

# Decolourisation of real textile waste using electrochemical techniques: Effect of electrode composition

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## Abstract

The present paper presents the study of the decolourisation of real textile effluent by constant current electrolysis in a flow-cell using a DSA<sup>®</sup> type material. The effect of using different anode materials (Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub>; Ti/Ir<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub>; Ti/Ru<sub>X</sub>Sn<sub>1-X</sub>O<sub>2</sub>, where X = 0.1, 0.2 or 0.3) on the efficiency of colour removal is discussed. Attempts to perform galvanostatic oxidation (40 and 60 mA cm<sup>-2</sup>) on the as-received effluent demonstrate that colour removal and total organic carbon (TOC) removal are limited. In this case the greatest degree of colour removal is achieved when anode containing 90% SnO<sub>2</sub> is used. If the conductivity of the effluent is increased by adding NaCl (0.1 mol L<sup>-1</sup>) appreciable colour/TOC removal is observed. The efficiencies of colour and TOC removal are discussed in terms of the energy per order ( $E_{EO}/\text{kWh m}^{-3} \text{order}^{-1}$ ) and energy consumption ( $E_C/\text{kWh kg}^{-1} \text{TOC}$ ), respectively. Finally, the extent of colour removal is compared to consent levels presented in the literature. © 2008 Elsevier B.V. All rights reserved.

**Keywords:** Decolourisation; Textile effluent; Electrochemical degradation

## 1. Introduction

It is well known that the textile industry produces large volumes of highly coloured waste and that the interruption of such waste into watercourses can interrupt many natural processes (e.g. photosynthesis; aerobic respiration [1]). In addition, the presence of highly coloured effluents in conventional water treatment stations is a considerable problem, limiting the effectiveness of traditional treatment methods. Industrial needs are continually being counterbalanced by the need to attend increasingly stringent legislation.

Various methods of colour removal have been presented in the literature, which are generally divided into chemical, physical and biological processes [2]. Biological processes are usually slower, require large storage areas and are not always totally efficient removing colour [1,2]. Physical and chemical methods are the most widely used, however, the former tends to result in the formation of solid waste that requires further treatment. Chemical processes are generally simpler in application and the

vast majority relies on the formation of a suitable oxidising agent (e.g. H<sub>2</sub>O<sub>2</sub>, •OH, O<sub>3</sub>). In such processes the main difference is the way in which the oxidising agent is generated, which can be by simple addition (e.g. hypochlorite addition) or by *in situ* generation methods (e.g. photochemical [3]; electrochemical [4,5]).

Obviously, from an electrochemical point of view the choice of electrode material is of fundamental importance. In this context, dimensionally stable anode (DSA<sup>®</sup>) materials have been widely studied for application in organic oxidation [6–8] and waste treatment systems [9]. DSA<sup>®</sup> materials are interesting for use in treatment systems as they present relatively long lifetimes and do not necessarily undergo the same poisoning phenomena associated with traditional electrode materials such as platinum. The most common DSA<sup>®</sup> material is the Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> anode, which has been extensively used in the chlor-alkali industry for a number of years [10].

When considering organic degradation, DSA<sup>®</sup> have been classified as ‘active’ or ‘non-active’, depending on its chemical nature [4,11]. Active electrodes mediate the oxidation of organic species via the formation of higher oxidation states oxides of the metal (MO<sub>X+1</sub>) whenever such higher oxidation state can be reached by the metal oxide (e.g. RuO<sub>2</sub> or IrO<sub>2</sub>)—leading to selective oxidation. Non-active electrodes present no higher

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oxidation state available and the organic species are directly oxidized by an adsorbed hydroxyl radical, generally resulting in complete combustion of the organic molecule (e.g.  $\text{SnO}_2$  or  $\text{PbO}_2$ ).

An important factor is the effluent's conductivity ( $\sigma$ /Coulombs), due to the fact that the greater the conductivity, the lower the ohmic-drop (resistance) across the electrochemical cell and the greater the efficiency of the process. Commonly, salts are added to the effluent in order to increase the conductivity and frequently  $\text{NaCl}$  ( $>3 \text{ gL}^{-1}$ , [12]) is used. The addition of chloride containing salts can be advantageous as highly oxidising species ( $\text{Cl}_2$ ,  $\text{ClO}^-$ ) are easily formed. On the other hand, there is concern that when simple chlorination is used to treat water containing organic material, highly toxic organic species can be formed. In recent studies it has been shown that chlorination of certain dyes can result in the formation of mutagenic compounds [13]. It is, however, interesting to note that when *in situ* generation of chlorine is employed such mutagenic species are not formed [14].

