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Photoelectrocatalytic oxidation of remazol turquoise blue and toxicological assessment of its oxidation products

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Abstract

The ability of photoelectrocatalytic oxidation to degrade the commercially important copper–phtalocyanine dye, remazol turquoise blue 15 (RTB) was investigated. The best experimental condition was optimized, evaluating the performance of Ti/TiO_2 thin-film electrodes prepared by sol–gel method in the decolourization of 32 mg L^{-1} RTB dye in 0.5 mol L^{-1} Na_2SO_4 pH 8 and applied potential of +1.5 V versus SCE under UV irradiation. Spectrophotometric measurements, high performance liquid chromatography, dissolved organic carbon (TOC) evaluation and stripping analysis of yielding solution obtained after 3 h of photoelectrolysis leads to 100% of absorbance removal from wavelength of 250–800 nm, 79.6% of TOC reduction and the releasing of up to 54.6% dye-bound copper (0.85 mg L^{-1}) into the solution. Both, original and oxidized dye solution did not presented mutagenic activity with the strains TA98 and TA100 of Salmonella in the presence and absence of S9 mix at the tested doses. Nevertheless, the yielding photoelectrocatalytic oxidized solution showed an increase in the acute toxicity for *Vibrio fischeri* bacteria, explained by copper liberation during treatment.

Keywords: Remazol turquoise blue; Mutagenic activity; Photoelectrocatalytic oxidation

1. Introduction

Among the synthetic dyes, the textile azo dyes with synthetic intermediates as contaminant and its products have undoubtedly attracted attention with regard to their potentiality to form toxic aromatic products with carcinogenicity and mutagenicity properties [1–14]. The Ecological and Toxicological Association of the Dyestuff Manufacturing Industry (ETAD) have reported that the highest rates of toxicity (LD50) were found amongst azo dyes [15]. Therefore, alternative methods for dye treatment have been widely investigated, including chemical oxidation with reagents such as: ozone, hydrogen peroxide, ozone/UV, hydrogen peroxide/UV and Fenton's reagent (hydrogen peroxide + Fe(II) and photocatalytic methods [16–19].

Among several photocatalyst, the TiO_2 semiconductor has received particular attention in the environmental sector because of its excellent chemical and good photoelectrochemical properties [20–26]. The use of TiO_2 particle suspensions or immobilized TiO_2 films, are widely employed to degrade organic wastes in water [27–33]. Photoelectrocatalysis has been an attractive way to increase the photocatalytic efficiency. By applying an electrochemical potential across a photoanode, on which the catalyst of TiO_2 film is supported, separation of photogenerated electrons and holes (e^-/h^+) is accelerated and the recombination of photogenerated charges is suppressed. Adsorbed water/OH^- groups are available as electron donor to yield hydroxyl radical ($OH^\bullet$), which is generation of powerful oxidants on the while oxygen can act as an electron acceptor to form the superoxide radical ion ($O_2^{\bullet -}$). Both species are strongly oxidizing and capable of degrading aromatic compounds as textile dye [28–30,33]. Among them, photoelectrocatalysis can be described as one of the common oxidation process that works successfully for textile dyes based on anthraquinone and azo dyes [28–30].

The decolouration of phtalocyanines dyes by using biodegradation [34–37] and advanced oxidation processes such as TiO_2/UV, Fenton and photo-Fenton reagent [38] have been described in the literature, but its degradation point to low efficiency of conventional treatment technologies. The best results obtained in the literature [33] for phtalocyanine dye degradation was achieved using a combined process of electrochemistry and

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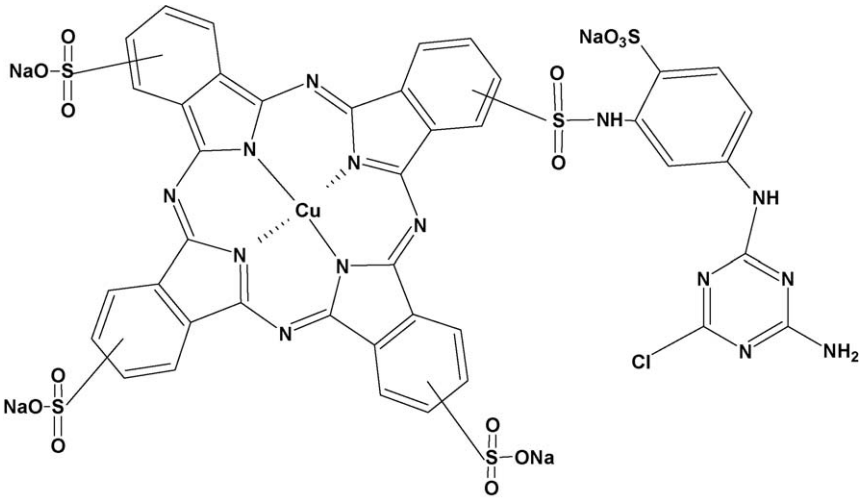

