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ENVIRONMENTAL APPLICATION OF Ti/TiO$_2$ ANODES PREPARED BY DC-MAGNETRON SPUTTERING: DEGRADATION OF ACID ORANGE 7

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Abstract

Ti/TiO$_2$ films were prepared by DC reactive magnetron sputtering followed by annealing in air at 400 ºC for 4 h. Structural tests have been performed to characterize the films, showing that the prepared films present 70% of anatase phase. When these results are compared with those from TiO$_2$ films grown on glass substrates with similar deposition parameters, it can be seen that Ti substrates favour the formation of rutile phase, which is not observed on the films supported on glass, indicating that the film structure is strongly influenced by the substrate's nature. The electrocatalytic oxidation of acid orange 7 aqueous solutions, with concentrations between 5 and 50 mg L^{-1}, was performed using Ti/TiO$_2$ electrodes, at applied current densities of 0.1 and 0.25 mA cm^{-2}. COD removal increased with applied current density and acid orange 7 initial concentration. The current efficiency also increased with initial concentration, showing that the process was mainly controlled by diffusion.

Key words: acid orange 7, DC-magnetron sputtering, decolourization, electrodegradation, TiO$_2$

1. Introduction

Several studies have demonstrated that TiO$_2$ is one of the most important semiconductors materials for environmental applications, presenting a band gap energy of about 3.2 eV. TiO$_2$ has three polymorphic forms of crystal structure: brookite, anatase and rutile, being the catalytic activity dependent on the crystal structure, crystal size distribution, surface roughness, surface hydroxyl group density etc. (Sonawane et al., 2004). Depending on the preparation method, TiO$_2$ can be obtained in one or in simultaneous phases, being the anatase phase the most efficient for environmental applications. However, lately it has been reported several studies, which demonstrate positive photocatalytic results for anatase/rutile mixture comparatively to the pure anatase TiO$_2$. Factors contributing to the enlarged photocatalytic activity include high surface area, high adsorption affinity and lower recombination rate (Kanna and Wongnawa, 2008). Over the past years, heterogeneous semiconductor photocatalysis using TiO$_2$ has been extensively studied for water and wastewater treatment (Chatterjee and Dasgupta, 2005; Favier et al., 2016; Fujishima et al., 2000; Irmak et al., 2004; Kartal et al., 2017; Ramaswamy et al., 2008).

TiO$_2$ semiconductor can be prepared as powders, in a slurry form, or as supported films. This latter configuration is advantageous since it avoids the posterior need for the recovery of the powders from

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the suspension and allows the utilization of the prepared material in continuous-flow systems. Thus, recent research work is being focused on the immobilization of the photocatalytic material on a supporting substrate.

Several different techniques can be used to prepare TiO$_2$ films (Habibi and Talebian, 2007; Liu et al., 2006; Papoutsi et al., 1994; Perathoner et al., 2007; Siefering and Griffin, 1990; Zhang et al., 1992) such as sol-gel method or anodization, using a liquid phase that is evaporated, ion beam techniques, chemical vapour deposition and direct current (DC) or radio frequency (RF) magnetron sputtering. Among them, the sputtering method presents several advantages especially because the structure and properties of sputtered TiO$_2$ films can be modified by changing the total working pressure, sputtering power, substrate temperature, bias power and other deposition parameters (Takeda et al., 2001; Wang et al., 1998). Recently, nanostructured anatase phase TiO$_2$ films were prepared by DC reactive magnetron sputtering, and the influence of O$_2$ partial pressure on TiO$_2$ growth was assessed.

It was found that structural, morphological and optical properties of the TiO$_2$ films are deeply influenced by the oxygen partial pressure and the sputtering power utilized in the preparation of the films (Sério et al., 2011a, 2011b, 2012). For this reason, it is crucial to characterize their properties according to the deposition parameters. In this context, a study of the influence of the crystallinity and preferred orientation of growth on the catalytic properties of TiO$_2$ films, prepared by DC reactive magnetron sputtering, was performed. The photocatalytic activity of nanocrystalline TiO$_2$ films was tested on the decolourization of Rhodamine 6G (Rh6G) aqueous solutions (Barrocas et al., 2013). The highest photocatalytic activity was observed for the film with anatase crystal structure that presented an orientation of growth along the direction (101) and that possessed only a vestigial rutile phase.