The aim of the current paper is the analysis of the effect of electrode material on the extent of colour removal of real waste originating from the textile industry. The waste was obtained from a textile factory, located in the state of São Paulo, in south-east Brazil. As the nature of the waste released from textile plants can vary from one day to the next, all assays in the current paper were carried out using a single batch of collected effluent. The extent of colour removal was evaluated by UV–vis spectroscopy, degree of total organic carbon removal and compliance with colour standards permitted by colour consents presented in the literatures [15,16].

## 2. Experimental

### 2.1. Solutions and reagents

The effluent was collected directly from the effluent-mixing tank, which received all the wastewater produced on the production line. Before reaching the mixing tank the effluent also received the addition of an anti-foaming agent. From the mixing tank the effluent is transferred to a biological treatment tank. After biological treatment the effluent is removed to the sewer. Due to commercial considerations the present authors were only permitted to obtain effluent samples from the *mixing tank*. For effluent characteristics see Section 3.

$\text{NaCl}$  (99%) was obtained from Malinkrodt and used without further purification.

### 2.2. Electrodes and reactor

A single-compartment filter-press cell (Fig. 1) was used with a DSA<sup>®</sup> type plate as the working electrode, which had a geometric area exposed to the solution of  $14 \text{ cm}^2$ , and a stainless steel cathode of the same area. The reactor was mounted by positioning the electrodes between Viton<sup>®</sup> and Teflon<sup>®</sup> spacers of varying thickness. A detailed description of the reactor has previously been presented in the literature [18]. Overall, the cell compartment containing the electrodes presented a volume of

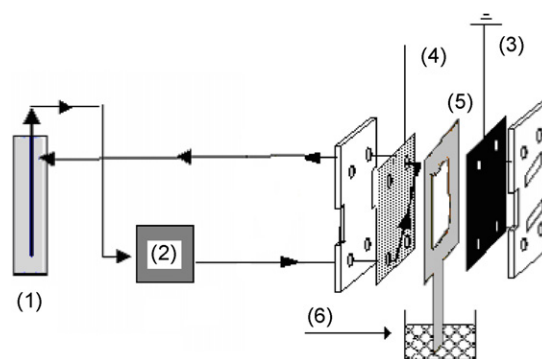


Fig. 1. Overall set-up of reactor and components: (1) electrolyte reservoir; (2) electric pump; (3) DSA<sup>®</sup>; (4) stainless-steel cathode; (5) membrane; (6) reference electrode.

$9 \text{ cm}^3$ . The electrolyte was passed through the cell by an electric pump at a flow velocity of  $425 \text{ cm}^3 \text{ min}^{-1}$ , ensuring that the electrolyte was refreshed within the cell approximately every 1.25 s.

The  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  electrode was obtained commercially from DeNora (Brazil). All the remaining electrodes were prepared by thermal decomposition of appropriate mixtures of precursor salts dissolved in 1:1 HCl (v/v) (as described in the literature [19]):  $0.2 \text{ mol L}^{-1} \text{ SnCl}_2 \cdot 2\text{H}_2\text{O}$  ( $\text{SnO}_2$ );  $0.2 \text{ mol L}^{-1} \text{ RuCl}_2 \cdot n\text{H}_2\text{O}$  ( $\text{RuO}_2$ );  $0.2 \text{ mol L}^{-1} \text{ TiCl}_4$  ( $\text{TiO}_2$ ) and  $0.2 \text{ mol L}^{-1} \text{ IrCl}_3$  ( $\text{IrO}_2$ ). After applying the salt mixture to a previously etched Ti plate, the mixture was heat treated at  $400^\circ\text{C}$  under a flow of  $\text{O}_2$  for 10 min. When, after various precursor additions, the desired mass was achieved, the electrode was treated at  $400^\circ\text{C}$  for a further hour.

A membrane (IONAC), which was open in the same manner as the spacers, was used not to separate the cell compartments but to provide an “*in situ*” probe connected to the reference electrode. The connection between the membrane walls, which was in contact with the working solution inside the cell, and the reference electrode was made by a membrane strip in contact with a bath of concentrated sulphuric acid (Fig. 2). All potentials were measured against the reversible hydrogen electrode (RHE).

