# Bubble annular photoeletrocatalytic reactor with TiO$_2$ nanotubes arrays applied in the textile wastewater

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## ABSTRACT

This study proposed a simple and effective annular bubble photoreactor using an array of TiO$_2$ nanotubes (NTs) prepared in situ by an anodisation process and used as photoanodes. The method is based on photoelectrocatalytic oxidation of the industrial textile wastewater (pH 7.83; conductivity 9.96 mS cm$^{-1}$; total dissolved solids 4.97 ppt; turbidity 0.04 NTU; colour 1146 mg/Pt; total organic carbon 5680 ppm and inorganic carbon 408.1 ppm) operating as follows: original pH of the effluent corrected to 2; current density of 9 mA cm$^{-2}$, commercial Hg high press lamp (250 W) irradiating at UV and visible region, and air bubble stirring of 700 mL min$^{-1}$. Using these optimised conditions, it was possible to obtain 90% colour removal (initial = 1.146 mg Pt), 66% COD reduction (initial = 5680 ppm) and 70% TOC removal after 3 h of treatment, reaching acceptable physicochemical properties for discharge.

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## Introduction

Discharged wastewater by some industries under uncontrolled and unsuitable conditions is causing significant environmental problems. The importance of pollution control and treatment is undoubtedly a key factor in the future. From an environmental overview, the treatment of textile industrial waste is a major problem in the textile sector. The textile industry and laundries consume large quantities of water; to dye 1 kg of cotton, 200 L of water is usually necessary, and large volumes of wastewater from different steps in the dyeing and finishing processes are produced [1]. Wastewater from printing and dyeing units is often rich in colour, and high diversity of chemicals, since the dyes include various compounds with different functional groups with a wide range in reactivity, solubility, volatility, stability, etc. [1]. In addition, the difficulty is increased due to the routine use of additives in the steps of assembling and fixing the dye to the fibre, such as wetting agents, antifoams, electrolytes, dispersing agents, pH adjusters, normalising agents, metal sequestrants and others [1]. Usually, these processes produce an effluent with high organic charge, high COD and BOD concentration, as well as many more hard-degradation and toxic/mutagenic materials [2,3]. This effluent can also contain particulate matter and sediments, oil and grease that cause the depletion of dissolved oxygen, which has an adverse effect on the aquatic ecological system. All of these problems result in greater difficulty treating dyeing wastewater [1], which can have a serious impact on natural water bodies and land in the surrounding area, as well on human health, if the discharge is irregular [3].

Nowadays, much more specific processes for water and wastewater treatments are required to meet severe regulatory standards regarding water quality, in particular with reference to the removal of refractory organic compounds, such as dyes, aromatics, pesticides, solvents, EDCs (endocrine disrupting chemicals) and PPCPs (pharmaceuticals and personal care products).

Among the emerging technologies for wastewater treatment, the advanced oxidation processes (AOP) has gained extraordinary attention [4–8]. They are a broad set of chemical oxidation treatments joined by the use of transient radical species, such as hydroxyl radicals (OH$^{\bullet}$) [9]. These species have high reactivity and non-selective action towards organic compounds, which are transformed in lower molecular weight intermediates, until their complete mineralisation to CO$_2$ and minerals [9–13].

In recent years, the possibility of integrating heterogeneous photocatalysis with electrochemical processes, in order to exploit their synergistic action, has been outlined. The benefit of coupling those processes is in the reduction of photogenerated electron-holes recombination, which is one of the main drawbacks of this process [14,15]. Furthermore, recent improvements in nano-technologies have allowed the production of nanostructured

forms of low costs [16]. In particular, the application of $TiO_2$ as photoanode in heterogeneous photoelectrocatalysis has generated considerable interest [17,18]. The process is based on the hydroxyl radical generation due to the photoinduced reactivity of $TiO_2$ nanotubes that promotes water oxidation under UV irradiation ($\lambda \leq 380$ nm) [14,15]

In our previous studies, we fabricated various $TiO_2$ nanotubes on titanium substrates with anodisation technology for the purposes of using photoelectrodes for the degradation of many types of organic pollutants, such as aromatic amines [19,20] and several dyes (textile and cosmetics dyes) [21,22] for use in water treatments. Nevertheless, application of the photoelectrocatalytic oxidation process for the treatment of effluent from wastewater is rare [23].

Hence, the present work focuses on the improvement of the reaction performance of $TiO_2$ nanotubes as photoanodes in the treatment of real textile effluent by coupling the photoelectrochemical process (PEC) using an annular bubble photoreactor. The discolouration and total organic carbon (TOC) removal were evaluated in order to assess the effectiveness of the proposed method.

## Experimental

### Preparation of $TiO_2$ electrode

Titanium samples (0.25 mm thick, 99.7% purity, from Sigma–Aldrich) with a geometric area of 56 $cm^2$ were degreased by successively sonication for 15 min in isopropanol, acetone and finally deionized water (DI), and then dried in an $N_2$ stream. Electrochemical anodisation of titanium was carried out by potentiostatic anodisation using a DC power supply (Minipa MPL-1303) in a two-electrode electrochemical cell using a ruthenium sheet as a counter-electrode. The interval between the working electrode and counter electrode was about 2 cm. The $TiO_2$ nanotube array was formed by anodising the Ti foil in organic electrolyte, which showed a dependence on the anodisation time. The present organic electrolyte was 0.25% ammonium fluoride (97.0%, Fisher) in glycerol (98.5%, Fisher) containing 10% volume Milli-Q water. The grown porous layers were annealed at 450 °C for 30 min in a furnace (model 650-14 Isotemp Programmable Muffle Furnace, Fisher Scientific) and were allowed to cool gradually back to ambient conditions. Bare $TiO_2$ NTs were tested to compare the efficiency and performance of decolourisation of wastewater.

The characterisations of $TiO_2$ NTs were studied and all of the results are reported by previously published references [19,20].

### Textile effluent

Textile effluent was collected from a textile factory (São Paulo, Brazil). It referred to the original disposal from the textile furnishing and finishing process and was collected after all steps involved in the production of jeans had been completed. The effluent sample was stored at 4 °C and used without any further treatment. Its physicochemical properties were: pH 7.83; conductivity 9.96 mS $cm^{-1}$; total dissolved solids 4.97 ppt; turbidity 0.04 NTU; colour 1146 mg/Pt; and total organic carbon 5680 ppm and inorganic carbon 408.1 ppm.

