during the oxidation of paper industry wastewater (without added NaCl) could be explained by considering that the presence of Ir and Co in the E2 RuO_2 matrix ($Ti/RuIrCo(40\%:40\%:20\%)O_x$ anode) decreased the evolution of an oxygen overpotential relative to that obtained in the presence of E1 (RuO_2); therefore, E2 was less effective in removing organic matter [23, 24, 29]. Ti/RuO_2 and $Ti/RuIrCo(40\%:40\%:20\%)O_x$ are DSA-type anodes with a low oxygen overpotential; hence, the electrochemical oxidation of organic compounds occurs together with the oxygen evolution reaction (OER). Comninellis *et al.* [29] reported that class I anodes ("active anodes") are anodes that mediate the conversion or selective oxidation of organics and, consequently, are good electrocatalysts for the oxygen evolution reaction. Our electrodes E1 and E2 fall within this category, and the oxygen evolution reaction is a side-reaction that competes with organic oxidation and lowers the efficiency of the overall process. The proposed oxidation mechanism in the presence of class I anodes is summarized in equations 1–4 [29]:

$$MO_x + H_2O \rightarrow MO_x(\cdot OH) + H^+ + e \qquad (1)$$

$$MO_x(\cdot OH) \rightarrow MO_{x+1} + H^+ + e \qquad (2)$$

$$R + MO_{x+1} \rightarrow RO + MO_x \qquad (3)$$

$$MO_{x+1} \rightarrow \frac{1}{2}O_2 + MO_x + H^+ + e \qquad (4)$$

The first step in the oxygen transfer reaction involves the discharge of water molecules to form adsorbed hydroxyl radicals on the electrode surface (MO_x) (Eq. 1). The strong interaction between the hydroxyl radical ($OH^{\cdot}$) and MO_x, could lead to the formation of an oxide with a higher oxidation state (Eq. 2). The surface redox couple MO_{x+1}/MO_x is thought to act as a mediator in the conversion or selective oxidation of organics (R) (Eq. 3). Equation 3 proceeds in competition with the oxygen generation reaction (Eq. 4). By contrast, class II anodes ("inactive" anodes) produce high overpotential values during the oxygen evolution reaction. The high overpotential favors the complete degradation of organic compounds through the formation of $MO_x(\cdot OH)$ active sites on the electrode surfaces (Eq. 5) [30].

$$MO_x(\cdot OH) + R \rightarrow MO_x + mCO_2 + nH_2O + e \qquad (5)$$

The oxygen evolution reaction could be favored in alkaline media [31]; therefore, if the electrochemical oxidation process in the presence of E1 and E2 produces a $pH > 7$, the pH can limit the oxidation of the organic matter.

3.3. Electrochemical oxidation of paper industry wastewater in the presence of NaCl (5.0 g/L) using the E1 and E2 anodes

Raw wastewater samples were supplemented with NaCl (5.0 g/L) and were subjected to electrochemical oxidation in the presence of each anode E1 and E2 under a constant potential difference (6 V) and were examined as a function of the electrolysis time. The NaCl concentration (5.0

g/L) was optimized in preliminary experiments. The COD, color, polyphenols, and pH are plotted as a function of the electrolysis time in Figs. 4.a–4.d, respectively, for each anode (E1 and E2).