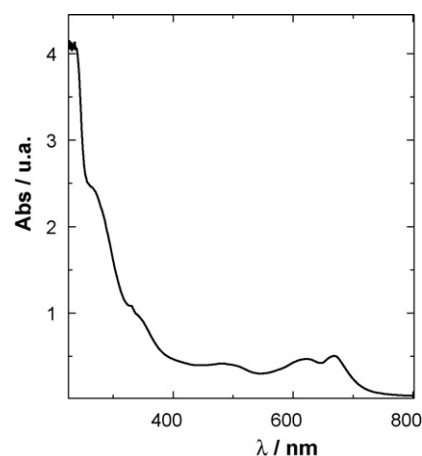


Fig. 2. UV–vis spectra of as-received effluent between 200 and 800 nm. Dilution 1:10.

All electrochemical measurements (cyclic voltammetry and galvanostatic electrolyses) were performed using a potentiostat/galvanostat (Autolab, model SPGSTAT30).

### 2.3. Analyses

The extent of colour removal was determined using UV–vis spectroscopy (path length 1 cm, apparatus: Varian Cary 5G) and monitoring the bands corresponding to the chromophores (490, 620 and 665 nm). Total organic carbon values were obtained using a TOC-V<sub>CPH</sub>, Shimadzu. Profiles of all these parameters were obtained by sampling solutions at predetermined time intervals during the degradation process.

### 2.4. Procedure

For each galvanostatic electrolysis 250 cm<sup>3</sup> of the effluent was transferred to the electrolyte reservoir. The appropriate current density was applied and aliquots (1 cm<sup>3</sup>) of the reaction mixture were removed, at predetermined intervals during the experiment, and submitted for analysis (TOC and UV–vis). Each experiment was performed for a time of 2 h.

### 2.5. Theoretical development

Guidelines presented by IUPAC indicate that the efficiency of an electrically driven oxidation process can be expressed according to the kinetic model that corresponds to the system under investigation [17]. Two specific figures of merit are presented:

1. The Electrical energy per unit mass ( $E_{EM}/\text{kWh kg}^{-1}$ ) is defined as the *electrical energy in kilowatt hours (kWh) required to bring about the degradation of a unit mass (1 kg) of a contaminant C in polluted water or air.*

For high organic concentrations, where the removal rate is phenomenologically *zero order* with respect to the substance [C] of interest:

$$E_{EM} = \frac{Pt1000}{VM(c_i - c_f)} \quad (1)$$

where  $P$ =rated power (kW),  $t$ =time (h),  $V$ =volume (L) treated,  $c_i$  and  $c_f$ =initial and final concentrations of [C] ( $\text{mol L}^{-1}$ ),  $M$ =molar mass ( $\text{g mol}^{-1}$ ). In the case of the substance of interest being the total organic carbon (TOC) content,  $M = 12 \text{ g mol}^{-1}$ . The factor of 1000 is used to convert grams to kilograms.

2. Electrical energy per order ( $E_{EO}/\text{kWh m}^{-3} \text{ order}^{-1}$ ) is defined as *electrical energy in kilowatt hours (kWh) required to bring about the degradation of a contaminant C by one order of magnitude in 1 m<sup>3</sup> (1000 L) of contaminated water or air.*

For low organic concentrations, where the removal rate is *first order* with respect to the substance [C] of interest, the  $E_{EO}$  is

given by:

$$E_{EO} = \frac{Pt1000}{V \log(c_i/c_f)} \quad (2)$$

In a recent study the present authors applied the both the  $E_{EO}$  and the  $E_C$  to the study of the electrochemical treatment of real effluent obtained from the textile industry [18]. In the present study the effluent obtained directly from the dye-house presented a high organic carbon concentration (typically  $225 \text{ mg L}^{-1}$ ), which tended to decrease with zero order kinetics and as result Eq. (1) is used to determine the electrical efficiency.

As in the previous study [18], the complex nature of the collected effluent meant that knowledge of the exact dye composition was not possible and as a result, the values needed for Eq. (1) for concentration ( $\text{mol dm}^{-3}$ ) were not obtainable for specific substances. However, measurements of the specific absorbance ( $\text{cm}^{-1}$ ) of the chromophore bands were possible. The chromophore bands were observed to decrease with first order dependence during treatment and as a result the absorbance is used in Eq. (5) instead of concentration. This should not be a problem as the expression  $\log(c_i/c_f)$  is dimensionless.

