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ORIGINAL PAPER

Pt film electrodes prepared by the Pechini method for electrochemical decolourisation of Reactive Orange 16

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Abstract Electrochemical decolourisation of Reactive Orange 16 was carried out in an electrochemical flow-cell, using as working electrodes a Pt thin film deposited on a Ti substrate (Pt/Ti) prepared by the Pechini method and a pure platinum (Pt) foil. Using the Pt/Ti electrodes better results for dye decolourisation were obtained under milder conditions than those used for pure Pt. For the Pt electrode, colour removal of 93 % ($\lambda = 493$ nm) was obtained after 60 min, at 2.2 V vs. RHE, using 0.017 mol L^{-1} NaCl + 0.5 mol L^{-1} H_2SO_4 solution. For the Pt/Ti electrode there was better colour removal, 98%, than for the Pt electrode. Moreover, we used 0.017 mol L^{-1} NaCl solution and the applied potential was 1.8 V. Under this condition after 15 min of electrolysis, more than 80% of colour was removed. The rate reaction constant, assuming a first order reaction, was 0.024 min^{-1} and 0.069 min^{-1}, for Pt and Pt/Ti electrodes, respectively.

Keywords Electrochemical decolourisation · Reactive dye · Polymeric precursor method · Pt electrode

1 Introduction

Textile dyes can be classified by the way they are fixed to the textile fiber (e.g. direct, reactive, acid) or by their chemical structure (e.g. azo, anthraquinone, indigoide). In the textile industry, 60% of the dyes used are azo dyes, in which the –N=N– group is connected to an aromatic ring. Reactive dyes are widely used due to their relatively easy application in the dyeing process and stability during wear. The textile industry produces large quantities of wastewater during the washing and dyeing process that contain large quantities of dye that are not fixed on the fiber surface, and as a result are disposed together with the textile effluent [1]. The presence of dyes at a concentration of less than 1 ppm can cause considerable colouration in water courses, affecting their transparency, gas solubility and can present carcinogenic and mutagenic properties [2, 3]. There are a number of ways to treat textile effluents; they are generally based on physical, chemical and biological treatments [4–6], such as chemical oxidation by ozone [7], UV radiation [8], hydrogen peroxide [9], hypochlorite [10], Fenton's reagent [11], and activated sludge [12], amongst others.

Among the methods described above, electrochemical advanced oxidation process (EAOP) has important advantages. These include the possibility that oxidizing agents are electrochemically produced at the anode without the need, in many cases, to add further chemical substances [13, 14], making the method applicable for a large range of pollutants. The space required is less than that of other methods and in some cases it can replace biological treatment processes.

One important aspect of the electrochemical process is economic, which is related to the method used to prepare the electrodes. The use of noble metals (e.g. Pt) on a large scale is generally not feasible on account of their high cost. In this sense, the possibility of employing Pt thin-film electrodes deposited on an inert substrate (e.g. Ti) is attractive as the catalytic properties are comparable or even better than bulk Pt electrodes at a small fraction of

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the cost [15]. Our laboratory has wide experience in the manufacturing of electrodes prepared by the sol-gel or Pechini routes [16–19]. In previous papers, we have described the preparation of Pt thin films [15, 20] and $Pt_xRuO_{2(1-x)}$ [21] for the oxidation of small organic molecules with improved catalytic activity. In light of this, the present study aims, for the first time, to investigate the decolourisation of Reactive Orange 16 (RO16) using Pt/Ti electrodes and pure Pt.

2 Materials and methods

2.1 Electrode preparation

The electrodes were prepared using a 10 × 5 × 0.5 mm titanium plate as substrate (TiBrasil 99.7%). The substrates were treated by sandblasting followed by chemical etching in hot aqueous oxalic acid (10% w/w) for 30 min. After the etching, the substrates were washed with Milli-Q water and dried at 130 °C. The precursor solution was prepared by dissolving citric acid (SYNTH) in ethylene glycol (MERCK) at 60 °C. To this solution, $H_2PtCl_6 \cdot 7H_2O$ (ALDRICH) was added at 1:12:96 molar ratios (Pt:CA:EG) [15]. The precursor solution was painted onto the substrate (Ti) and then treated at 130 °C for 30 min to eliminate water and then at 300 °C for 10 min to eliminate the organic material, producing the metallic film. This procedure was repeated 3 times and after the third calcination, the sample was cooled at 5 °C min^{-1}. All materials were produced in static air atmosphere [15] and an electrode with a roughness factor [22] of 12.51 was obtained.

