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ORIGINAL PAPER

Mutagenic activity removal of selected disperse dye by photoeletrocatalytic treatment

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Abstract The degradation of black dye commercial product (BDCP) composed of C.I. Disperse Blue 373, C.I. Disperse Orange 37, C.I. Disperse Violet 93 dyes was investigated by photoelectrocatalysis process. The dyes have shown high mutagenic activity with *Salmonella* strain YG1041 and TA98 with and without S9. Samples of BCPD dye submitted to conventional chlorination and photoelectrocatalytic oxidation were compared monitoring its products by HPLC using a diode array detector, spectrophotometry UV–vis, TOC removal, and mutagenicity potency. The photoelectrocatalytic method operating with Ti/TiO_2 as anode at +1.0 V and UV illumination presented fast oxidation of test solutions containing 10 mg L^{-1} of dye in 0.1 mol L^{-1} NaCl pH 4.0 leading to 100% of discoloration, 67% of mineralization, and negative response to all tested *Salmonella* strains. The formation of $Cl^{\bullet}$, $CL_2^{\bullet}$ on photoelectrocatalytic medium improved the efficiency of the method in relation to conventional chlorination method that promoted 100% of discoloration, but only 8% of TOC removal and more mutagenic product.

Keywords Mutagenic activity · Disperse dyes · Photoelectrocatalytic oxidation · Chlorination of azo dyes

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1 Introduction

A novel class of mutagenic compounds derived from dinitrophenyl azo dyes was isolated in rivers in Japan, accounting, in same cases, for at least 50% of the mutagenic activity detected in the water bodies [1–6]. The dyes are converted to non-chlorinated derivatives of the PBTA compounds (non-ClPBTA) in which the NO_2 group is reduced to NH_2 by treatment with reducing reagents such as sodium hydrosulfite during the treatment of dye processing plant effluents. The PBTA compounds are formed from the non-ClPBTAs by chlorination reagents such as sodium hypochlorite during the sewage treatment process [1, 3–5, 7, 8]. According to Shiozawa et al. [3] the mutagenic activity of PBTAs, detected with the strain TA98 and YG1024 of *Salmonella typhimurium* in the presence of metabolic activation is around 60 times greater than the corresponding parental azo dye. A study performed with PBTA1, PBTA2, and related azo dyes showed that these compounds are cytotoxic for Chinese hamster lines CHL and V79-MZ, inducing multilobed nuclei and binucleated cells. This study suggests that these compounds affect not only DNA but also structural and regulatory proteins involved in cell division [7].

Cristais river in the metropolitan region of São Paulo, Brazil, was contaminated by mutagenic effluents released by a dye processing plant located 6 km upstream from a drinking water treatment plant (DWTP) [9, 10]. In this area, the river water, sediment, drinking water, and DWTP sludge showed mutagenic activities [10]. A black dye commercial product (BDCP) (CVS) was, at least partially, responsible for the mutagenic activity detected in all these samples, except for the drinking water [9]. But, the results obtained with *Salmonella* assay using nitroreductase and O-acetyltransferase overproducing strains and different

extraction procedures indicated that all samples, including the drinking water, showed mutagenic activity that was related to the presence of BCPD dye and its derivative compounds [11–14].

Previous work [9–14] have indicated that the commercial product BCPD is composed of three disperse azo dyes: C.I. Disperse Blue 373, C.I. Disperse Orange 37, and Disperse Violet 93, whose structures are shown in Fig. 1. Each component of the BCPD was shown to have mutagenic strengths of 6,300, 4,600, and 280 revertants μg^{-1} for YG1041 with S9, respectively [14]. The drinking water treated in the DWTP also presented mutagenic activity, which in this case serves a population of 60,000 inhabitants [12].