### NTs Photoelectrochemical bubble reactor

The 4 L photoelectrocatalytic bubble column reactor, which was specifically designed for operation with strongly, absorbing solutions such as textile effluent, was constructed from PVC pipe (Fig. 1). An excellent mass transfer can be achieved in this reactor by gas-sparging with small bubbles generated by passing gas
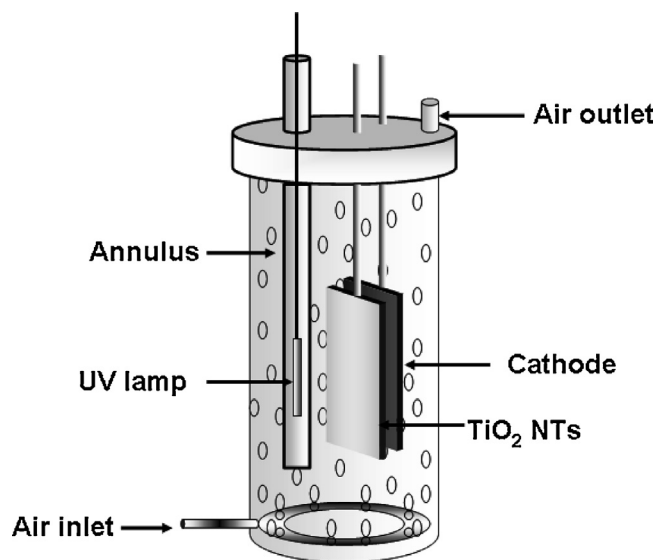


**Fig. 1.** Representative scheme of an annular bubble photoelectroreactor used in the wastewater decolourisation.

through a silicon hose with a hole of 1 mm and a 1 cm space between each hole distributor at its base. The reactor was used in 2-electrode mode, with all currents quoted with respect to the counter electrode. The $TiO_2$ NTs arrays worked as an anode and a ruthenium sheet of same area as a cathode. This system was connected in a power supply and a specific current was applied under these components. To compare the efficiency of this bubble reactor, the silicone hose was removed of the bottom and changed by a magnetic stirrer. The space between each electrode was configured to keep exactly in the same position and neither silicon hose nor magnetic stirrer was able to disrupt the system.

The light sources were 125 W and 250 W Hg high pressure lamps positioned inside a quartz tube and inserted in the middle of a photoelectroreactor, as shown in Fig. 1.

### PEC experiments under artificial UV light

Here, 125 and 250 W mercury lamps (Philips, with a maximum wavelength of 365 nm) were placed about 3 cm away from and parallel to the $TiO_2$ NT anode. However, we have to point out that when the electrode was immersed in the textile effluent, the effective light intensity reaching the electrode surface declined, depending upon the composition and colour of the sample solution. The cell and lamp were placed in the photoreactor, and the electrodes were connected to a DC power supply before a specific current was applied. All measurements were carried out using a constant airflow of 700 mL $min^{-1}$ of compressed air.

During the photoelectrocatalytic treatment, aliquots were withdrawn at controlled times and decolourisation and degradation was monitored with a Hanna colorimeter in a 10 mm quartz cell and the mineralisation of organic matter and inorganic carbon with a total organic carbon analyser (TOC - $V_{CPN}$, Shimadzu, Japan). The COD results were achieved using a COD Photometer Macherey-Nagel model PF-3. The pH, conductivity and total dissolved solids were achieved by Hanna and turbidity by Microquímica.

## Results and discussion

### FEG-SEM images of $TiO_2$ NTs

The electrodes achieved and used in PEC processes are shown in Fig. 2I. The morphology of $TiO_2$ NT electrodes obtained during
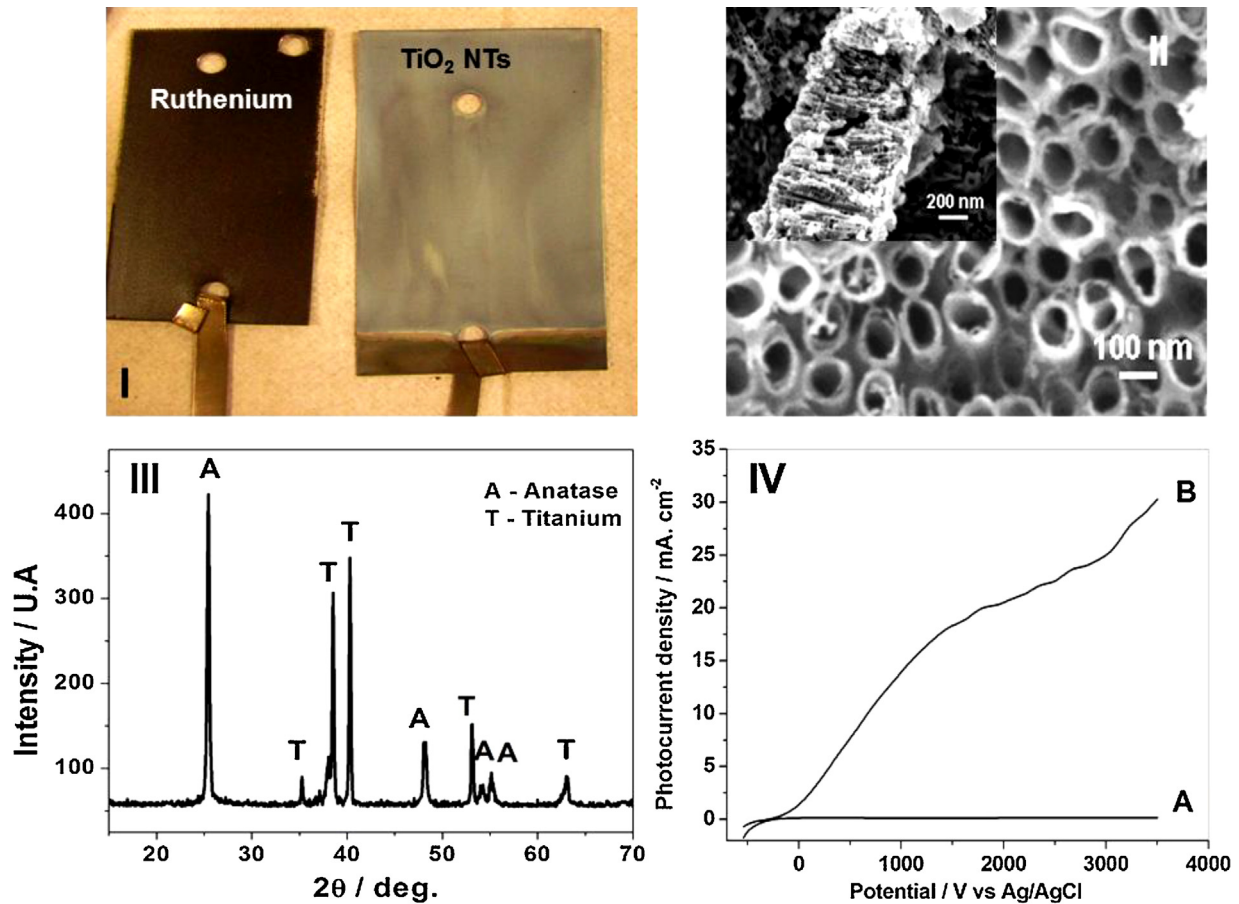
**Fig. 2.** (I) Pictures of samples used in PEC process of ruthenium and $TiO_2$ NTs arrays; (II) FEG-SEM images (top view and insert cross-section); (III) X-ray diffraction of $TiO_2$ nanotube arrays annealed at 450 °C for 30 min and (IV) linear sweep voltammogram curves of $TiO_2$ nanotubes arrays in 0.1 M $Na_2SO_4$ solution pH 6.5 in the dark (A) and UV illumination (B).