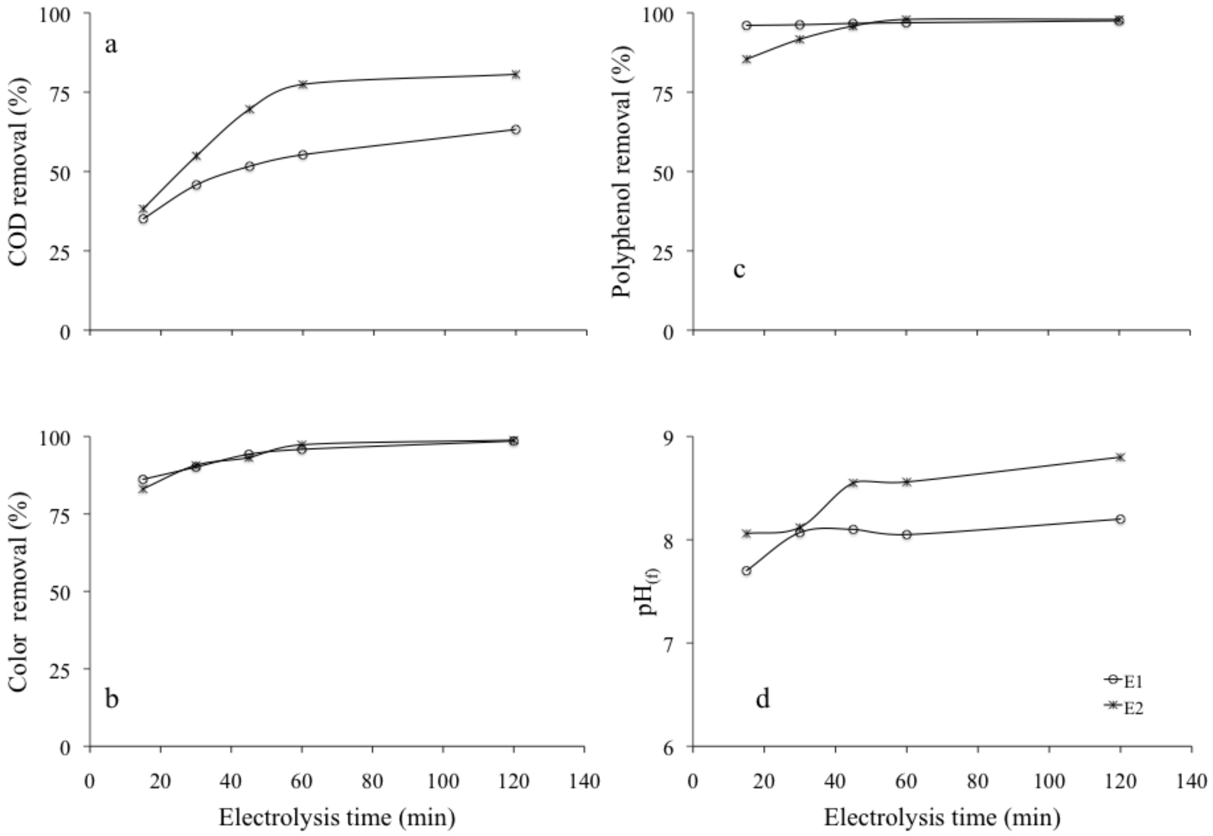

Figure 4. Percent removal of (a) COD, (b) color, and (c) polyphenols. (d) pH of the wastewater as a function of the electrolysis time. Anodes: E1 (Ti/RuO_2) and E2 ($(Ti/RuIrCo(40\%:40\%:20\%)O_x$). pH (initial) = 6.2, cell potential difference of 6 V, with the electrolyte NaCl (5.0 g/L).

The electrochemical oxidation of paper industry wastewater in the presence of anodes E1 and E2 differed, depending on the presence or absence of NaCl. The addition of NaCl increased the capacity of the E1 and E2 anodes to reduce the COD, color, and polyphenol content; therefore, NaCl favored the oxidation process; however, the COD removal percentage curves obtained from E1 and E2 in the presence of NaCl (Fig. 4a) revealed that the E2 anode was more effective than the E1 anode in reducing the COD over the electrolysis time examined. A 60 min electrolysis time provided a COD removal percentage of 77% in the presence of E2 and a 55% value in the presence of E1. The E2 anode was therefore capable of doubling the COD value obtained from the E1 anode in the absence of NaCl. The curves corresponding to the percentage removal of color and polyphenols in the presence of the anodes E1 and E2 (Fig. 4.b and 4.c) displayed similar trends during electrolysis. The percentage color removal was 87–97% during the 15–60 min electrolysis window, whereas the polyphenol removal percentage was 97% after 15 min electrolysis in the presence of the E1 anode. This value varied from 85 to 97% during a 15–60 min electrolysis window in the presence of the E2 anode. These results revealed that NaCl improved the performances of the E1 and E2 anodes toward the removal of COD, color, and polyphenols within relatively short electrolysis times. In the absence of NaCl, longer electrolysis times were needed to significantly remove the COD, color, and polyphenols. It is important to note that in the absence of NaCl, the greatest COD removal value was obtained in the presence of the E1 anode. The E2 anode afforded the best performance in the presence of NaCl. Figure 4.d shows that the pH increased with the electrolysis time, and the solution acquired a basic character, as the absence of NaCl (Fig. 3.d). The pH values were higher with the addition of NaCl and in the presence of the E2 anode. Similar behaviors have been observed in the electrochemical oxidation of organic matter in the presence of other DSA anodes, including Ti/RuO_2 [15], Ti/$(RuO_2)_{0.70}(Ta_2O_5)_{0.30}$, Ti/$Ru_{0.30}Ti_{0.70}O_2$, Ti/$Ru_{0.30}Sn_{0.70}O_2$, Ti/$Ru_{0.30}Pb_{0.70}O_2$, and Ti/$Ir_{0.30}Sn_{0.70}O_2$ [32], Ti/$Ru_{0.3}Ti_{0.7}O_2$ [33]. The effect of NaCl on the electrooxidation process has been discussed by Comninellis and Nerini [34]. The NaCl supporting electrolyte increases the rate of degradation of organic matter through an indirect oxidation mechanism involving active chlorine (hypochlorite), which is generated electrochemically. The electrochemical generation of hypochlorite/chlorine in a solution containing chloride ions proceeds according to the equations 6–8.