An attractive process popularized in the past few years for degrading organic pollutants is the photoelectrocatalysis. The technique is based on combining process of the heterogeneous photocatalytic process operating on a catalyst as TiO_2 immobilized on Ti foil under UV irradiation and a positive potential higher than flat band potential of the semicondutor. This configuration allows the more effective separation of photogenerated charges thereby increasing the lifetime of electron–hole pairs [15] and decreasing the recombination rate of the generated charges with excellent application for the remediation of textile dyes [16–22]. Nevertheless, there is no work reported in the literature dealing with removal of dyes with confirmed mutagenic activity.

Therefore, the objective of this work was to optimize a photoelectrocatalytic treatment to removal all components present (C.I. Disperse Blue 373, C.I. Disperse Orange 37, and Disperse Violet 93) in the commercial CVS dye (chemical structures shown in Fig. 1) and also test its influence on the mutagenic properties of these compounds or its byproducts generated. The process is compared with conventional chlorination process usually adopted in DWTP.

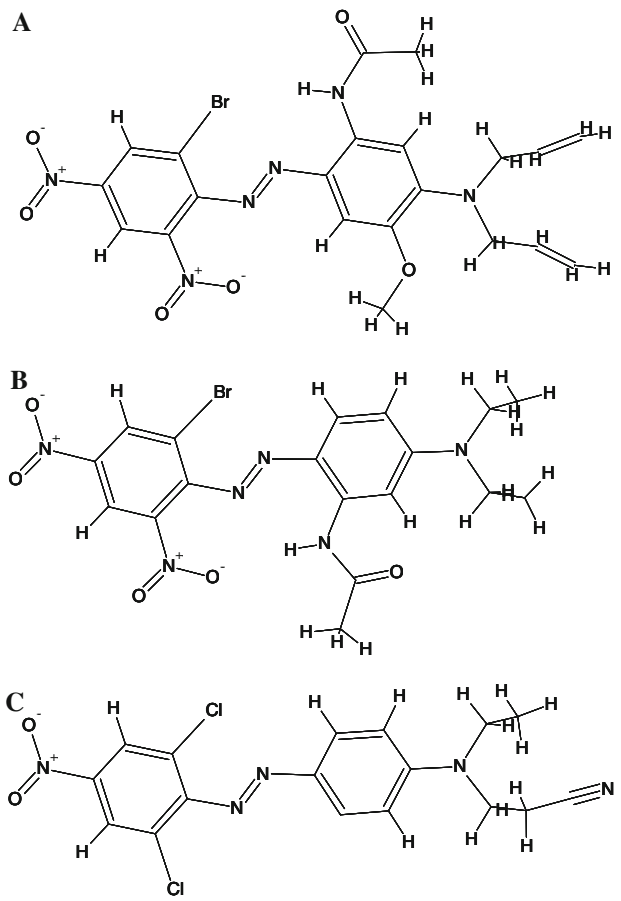

Fig. 1 Chemical structures of the components of CVS dye assigned as **a** C. I. Disperse blue 373; **b** C.I. Disperse violet 93; and **c** C. I. Disperse orange 37 dyes

2 Materials and methods

2.1 HPLC analysis

The BCPD commercial dye sample was kindly provided by a Textile industry. Stock solution of the BCPD dye was prepared by dissolving the commercial sample in acetonitrile (J. T. Baker) HPLC grade and deionized water (Milli-Q® System—Millipore, Milford, MA, USA) in the proportion 50:50, v/v. The disperse dyes: Disperse Orange 37 (DO37), Disperse Violet 93 (DV93), and Disperse Blue 373 (DB373) (Fig. 1), chemical components of the commercial sample of BCPD dye, were extracted in silica-gel 60H (Merck—0.063–0.200 mm) compacted in a glass column. A mixture of hexane (Synth p.a.) and ethylacetate (Synth p.a.) (80:20 v/v) was used to elute the components of the BCPD samples. The major fractions were purified in Sep-Pak C18 (Millipore, Milford, MA, USA) cartridges, pre-conditioned and eluted with acetonitrile. After the elution, the aliquots were dried in a rotating evaporator under a flow of ultrapure N_2, and then tested as to their purity using a high performance chromatography technique with diode array detection (HPLC-DAD-Shimadzu, model SCL-10AVP). Next each component was analyzed by mass spectrometry (UltrOTOFQ—ESI-TOF Mass Spectrometer—Bruker Daltonics, Billerica, MA, USA) and ^{1}H and ^{13}C NMR spectroscopy in a DMSO-d_6 (Varian INOVA 500 spectrometers at 500 MHz). The chromatograms and obtained spectra confirmed the structures previously identified [10, 11]. These samples of C.I. Disperse Orange 37 (DO37), C.I. Disperse Violet 93 (DV93), and C.I. Disperse Blue 373 (DB373) were used to construct analytical curves in order to spike the environmental samples and also to analyze the collected samples using the standard addition method.