Fig. 1. Molecular structure of the remazol turquoise blue 15 dye.

photoelectrochemistry. After 4 h of potential controlled electrolysis at −1.2 V on a cathode of platinum, followed by more 6 h of photoelectrocatalytic oxidation on Ti/TiO_2 operating on UV illumination and potential of +1.5 V, the results point to 100% of colour removal and 83% of TOC decay of copper–phtalocyanine complex.

Although photoelectrocatalysis is used increasingly to degrade the recalcitrant compounds, still little is known about the toxicity of the products formed during the treatment. Taking into consideration that metallophtalocyanine dyes could liberate the metal present in the complex to the final solution, this evaluation cannot be underestimated since the yielding solution could present higher toxic potential than their original compound. In addition, it was not found in the literature studies evaluating the copper–phtalocyanine dye mutagenicity.

The aim of the present study was to promote the photoelectrocatalytic oxidation of the remazol turquoise blue dye (Fig. 1) on a nanoporous thin-film electrode Ti/TiO_2 using different electrolytes and a simple photoelectrochemical reactor constructed with germicide lamp. The solution of the dye as well as its photoelectrocatalyzed product was evaluated for mutagenic activity in the Salmonella/microsome microsuspension assay and for acute toxicity with the marine luminescent bacteria *Vibrio fischeri* [39–41].

2. Experimental

2.1. Apparatus and procedure

The photoelectrocatalytic experiments were performed in a photoelectrochemical reactor of two compartments illustrated in Fig. 2. A Nafion® 117 membrane was used to separate both compartments while allowing electrolyte contact. The photoactive area of the working electrode acting as anode Ti/TiO_2 was prepared by sol–gel method, as cited previously in the literature [23–26]. Both sides of the photoanode (8 cm^2) was illuminated by two germicide lamp operating on UV light source (315–400 nm) mounted 5 cm in front of each side of the working electrode in the cell. The light intensity of 8 W cm^{-2} was measured with an International Light Inc. photometer, model IL 1400A. The compartment containing the platinum counter electrode was not directly exposed to the UV illumination. The reference electrode was a saturated calomel electrode (SCE) placed close to the working electrode using a bridge tube containing a Vycor frit tip. A Potentiostat/Galvanostat EG&G PARC model 283 controlled by the Electrochemical 270 software was used to bias the photoanode in the photoelectrocatalytic experiments.

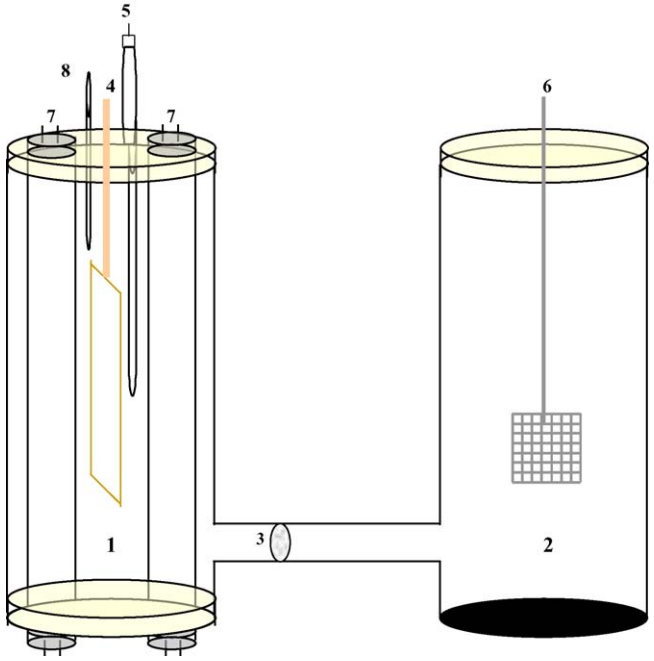

Fig. 2. Photoelectrocatalytic reactor with two compartment. Anodic compartment (1) and cathodic compartment (2) separated by a Nafion® 117 membrane (3). Photoanode of Ti/TiO_2 prepared by sol–gel method (4) illuminated by two commercial germicide lamp Phillips of 4 W cm^{-2} operating on UV light source (315–400 nm) mounted 5 cm in front of each side of the working electrode in the cell (7). A platinum gauze used as counter electrode (6) and a saturated calomel electrode (SCE) placed close to the working electrode using a bridge tube containing a Vycor frit tip (5). (8) Air bubble.