On the other hand, TiO$_2$ immobilized in film form allows also its use in the field of environmental electrochemistry, as electrocatalyst, with or without photo assisted process, for the electrolysis of organic and inorganic pollutants, either as cathode or as anode, in the electroreduction or in the electrooxidation of those compounds (Babu et al., 2011; Chekin et al., 2013; Haizhang et al., 2007; Hou et al., 2009; Li et al., 2000; Liu et al., 2010; Milsom et al., 2007; Valdez et al., 2012; Wang et al., 2013).

The mechanism of the anodic oxidation of organic molecules is mediated by $^{\bullet}$OH and the degradation can take place via complete combustion or conversion of the organic compounds. In the latter case, if the resulting by-products are more biodegradable than the parent compounds, it may correspond to a successful process. Anyway, to employ the film as electrode it is important to have the film deposited on a conductive substrate. In this paper, it is presented a study of the performance of TiO$_2$ films on Ti substrate, prepared by DC reactive magnetron sputtering, in the degradation of a model azo dye, Acid Orange 7 (AO7), by electrocatalytic oxidation.

2. Material and methods

2.1. Preparation and characterization of the TiO$_2$ films

The TiO$_2$ films used as electrodes in the electrodegradation assays were deposited by DC reactive magnetron sputtering on titanium substrates (0.25 mm thick) at room temperature in a custom made system. The sputtering target was a titanium disc (Goodfellow, 99.99% purity), with 64.5 mm diameter and 4 mm thickness. Prior to deposition, Ti substrates were successively cleaned in a concerted sequence using a 9 M HCl aqueous solution and deionized water, being the duration of each step 5 min. Substrates were then dried with N$_2$ gas, to remove vestigial organic matter. Before introducing the gas mixture, the system was driven to a base pressure of 10^{-5} Pa by a turbomolecular pump. Pure Ar and O$_2$ (Air Liquide, both 99.99% purity) were utilized for the deposition, and their partial pressures were controlled separately by mass flow meters. Several preliminary tests were carried out using the same deposition parameters as described in detail elsewhere, in order to obtain TiO$_2$ films with anatase/rutile mixture (Sério et al., 2011a). The best results were obtained for a constant total pressure, P$_T$, during the deposition of 0.8 Pa and an oxygen partial pressure of 0.12 Pa (i.e., 15% of P$_T$). The sputtering power was maintained at 1000 W, during 80 min. Before the deposition of the TiO$_2$ films by sputtering, a movable shutter was placed between the target and the substrates and the distance between them was maintained constant at 100 mm. The target surface was pre-sputtered in Ar, for 5 min, for cleaning.

To improve the effective area, the TiO$_2$ films were deposited in both sides of the titanium substrates. In order to improve the crystalline growth of the sputtered films, they were annealed in a tubular furnace at 400 ºC for 4 h, in air atmosphere. The structural characterization of the films was carried out by X-ray diffraction (XRD) on a Philips Analytical PW 3050/60 X'Pert PRO (theta/2 theta) equipped with X'Celerator detector operating with monochromatized Cu Kα_{α} radiation in Bragg-Brentano geometry. Diffractograms were obtained by continuous scanning in a 2θ-range of 20º to 90º with a 2θ-step size of 0.02º and a scan step time of 20 s. The cell parameters were calculated by a least-square method, the Checkcell program, available online as freeware (http://www.ccp14.ac.uk/mirror/mirror.htm).