$$2Cl^- \rightarrow Cl_2 + 2e \qquad (6)$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \qquad (7)$$

$$HClO \rightarrow H^+ + ClO^- \qquad (8)$$

The hypochlorite ion is a powerful oxidizing agent and is referred to as “active chlorine” [35]. Pollutants are destroyed in the bulk solution through an oxidation reaction with this generated oxidant (Eq. 8). Given that the best COD removal performance was observed in the presence of NaCl and the E2 anode, therefore, the E2 anode (Ti/RuIrCo(40%:40%:20%)O_x) may have a greater capacity for producing hypochlorite ions (eq. 6–8). The indirect mechanism may be favored on the E2 anode (Ti/ RuIrCo(40%: 40%: 20%)O_x); therefore, the removal of COD may exceed that obtained in the presence of the E1 anode (Ti/RuO_2).

3.4. UV-Vis Spectroscopy

Figures 5.a–5.b show the UV-Vis spectra of paper industry wastewater subjected to electrochemical oxidation in the presence of the E1 and E2 anodes without (Fig. 5a) or with (Fig. 5b) the NaCl addition, under identical conditions (6 V cell potential and 60 min electrolysis time). For comparison purposes, Figs. 5.a and 5.b show the UV-Vis spectrum of raw paper industry wastewater. The UV-Vis spectrum of the raw wastewater displayed an absorption band between 250 and 300 nm associated with π-π electronic transitions in the aromatic organic compounds. In the absence of NaCl (Fig. 5a) the UV-Vis spectra of the wastewater after electrochemical oxidation treatment depended on the type of anode used. The E1 anode removed the absorption band between 250 and 300 nm, whereas the E2 anode reduced the intensity of the absorption band and slightly shifted the peak toward longer wavelengths. These results confirmed that without NaCl, the E1 anode was more effective in removing organic matter than the E2 anode under identical applied potentials and electrolysis times.