The concentration of remazol turquoise blue dye (C.I.74459, purchased from Sigma–Aldrich), FW 1282.97, in the solution was monitored by measuring the absorbance of samples of the dye solution at controlled time using a Hewlett Packard 8453 spectrophotometer operated at 200–800 nm in a quartz cell. Typical UV–vis absorption spectra of copper–phtalocyanine dye present four characteristics bands. The two intense bands at 674 and 610 nm are attributed due π–π^* transitions, usually referred to as Q-bands. The other characteristics band is the Soret band observed at 332 nm. The peak at 270 nm is attributed to the bis-monochlorotriazine groups and other aromatic sites in the molecule.

Dissolved organic carbon (TOC) was monitored using the Total Organic Carbon Analyzer (Shimadzu 5000A). A high performance liquid chromatography Shimadzu Model 10 AVP equipped with a photodiode array detector (200–800 nm) was used to separate and identify products and intermediates of the dye oxidation. The separation column was G-ODS (4 mm × 250 mm, 5 μm) and the mobile phase was ammonium acetate 10 mmol L^{-1} (eluent A) and methanol (B) operating under gradient elution on flow rate of 1.0 mL min^{-1}. The best separation was obtained for: 0–8 min 100% A, 48–50 min 50% A, 52–60 min 100% A.

The content of copper ions released during photoelectrocatalytic experiments, in both anode and cathode compartments were determined by the anodic stripping voltammetry method using mercury films calibrated previously to a minimum detectable concentration of copper of 3.18 μg L^{-1}. The general procedure for carrying out anodic stripping voltammetry was as follows. The stirrer was switched on and the solution containing copper standard solution and mercury(II) in nitrate medium was purged with nitrogen gas for 15 min. The accumulation potential of −0.8 V was then applied to the working electrode, whilst still stirring the solution. After deposit of metal/mercury amalgam, there was a 10 s quiescent period with the stirring stopped and a potential scan from −0.5 to 0.1 V was applied. Unless otherwise stated the following parameters were used: accumulation time of 5 min and linear scan of 50 mV s^{-1}.

The mutagenic activity was evaluated using the Salmonella/microsome microsuspension assay [39] using the strains of *Salmonella typhimurium* TA98 (his D3052, rfa, Δbio, ΔuvrB, pKM101) and TA100 (hisG46, rfa, Δbio, ΔuvrB, pKM101). The metabolic activation was provided by Araclor 1254 induced Sprague Dawley rat liver S9 mix [40] and necessary cofactors at the concentration of 4% (v/v) [40]. The positive controls were 4-nitroquinoline at 0.125 μg/plate and 2-aminoanthacene at 0.625 μg/plate for both strains, in the absence and presence of S9 mix, respectively. Samples were considered positive when significant ANOVA and dose response were obtained. The samples before and after the oxidation process (dye plus vehicle) were dissolved in sterile ultra pure water in a concentration of 360 mg L^{-1} (containing 0.8 mg L^{-1}). The vehicle used were sodium sulphate, and a solution of this salt at the same concentration cited above was also tested (negative control). Doses were tested in triplicates and corresponded to 1, 2, 4 and 8 μg of dye per plate both in the presence and absence of S9 mix.

Acute toxicity test were performed with *V. fischeri*, a marine luminescent bacteria according with ISO 11348-3 [41]. We measured the luminescence with a Microtox model 500 Analysis (Azur Environment, Delaware, USA). Several doses were evaluated and the sodium sulphate was tested separately as a negative control. Serial dilutions (1:2) were performed from a solution of 320 mg mL^{-1}. The results were expressed as the % of light inhibition as well as in CE20, which is the effective concentration that causes 20% of light inhibition after 15 min of exposure. The lower the CE20 the more toxic is the sample analyzed. The dye solution presented a blue colouration that could cause interference in the light measurement. For the correction of this artifact the assay was performed with a modification that allows the differentiation of the real toxicity from the light inhibition due to the colour of the sample also according to ISO 11348-3 [42].