The high performance liquid chromatographic analyses were carried out in a Shimadzu SCL-10AVP apparatus coupled with a diode array detector. The chromatograms were investigated between 200 and 800 nm, and the maximum wavelengths selected to analyze the disperse dyes DO37, DV93, and DB373 were 428, 562, and 592 nm, respectively. The HPLC analysis was performed in a reversed-phase column Shimadzu CLC-ODS (C18) (25 cm × 4.6 mm × 5 μm, 100 A) connected to a guard column Shimadzu CLC-ODS (C18) (1 cm × 4.6 mm × 5 μm, 100 A). All solutions were filtered before the analysis in a 0.45-μm PTFE filter. The best experimental conditions under optimized isocratic mode were: a mobile-phase acetonitrile/water 85:15 v/v, a flow rate of 1.0 mL min^{-1}, and a column temperature of 40 °C. The analysis time was 15 min, and all the analyses were carried out in triplicate. The results were compared with an HPLC coupled to a UV–Vis detector (ProStar Varian HPLC apparatus with two high pressure gradient pumps (model 210/215)) operating under isocratic conditions coupled to a UV–Vis spectrophotometric detector (Varian ProStar 320).

Taking into account the injected volumes, we calculated the respective masses of the dyes DO37, DV93, and DB373 and the analytical curves were constructed by plotting the peak area versus amount (mass). The concentration of each disperse dye in the analyzed sample was obtained by a linear regression of these analytical curves. All the chromatographic measurement of samples collected from photoelectrocatalytic and chlorinated treatments were carried out in triplicate.

2.2 Chlorination of the BCPD dye

Samples of 1 mg L^{-1} of BCPD dye, commercialized as a mixture of three azo dyes: C.I. Disperse Blue 373, C.I. Disperse Violet 93, and C.I. Disperse Orange 37 [10–13], were submitted to conventional chlorination step, which simulated the process usually adopted in the DWTP. Briefly, this treatment consisted of: pH correction with the application of NaOH, pre-chlorination with chloride gas (Cl_2), addition of aluminum sulfate, flocculation, coagulation, and flotation. The final concentration of the residual free chlorine in the treated water was kept around 1.5 mg L^{-1} as required by Brazilian Federal Law [18]. The free active chlorine in the solution was quantified by colorimetric method based on *N*,*N*′-diethyl-*p*-phenylenediamine (DPD) reaction according to Official method [19].

2.3 Evaluation of the mutagenic activity

The *Salmonella* mutagenicity test was performed using the microsuspension method [10, 11]. To evaluate the solution of the dye and the product of chlorination and photoelectrocatalytic treatments, it was used the strains TA98 (HisD3052, rfa, Δbio, ΔuvrB, pKM101) and the nitroreductase and *o*-acetyltransferase overproducing strain, YG1041, which is derived from TA98, in the presence and absence of S9 mix containing 4% (v/v) lyophilized Aroclor-1254-induced rat liver S9 fraction (Moltox Inc.) and cofactors. The dried extract was re-suspended in DMSO just before the test. Five different doses at minimum dose of 0.1 mL equivalent and maximal dose of 30 mL equivalent were tested in duplicate. Positive controls were 4-nitroquinoline-1-oxide (Sigma) at 0.125 μg/plate for TA98, 4-nitro-*o*-phenylene-diamine at 0.25 μg/plate for YG1041, and 2-nitrofluorene at 25 μg/plate for YG1042 without S9, respectively; and 2-aminoanthacene (Sigma) at 0.03125 μg/plate for these strains with S9. Results were statistically analyzed using the Salanal computer program, with the Bernstein model, and expressed as revertants L^{-1} equivalent of water.