It should, however, be noted that the removal of colour is not necessarily a sufficient indication of the suitability of effluent to be discharged in to the sewer or water courses and other parameters need to be taken in to consideration. In the present study the extent of total organic carbon (TOC) removal and the associated energy consumption are also considered.

## 3. Results and discussion

### 3.1. Effluent characteristics

The as-received effluent presented the UV–vis spectrum (200–750 nm) given in Fig. 2. Bands can be observed at 490 (orange), 620 (blue–green) and 665 nm (blue–green) and consequently the effluent presented overall a blue–green colour. The pH of the as-received effluent was 6.9 and the total organic carbon (TOC) analysis of various samples of the collected effluent indicated an average carbon content of  $\sim 225 \text{ mg dm}^{-3}$ .

For an electrochemical reaction to proceed with efficiency, it is necessary that the reaction mixture presents relatively high conductivity. Usually a salt (e.g. NaCl, typically at values  $>3 \text{ g dm}^{-3}$  [12]) is added as a conducting component in electrochemical treatment systems. However, textile waste can contain large quantities of inorganic salts, which import conductivity to the effluent. From the point of view of reagent savings, it is interesting to study the degradation without the addition of further salts. The electrical conductivity of the as-received effluent (without addition of salts) was measured at  $2.1 \text{ mS cm}^{-1}$ . In the present study the effect of performing galvanostatic electrolyses in the absence (as-received effluent) and in the presence of NaCl ( $0.1 \text{ mol dm}^{-3}$ ) is discussed, considering also the nature of the electrode material.

### 3.2. Cyclic voltammetry

Cyclic voltammetry is a useful technique for probing the processes that occur at the electrode/solution interface [20]. The measurement of the current that results as the potential is varied can provide valuable insight into the reactions that occur at the electrode surface. In addition, it is widely accepted that cyclic voltammetry offers the most sensitive *in situ* characterisation of oxide materials [10]. In the case of the oxide electrodes used in this study, the voltammetric experiments were performed in the potential region where no permanent modification of the oxide surface occurs (0.4–1.4 V vs. RHE).

Fig. 3 presents the cyclic voltammograms of the Ti/Ru<sub>0.1</sub>Sn<sub>0.9</sub>O<sub>2</sub> electrode in solutions of effluent, with and without the addition of NaCl (1.0 g L<sup>-1</sup>). In the as-received effluent (curve 1), the Ti/Ru<sub>0.1</sub>Sn<sub>0.9</sub>O<sub>2</sub> electrode presents typical voltammetric behaviour, i.e. a broad, featureless region between 0.4 and 1.2 V followed by a rapid current increase at potential values >1.2 V, which corresponds to the onset of the oxygen evolution reaction (OER). The addition of NaCl (1.0 g dm<sup>-3</sup>, curve 2) to the effluent results in a decrease in the potential of the onset of the OER of approximately 50 mV (NaCl) and similar results are observed for the other electrodes studied. When NaCl is present in the reaction mixture, there is also the possibility that Cl<sub>2</sub> gas is formed at the anode. In this case, the current increase at potentials >1.2 V is also due to the chlorine evolution reaction (CER).

As a comparison, the voltammetric profile of the Ti/Ru<sub>0.1</sub>Sn<sub>0.9</sub>O<sub>2</sub> electrode was obtained in solution of NaCl (0.10 mol L<sup>-1</sup>) dissolved in deionised water, and is also presented in Fig. 3 and compared to the same concentration in the effluent. From Fig. 3 it can be observed that there is a much higher current in the pure electrolyte, indicating that, when the effluent is present, there is a considerable interaction between the components of the effluent and the electrode surface. This interaction probably inhibits both the Cl<sub>2</sub> and O<sub>2</sub> evolution reactions.

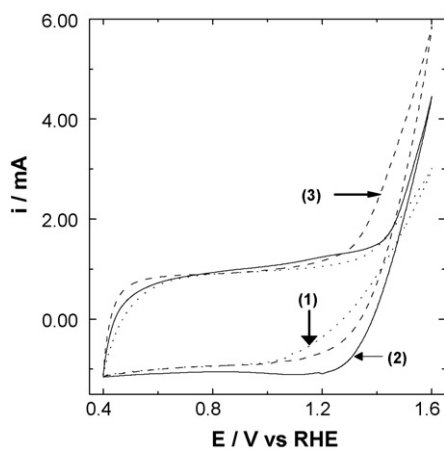


Fig. 3. Cyclic voltammogram of effluent with and without salt added: (curve 1) as-received effluent; (curve 2) effluent in 0.1 mol L<sup>-1</sup> NaCl; (curve 3) 0.1 mol L<sup>-1</sup> NaCl in distilled water. Sweep rate = 50 mV s<sup>-1</sup>.