3. Results and discussion

3.1. Photoelectrocatalytic oxidation of copper–phtalocyanine dye

Fig. 3 shows the effect of supporting electrolyte on the performance of the TiO_2 thin-film electrodes to promote the discolouration of 38.5 mg L^{-1} copper–phtalocyanine dye. The photoelectrocatalytic oxidation of the dye solution in 0.5 mol L^{-1} NaCl (Curve A); 0.5 mol L^{-1} Na_2SO_4 (Curve B); 0.5 mol L^{-1} $NaNO_3$ (Curve C) at pH 7.0 was carried out using UV light and applied potential (E_{app}) of +1 V (versus SCE). In the same graph, the results also exhibited the discolouration in 0.5 mol L^{-1} NaCl under heterogeneous photocatalysis operating under open circuit (Curve D). The results are expressed as a fractional conversion (f) of the dye and plotted in a time-dependent scale. The fractional conversion is the ratio of dye concentration variation at time t (C_t) to the initial dye concentration (C_0) in solution at $t = 0$. Concentration was determined by monitoring the absorbance of the dye following the most intense band at wavelength of 674 nm

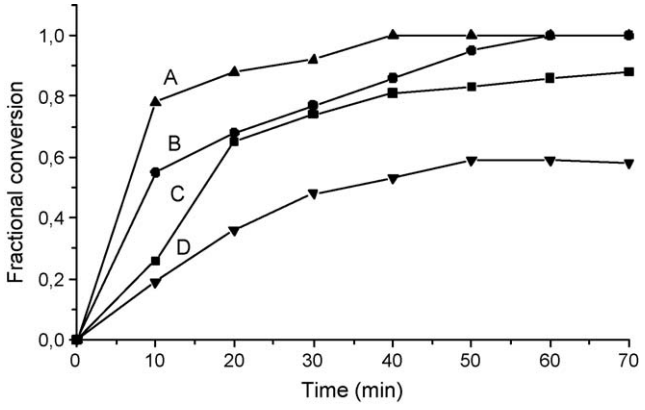

Fig. 3. Effect of supporting electrolyte on the photoelectrocatalytic oxidation of remazol turquoise blue 15 dye as a function of treatment time. Dye solution = 38.5 mg L^{-1} in 0.5 mol L^{-1} NaCl (A); 0.5 mol L^{-1} Na_2SO_4 (B); 0.5 mol L^{-1} $NaNO_3$ (C) at pH 7.0 under applied potential (E_{app}) = +1 V (vs. SCE), on Ti/TiO_2 thin-film anode and UV irradiation. (D) Photocatalysis on Ti/TiO_2 in 0.5 mol L^{-1} NaCl, under UV light without applied potential electrode. Aliquots removed each 10 min and absorbance monitored at 674 nm.

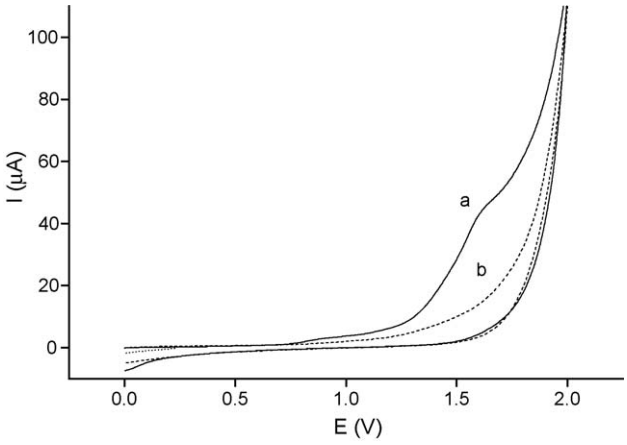

Fig. 4. Cyclic voltammograms obtained for oxidation of 129 mg L^{-1} of remazol turquoise blue 15 dye in 0.5 mol L^{-1} Na_2SO_4 on glassy carbon electrode (a) and for supporting electrolyte (b).