electrodeposition at 30 V in 0.25% $NH_4F$, 10% water in glycerol as an electrolyte was evaluated by using FEG-SEM images (Fig. 2II). The images show that the $TiO_2$ layer consists of nanotubular arrays with a uniform tube diameter of about 100 nm; a wall thickness of 10 nm and a length of around 1.5 μm. The formation of

nanotubular arrays was the result of competition reactions involving both the electrochemical oxidation of titanium on the metal surface and the chemical dissolution of the formed $TiO_2$ layer by fluorides in the electrolyte [19,20,24–27]. The use of highly viscous neutral electrolytes was adopted to control the steady
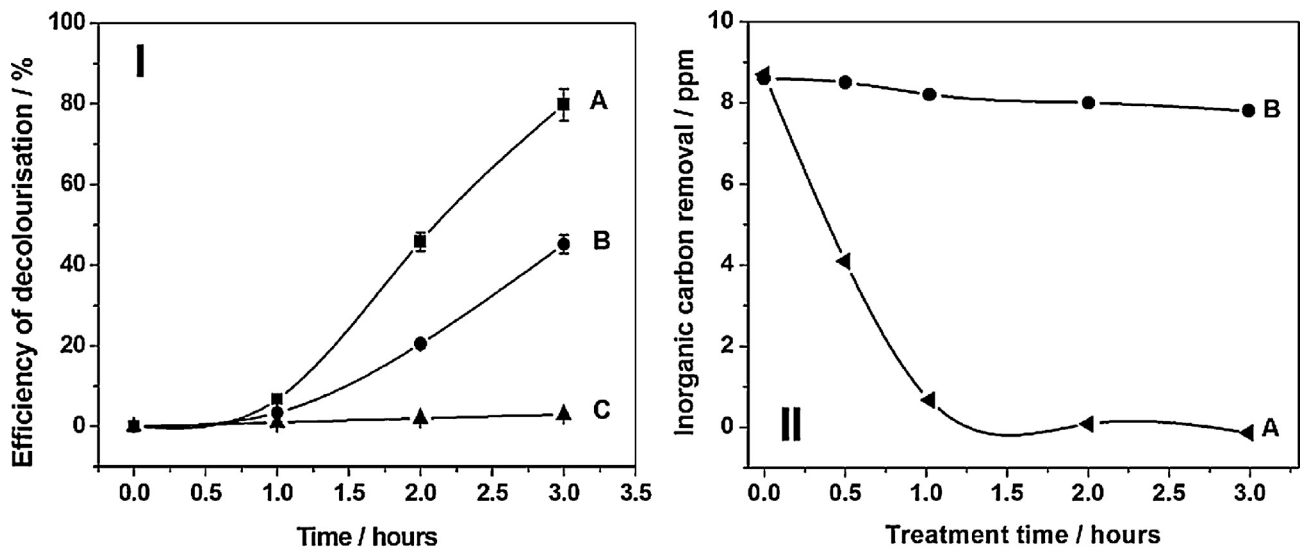


**Fig. 3.** Efficiency of decolourisation (I) and dissolved inorganic carbon removal (II) during 4 L of wastewater pH 2, treated using $TiO_2$ NT photoanode under air flow (700 mL min$^{-1}$); a current density of 9 mA cm$^{-2}$ and commercial light irradiating at UV + vis light 250 W of power under bubble mixing (A) and mechanical mixing (B) and bare $TiO_2$ NTs (C).

process [25–27], promoting chemical drilling at the bottom of the nanotubes. On the other hand, the use of $NH_4F$ as a neutral electrolyte creates a mild anodic oxidising environment, which essentially minimises the rate of chemical dissolution of the $TiO_2$ nanotube wall in comparison with acidic solutions [26]. As a result, it is possible to generate $TiO_2$ films with an ordered architecture, which can provide a unidirectional electric channel on the catalyst which improves the photoactivity.

### X-ray diffraction (XRD)

Fig. 2III shows an X-ray diffraction (XRD) patterns of nanotubes obtained after 50 h at 30 V, as mentioned previously, submitted to annealing at 450 °C. Results indicate that the diffraction peaks at about $2\theta$ 25.5°, 37.3°, 38.1°, 48.2°, 54.2°, and 55.2° can be indexed to the (1 0 1), (1 0 3), (0 0 4), (2 0 0), (1 0 5), and (2 1 1) crystal faces of anatase $TiO_2$. It is necessary to note that the rutile peak is much lower than the anatase peak, so it is reasonable to neglect the influence of such trace rutile content on the $TiO_2$ nanotubular arrays. The results are good since anatase is the higher activity form because it preserves more OH radical active surface sites [24,28,29]. This is a good indicator that the $TiO_2$ nanotubular arrays could contribute significantly to the photoactivity of the material.