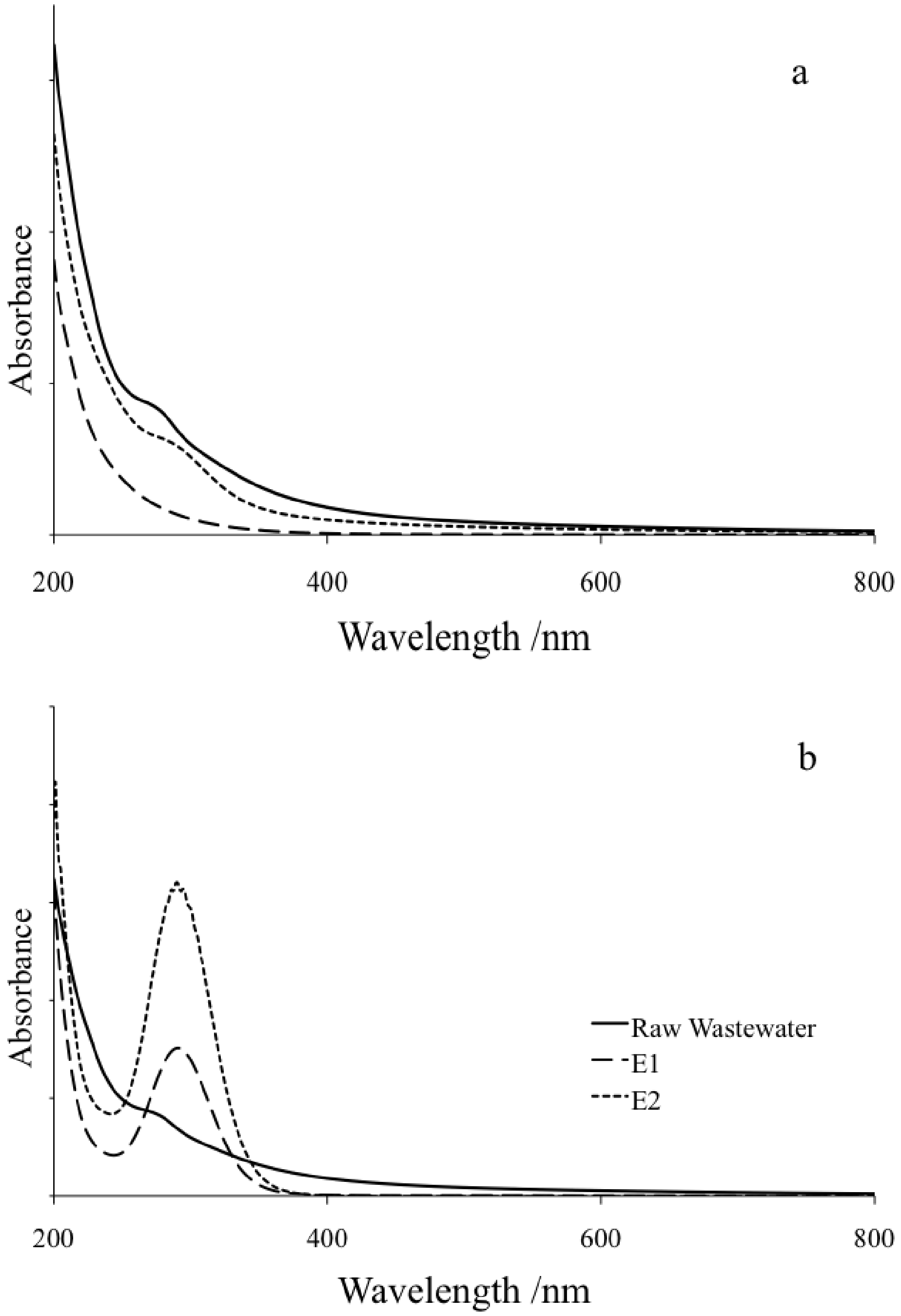

Figure 5. UV-Vis spectra of the paper industry wastewater after electrochemical oxidation at the E1 or E2 anodes. Anodes: E1 (Ti/RuO_2) and E2 (Ti/RuIrCo(40%:40%:20%)O_x). pH (initial) = 6.2, cell potential difference of 6 V. a) without NaCl, or b) with NaCl (5.0 g/L).

In the presence of NaCl, the UV-Vis spectra (Fig. 5b) were significantly different from those shown in Fig. 5a due to the presence of an intense peak at 290 nm, which developed and increased in intensity during the electrolysis process. The absorption peak at 290 nm was attributed to hypochlorite ions generated in situ as it was reported by Feng *et al.* [35]. They demonstrated that the identity of the active chlorine species in a solution depended fundamentally on the pH. At pH < 7, HClO predominated, whereas hypochlorite ions predominated at pH > 7. Our results suggest that the electrooxidation of contaminants at either anode, E1 or E2, proceeds via an indirect oxidation mechanism with the participation of hypochlorite ions. It is worth noting that the indirect oxidation mechanism is influenced by the properties of the electrode material, as evident in the performances of the anodes with respect to the removal of COD, color, and polyphenols via electrolysis, without or with the addition of NaCl (5 g/L). In the absence of NaCl, the best performance was obtained from the E1 anode. By contrast, in the presence of NaCl (5 g/L), the best performance was obtained from the E2 anode, in this case, the direct and indirect oxidation mechanisms occurred simultaneously during the electrooxidation process; therefore, an electrode material that promotes direct oxidation may not promote the indirect mechanism and vice versa, as observed here. Consequently, the electrode material is fundamental to the electrochemical oxidation process, as discussed by Comninellis *et al*. [22, 36].