2.2 Electrochemical reactor

RO16 decolourisation was performed in an electrochemical flow-cell, as previously reported [23, 24]. The working electrodes (WE) were a Pt/Ti electrode or a Pt plate, both with a geometric area of 2 cm^2 exposed to the solution. A stainless steel plate of the same area was used as the counter electrode (CE). All potentials are referred to the reversible hydrogen electrode (RHE). An IONAC membrane (opened in the center) was introduced through the cell, to achieve electrical contact between the electrolyte solution and the reference electrode [24], but did not separate the cell. This membrane was immersed in a solution of 0.5 mol L^{-1} H_2SO_4 in which the RHE was placed. The distance between the CE and WE was controlled with Viton and Teflon spacers. The electrolyte flow through the cell was 1.24 L h^{-1} and the dye solution was pumped from the electrolyte reservoir through the cell using a peristaltic pump.

2.3 Electrochemical characterization

Voltammetric profiles of the electrodes were investigated to characterize the electrochemical processes occurring at the electrode/surface interface. All current densities are normalized by the electrochemical area calculated from the adsorption/desorption of hydrogen at the platinum surface in order to avoid area effects. Solutions of RO16 (35 mg L^{-1}) were prepared by dissolving the dye in aqueous solutions of 0.5 mol L^{-1} H_2SO_4 and 0.017 mol L^{-1} NaCl. Electrolyses were performed at two potentials, 1.8 and 2.2 V, and electrolyte samples were collected at different times during electrolysis (0, 15, 30, 45, and 60 min). All measurements were performed at 25 ± 2 °C.

2.4 UV-vis spectroscopy

The extent of colour removal was determined using UV-vis spectroscopy (Shimadzu Multispec 1501) by monitoring the band corresponding to the RO16 chromophore ($\lambda = 493$ nm).

3 Results and discussion

The first tests were carried out using only 0.5 mol L^{-1} H_2SO_4, blank solution, and the voltammetric results showed a typical electrochemical profile for a Pt electrode in this electrolyte, as shown in Fig. 1. The Pt/Ti electrode presented an anodic charge approximately three times

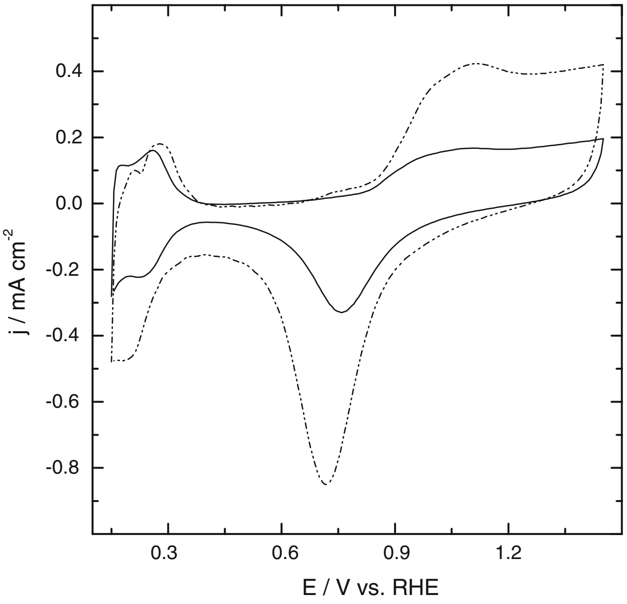

Fig. 1 Voltammetric profile of Pt/Ti and polycrystalline Pt electrodes, both in H_2SO_4 (0.5 mol L^{-1}) medium. (—) Pt and (·····) Pt/Ti electrodes. $v = 100$ mV s^{-1}