### Photoactivity

The electrode photoactivity was evaluated by recording the photocurrent vs. applied potential for $TiO_2$ NTs (Fig. 2IV) in 0.1 mol $L^{-1}$ sodium sulphate pH 6.5 under and without UV irradiation. The respective voltammetric curves are shown in Fig. 2IV. The observed dark current was found to be negligible, see Fig. 2IV, curve A. However, high photocurrent density was greatly increased under UV irradiation at potential higher than $-0.25$ V vs. Ag/AgCl and the current values are constant after reaching a potential of $+1.5$ V, as shown in Fig. 2IV, curve B. The photoelectrochemical current density reflects the generation, separation and transfer efficiency of photo-excited electrons from the valence to the conduction band of $TiO_2$. Therefore, the crystallised $TiO_2$ nanotubular array can act effectively as a novel photoelectrochemical material to be incorporated into promising technological applications, such as a good photocatalyst. Since there is superior electron transport, the decreases in the photoelectrocatalytic oxidation efficiency resulting from the recombination process is reduced.

### Wastewater decolourisation optimisation

Fig. 3 shows the real effects of airflow in the PEC system used to treat 4 L of wastewater pH 2, treated using the $TiO_2$ NT photoanode under air flow (700 mL $min^{-1}$); a current density of 9 mA $cm^{-2}$ and commercial light irradiating at UV + vis light. Fig. 3I illustrate the decolourisation of the original wastewater textile industry submitted to 3 h of photoelectrocatalysis. As can be observed in Fig. 3I, curve A, the decolourisation of wastewater submitted to the PEC process achieved 81% using bubbles, while the mechanical movement promoted only 41% colour removal (Fig. 3I, curve B). In Fig. 3I, curve C, a bare $TiO_2$ NTs was tested to compare their efficiency in relation with $TiO_2$ NTs annealed and less of 2% was observed after 3 h of experiments. These results corroborate with the expected ones, where systems whose bubbles are used to mix or shake solutions can increase the mass transference inside a reactor and improve the surface of contact between electrode/ solution interfaces. On the other hand, the bubbles system can be related to the removal of carbonate and/or bicarbonate ions from bulk solution. The low yield when bare $TiO_2$ NTs was studied is due the absence of anatase phase. This phase is fundamental for

photocatalytic process because it is responsible to generate the excitons that convert holes to hydroxyl radicals.

In order to test the photoelectrocatalytic efficiency the discoloration of the wastewater was conducted by electrocatalysis (current density of 9 mA + catalyst) and photocatalysis (UV/vis irradiation + catalyst). The percentage of discoloration obtained after180 min of treatment showed maximum of 6% and 45%, respectively. These results illustrate the importance of photoelectrocatalysis PEC that reached 81% of colour removal.

Fig. 3II compares the inorganic carbon removal (IC) monitored during the treatment of original wastewater at pH 2 with and without the bubble system. In this case, when bubbles are used at acidic medium, the IC removal is promoted in the first hour of the experiment (Fig. 3II, curve A), while a slower IC removal was observed in the mechanical mix (Fig. 3II, curve B).

This result was expected due to carbonate and bicarbonate ions acting as a radical scavenger and causing the suppression of free hydroxyl radicals [Eqs. (1) and (2)] to degrade the organic pollutant [26]. Hydroxyl radicals produced are converted to the hydroxide ion, thereby decreasing the concentration of these oxidising agents. As a consequence, the photodegradation process occurs at a very slow rate, only depending on the reaction of dye molecules at the electrode surface.

$$HCO_3^- + OH^\bullet \rightarrow CO_3^{-\bullet} + H_2O \tag{1}$$

$$CO_3^{2-} + OH^\bullet \rightarrow CO_3^{-\bullet} + OH^- \tag{2}$$

Therefore, the reduction of these species present in the wastewater can promote an increase in the performance of treatment by AOP.

### Dilution of wastewater

Fig. 4 shows the effects of dilution of the original wastewater in the performance of decolourisation. The original effluent presented a high intensity colour (1146 mg Pt) and turbidity of 0.04 NTU. In this condition, some of the UV irradiation from the lamp is partially absorbed, decreasing the intensity of photons that can be on the $TiO_2$ surface. As the PEC process depends on e/-h+ generation on the electrode surface due to irradiation with $\lambda > 380$ nm and concomitant water adsorption for conversion to $OH^\bullet$ radicals, there is a reduction of colour of the effluent. Dilution with tap water improved the discolouration, as shown in Fig. 5I,
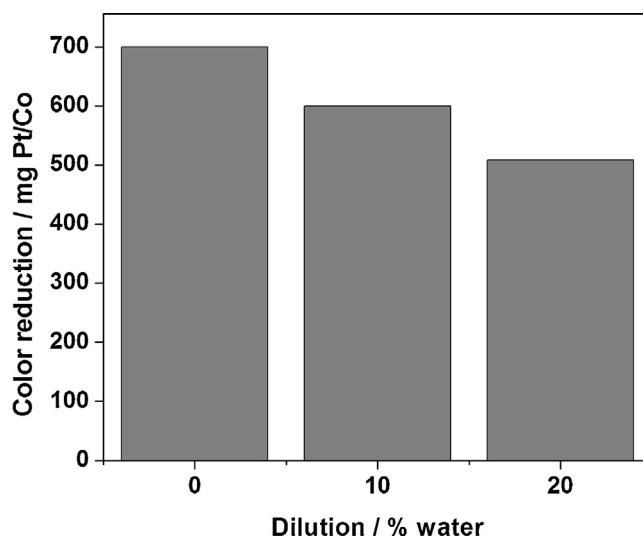