2.4 Photoeletrocatalytic degradation of BCPD solution

All photoelectrochemical experiments were conducted using Ti/TiO_2 thin-film photoelectrodes. The electrodes were prepared by coating a titanium foil back contacts (0.05 or 0.5 mm thick, Goodfellow Cambridge Ltd) with TiO_2 colloidal suspensions, using a sequence of four repetitions of dipping, drying, and firing at 300 °C for 3 h. Further details concerning this procedure and characterization of these thin-film electrodes are available in the literature [20, 21]. The photoelectrocatalytic oxidation experiments were performed in a 150 mL photoelectrochemical reactor (Fig. 2) equipped with water refrigeration using an ultra-thermosthatic bath (Nova Técnica, Brazil). In the cell was positioned a working electrode, an auxiliary electrode, and a saturated calomel electrode (SCE) placed close to the working electrode using a bridge tube containing a Vycor frit tip. The photoactive area of the anode (TiO_2) was 9 cm^2 and it was illuminated with UV light source (315–400 nm) using a 125 W Philips medium pressure mercury lamp ($I = 9.23$ W m^{-2}) without the glass, inserted in a quartz bulb separated 2.5 cm from the photoanode. The dye aqueous solution was placed in the reactor and the photoelectrochemical process was carried out by bubbling compressed air. A Pt gauze electrode (4 cm^2) was used as counter electrode. The controlled potential electrolysis were carried out using the same compartment cell, where the Pt gauze (4.0 cm^2) acted as cathode and the other Pt gauze (4 cm^2) acted as anode, without UV illumination.

A Potentiostat/Galvanostat EG&G PARC model 283 controlled by the Electrochemical 270 software was used to bias the photoanode in the photoelectrocatalytic oxidation experiments and also to control the potential and to record

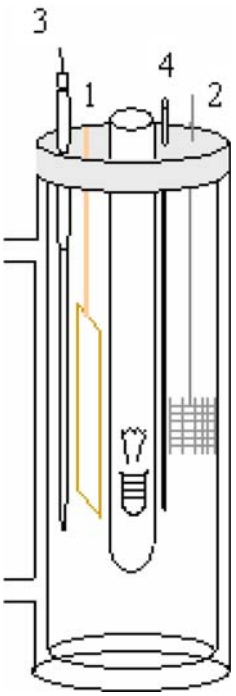

Fig. 2 Schematic diagram of the photoelectrochemical reactor constructed in glass water refrigerated by an ultra-thermostatic bath containing: (1) reference electrode; (2) working electrode; (3) quartz bulb; (4) air; (5) counter electrode; (6) and (7) water circulation; (8) lamp of 125 W Philips medium pressure mercury without the glass