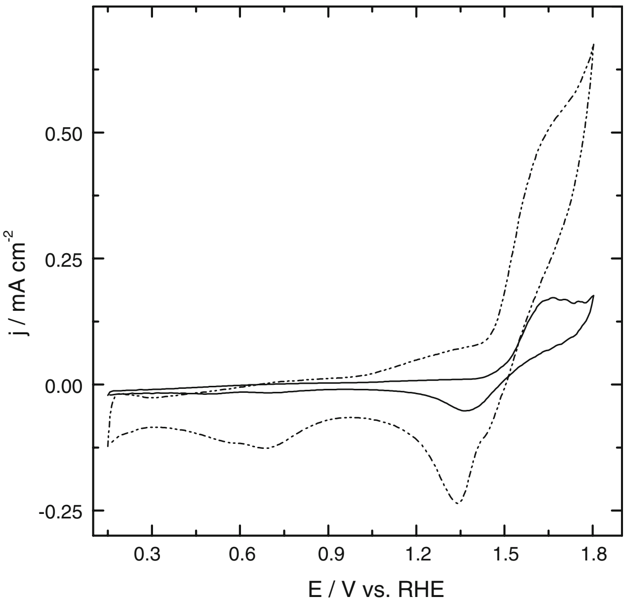

Fig. 2 Voltammetric profile using (·····) Pt/Ti electrode and (—) Pt electrode both in medium of $H_2SO_4 + NaCl + RO16$. $v = 100\ mV\ s^{-1}$

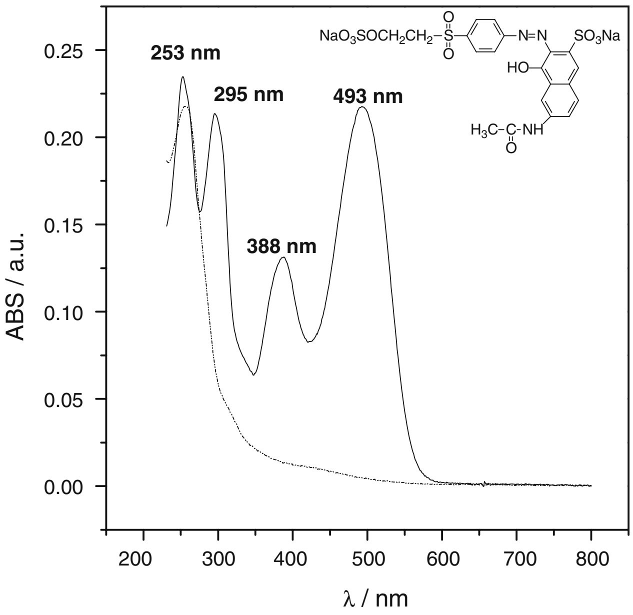

Fig. 3 Molecular structure of RO16 and UV-vis spectra (—) before and (·····) after 60 min of electrolysis (1.8 V), using NaCl (0.017 mol L^{-1})

greater than the polycrystalline Pt electrode. This result is explained by the pretreatment applied to the titanium plate, which includes sandblasting for cleaning and increasing the surface roughness [14] to promote platinum adhesion.

When Cl^- is present in the electrolyte, for the Pt/Ti electrode, in the region of 1.5 V, where Cl_2 production begins, the current is about 11 times greater when compared to the polycrystalline Pt electrode (Fig. 2).

In the electrochemical process, pollutants can be destroyed by direct and/or indirect oxidation processes. In the direct process the dye is adsorbed on the surface of the electrode and is destroyed by direct electron transfer [24]. In the indirect process decolourisation is achieved by in-situ production of strong oxidizing species such as chlorine/hypochlorite produced electrochemically on the electrode [24]:

$$\text{Anode:}\quad 2Cl^- \rightarrow Cl_2 + 2e^- \tag{1}$$

$$\text{Cathode:}\quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

$$\text{Solution:}\quad Cl_2 + 2OH^- \rightarrow H_2O + ClO^- + Cl^- \tag{3}$$

$$HOCl \leftrightarrow H^+ + OCl^- \tag{4}$$

$$\text{Dye} + OCl^- \rightarrow \text{intermediates} \rightarrow CO_2 + Cl^- + H_2O \tag{5}$$

With the use of these electrodes the contribution of direct process was small, making it necessary to add 0.017 mol L^{-1} NaCl, which promoted the electrochemical formation of chlorine/hypochlorite.