**Fig. 4.** Colour reduction of wastewater as a function of different percentages of tap water dilution.
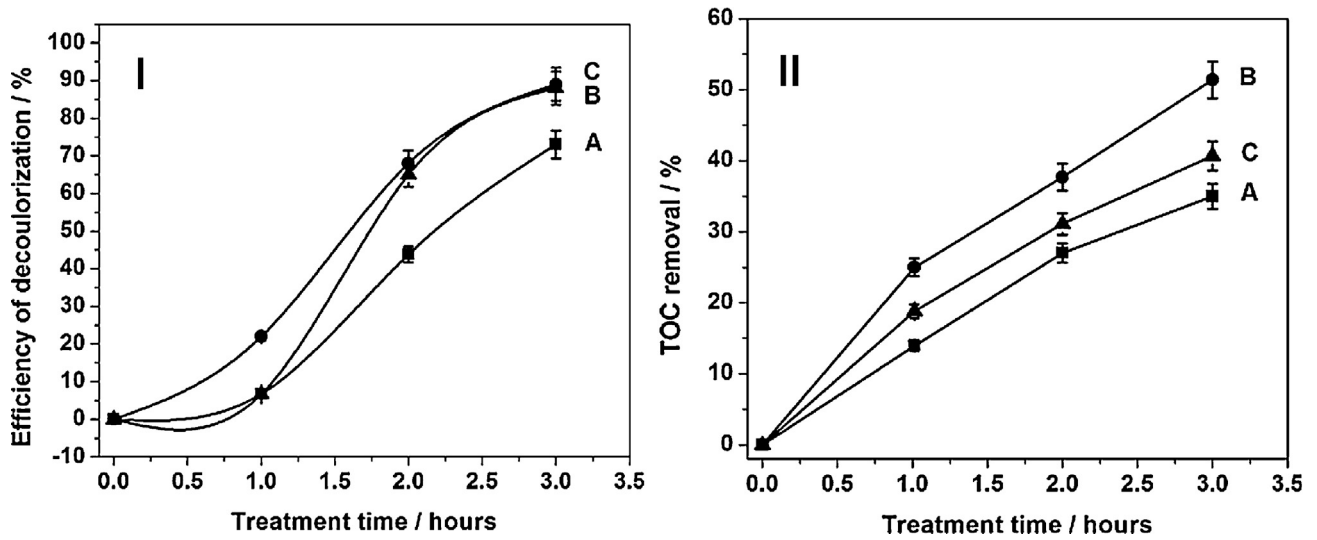
**Fig. 5.** Efficiency of decolourisation (I) and TOC removal (II) of wastewater in: no dilution (A); 10% (B) and 20% (C) tap water. Conditions: pH 2; a current density of 9 mA cm$^{-2}$ and commercial light irradiating at UV + vis light 250 W of power and under air flow of 700 mL min$^{-1}$.
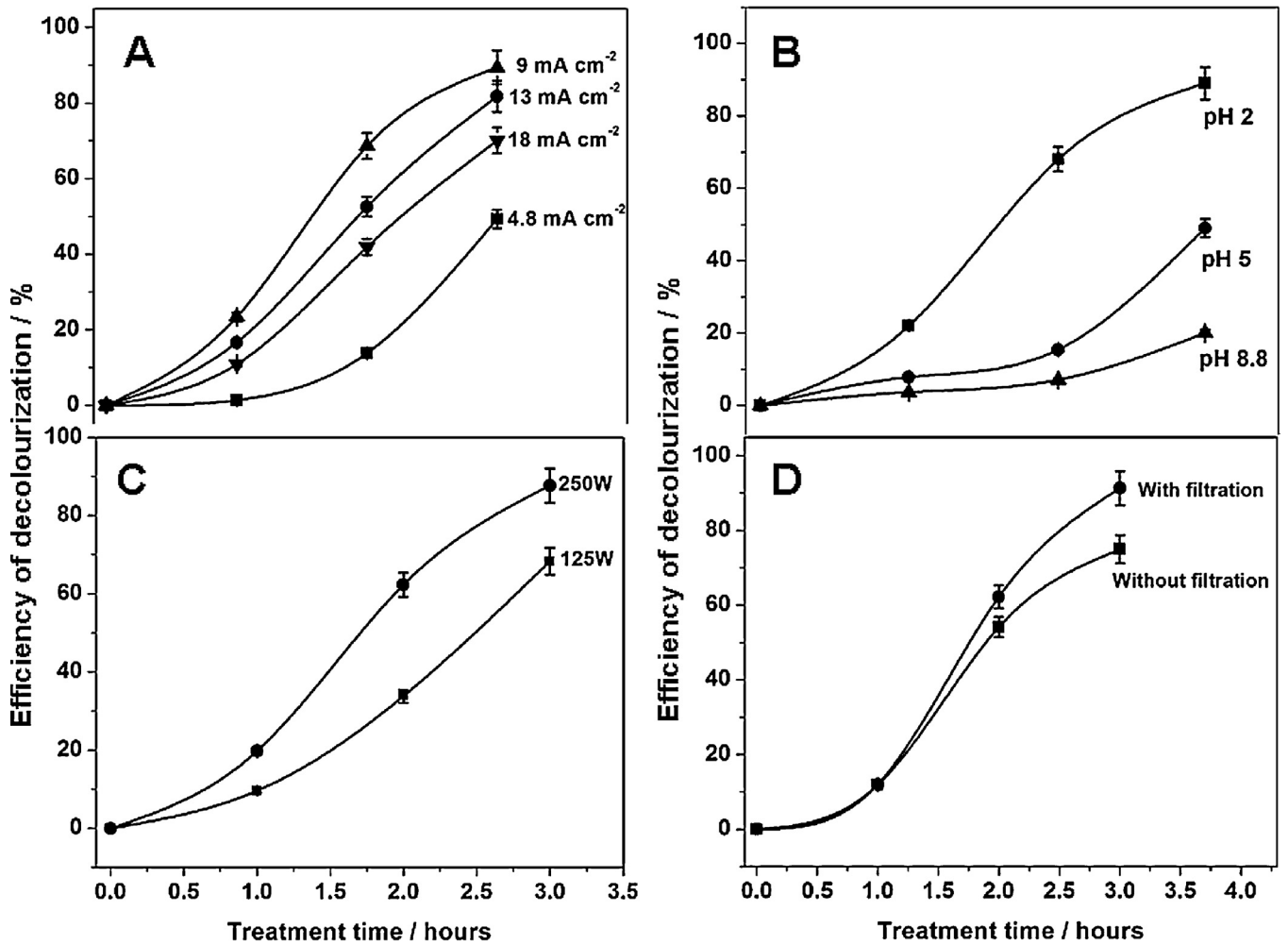


**Fig. 6.** Efficiency of decolourisation as a function of treatment time under different conditions, such as: density current (A); pH of solution (B); power lamps (C) and filtration of system (D).

indicating that a simple step of dilution can improve the economic feasibility.