### 3.3. Galvanostatic electrolyses of as-received effluent

The effect of electrode material on the extent of colour removal was studied by performing galvanostatic electrolyses (40 mA cm<sup>-2</sup>) for 2 h on the as-received effluent. The results were accompanied by UV–vis spectroscopy and TOC analyses. In Fig. 4a the UV–vis profile of the as-received effluent before and after electrolysis at SnO<sub>2</sub>-containing electrodes is presented and it can be seen that the rate of colour removal across the visible range (400–750 nm) is limited. Table 1 presents the extent of colour removal and it can be observed that it is greater when the Ti/Ru<sub>0.1</sub>Sn<sub>0.9</sub>O<sub>2</sub> anode is used. The greater activity of the Ti/Ru<sub>0.1</sub>Sn<sub>0.9</sub>O<sub>2</sub> is due to the activity of SnO<sub>2</sub> for organic oxidation [4] and this is borne out by Fig. 4b in which a clear dependence of the rate of colour removal on the SnO<sub>2</sub> content can be observed. The results presented in Fig. 4b indicate that the “non-active” nature of the SnO<sub>2</sub> promotes the more rapid removal of the colour content and it is also possible to note that the reduction of the SnO<sub>2</sub> content results in a decrease in the colour removal to levels observed for the Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> and Ti/Ir<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> anodes. However, as a whole, it can be observed that the extent of colour removal is incomplete when electrolysis at 40 mA cm<sup>-2</sup> is performed on the as-received effluent, independent of the electrode material.

The removal of colour follows pseudo-first order kinetics and this is shown in Fig. 5 (colour removal) and Fig. 5 inset (ln(C)/(C<sub>0</sub>)) for the Ti/Ir<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> electrode, using the peak at 690 nm as an illustrative example. As the removal of colour presents pseudo-first order dependence, the energy per order (E<sub>EO</sub>) can be applied (Table 1) [18]. From the values presented in Table 1, it can be observed that the E<sub>EO</sub> values are high when compared to those presented by Daneshvar et al. [21] when working with various acid dyes. It should be noted, however, that in the current study *real* effluent was studied, indicating the complex nature of correlation between simulated lab-scale and full-scale treatment systems. As the cell operating potential is

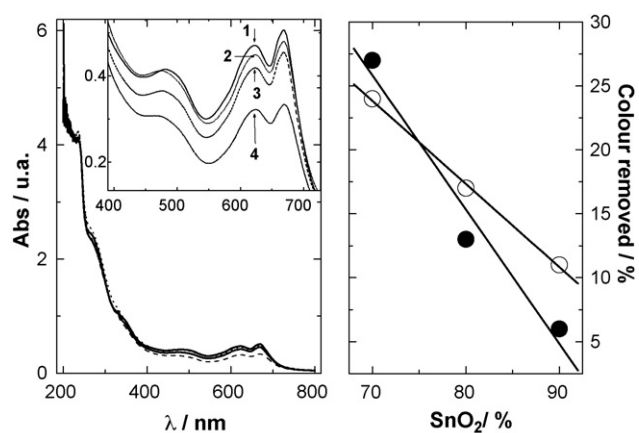


Fig. 4. (a) Effect of direct electrolysis at SnO<sub>2</sub>-containing electrodes (40 mA cm<sup>-2</sup>) on the UV–vis spectra (200–800 nm) of the as-received effluent. Dilution 1:10 (inset): expansion of visible region (400–750 nm). Curves (1) as-received effluent; (2) Ti/Ru<sub>0.3</sub>Sn<sub>0.7</sub>O<sub>2</sub>; (3) Ti/Ru<sub>0.2</sub>Sn<sub>0.8</sub>O<sub>2</sub>; (4) Ti/Ru<sub>0.1</sub>Sn<sub>0.9</sub>O<sub>2</sub>. (b) Effect of SnO<sub>2</sub> content on the removal of colour (690 nm) at different current densities: (●) 40 and (○) 60 mA cm<sup>-2</sup>.