2.2. AO7 degradation assays

The TiO$_2$ films prepared by sputtering technique, followed by annealing (Ti/TiO$_2$), were used as anodes in the AO7 (Fig. 1) electrocatalytic oxidation. Titanium foils are often used as substrate for the preparation of anodes from metal oxides materials.
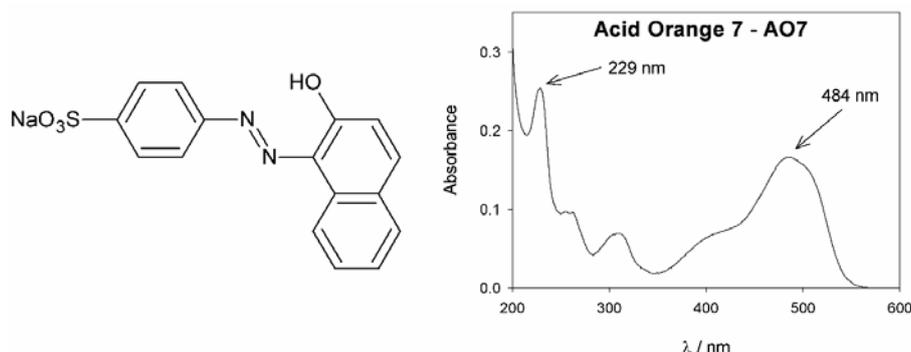
Fig. 1. Molecular structure and UV-Vis absorption spectrum of the azo dye AO7

However, during the anodic oxidation assays, particularly at high current densities, titanium oxidizes and forms an interlayer between the substrate and the metal oxide that drastically reduces the conductivity of the material, preventing its use as anode (Montilla et al., 2004a, 2004b; Zanta et al., 2003). In this work, it was tried to use this well-known problem as an advantage. Thus, Ti plates, without (Ti) and with (Ti(tt)) thermal treatment at 400 ºC, were also used as anodes in degradation assays, to test if the oxidation of the Ti foil during the anodic degradation assay can lead to significant AO7 electrocatalytic degradation rates.

For the electrocatalytic assays, a potenciostat/galvanostat VoltaLab PGZ 301 and a one-compartment three-electrode cell were used. The anodes, Ti, Ti(tt) and Ti/TiO$_2$ and the cathode, a stainless steel foil, had a geometric area of 20 cm^2. As reference electrode, an Ag/AgCl,KClsat was used. All the assays were performed at room temperature with stirring, being the processed solution volume 200 mL and the applied current densities 0.1 and 0.25 mA cm^{-2}. Low applied current densities were used in order to obtain higher current efficiencies, since the dye concentrations used were very low.

The degradation assays were performed using AO7 aqueous solutions with different initial dye concentrations, 5.0, 12.5 and 50.0 mgL^{-1}, and containing Na$_2$SO$_4$, 5 g L^{-1}, as background electrolyte. The reagents AO7, C$_{16}$H$_{11}$N$_2$NaO$_4$S (Aldrich, >85%), and Na$_2$SO$_4$ (Merck, 99.5%) were used as purchased, without further purification.

During the assays, samples were collected periodically and monitored by UV-Vis absorption spectrophotometry, in the range of 200-600 nm, using a Shimatzu UV-1800 spectrophotometer. Chemical oxygen demand (COD) determinations, using closed reflux and titrimetric method (Eaton et al., 2005), were also performed for the assays run with 12.5 and 50 mg L^{-1} AO7 initial concentration, and COD values of 19±1 and 75±2 mg L^{-1} were obtained, respectively, for the initial solutions. For the assays performed with AO7 initial concentration of 5 mgL^{-1}, COD determinations were not performed because the COD value for this solution is below the quantification limit of the method used. Prior to the degradation assays,

the AO7 solutions where left for one hour, with stirring, in the electrochemical cell completely assembled. UV-Vis spectra of the initial solutions and of the samples collected after one hour stirring were compared, in order to exclude removal of the dye from solution due to adsorption onto the different anodes' surface.

3. Results and discussions

3.1. Structural properties

Since the as-deposited films XRD analysis revealed amorphous nature, the samples were thermal annealed at 400 ºC in air during 4 h in order to allow TiO$_2$ crystallization. Similar behaviour was previously described for the TiO$_2$ films deposited by DC reactive magnetron sputtering, but on glass substrates (Sério et al., 2011a, 2011b, 2012). Fig. 2 shows the XRD pattern of the annealed TiO$_2$ film deposited on the titanium substrate. The XRD pattern analysis shows a mixture of anatase and rutile phases in TiO$_2$ film (beyond the typical peaks of the anatase phase, another peak at d = 3.25 Å appears, which corresponds to the (110) plane of rutile TiO$_2$ – rutile's most stable plane). The amount of anatase phase was evaluated from the integrated intensity of the XRD peaks using the (Eq. 1) (Cullity, 1978):

$$W_A = \frac{1}{1 + 1.265 \times I_R / I_A} \qquad (1)$$

where W_A is the mass fraction of anatase, I_A (101) and I_R (110) denotes the integrated main peak intensities of anatase and rutile, respectively.