As can be seen in Fig. 4, approximately 14% and 28% colour reduction of wastewater is obtained when 10% and 20% tap water is submitted to the PEC process, respectively. In addition, this dilution promoted around 90% discolouration after 3 h of treatment, while the original effluent reached 71% (Fig. 5I). At the same time, the TOC removal analyses revealed a maximum of 54% when 10% tap water was added, while the treatment without dilution was responsible for only 33% mineralisation. It is expected that 20% tap water could promote a higher discolouration than 10%; however, the opposite effect was observed. This behaviour could be explained as a function of conductivity of the solution (8.71 mS cm$^{-1}$ for 10% and 7.48 mS cm$^{-1}$ for 20% dilution). In an electrolytic process, the conductivity of the solution affects the efficiency of current intensity, voltage, and the consumption of electrical energy. The conductivity must be high in order to ensure good ion transfer in the solution. In this situation, a minimal difference was responsible for 15% of the TOC removal.

### Optimisation of treatment conditions

In order to increase the PEC performance in the discolouration of the wastewater other parameters was optimised, such as current applied, pH, irradiance and filtration system. All of the studies were carried out using a TiO$_2$ NT electrode in wastewater corrected to pH 2, with an airflow of 700 mL min$^{-1}$ and 10% tap water dilution.

Fig. 6A indicates the effect of effluent discolouration when treated under UV irradiation and current density ranging between 4.8 and 18 mA cm$^{-2}$. The results show that the discolouration increased significantly at 9 mA cm$^{-2}$, where 90% of the original colour was removed after 3 h of PEC treatment. Higher and lower values of current were not able to reach a desirable intensity of colour removal. As expected, application of an appropriate density current across the electrodes, which suppresses electron/hole recombination at the surface of the semiconductor, is necessary. At small current densities, there is a low influence on the separation of charges generated during photoirradiation [30]. Nevertheless, a current density higher than 9 mA cm$^{-2}$ promotes concomitant oxidation of water to oxygen, decreasing the efficiency of forming hydroxyl radicals and decreasing the PEC efficiency in dye discolouration.

Fig. 6B illustrates the influence of the original pH of the wastewater (2.5, 5.0 and 8.8) in the performance of decolouration. The measurements were taken for wastewater at corrected original pH treated over 3 h with a TiO$_2$ nanotubes array as the photoanode, under a constant current of 9 mA cm$^{-2}$ and under UV irradiation. 90% of discolouration was observed at acid medium. At pH 5 and pH 8.8 the colour removal decreases to 51% and 19%, respectively. Probably the amount of carbonates in the original water is responsible to trap hydroxyl radical. Therefore, the process is less effective for the organic content degradation. On the other hand, at pH 2, the adsorption of dye on the electrode surface is more efficient since carbonate removal is more effective and adsorption of dye by electrostatic interaction on the electrode surface is improved since in this pH it is protonated (isoelectric point around 5.3) [31] improving the success of treatment.

Fig. 6C shows the effects of irradiance in the wastewater discolouration. The graphs compare the performance of textile effluent during 3 h of treatment for TiO$_2$ NT under the bubble system, at pH 2 under UV–vis irradiation from different lamps. 91% of colour removal was reached when the semiconductor was irradiated by a 250 W lamp and only 70% when irradiated by a 125 W lamp, suggesting higher irradiance increases the efficiency due increases of hydroxyl radical generation.

During all experiments, the presence of small black-coloured particles in the solution (turbidimetry 0.04 NTU) was observed, which persisted up to the first hour of PEC treatment, but was removed under longer electrolysis conditions. These components could be associated with other compounds in solution with lower solubility. These particles can absorb or reflect the light, preventing the entire amount of radiation from reaching the TiO$_2$ NT surface. Thus, the removal of these particles by the filtration process was evaluated. Fig. 6D shows the effects of this previous filtration on the performance of wastewater discolouration. It is evident that removing these compounds increases the performance of the treatment by around 20% in comparison to when the wastewater is treated by filters. Therefore, the use of this option is recommended mainly in economic situations where a new physical component will be part of a treatment system and a great quantity of particles must be treated before correct disposal.

### COD and TOC analysis

Thus, our findings indicate that wastewater from textile effluents can be successfully treated using TiO$_2$ NTs arrays as the photoanode in a PEC system optimised with 10% dilution of the original effluent, correction to pH 2, bubbling with an airflow of 700 mL min$^{-1}$, applying a current density of 9 mA cm$^{-2}$ and being irradiated by a 250 W Hg lamp with a quartz bulb. In order to monitor the efficiency of treatment, besides the discolouration, the COD reduction and TOC removal were analysed, the results of which are shown in Fig. 7.

The COD analysis showed that a reduction by up to 60% is seen after 3 h of treatment, while the TOC value achieved 70% mineralisation. These results are somewhat higher than those of the other systems [32], indicating that the proposed PEC reactor can be competitive in comparison to other similar systems for the treatment of textile wastewater in pilot-scale operations [33,34].

Under these optimal conditions, Table 1 summarises the efficiency of the PEC process under physicochemical parameters. The chemical oxygen demand (COD) and total organic carbon (TOC) concentration were reduced in the effluent by 73% and 66%, respectively, after 3 h of photoelectrocatalytic oxidation. The reduction in conductivity values was not nearly as impressive, since dye mineralisation can also generate some inorganic ions, such as ammonium and nitrate. Taking into consideration that a solution of pure water presents turbidity lower than 0.04 NTU, the
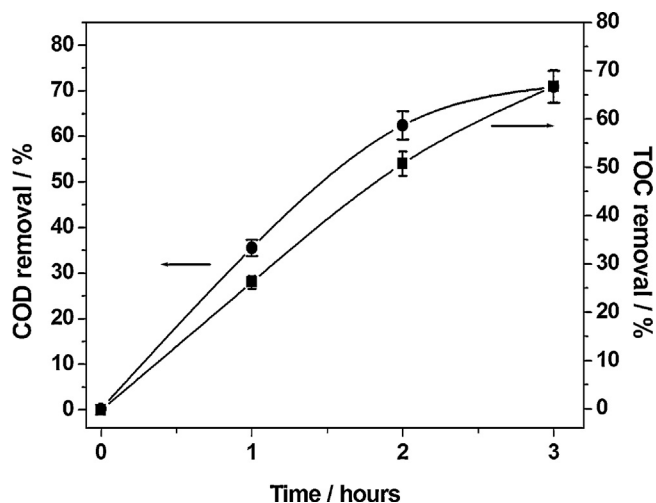


**Fig. 7.** COD removal and TOC removal under optimised conditions: 10% dilution of tap water; pH 2; airflow of 700 mL min$^{-1}$, current density of 9 mA cm$^{-2}$ and irradiated by a 250 W Hg lamp with a quartz bulb.