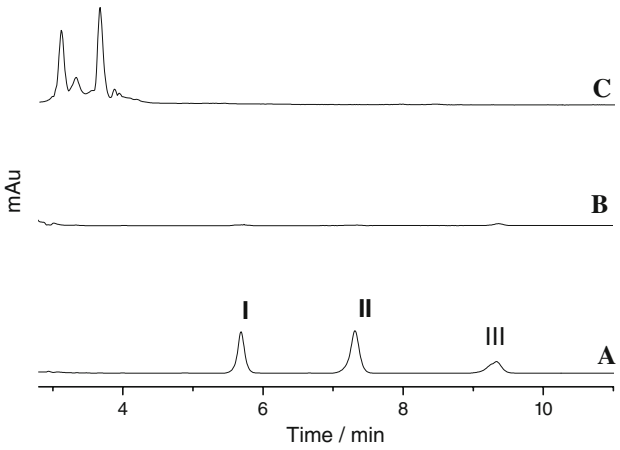

Fig. 3 HPLC chromatograms with diode array detection for 2.5 mg L^{-1} of CVS dye (*A*) showing the peaks of components: (I) C.I. Disperse Blue 373; (II) C.I. Disperse Violet 93; and (III) C.I. Disperse Orange 37 before (*A*) and after (*B*) 60 min of photoelectrocatalytic oxidation under $E = 1$ V and UV illumination, in NaCl 0.025 mol L^{-1}, pH 4.0 and (*C*) chlorination treatment. Mobile phase: acetonitrile:water (85:15 v/v). Flow rate—1 mL min^{-1} and controlled temperature—30 °C

the current decrease in function of time during electrolysis at controlled potential.

3 Results and discussion

3.1 Photoelectrocatalytic oxidation of BCPD

Figure 3 (curve A) shows a typical chromatographic separation for commercial BCPD dye, where three main dyes components were identified at $t_{r1} = 5.71$ (C.I. Disperse Blue 373; blue dye), $t_{r2} = 7.34$ (C.I. Disperse Violet 93; violet dye), and $t_{r3} = 9.39$ (C.I. Disperse Orange 37; orange dye). The attribution was carried out by individual detection of each component separated as described in Sect. 2.

The corresponding spectra in the UV–vis range recorded in the hydrodynamic conditions of HPLC couple to diode array obtained for each component of BCPD dye (Graphs 1, 2, 3) are shown in curve A of Fig. 4. Each spectra presents a set of characteristics bands at 595 (intense peak), 287, 210 nm for DB373 dye; at 562 (intense peak), 299, 236, 215 for violet dye and at 433 (intense band), 310, 272 for orange dye.

In order to further investigate the full potential of the photoelectrocatalytic approach, the product generated after 1-h period of photoelectrolysis of 2.5 mg L^{-1} of BCPD dye in NaCl 0.25 mol L^{-1} at pH 4 with the photoanode biased at +1.0 V were investigated by HPLC with a diode array detector. Figure 3 (curve B) shows the correspondent chromatograms recorded for treated sample. It is possible to see that the chromatograms do not shown any signal for the main peak due DB373 (peak I), DV93 (peak II), and DO37 (peak III). The absorption spectra recorded for each component after 1-h of photoelectrocatalytic oxidation of BCPD dye also exhibited the absence of absorbance bands, as shown curve B of Fig. 4.

The performance of photoelectrocatalytic treatment on each individual component of BCPD dye can be better analyzed on Fig. 5 (curves B, C, and D). One hundred percent of dye removal was observed by monitoring the chromatographic area of each dye after 5 min of treatment. It is important to notice that concentration was determined adopting an analytical methodology calibrated to reach a limit of detection (LOD) evaluated as the signal-to-noise ratio equal to 0.09 ng (DO37), 0.84 ng (DV93), and 0.08 ng (DB373).

In agreement with our previous findings [20, 22], it has been suggested that in the presence of chloride solution as supporting electrolyte the main degradation route of azo dye involves the action of $CL_2^{\bullet -}$ and $Cl^{\bullet}$ radicals electrogenerated during the heterogeneous oxidation process. The high oxidative power of these radicals, standard potential of $E^0_{Cl^{\bullet}/Cl^-} = 2410$ V versus NHE and $E^0_{Cl_2^{\bullet}/2Cl^-} = 2.090$ V versus NHE [22], leads to high efficiency of the adopted method to remove the dye up to level of traces in few minutes of treatment. It is supposed that adsorbed chloride ions on the semiconductor surface acting as an anode could be oxidized by holes generated under UV irradiation leading to formation of $Cl^{\bullet}/HOCl^{\bullet}$ species, which can be used to degrade the organic pollutant or to form active chlorine (Cl_2, HClO, ClO^-) in solution in absence of organic compounds [20].