The prepared films present a percentage of the anatase phase equal to 70, being this result very different from the one obtained in a previous study performed by Sério et al. (2011a). The main difference between the present work and the previous study is the use of a different substrate. In the case of the previous work, the substrates were glass slides and not titanium substrates, and the TiO$_2$ films deposited on glass substrates at P = 1000 W and with 15% O$_2$ (using the same deposition parameters) presented only the anatase phase with a preferential growth of the reflection (004) along the c axis (Sério et al., 2011a).
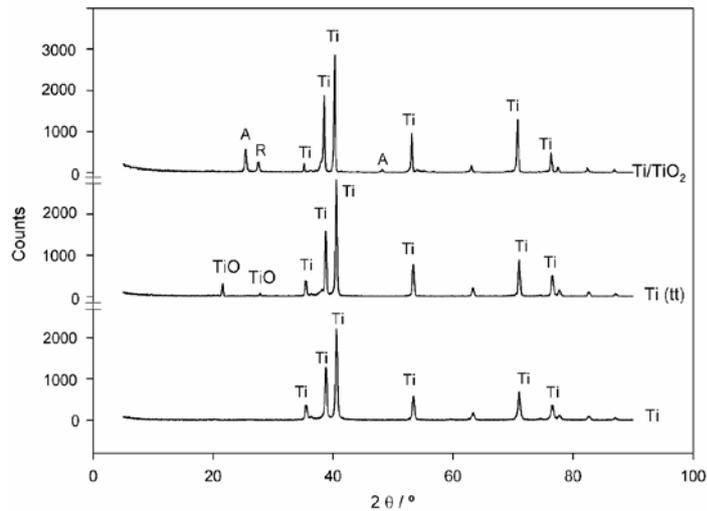
Fig. 2. XRD patterns of the different anode materials: Ti – titanium substrate; Ti(tt) - titanium substrate with thermal annealing at 400 ºC; Ti/TiO$_2$ – TiO$_2$ film prepared by DC reactive magnetron sputtering on titanium substrate annealed at 400 ºC (Peaks indexing: A – Anatase; R – Rutile; Ti – Titanium)

Comparing both studies, it can be concluded that Ti substrates seem to favour the formation of rutile phase and therefore the film structure is influenced by the substrate's nature. This study further shows that the substrate nature is a key factor during the film growth processes since it strongly influences the adatom mobility and therefore affects the growth mechanisms. In fact, it is well known that the film growth direction is highly affected by the surface morphology and roughness of the substrate that can also determine the appearance of just one phase or a mixture of phases. For example, some reports show that higher-quality anatase films grow better on (001) LaAlO$_3$ substrates than on (001) SrTiO$_3$ substrates, due to the improved lattice match (Kennedy and Stampe, 2003). Kitazawa et al. (2006) have observed a mixture of rutile and anatase when films deposition was on a-Al$_2$O$_3$ and pure anatase on LaAlO$_3$ substrate. These reports showed that, using the same deposition parameters, it is possible to obtain TiO$_2$ films with distinct preferential orientation of growth just due to the use of a different substrate. The observed peaks in Fig. 2 corresponding to anatase-TiO$_2$ phase could be indexed based on the single-phase anatase structure.

The cell parameters were refined by a least-square method and the obtained values, a=3.777 and c=9.518 Å (space group I_{41}/amd), agree well with those reported for anatase TiO$_2$ phase in the JCPDS ASTM no. 21-1272. The average grain size (D) was calculated from the anatase (101) and rutile (110) peaks at $2\theta = 25.3^o$ and 27.3^o, respectively, using Scherrer's Equation (Eq. 1) (Cullity, 1978). For the anatase phase, the D value was 49 nm and for rutile was 38 nm. Under the same conditions, the estimated grain size for anatase TiO$_2$ films on glass substrates was 64 nm (Sério et al., 2011a), which is higher than the one obtained in this work. This may be due to the inhibition of the grain growth as a result of the formation of phase boundaries between the nanocrystalline anatase and rutile phases, i.e., the presence of rutile phase blocks the growth of grains, resulting in a decrease in the average crystallite size for the anatase or rutile phases.