The UV-Vis spectra shown in Fig. 5b reveal that under fixed oxidizing conditions, the absorption peak at 290 nm, assigned to hypochlorite ions, was more intense in the presence of the E2 anode compared to the E1 anode, suggesting that the E2 anode produced greater amounts of the hypochlorite ion that the E1 anode. This hypothesis explains the better performance observed at the E2 anode in the removal of COD.

The quality measures of the paper mill wastewater parameters before and after electrochemical oxidation treatment with the E1 and E2 anodes are listed in Table 2. These results highlight the effectiveness of the E1 and E2 anodes at 6 V, an initial pH of 6.2, and an electrolysis time of 120 min, in the absence or presence of NaCl (5.0 g/L). Mahes *et al.* [6] reported that the addition of sodium chloride may be necessary to increase the electrical conductivity of wastewater. High concentrations of chloride ions and salts in water can improved the performance and effectiveness of electrochemical processes and can decrease the energy consumption. In this study, the Ti/RuO_2 and Ti/RuIrCo(40%:40%:20%)Ox anodes performed well in promoting wastewater oxidation.

Table 2. Paper industry wastewater characteristics before and after of oxidation treatment with the E1 or E2 anodes, in the absence or presence of NaCl (5.0 g/L).

Parameters	Paper mill wastewater				
	Raw	After electrochemical treatment*			
		E1: Ti/RuO_2		E2: Ti/RuIrCo(40%;40%;20%)Ox	
		Without NaCl	NaCl (5 g/L)	Without NaCl	NaCl (5 g/L)
pH	6.2 (initial)	8.5	8.2	7.7	8.8
COD (mg L^{-1})	2585	1156	950	1647	501

Color (m^{-1})	101.5	2.3	1.5	21.8	1.2
Turbidity (NTU)	486	5	10	100	4
TDS ($mg\ L^{-1}$)	2.1	1.45	4.6	2.2	6.1
Chloride concentration ($mg\ L^{-1}$)	80	-	205	-	221
Total Polyphenols ($mg\ L^{-1}$)	48	2	1.2	9	1
Conductivity ($mS\ cm^{-1}$)	2.9	2.10	8.0	3.55	10.29

* Potential difference: 6 V; pH: 6.2; electrolysis time: 120 min.

4. CONCLUSIONS

The electrochemical oxidation of paper industry wastewater was studied using the dimensionally stable anodes E1 (Ti/RuO_2) and E2 (Ti/RuIrCo). Both anodes reduced the COD content, color, and polyphenol content; however, the removal capacity depended on the electrode material, the presence of NaCl as a supporting electrolyte, and the electrolysis time. In the absence of NaCl, the E1 anode provided the greatest reductions in COD, color, and polyphenols. The maximum COD removal values were 55% at the E1 anode and 36% at the E2 anode. The electrochemical oxidation process appeared to occur through a mechanism that was directly limited by the oxygen evolution reaction, which occurred simultaneously at the electrode. In the presence of NaCl (5.0 g/L), both anodes (E1 and E2) provided greater COD, color, and polyphenol removal at relatively short electrolysis times. In this case, the E2 anode performed best in COD removal (80%). Under these conditions, the electrochemical oxidation process appeared to occur through both mechanisms (direct and indirect); however, the indirect mechanism was favored by the E2 anode over the E1, which could explain the fact that a greater COD removal occurred in the presence of the E2 (Ti/RuIrCo (40%:40%:20%)O_x) anode.

ACKNOWLEDGEMENTS
The authors thank the Consejo Nacional de Ciencia y Tecnología México (CONACYT) for financial support [CB-2012-178166].