Table 1  
Figures of merit associated with galvanostatic oxidation (40 or 60 mA cm<sup>-2</sup>) of the as-received effluent

Electrode	j/mA cm <sup>-2</sup>	E <sub>cell</sub> (V)	Energy per order		620		660		TOC removed	
			490		%		%		%	
			E <sub>EO</sub> (kW h m <sup>-3</sup> order <sup>-1</sup> )	%	E <sub>EO</sub> (kW h m <sup>-3</sup> order <sup>-1</sup> )	%	E <sub>EO</sub> (kW h m <sup>-3</sup> order <sup>-1</sup> )	%	E <sub>c</sub> (kW h kg <sup>-1</sup> )	TOC
Ti/Ru <sub>0.1</sub> Sn <sub>0.9</sub> O <sub>2</sub>	40	11.5	617	27	377	31	320	3.49	4926	
	60	14.5	874	23	858	25	780	2.97	7296	
Ti/Ru <sub>0.2</sub> Sn <sub>0.8</sub> O <sub>2</sub>	40	11.5	852	12	928	10	1069	3.73	4603	
	60	15.5	1204	22	941	21	1017	3.43	6744	
Ti/Ru <sub>0.3</sub> Sn <sub>0.7</sub> O <sub>2</sub>	40	12.5	2279	7	1777	6	1918	5.64	3312	
	60	14.5	1925	17	1204	16	1286	3.93	5515	
Ti/Ir <sub>0.3</sub> Ti <sub>0.7</sub> O <sub>2</sub>	40	12.3	1748	8	1522	8	1522	5.25	3502	
	60	15.5	1590	16	1376	17	1287	3.34	6936	
Ti/Ru <sub>0.3</sub> Ti <sub>0.7</sub> O <sub>2</sub>	40	13.0	1286	7	1769	7	1744	4.40	2950	
	60	16.0	971	23	947	21	1050	4.20	5700	

high (see Table 2), the  $E_{EO}$  values are also correspondingly high, which indicates that electrochemical oxidation of the as-received effluent is not economically efficient.

If the current density is increased to 60 mA cm<sup>-2</sup>, little or no increase in the extent of colour removal is observed and as the cell potential increases with increased current density, there is a concomitant increase in the  $E_{EO}$  values (Table 1).

The extent of organic removal is presented in Table 1. The quantity of TOC removed can be observed to vary from minimum of ~3.5% (Ti/Ru<sub>0.1</sub>Sn<sub>0.9</sub>O<sub>2</sub>) to a maximum of ~5.6% (Ti/Ru<sub>0.3</sub>Sn<sub>0.7</sub>O<sub>2</sub>) after 2 h of electrolysis at 40 mA cm<sup>-2</sup>.

Increasing the current density to 60 mA cm<sup>-2</sup> results in a decrease in the amount of TOC removed, with a maximum of 4.2% being removed for the Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> electrode. The energy consumption ( $E_c$ ) associated with the removal of the TOC content is presented in Table 1 for the different electrode compositions studied and it can be observed that the energy consumption is high in all cases ( $\geq 3000$  kW h kg<sup>-1</sup> at 40 mA cm<sup>-2</sup> and  $\geq 5500$  kW h kg<sup>-1</sup> at 60 mA cm<sup>-2</sup>), which again indicates the difficulty associated with treating real effluent solutions. The electrical current passed at the electrode ( $I_{total}$ ) is divided into current used to degrade the effluent ( $I_{degrade}$ ) and that used to form O<sub>2</sub> in the oxygen evolution reaction ( $I_{OER}$ ).

$$I_{total} = I_{degrade} + I_{OER} \quad (3)$$

As the current density is increased, the contribution of  $I_{OER}$  greatly increases, resulting in a decrease in the efficiency of degradation—as seen in Table 1.

### 3.4. Galvanostatic electrolyses of effluent with 0.1 mol dm<sup>-3</sup> NaCl

The galvanostatic electrolysis of the effluent with the addition of NaCl (0.1 mol dm<sup>-3</sup>) was performed at 40 mA cm<sup>-2</sup>. The

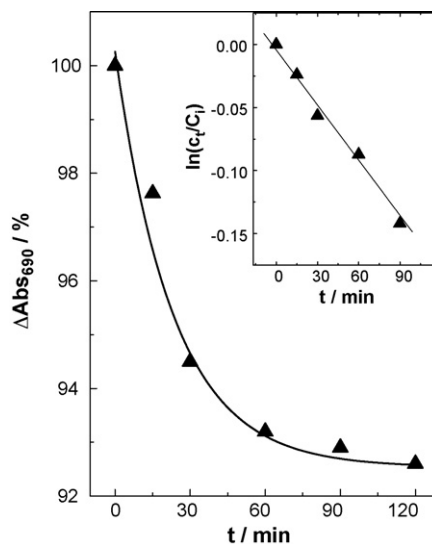


Fig. 5. Variation of absorbance at 690 nm during electrolysis at 40 mA cm<sup>-2</sup> of the as-received effluent at the Ti/Ir<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> electrode. Inset: first order plot of results presented in this figure:  $c_0$  and  $c_t$  represent initial concentration and concentration after a given time,  $t$ , respectively.