Fig. 3 shows SEM images of the TiO$_2$ films deposited over the Ti substrate by DC reactive magnetron sputtering and annealed at 400 ºC. The film presents a uniform coating with the outer layer still incomplete.
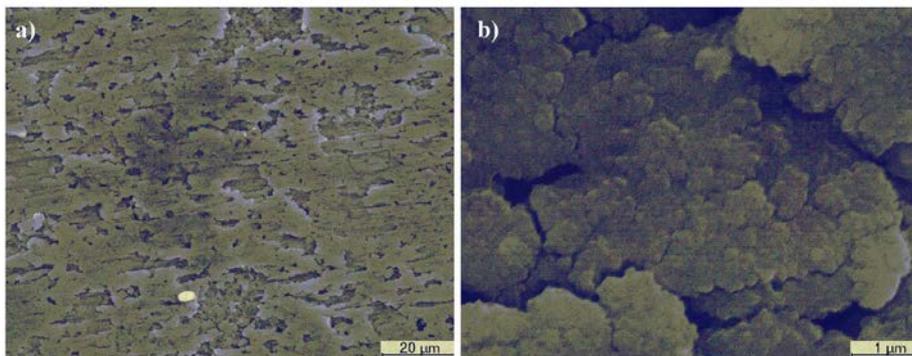

Fig. 3. SEM micrographs of the annealed Ti/TiO$_2$ films deposited by DC reactive magnetron sputtering on titanium substrates with different magnifications: a) x1000; b) x20000

The growth of the film seems parallel oriented, being the growth unit, granules lower than 1 μm in size. Analysing the SEM image with higher magnification it also can be observed agglomerates of grains or particulates distributed over the substrate surface with a 'blooming flower-like' appearance. Comparing these results with the ones presented by TiO₂ films prepared with the same experimental conditions, but on a glass substrate (Sério et al., 2011a), although it is also observed a surface with a 'blooming flower-like' appearance, there are other features in the films morphology namely the parallel oriented growth, revealing that the Ti substrate strongly influences the TiO₂ film's morphology as a consequence of its influence over the growth mechanism.

The qualitative estimation of the mechanic stability of the TiO₂ films was examined using a standard Scotch tape (STT, 3M, 600-1-18D) test, and it was found for all of them a strong adhesion strength of the TiO₂ films to the substrate.

3.2. Degradation assays

The influence of the anode material and of the current density on the degradation efficiency was studied with solutions containing 50 mg L^{-1} of AO7, using Ti, Ti(tt) and Ti/TiO₂ anodes, at applied current intensities of 0.1 and 0.25 mA cm^{-2}. The obtained results are presented in Fig. 4. In Fig. 4 a) to d), the ratios between the initial absorbance and the absorbance of the different samples collected during the assays are presented for 229 and 484 nm. These wavelengths are characteristic of AO7 molecule, being the former due to the aromatic rings and the later related to the azo bond. For the three anode materials tested, at both current densities, the decrease in absorbance is higher at 484 nm than at 229 nm, pointing to a degradation mechanism involving as first step the breaking of the azo bond, followed by the opening of the aromatic rings, by oxidation, with the consequent decrease in COD (Fig. 4 e and f).

For the lowest current density assayed, the highest absorbance decays were obtained with Ti(tt) anodes and the highest COD removals were obtained for the Ti/TiO₂ anodes, showing that at these experimental conditions this later anode is more effective in the oxidation of the products formed by the azo bond breaking, i.e., electrons are not preferentially used in breaking azo bonds but they simultaneously oxidize the intermediates formed. This higher oxidation efficiency promoted by the Ti/TiO₂ anodes is probably due to its catalytic properties, that maintain the reaction products adsorbed on the anode's surface, i.e., in the electrochemical reaction zone, promoting the conversion into more oxidized products.