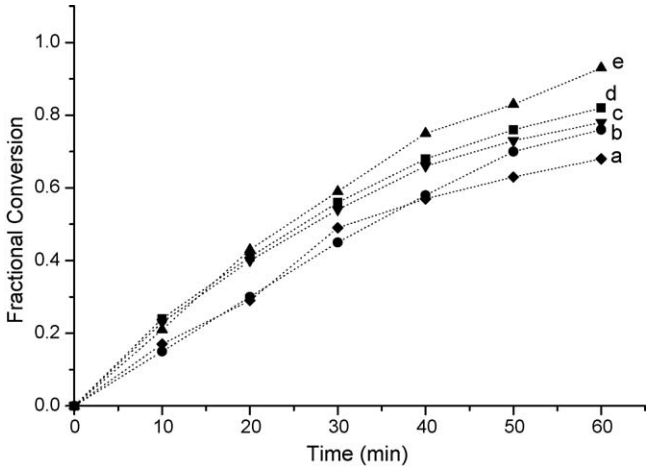

Fig. 5. Effect of pH variation in solutions 0.5 mol L^{-1} Na_2SO_4 on the photoelectrocatalytic oxidation of 5×10^{-5} mol L^{-1} remazol turquoise blue 15 dye on a TiO_2 thin-film electrode biased at $E = +1.0$ V vs. SCE. Curves: (a) pH 4; (b) pH 6; (c) pH 10; (d) pH 12; (e) pH 8.

assigned as band Q attributed to π–π^* transition due phtalocyanine ring.

In all supporting electrolyte, the results obtained indicate that the potential increases drastically the oxidation constant rate of the dye solution. After 70 min of photoelectrolysis the maximum fractional conversion is around 50% under open circuit, but the discolouration reaches 100% in NaCl under potential of +1.0 V. As observed previously in another photoelectrocatalytic reaction [33] applying a bias potential (E_{app}) from +0.6 to +1.0 V the colour removal rate is practically constant, but its increases markedly at E_{app} higher than 1.0 V. This behavior indicates that under applied potential higher than flat band potential of the semiconductor there is a significant increasing on the efficiency of the photocatalytic activity of the TiO_2/Ti electrode and thereby increases the reaction rate of dye oxidation. Nevertheless, maximum values are obtained at potential of +1.5 V, where probably there is a synergic effect of the dye oxidation on the electrode surface, which usually presents an oxidation peak at +1.54 V versus SCE on cyclic voltammograms recorded on glassy carbon electrode, as illustrate in Fig. 4. So, $E_{app} = +1.5$ was adopted in the further experiments.

The discolouration of RTB in $NaNO_3$ medium leads to a maximum of 88% after 70 min of electrolysis. This colour removal also does not follow a first order reaction. The lower efficiency compared to other electrolyte (Na_2SO_4 and NaCl) is explained taking into consideration that usually UV irradiation can promote a competitive photolytic degradation of nitrate to nitrite [42] in solution $[NO_3^- + H_2O + h\nu \rightarrow NO_2^{\bullet} + OH^{\bullet} + OH^-]$, decreasing the photon efficiency. To confirm this hypothesis, aliquots removed after 60 min of photoelectrochemical oxidation of 0.5 mol L^{-1} $NaNO_3$ in pH 7 on Ti/TiO_2 photoanode conducted under UV illumination and applied potential of +1 V, were analyzed by using a qualitative assay. A white precipitate was obtained due reaction of $Ag^+ + NO_2^- \rightarrow AgNO_2$ (s), confirming that nitrite are being produced during the photoelectrocatalytic experiment.

The relationship between $\ln C/C^0$ and time for NaCl and Na_2SO_4 was linear, suggesting a kinetic of pseudo first order reaction with a rate constant (k) of dye consumption (mol L^{-1}) measured as function of time of $-0.0550\ min^{-1}$ and $-0.0387\ min^{-1}$, respectively. These results indicate that the colour removal of remazol turquoise blue solution occurs very fast in both electrolytes, but is higher in chloride medium. Although some preliminary results obtained in the literature [30] point to presence of harmful chlorinated compounds as side products after the photoelectroxidation of azo dyes in NaCl medium, sulphate medium was chosen as better alternative to promote the degradation process of remazol turquoise blue dye, since the generation of chloro-aromatic hydrocarbons due partial decomposition should be health concern [43].