According to Feng [25], HOCl is a weak acid that has a conjugated base, OCl^-, which is strongly dependent on pH. Their pK_a is 7.5 at 25 °C, and the predominant form of free chlorine is HOCl, about 99% for pH > 5, and OCl^- is predominant for pH > 9. An interesting point is that the Pt/Ti electrode is effective in approximately neutral pH (pH = 6.8), while the polycrystalline Pt electrode is only effective at lower pH. At this pH, about 80% of the free chlorine is also HOCl, and the other 20% the OCl^- form.

Several peaks are observed in the spectrum at the beginning of the reaction as shown in Fig. 3. The peak observed in the UV region at 295 nm is due to the gamma acetylated acid structure [26], which is a precursor in RO16 synthesis, the peak observed at 254 nm is indicative of benzene rings [26], the peak 386 nm is probably associated to the azo group [26]. Finally, the peak at 493 nm [8, 26] is associated to the chromophore group and is used to accompany the extent of colour removal. After 60 min of electrolysis a significant decrease in the peak at 493 nm is observed, which is associated with the decolourisation process. At the end of the oxidation reaction, the spectrum shows a peak at 254 nm, probably due to benzene molecules, and this band originates from $\pi \rightarrow \pi^*$ transitions. As the time of decolourisation was 1 h it is expected that, using a long period of electrolysis, these compounds will be mineralized.

The Pt/Ti electrode promoted better colour removal when compared to the Pt electrode in all cases. An initial study with the bulk Pt electrode indicated that the maximum efficiency for colour removal is obtained in H_2SO_4 (0.5 mol L^{-1}, pH = 0.6) + NaCl (0.017 mol L^{-1}), whereas for the Pt/Ti the best result is observed in NaCl (0.017 mol L^{-1}, pH = 6.8). Under these conditions, the best result for bulk Pt in terms of colour removal was

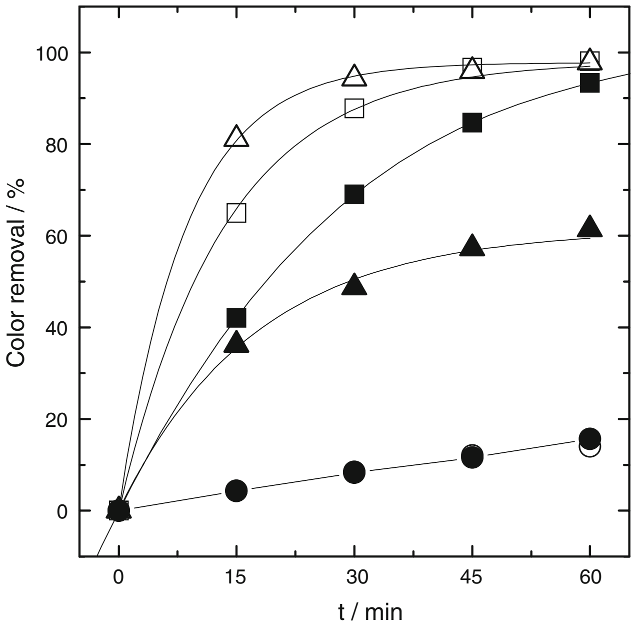

Fig. 4 Colour removal: (Δ) Pt/Ti in 0.017 mol L^{-1} NaCl at 1.8 V; (□) Pt/Ti in 0.017 mol L^{-1} NaCl at 2.2 V; (▲) Pt in 0.5 mol L^{-1} H_2SO_4 at 1.8 V; (■) Pt 2.2 V in 0.5 mol L^{-1} H_2SO_4; (○) Pt in 0.017 mol L^{-1} NaCl at 1.8 V; (●) Pt in 0.017 mol L^{-1} NaCl at 2.2 V

obtained at an applied potential of 2.2 V, while for the Pt/Ti electrode the best result was at 1.8 V.