Another factor that may contribute to this high oxidation efficiency is the low dye concentration that increases the importance of the diffusion step of the dye molecules to the electrode's surface, thus

increasing the probability for the complete degradation of the already adsorbed molecules. Similar behaviour was observed for the highest applied current density, although UV-Vis absorption spectra results for Ti(tt) and Ti/TiO₂ anodes were coincident. This match in the absorbance results, at both wavelengths, and the decrease in the difference of the COD removal results, must be related with the increasing control by the diffusion step, because AO7 molecules arrive at the reaction zone with similar flux for both current densities. Since AO7 concentration is equal, but the flux of electrons available for the oxidation reaction is higher at higher current densities, leading to a more efficient oxidation, the importance of the catalytic effect is reduced. Although with the increase in current density the diffusion step becomes more significant, the process at both current densities seems current controlled, since an increase in the current density clearly promotes an increase in the degradation rate. The poorest degradation results were presented by Ti anode, which was already expected. However, the behaviour of the material seemed to improve with time, mainly the COD removal rate, particularly for the highest current density applied, which may be related with some degree of oxidation that Ti was acquiring during the oxidation assay.

An AO7 electrocatalytic degradation study was performed by Hou et al. (2009) at a TiO₂ anode prepared by immobilizing TiO₂ film onto activated carbon fibers, to obtain a 3D TiO₂/ACF, and the results were compared with those from a Ti/TiO₂ 2D films. These authors had observed higher decreases in absorbance with time than those presented in this study. However, comparison is difficult, since in that study the applied charge is given as potential bias and not in current density.