References

1. D. Pokhrel, T. Viraraghavan, *Sci. Total Environ.*, 333 (2004) 37
2. M. Ali and T. R. Sreekrishnan, *Advances in Environmental Research*, 5 (2001) 175
3. M. Xu, Q. Wang, Y. Hao, *J. Hazard. Maters*. 148 (2007) 103
4. J.Liang, S. Komarov, N. Hayashi, E. Kasai, *Ultrason. Sonochem.*, 14 (2007) 201–207
5. K.V. Rajeshwari, M. Balakrishnan, A. Kansal, K. Lata, V.V.N. Kishore, *Renew Sustain Energy Rev.*, 4 (2000) 135
6. S. Mahesh, B. Prasad, I. D. Mall, I. M. Mishra, *Ind. Eng. Chem. Res.*, 45 (2006) 2830
7. P. Malavyva and V. S. Rathore, *Bioresource Technol.*, 98 (2007) 3647
8. A.C. Rodrigues, M. Boroski, N. S. Shimada, J. C. Garcia, J. Nozaki and N. Hioka, *J. Photoch. Photobio A*, 194 (2008) 1
9. S. Khansorthong, M. Hunsom, *Chem. Eng. J.*, 151 (2009) 228
10. E.-S.Z. El-Ashtoukhy, N.K. Amin, O. Abdelwahab, *Chem. Eng. J.*, 146 (2009) 205
11. M. R. Assalin, E. dos Santos Almeida, N. Durán, *Int. J. Environ. Res. Public Health.*, 6 (2009) 1145

12. K. Eskelinen, H. Särkkä, T.A. Kurniawan, M.E.T. Sillanpää, *Desalination*, 255 (2010) 179
13. M. Gotsi, N. Kalogerakis, E. Psillakis, P. Samaras, D. Mantzavinos, *Water Res.*, 39 (2005) 4177
14. Carlos A. Martínez-Huitle and Sergio Ferro, *Chem. Soc. Rev*., 35 (2006) 1324
15. I. D. dos Santos, J.C. Afonso, A. J. B. Dutra, *J. Braz. Chem. Soc.*, 22 (2011) 875
16. Norazzizi Nordin, Siti Fathrita Mohd Amir, Riyanto, Mohamed Rozali Othman, *Int. J. Electrochem. Sci.*, 8 (2013) 11403
17. M. Ugurlu, M.H. Karaoglu, I. Kula, *Polish J. of Environ. Stud.*, 15 (2006) 647
18. R.T. Pelegrini, R. S. Freire, N. Duran, R. Bertazzoli, *Environ. Sci. Technol.*, 35 (2001) 2849
19. B.Wang, W. Kong, H. Ma, *J. Hazard Mater*., 146 (2007) 295
20. A.P. Buzzini, D.W. Miwa, A.J. Motheo, E.C. Pires, *Water Sci. Technol*., 54 (2006) 207
21. T. Zayas, M. Picazo, L. Salgado, *Journal of Water Resource and Protection*, 3 (2011) 32
22. M. Panizza in C. Comninellis and G. Chen (eds.), *Electrochemistry for the Environment*, Chap. 2, p. 25, Springer Science (2010)
23. Tiang Dian, Lin Xuan, Cui Xiong, Yan Qi, *Transactions of Nfsoc*, 6 (1996) 85
24. S. Kulandaisamy, J. Prabhakar Rethinaraj, S.C. Chockalingam, S. Visvanathan. K.V. Venkateswaran, P. Ramachandran, V. Nandakumar, *J. Appl. Electrochem.*, 27 (1997) 579
25. S. Trasatti, *Electrochim. Acta* 36 (1991) 225
26. J.D. Box, *Water Res*., 17 (1983) 511
27. J. F. C. Boodts, S. Trasatti, *J. Electrochem. Soc.*, 137 (1990) 3784
28. T.A.F. Lassali, L.O.S. Bulhões, L.M.C. Abeid, J.F.C. Boodts, *J. Electrochem. Soc.*, 144 (1997) 3348
29. C. Comninellis, *Electrochim. Acta*, 39 (1994) 1857
30. O. Simond, V. Schaller, Ch. Comninellis, *Electrochim. Acta*, 42 (1997) 2009
31. S. Ardizzone, S. Trasatti, *Adv. Colloid. Interf*., 64 (1996) 173
32. S.A. Neto, A.R. de Andrade, *Electrochim. Acta*, 54 (2009) 2039
33. Malpass G.R.P., Miwa D.W., Mortari D.A., Machado S.A.S., Motheo A.J., *Water Research*, 41 (2007) 2969
34. C. Comninellis and A. Nerini, *J. Appl. Electrochem*., 25 (1995) 23
35. Feng Y., Smith D. W. and Bolton J. R., *J. Environ. Eng. Sci.*, 6 (2007) 277
36. A. Kapałka, G. Fóti, C. Comninellis, *J. Appl. Electrochem*., 38 (2008) 7