**Table 1**
Results of the photodegradation parameters.

| Physicochemical parametes | Textile wastewater | |
|---|---|---|
| | Before | After |
| COD/mg L$^{-1}$ | 752 | 203 |
| TOC/mg L$^{-1}$ | 750 | 250 |
| pH | 2.0 | 2.0 |
| Conductivity/mS cm$^{-1}$ | 9.96 | 9.8 |
| Turbidity/NTU | 0.04 | 0.04 |
| Total dissolved solid/ng L$^{-1}$ | 4.97 | 4.94 |
| Colour/mg PT | 1146 | 110 |
| Energy consumption/kWh kg$^{-1}$ | – | 3882 |

turbidity grade obtained for effluent samples before and after treatment did not show any significant reduction. The experimental pH values do not change after fixation at pH 2 and the energy consumption indicates values of 3882 kWh/kg$^{-1}$. Further studies are required to improve the application for high volumes of effluent, with a view to the future application of the developed process in industrial wastewater treatment.

Electric energy per mass ($E_{EM}$) is the electric energy in kilowatt-hours [kWh] required to bring about the degradation of a unit mass (e.g. one kilogram, kg) of a contaminant C in polluted water or air.

The $E_{EM}$ value [kWh/kg] can be calculated from Eq. (3):

$$E_{EM} = \frac{Pt10^6}{V(\gamma_i - \gamma_f)} \qquad (3)$$

$P$ is the rated power [kW] of the advanced oxidative process system, $V$ is the volume [L] of water in the time $t$ [h], factor of $10^6$ converts g to kg, and mass concentrations are used ($\gamma = m/V$) (usual unit mg/L) [35].

## Conclusion

Our findings indicate that the annular bubble photoreactor using a TiO$_2$ nanotube array as a photoanode has proven to be a good alternative for the treatment of textile wastewater, representing a powerful mean for the abatement of refractory and/or toxic pollutants in wastewaters from the textile industry. These pollutants can be directly degraded on the surface of the semiconductor by holes and/or hydroxyl radicals and adsorbed pollutants on the electrode surface. The method is rapid, simple and efficient. Using the optimised conditions of 10% dilution of the original effluent, correction to pH 2, bubbling with 700 mL min$^{-1}$ of airflow, applying a current density of 9 mA cm$^{-2}$ and irradiation by a 250 W Hg lamp inserted in a quartz bulb, it was found that the PEC process was able to reach 90% of the original colour of the effluent and promote up 70% mineralisation and COD reduction by 66% after 3 h of treatment.

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## References

[1] C.C.I. Guaratini, M.V.B. Zanoni, Corantes têxteis, Quim. Nova 23 (2000) 71–78, doi:http://dx.doi.org/10.1590/S0100-40422000000100013.

[2] D.P. Oliveira, P.A. Carneiro, M.K. Sakagami, M.V.B. Zanoni, G.A. Umbuzeiro, Chemical characterization of a dye processing plant effluent–identification of the mutagenic components, Mutat. Res. 626 (2007) 135–142, doi:http://dx.doi.org/10.1016/j.mrgentox.2006.09.008.

[3] Z. Wang, M. Xue, K. Huang, Z. Liu, Advances in treating textile effluent, InTech (2011) , doi:http://dx.doi.org/10.5772/1039.

[4] Q. Yang, P. Ling Ang, M.B. Ray, S.O. Pehkonen, Light distribution field in catalyst suspensions within an annular photoreactor, Chem. Eng. Sci. 60 (2005) 5255–5268, doi:http://dx.doi.org/10.1016/j.ces.2005.02.067.

[5] M.F. Kabir, E. Vaisman, C.H. Langford, A. Kantzas, Effects of hydrogen peroxide in a fluidized bed photocatalytic reactor for wastewater purification, Chem. Eng. J. 118 (2006) 207–212, doi:http://dx.doi.org/10.1016/j.cej.2006.02.003.

[6] G.G. Bessegato, T.T. Guaraldo, M.V.B. Zanoni, Modern electrochemical methods in nano, surface and corrosion science, InTech (2014) , doi:http://dx.doi.org/10.5772/57202.

[7] Y. Liu, L. Hua, S. Li, Photocatalytic degradation of Reactive Brilliant Blue KN-R by TiO2/UV process, Desalination 258 (2010) 48–53, doi:http://dx.doi.org/10.1016/j.desal.2010.03.050.

[8] H.J. Yun, H. Lee, J.B. Joo, N.D. Kim, M.Y. Kang, J. Yi, Facile preparation of high performance visible light sensitive photo-catalysts, Appl. Catal. B 94 (2010) 241–247, doi:http://dx.doi.org/10.1016/j.apcatb.2009.11.014.

[9] S. Parsons, Advanced Oxidation Processes for Water and Wastewater Treatment, IWA Publishing, London, 2004. . (accessed 5.11.14) http://www.iwa-publishing.com/template.cfm?name=isbn1843390175.

[10] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, Recent developments in photocatalytic water treatment technology: a review, Water Res. 44 (2010) 2997–3027, doi:http://dx.doi.org/10.1016/j.watres.2010.02.039.

[11] S. Mozia, Photocatalytic membrane reactors (PMRs) in water and wastewater treatment. A review, Sep. Purif. Technol. 73 (2010) 71–91, doi:http://dx.doi.org/10.1016/j.seppur.2010.03.021.

[12] J.M. Poyatos, M.M. Muñio, M.C. Almecija, J.C. Torres, E. Hontoria, F. Osorio, Advanced oxidation processes for wastewater treatment: state of the art, Water Air Soil Pollut. 205 (2009) 187–204, doi:http://dx.doi.org/10.1007/s11270-009-0065-1.

[13] M.I. Badawy, M.Y. Ghaly, T.A. Gad-Allah, Advanced oxidation processes for the removal of organophosphorus pesticides from wastewater, Desalination 194 (2006) 166–175, doi:http://dx.doi.org/10.1016/j.desal.2005.09.027.

[14] A. Fujishima, X. Zhang, D. Tryk, TiO$_2$ photocatalysis and related surface phenomena, Surf. Sci. Rep. 63 (2008) 515–582, doi:http://dx.doi.org/10.1016/j.surfrep.2008.10.001.