The performance of the photoelectrocatalytic degradation of 2.5×10^{-5} mol L^{-1} of remazol turquoise blue dye solution at different pH values, was investigated testing the discolouration process in 0.50 mol L^{-1} Na_2SO_4 at acid, neutral and alkaline medium. The photoelectrocatalytic oxidation was conducted on TiO_2 thin-film electrodes under UV illumination and +1 V and the pH values maintained constant during the experiments. This was necessary because the pH of the solution in the anode compartment is decreased due to evolution of oxygen from the anode surface. As these reactions acidify the anode, the hydrogen evolution generates a concomitant increasing of the pH at the cathode. The results expressing the effect of pH on the fractional conversion (f) of the colour dye in function of time are shown in Fig. 5. Maximum colour removal was obtained at pH 8. In addition, this pH value could be offering some advantages to treat the effluent from textile industry, since usually its effluent is slightly alkaline. This fact occurs because commonly the fixation of reactive dyes onto the fibre is carried out at alkaline condition to favour the covalent bond between reactive group and the hydroxyl or amine groups present in the cellulose or wool fibre, for example.

Fig. 6, exhibits the UV–vis spectra obtained before and after 3 h of photoelectrocatalysis oxidation of 32 mg L^{-1} of copper–phtalocyanine solution in Na_2SO_4 0.5 mol L^{-1}, pH 8, $E_{app} = 1.5$ V. The degradation process induces the total suppres-

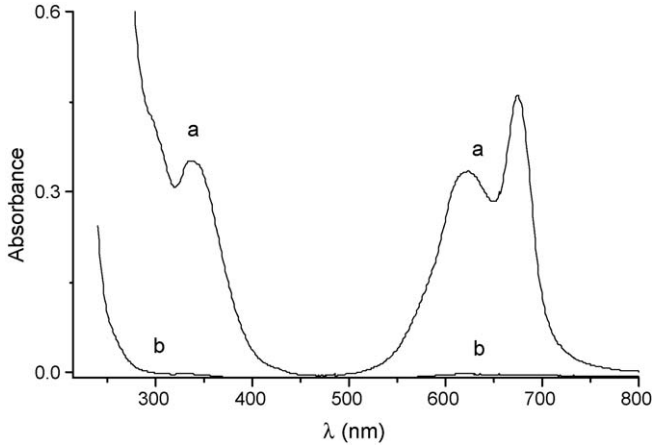

Fig. 6. Absorbance decay before (a) and after 3 h (b) of photoelectrocatalytic oxidation of 32 mg L^{-1} of remazol turquoise blue 15 dye in 0.5 mol L^{-1} Na_2SO_4 on TiO_2 thin-film electrodes at +1.5 V and UV irradiation.

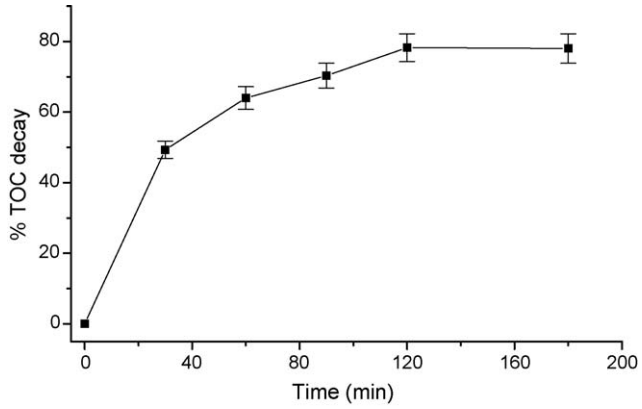

Fig. 8. Percentage of dissolved organic carbon removal as a function of time of photoelectrocatalytic treatment of 32 mg L^{-1} of copper–phtalocyanine dye on TiO_2 thin-film electrode in Na_2SO_4 0.5 mol L^{-1} in pH 8. E_{app} = 1.5 V.

sion of the absorbance signals on 674, 620 and 332 nm (due metallophtalocyanine group) and at 270 nm, mainly related with aromatics sites in the molecule, indicating that the process are efficient to remove colouration of RTB dye solution.