The influence of the AO7 concentration and of the current density was studied using the Ti/TiO₂ anode, at two different applied current densities and with three different initial AO7 concentrations. The obtained results are presented in Fig. 5. The absorbance decays, at both wavelengths under observation, increased with current density, being higher for the values at 484 nm, for the reasons already pointed out. Concerning the influence of the initial concentration, although the relative decays in absorbance were similar, the absolute decays clearly increased with initial AO7 concentration (see insets of parts a to d of Fig. 5), showing the importance of the molecules diffusion for the lower concentrations. The COD removal (Fig. 5e) followed a similar trend that was even more obvious for the highest applied current density, i.e., when the current control was lower and the diffusion component became more important. The assay performed with 50 mg L^{-1} AO7 initial concentration at 0.1 mA cm^{-2} presented a very low COD removal rate after 3 h assay. This abnormal behaviour can be due to the polarization of the electrode's surface by some polymeric substances that were formed at very low applied potential and relative high organics concentration, which must be the case.
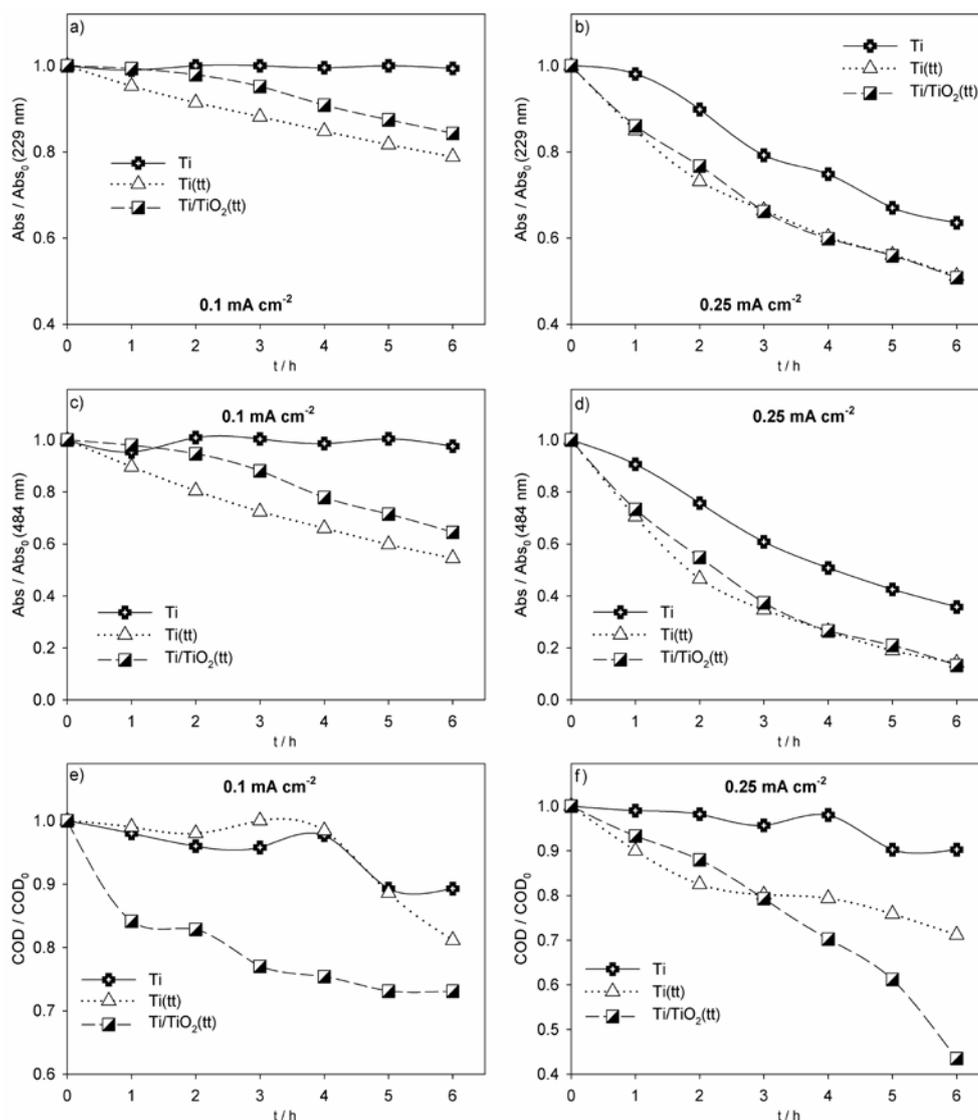
Fig. 4. Variation in time of relative absorbance removal, measured at two different wavelengths (a to d), and relative COD removal (e and f) for the electrodegradation assays of 50 mg L^{-1} AO7 solutions, performed at two different current densities (0.1 mA cm^{-2} – a, c and e; 0.25 mA cm^{-2} – b, d and f), using three different anode materials: Ti, Ti(tt) and Ti/TiO$_2$ Background electrolyte – 5 g L^{-1} sodium sulfate aqueous solutions