In Fig. 4 the comparison between the colour removal using the polycrystalline Pt/Ti electrode in NaCl (0.017 mol L^{-1}) and the Pt electrode in H_2SO_4 (0.5 mol L^{-1}) + NaCl (0.017 mol L^{-1}) is presented. The Pt/Ti electrode also gave a greater rate of colour removal, removing 80% of colour in 15 min, while the Pt electrode removed only 40% in the same time period. It is also interesting to note that the extent of colour removal for the Pt electrode in NaCl (0.017 mol L^{-1}), without H_2SO_4 (0.5 mol L^{-1}), results in lower levels of removal (10–15%, Fig. 4) regardless of the applied potential.

It is important to stress that the best results for Pt/Ti electrodes were obtained at 1.8 V, comparing the initial stages of the reaction. This fact could indicate a change in the reaction mechanism, probably caused by adsorption of chemical species formed at 2.2 V or adsorption of Cl^-, showing a strong tendency to adsorb on metal surfaces.

For low organic concentrations, where the removal rate is phenomenologically first order with respect to the substance [C] of interest, the electrical energy per order (E_{EO}/kWh m^{-3} $order^{-1}$) is given by [24]:

$$E_{EO} = \frac{P \times t \times 1000}{V \times \log(C_i/C_f)} \quad (6)$$

E_{EO} is an important factor because it supplies the energy consumption associated to each process and permits comparison between electrodes within the same concentration range.

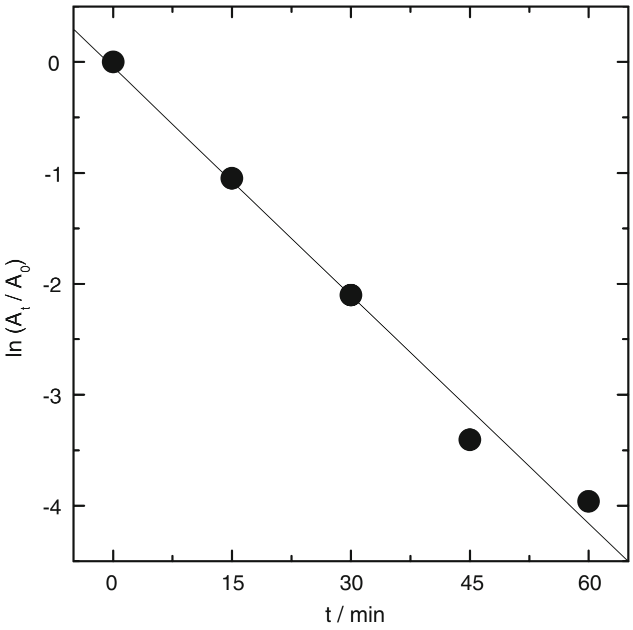

Fig. 5 Pseudo-first order plot for RO16 decolourisation using Pt/Ti electrode in 0.017 mol L^{-1} NaCl. A_0 and A_t denote absorbance at $t = 0$ and at time t during electrolysis, respectively

In Fig. 5 the change in the absorbance is presented as a function of time showing that the reaction under the conditions investigated is of first order. Using this data, it was possible to calculate the rate constant, *k*, and energy per order which are presented in Table 1.

As shown in Table 1, the energy per order for colour removal using the Pt/Ti electrode is approximately half that obtained using the Pt electrode, and the rate of colour removal is three times greater for Pt/Ti.

Electrolyses were carried out in the oxygen evolution region and by using these potentials anode poisoning is avoided, because poisoning species can be oxidized only at high anode potentials in the region of water discharge with simultaneous oxygen evolution, which allows regeneration of the anode surface during oxidation [27]. However, at high potentials, the side reactions of oxygen evolution may be more dominant, and energy consumption may increase [28].