In addition, the products were also examined by HPLC equipped with a diode array detector operating at wavelength from 250 to 800 nm. The chromatograms before and after oxidation of 32 mg L^{-1} of copper–phtalocyanine dye used as standard solution are exhibited in Fig. 7. The original solution under gradient elution (Curve a) exhibits an intense peak due to copper–phtalocyanine dye with a retention time of t_r = 34 min detectable in all wavelength of 671, 621 and 342 nm (but a wavelength of 342 nm was chosen for analytical purpose) and several small shoulder due impurities detected in the original sample. After photoelectrocatalysis the main peak is dramatically diminished yielding a final chromatogram (Curve b), where is still observed only a residue of the dye content at concentrations

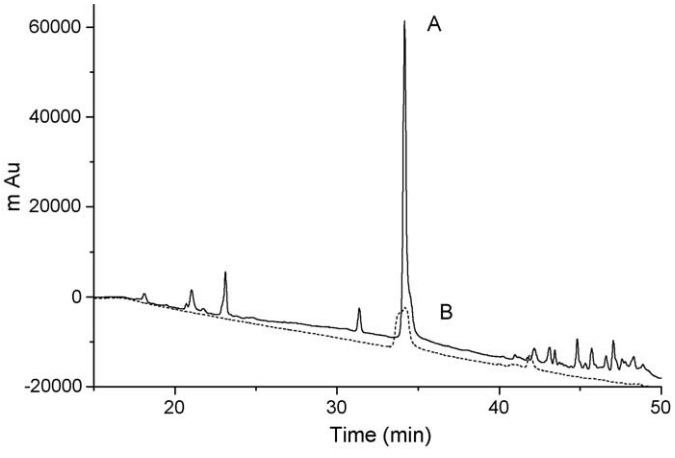

Fig. 7. HPLC chromatograms with detection at diode array for 32 mg L^{-1} of commercial remazol turquoise blue 15 dye in Na_2SO_4 0.5 mol L^{-1} pH 8 before (a) and after (b) photoelectrocatalytic oxidation on the TiO_2 thin-film electrode biased at +1.5 V. Column G-ODS (4 mm × 250 mm, 5 μm); mobile phase: ammonium acetate 10 mmol L^{-1} (eluent A) and methanol (eluent B) operating under gradient elution on flow rate of 1.0 mL min^{-1}. Setting parameters: 0–8 min 100% A, 48–50 min 50% A, 52–60 min 100% A. Wavelength of 342 nm.

of 2 mg L^{-1} (determined by area calibration curve). This result indicates that the dye content is markedly reduced and all the impurities present in the sample were removed during photoelectrocatalysis. In addition the analysis of the chromatograms obtained by HPLC coupled to diode array have not shown other detectable products.

Finally, the same solution submitted to photoelectrolysis was evaluated by TOC measurements. The results obtained from TOC experiments after 3 h of photoelectrocatalysis of 32 mg L^{-1} of dye in 0.5 mol L^{-1} Na_2SO_4 pH 8 are shown in Fig. 8. As can be seen a maximum of 79.6% of mineralization is reached after 3 h of photoelectrocatalysis. The results suggest that there is no total mineralization of the dye solution to CO_2 but the photoelectrocatalytic results are very significant when compared to other processes described in the literature [34–38] and very close to that obtained photoelectrochemical reactor with only one compartment [33].

To follow the copper content present after degradation of copper–phtalocyanine complex during the photoelectrocatalysis, anodic stripping voltammetric was carried out using mercury films electrode. For this, it was analyzed the free copper ions present into the yielding solution of the catholyte and anolyte and the copper accumulated in the photocathode (Pt gauze) after 3 h of treatment using the photoelectrocatalytic process. The amount of copper collected on the Pt gauze was 0.0011 ± 0.0004 mg, which is not considerable in the process. Nevertheless, the level of free copper released in the anodic compartment during the photoelectrolyzed process is 0.85 ± 0.09 mg L^{-1}. These results indicate that at least 54% of the copper present in the complex was released during the photoelectrocatalyze process and are present in the form of Cu(II) in the transparent solution.

Table 1 shows the results obtained for the Salmonella/microsome microsuspension assay. In this test an increase in the number of revertants per plate in relation to the doses tested would indicate mutagenic activity of the sample tested. As it can be observed in Table 1 no increase in the number of revertants per plate was detected when compared to the negative control in any of the doses tested for both treated and untreated dye solution. Although at doses that corresponded to 4 and 8 μg of

Table 1
Mean of the number of revertants per plate obtained in the Salmonella/microsome microsuspension assay with the strains of *Salmonella typhimurium* TA98 and TA100 with and without metabolic activation (S9 mix) for the doses tested (expressed in μg of dye per plate in relation to the treatment solution, see material and methods for details)