Table 2  
Figures of merit associated with galvanostatic oxidation (40 mA cm<sup>-2</sup>) of the as-received effluent +0.1 mol L<sup>-1</sup> NaCl

Electrode	E <sub>cell</sub> (V)	Energy per order		620		660		TOC removed	
		490		%		%		%	
		E <sub>EO</sub> (kW h m <sup>-3</sup> order <sup>-1</sup> )	%	E <sub>EO</sub> (kW h m <sup>-3</sup> order <sup>-1</sup> )	%	E <sub>EO</sub> (kW h m <sup>-3</sup> order <sup>-1</sup> )	%	E <sub>c</sub> (kW h kg <sup>-1</sup> )	TOC
Ti/Ru <sub>0.1</sub> Sn <sub>0.9</sub> O <sub>2</sub>	5.6	37	90	29	95	27	96	25.3	327
Ti/Ru <sub>0.2</sub> Sn <sub>0.8</sub> O <sub>2</sub>	5.2	34	91	30	93	28	94	26.8	287
Ti/Ru <sub>0.3</sub> Sn <sub>0.7</sub> O <sub>2</sub>	5.2	34	91	42	85	43	84	23.9	325
Ti/Ir <sub>0.3</sub> Ti <sub>0.7</sub> O <sub>2</sub>	5.9	58	79	48	85	45	87	25.1	352
Ti/Ru <sub>0.3</sub> Ti <sub>0.7</sub> O <sub>2</sub>	5.5	28	95	26	96	26	96	44.4	159

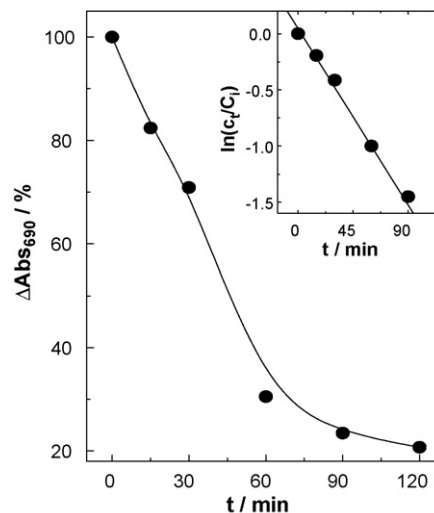


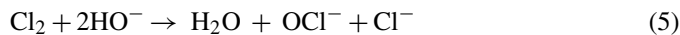
Fig. 6. Variation of absorbance at 690 nm during electrolysis at 40 mA cm<sup>-2</sup> of the effluent +0.1 mol L<sup>-1</sup> NaCl at the Ti/Ir<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> electrode. Inset: first order plot of results presented in main figure; A<sub>i</sub> and A<sub>t</sub> represent initial concentration and concentration after time, *t*, respectively.

conductivity of the electrolyte was observed to increase from 2.41 to 11.45 mS cm<sup>-1</sup> and this is reflected in the lower cell potential during electrolysis (Table 2).

Table 2 presents the effect on colour removal (in terms of % and E<sub>EO</sub>) of the electrode material and these values can be compared to those in Table 1. As observed during electrolysis of the as-received effluent, the removal of colour displays first order dependence, as illustrated for the Ti/Ir<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> in Fig. 6. Overall, the presence of NaCl aids the removal of both the colour and the TOC content, with levels of removal reached that are far greater than in the absence of NaCl. The reasons for the rapid removal of colour in the presence of NaCl are well known and are due to the electrochemical formation of chlorine gas (Cl<sub>2</sub>) at the anode [22]:



The subsequent reaction of Cl<sub>2</sub> with HO<sup>-</sup> formed at the cathode results in the formation of hypochlorite (ClO<sup>-</sup>):



Subsequently the oxidation of the dye is achieved [23]:



Colour removal for the SnO<sub>2</sub>-containing electrodes (90–95%) is similar to that observed for the TiRu<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> electrode under the same conditions (~95% Fig. 6). On the other hand, the Ti/Ir<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> electrode presents a lower level of removal (~85%) over the chromophore range, which is probably due to the different chlorine evolution kinetics at this electrode compared to the TiRu<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> [10].