[15] V. Brezová, S. Gabcová, D. Dvoranová, A. Stasko, Reactive oxygen species produced upon photoexcitation of sunscreens containing titanium dioxide (an EPR study), J. Photochem. Photobiol. B 79 (2005) 121–134, doi:http://dx.doi.org/10.1016/j.jphotobiol.2004.12.006.

[16] H. de Lasa, B. Serrano, M. Salaices, Photocatalytic Reaction Engineering, Springer US, Boston, MA, 2005, doi:http://dx.doi.org/10.1007/0-387-27591-6.

[17] M. Sanchez, M.J. Rivero, I. Ortiz, Photocatalytic oxidation of grey water over titanium dioxide suspensions, Desalination 262 (2010) 141–146, doi:http://dx.doi.org/10.1016/j.desal.2010.05.060.

[18] M. Bestetti, D. Sacco, M.F. Brunella, S. Franz, R. Amadelli, L. Samiolo, Photocatalytic degradation activity of titanium dioxide sol–gel coatings on stainless steel wire meshes, Mater. Chem. Phys. 124 (2010) 1225–1231, doi:http://dx.doi.org/10.1016/j.matchemphys.2010.08.062.

[19] J.C. Cardoso, T.M. Lizier, M.V.B. Zanoni, Highly ordered TiO$_2$ nanotube arrays and photoelectrocatalytic oxidation of aromatic amine, Appl. Catal. B 99 (2010) 96–102, doi:http://dx.doi.org/10.1016/j.apcatb.2010.06.005.

[20] J.C. Cardoso, M.V.B. Zanoni, Structural effects of nanotubes, nanowires, and nanoporous Ti/TiO$_2$ electrodes on photoelectrocatalytic oxidation of 4,4-oxydianiline, Sep. Sci. Technol. 45 (2010) 1628–1636, doi:http://dx.doi.org/10.1080/01496395.2010.487721.

[21] G.G. Bessegato, J.C. Cardoso, M.V.B. Zanoni, Enhanced photoelectrocatalytic degradation of an acid dye with boron-doped TiO$_2$ nanotube anodes, Catal. Today 240 (2014) 100–106, doi:http://dx.doi.org/10.1016/j.cattod.2014.03.073.

[22] G.G. Bessegato, J.C. Cardoso, B.F. da Silva, M.V.B. Zanoni, Enhanced photoabsorption properties of composites of Ti/TiO$_2$ nanotubes decorated by Sb2S3 and improvement of degradation of hair dye, J. Photochem. Photobiol. A 276 (2014) 96–103, doi:http://dx.doi.org/10.1016/j.jphotochem.2013.12.001.

[23] M.A. Paschoal, The photoelectrocatalytic oxidative treatment of textile wastewater containing disperse dyes, Desalination 249 (2009) 1350–1355, doi:http://dx.doi.org/10.1016/j.desal.2009.06.024.

[24] J.M. Macak, H. Tsuchiya, L. Taveira, S. Aldabergerova, P. Schmuki, Smooth anodic TiO$_2$ nanotubes, Angew. Chem. Int. Ed. Engl. 44 (2005) 7463–7465, doi:http://dx.doi.org/10.1002/anie.200502781.

[25] J.M. Macak, S.P. Albu, P. Schmuki, Towards ideal hexagonal self-ordering of TiO$_2$ nanotubes, Phys. Status Solidi–Rapid Res. Lett. 1 (2007) 181–183, doi:http://dx.doi.org/10.1002/pssr.200701148.

[26] G.K. Mor, O.K. Varghese, M. Paulose, N. Mukherjee, C.A. Grimes, Fabrication of tapered, conical-shaped titania nanotubes, J. Mater. Res. 18 (2011) 2588–2593, doi:http://dx.doi.org/10.1557/JMR.;1; 2003.0362.

[27] K. Shankar, G.K. Mor, H.E. Prakasam, O.K. Varg hese, C.A. Grimes, Self-assembled hybrid polymer-TiO$_2$ nanotube array hetero junction solar cells, Langmuir 23 (2007) 12445–12449, doi:http://dx.doi.org/10.1021/la 7020403.

[28] J.M. Macak, K. Sirotna, P. Schmuki, Self-organized porous titanium oxide prepared in Na2SO4/NaF electrolytes, Electrochim. Acta 50 (2005) 3679–3684, doi:http://dx.doi.org/10.1016/j.electacta.2005.01.014.

[29] J.M. Macák, H. Tsuchiya, P. Schmuki, High-aspect-ratio TiO$_2$ nanotubes by anodization of titanium, Angew. Chem. Int. Ed. Engl. 44 (2005) 2100–2102, doi:http://dx.doi.org/10.1002/anie.200462459.

[30] H.G. Oliveira, D.C. Nery, C. Longo, Effect of applied potential on photocatalytic phenol degradation using nanocrystalline $TiO_2$ electrodes, Appl. Catal. B 93 (2010) 205–211, doi:http://dx.doi.org/10.1016/j.apcatb.2009.09.030.

[31] M.V.B. Zanoni, J.J. Sene, M.A. Anderson, Photo electrocatalytic degradation of Remazol Brilliant Orange 3R on titan ium dioxide thin-film electrodes, J. Photochem. Photobiol. A 2 (003) (2015) 55–63, doi:http://dx.doi.org/10.1016/S1010-6030(02)00320-9.

[32] X. Hao, H. Li, Z. Zhang, C. Fan, S. Liu, Y. Sun, Modeling and experimentation of a novel labyrinth bubble photoreactor for degradation of organic pollutant, Chem. Eng. Res. Des. 87 (2009) 1604–1611, doi:http://dx.doi.org/10.1016/j.cherd.2009.06.002.

[33] D. Dogan, H. Türkdemir, Electrochemical oxidation of textile dye indigo, J. Chem. Technol. Biotechnol. 80 (2005) 916–923, doi:http://dx.doi.org/10.1002/jctb.1262.

[34] A. Kunz, P. Peralta-Zamora, S.G. de Moraes, N. Durán, Novas tendências no tratamento de efluentes têxteis, Quim. Nova 25 (2002) 78–82, doi:http://dx.doi.org/10.1590/S0100-40422002000100014.

[35] J.R. Bolton, K.G. Bircher, W. Tumas, C.A. Tolman, Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems (IUPAC Technical Report), Pure Appl Chem. 73 (2001) 627–637, doi:http://dx.doi.org/10.1351/pac200173040627.