COD absolute removal is plotted against the charge passed for the different assays in Fig. 5f. For equal applied current density the current efficiency increases with AO7 initial concentration and for equal AO7 initial concentration the current efficiency increases with the decrease in current intensity, for charges up to 500 C.

4. Conclusions

Ti/TiO$_2$ films were prepared by DC reactive magnetron sputtering on titanium substrate, followed by annealing in air at 400 °C for 4 h to form the anatase/rutile mixture. The use of titanium substrate instead of glass for the deposition of TiO$_2$ led to the formation of rutile phase, showing that the film structure is influenced by the substrate's nature. The electrocatalytic behaviour of the Ti/TiO$_2$ electrode in

the degradation of AO7 was compared with that of a titanium foil and a titanium foil annealed at 400 °C. This latter material presented in the XRD pattern two peaks assigned to TiO.

When comparison is possible (i.e., assays run with identical experimental conditions), the best COD removals were attained with the Ti/TiO$_2$ anode. There was also some improvement in the results obtained with Ti(tt) when compared to those from the titanium foil anode that must be due to the TiO formed during the annealing.

In general, for the tested materials, the removal of COD increased with current density and with AO7 initial concentration. The electrical charge efficiency also increased with AO7 initial concentration, showing that for the applied current densities and AO7 initial concentrations used, the process was mainly controlled by the diffusion of the dye molecules towards the reaction zone.
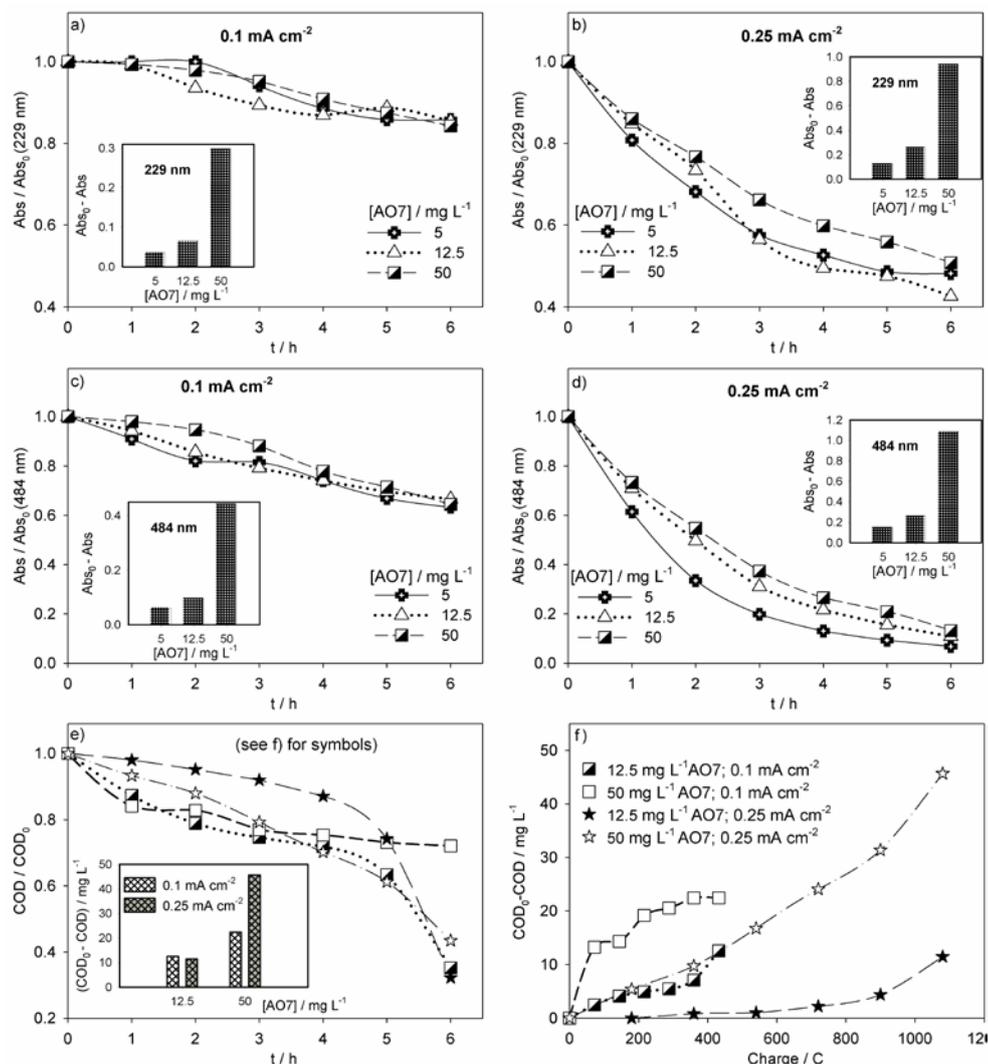
Fig. 5. Variation in time of relative absorbance removal, measured at two different wavelengths (a to d) and of relative COD removal (e) and variation of absolute COD removal with applied charge (f) for the electrodegradation assays of AO7 solutions, performed at two different current densities (0.1 mA cm^{-2}: a, c, e and f; 0.25 mA cm^{-2}: b, d, e and f), with three different AO7 concentrations (5, 12.5 and 50 mg L^{-1}), using Ti/TiO$_2$ as anode material and 5 g L^{-1} sodium sulfate aqueous solutions as background electrolyte. Insets: Absolute removals of Abs (a,b – 229 nm; c,d – 484 nm) and COD (e) for the assays whose results are presented in the main respective graphics

Although the Ti/TiO$_2$ films showed to be electrochemical and mechanically stable in the experimental conditions tested and effective in the degradation of the azo dye AO7, they did not allow the use of higher current densities, needed in the case of polluted samples with higher COD content. Thus, to improve the mechanical and electrochemical stabilities at higher current densities, new investigation has to be performed, namely to improve the adherence of TiO$_2$ sputtered film on the titanium substrate.

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