The addition of NaCl results in a considerable increase in the extent of TOC removed during electrolysis. As can be observed in Table 2, the level of TOC reaches up to ~44% in the case of the Ti/Ru<sub>0.3</sub>Ti<sub>0.7</sub>O<sub>2</sub> electrode, which represents a ten-fold increase compared to direct electrolysis of the as-received effluent. For

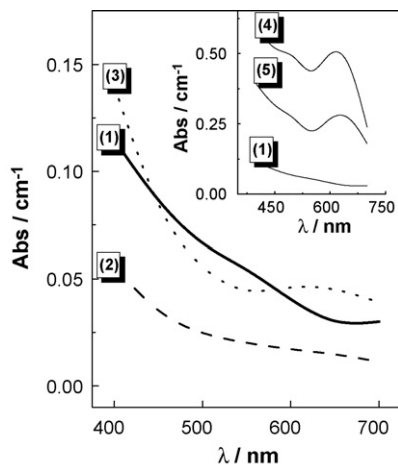


Fig. 7. Comparison of colour removal obtained in present study with colour consents presented in the literature [15]. (1) Colour consent; at  $40 \text{ mA cm}^{-2}$  in  $0.10 \text{ mol L}^{-1}$  NaCl for (2)  $\text{Ti/Ru}_{0.1}\text{Sn}_{0.9}\text{O}_2$ ; (3)  $\text{Ti/Ir}_{0.3}\text{Ti}_{0.7}\text{O}_2$ . Inset: as-received effluent: (4) before and (5) after electrolysis at  $60 \text{ mA cm}^{-2}$  at the  $\text{Ti/Ru}_{0.1}\text{Sn}_{0.9}\text{O}_2$  electrode.

the  $\text{SnO}_2$ -containing electrodes the extent of TOC removed remains practically constant in the region of 25%. This difference is probably due to the fact that the  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  electrode has been extensively used for the production of  $\text{Cl}_2$  [10] and as such is “designed” to optimize reaction 1—favouring the subsequent degradation pathways in reactions 2 and 3.

The energy consumption ( $E_c$ ) for TOC removal was calculated and is presented in Table 2. The  $\text{Ti/Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$  electrode operates at a cell voltage of 5.5 V, which is between 0.25 and 0.3 V greater than the  $\text{Ti/Ru}_{0.2}\text{Sn}_{0.8}\text{O}_2$  and  $\text{Ti/Ru}_{0.3}\text{Sn}_{0.7}\text{O}_2$  electrodes, but the overall energy expended per kg of organic material is approximately half that needed for the other electrodes.

### 3.5. Colour standards

The levels of colour permitted in effluent discharge may vary from place to place, depending on the concentration of industries producing highly coloured effluent along a given course of water. Fig. 7 presents typical colour consents (line 1), as presented [15,16] for discharge into receiving waters. The values in Fig. 7 are compared for some of the conditions employed in the present study. From Fig. 7 (inset) it can be observed that the original effluent (line 4) presents unacceptable colour levels and treatment of the as-received effluent at  $60 \text{ mA cm}^{-2}$  (line 5) have little effect. When NaCl is added (lines 2 and 3) it can be seen that for reduction in colour levels the nature of the electrode material is important in achieving the level required.

## 4. Conclusions

The present study demonstrates that total removal of the colour present in real textile effluent is possible when NaCl is added to the electrolyte and high current densities are employed. When the *as-received* effluent is treated without the addition of

NaCl both colour and TOC removal are limited. The best results in this case are obtained when the  $\text{Ti/Ru}_{0.1}\text{Sn}_{0.9}\text{O}_2$  electrode is used, probably due to the greater chance of the formation of highly oxidising hydroxyl radicals at this material.

The values of the energy per order ( $E_{EO}/\text{kWh m}^{-3} \text{ order}^{-1}$ ) for colour removal are considerably higher than those presented in the literature for pure dye solutions, reflecting the complex nature of the effluent studied.

The present study demonstrates the possibility of total colour removal from highly coloured effluents, depending on the type of electrode and the nature of the active species generated at the electrode surface.

The authors understand that although the removal of colour is important, it is not necessarily an indication that the effluent is fit to be released in to the sewer system. In this light our continuing studies concern the variation of toxicity before and after the treatment.

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