Table 1 Parameters obtained after 60 min of the electrolysis of Reactive Orange 16 in 0.017 mol L^{-1} NaCl using Pt/Ti and polycrystalline Pt electrodes

Parameter	Pt	Pt/Ti
Colour removal (%)	93	98
k (min^{-1})	0.024	0.069
Energy by order (kW h m^{-3} $order^{-1}$)	1.06	0.49

4 Conclusions

The decolourisation of aqueous Reactive Orange 16 solution using a thin film of platinum deposited on a Ti substrate as working electrode was investigated. Three important aspects of these materials must be stressed: (1) the cost of the electrodes is a small fraction of a platinum electrode once the film thickness is about 7 micron, which leads to 15 mg of Pt per cm^2; (2) the electrochemical surface area can be easily controlled by the preparation conditions; (3) a significant enhancement in the reaction rate constant was observed. The Pt/Ti electrode gave better colour removal than the Pt electrode and, as a result, the applied potential required for colour removal was lower (1.8 V). In addition, in 15 min of electrolysis more than 80% of colour was removed using only 0.017 mol L^{-1} NaCl, without the need to add H_2SO_4 (0.5 mol L^{-1}). Considering the results presented the Pt/Ti electrode shows favourable characteristics for application in environmental electrochemistry.

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References

1. Kunz A, Peralta-Zamora P, de Moraes SG, Duran N (2002) Quim Nova 25(1):78
2. Carneiro PA, Osugi ME, Fugivara CS, Boralle N, Furlan M, Zanoni MVB (2005) Chemosphere 59(3):431
3. Meric S, Kaptan D, Olmez T (2004) Chemosphere 54(3):435
4. Isik M (2004) Enzyme Microb Technol 35(5):399
5. Libra JA, Borchert M, Vigelahn L, Storm T (2004) Chemosphere 56(2):167
6. Ong SA, Toorisaka E, Hirata M, Hano T (2005) Sep Purif Technol 42(3):297
7. Gutowska A, Kaluzna-Czaplinska J, Jozwiak WK (2007) Dyes Pigm 74(1):41
8. Bilgi S, Demir C (2005) Dyes Pigm 66(1):69
9. Baldrian P, Merhautova V, Gabriel J, Nerud F, Stopka P, Hruby M, Benes MJ (2006) Appl Catal B 66(3–4):258
10. Bredereck K, Schumacher C (1993) Dyes Pigm 21(1):45
11. Kusic H, Koprivanac N, Srsan L (2006) J Photochem Photobiol A 181(2–3):195
12. Arslan-Alaton W, Eremektar G, Babuna FG, Selcuk H, Orhon D (2004) Fresenius Environ Bull 13(10):1040
13. Kraft A, Stadelmann M, Blaschke M (2003) J Hazard Mater 103(3):247
14. Troster I, Fryda M, Herrmann D, Schafer L, Hanni W, Perret A, Blaschke M, Kraft A, Stadelmann M (2002) Diamond Relat Mater 11(3–6):640
15. Freitas RG, Oliveira RTS, Santos MC, Bulhoes LOS, Pereira EC (2006) Mater Lett 60(15):1906
16. Terezo AJ, Pereira EC (2000) Electrochim Acta 45(25–26):4351
17. Terezo AJ, Pereira EC (2002) Mater Lett 53(4–5):339
18. Villullas HM, Mattos-Costa FI, Bulhoes LOS (2003) J Electroanal Chem 545:89
19. Villullas HM, Mattos-Costa FI, Nascente PAP, Bulhoes LOS (2004) Electrochim Acta 49(22–23):3909
20. Freitas RG, Santos MC, Oliveira RTS, Bulhoes LOS, Pereira EC (2006) J Power Sourc 158(1):164
21. Freitas RG, Marchesi LF, Oliveira RTS, Mattos-Costa FI, Pereira EC, Bulhoes LOS, Santos MC (2007) J Power Sourc 171(2):373
22. Reiner A, Steiger B, Scherer GG, Wokaun A (2006) J Power Sourc 156(1):28
23. Malpass GRP, Motheo AJ (2001) J Appl Electrochem 31(12):1351
24. Malpass GRP, Miwa DW, Mortari DA, Machado SAS, Motheo AJ (2007) Wat Res 41(13):2969
25. Feng YG, Smith DW, Bolton JR (2007) J Environ Eng Sci 6(3):277
26. Catanho M, Malpass GRP, Motheo AJ (2006) Quim Nova 29(5):983
27. Comninellis C (1994) Electrochim Acta 39(11–12):1857
28. Bejankiwar R, Lalman JA, Seth R, Biswas N (2005) Water Res 39(19):4715