Sample	Dose μg of dye/plate	TA98		TA100	
		−S9	+S9	−S9	+S9
Before treatment	0	53.00 (6.75)	51.40 (6.11)	110.60 (9.63)	117.40 (6.54)
	1	48.00 (6.08)	52.67 (4.62)	107.33 (10.1) (10.1) (10.1) (10.12)	117.33 (9.87)
	2	53.00 (2.65)	46.00 (6.08)	109.00 (7.55)	118.67 (0.03)
	4	48.33 (3.79)	40.67 (2.08)	109.00 (9.54)	110.33 (17.8)
	8	50.33 (5.03)	39.00 (2.65)	114.33 (2.08)	112.00 (7.00)
After treatment	0	53.00 (6.75)	51.40 (6.11)	110.60 (9.63)	117.40 (6.54)
	1	56.67 (5.03)	50.00 (5.57)	116.67 (18.6)	130.67 (7.64)
	2	49.67 (2.52)	23.00[a] (4.36)	118.00 (6.08)	103.33 (6.43)
	4	0[a]	19.33 (7.77)	81.33[a] (16.7) (16.65)	86.00[a] (12.0)
	8	0[a]	12.67[a] (1.53)	67.67[a] (10.7)	72.00[a] (3.46)
	Positive control[b]	1440	520	2030	1900

[a] Counts below the control indicates killing of the exposed bacteria (toxicity).
[b] 4-Nitroquinoline at 0.125 μg/plate without S9; 2-aminoanthracene at 0.625 μg/plate with S9.

the treated dye per plate a decrease of the number of revertants was observed, indicating a toxic effect for the tested strains. Because of these results we evaluated the same dye solution in an acute toxicity assay, using the marine luminescent bacteria *V. fischeri*. In this assay the reduction of light emission by the bacteria indicates toxicity in the analyzed sample.

Fig. 9 summarizes the results obtained for the sodium sulphate used as supporting electrolyte, treated and untreated dye solution. All samples showed some degree of light reduction depending on the dose tested, but the highest toxicity was observed for the treated dye solution. From the graphs the CE20 (15 min) was calculated for each sample. For the sodium sulphate it was 80 mg mL^{-1}, for the dye solution, 62 mg mL^{-1} (after colour correction) and for the treated dye solution 21 mg mL^{-1}. The lower the CE20 more toxic is the sample. This increase in toxicity could be explained by the release of free cooper ions during the degradation of the dye. Concentrations of copper that show toxic effect for *V. fischeri* is around 0.3 mg L^{-1} [44] and the concentration of free copper detected in the solution after treatment was 0.85 mg L^{-1} as already cited above.

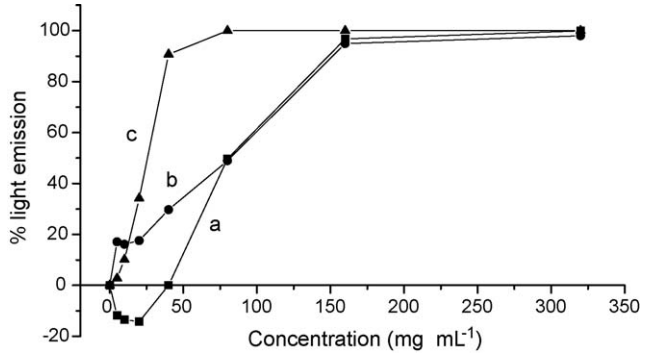

Fig. 9. Percentage of light inhibition of the marine luminescent bacteria *Vibrio fischeri* in relation to the tested concentrations. Sodium sulphate (Curve a) presented a CE20 (15 min) of 80 mg mL^{-1}; the dye solution before treatment 62 mg mL^{-1} (Curve b) and after treatment, 21 mg mL^{-1} (Curve c).

4. Conclusion

Despite the fact that the decolourization of textile waste is based on optimal solution acceptable to treatment plants, we must continue to strive for both decolourization as well as complete mineralization and the final evaluation of the efficiency of the treatment should be complemented with toxicological assays. Our results indicate that copper–phtalocyanine dye solution can be degraded by photoelectrocatalysis using a simple reactor operating with two germicide UV light and potential of +1.5 V very rapidly when compared to alternative oxidation process. Nevertheless, due to liberation of copper ions during the treatment, it is important that they are removed or reduced to safe concentrations [45] before the treated effluent is released to the aquatic environment.

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