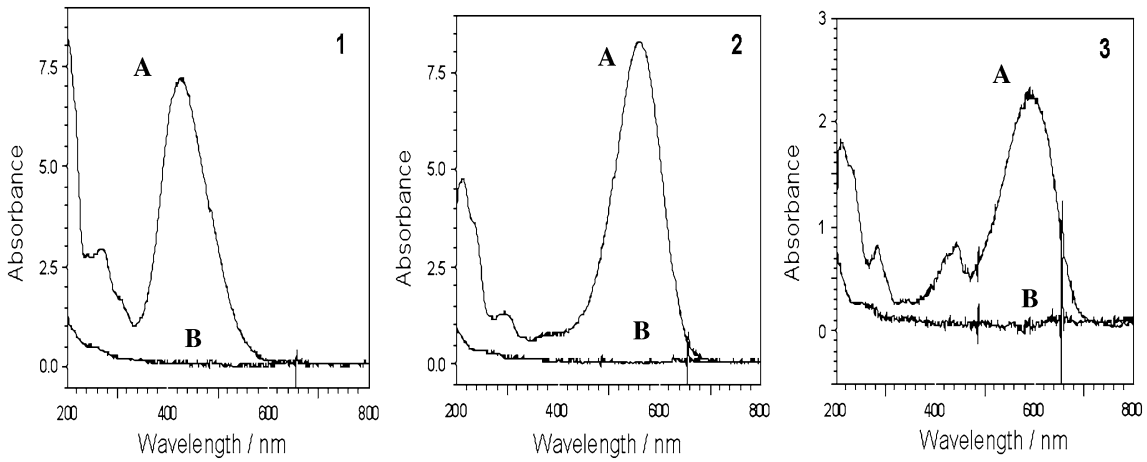

Fig. 4 UV–vis absorption spectra obtained for (1) C.I. Disperse Blue 373; (2) C.I. Disperse Violet 93; and (3) C.I. Disperse Orange 37 present in a sample of 2.5 mg L^{-1} of CVS dye separated on HPLC and recorded at diode array detector from 200 to 800 nm, chosen taking into consideration the retention time of each peak on the chromatograms before (*A*) and after 60 min of photoelectroctalytic oxidation (*B*)

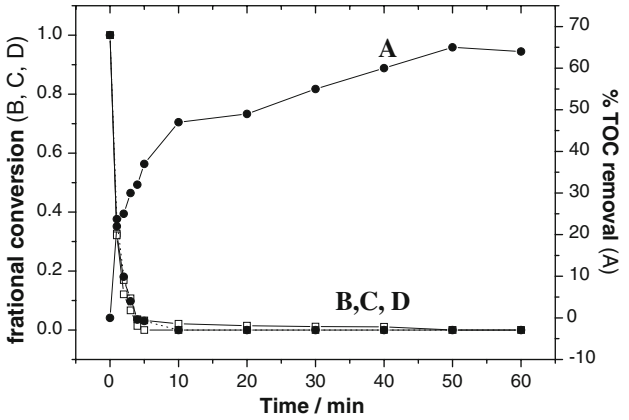

Fig. 5 (*A*) Total organic carbon removal of 10 mg L^{-1} BCPD treated by photoelectrocatalytic oxidation. (*B–D*) Degradation of BCPD dye during 1 h of photoelectrolytic treatment of 10 mg L^{-1} of BCPD dye in NaCl 0.10 mol L^{-1} at pH 4, with the photoanode biased at +1.0 V and UV irradiation. Components of BCPD dye separated by chromatographic signal (CLAE/DAD) (*filled circle*) DB373 (*filled triangle*) DO37 (*filled square*) DV93

The effect of initial chloride concentration on the photoelectrocatalytic oxidation of BCPD was examined between 0.010 and 0.250 mol L^{-1}, using UV irradiation. Results obtained indicate that a minimum concentration of 0.010 mol L^{-1} was necessary to reach at least 50% of dye removal after 60 min of treatment. The time of electrolysis to reach 100% of dye removal increased proportionally to increases in initial NaCl concentration up to 0.1 mol L^{-1}. Above these values, dye removal is almost constant and it was adopted in the further experiments.

The effect of pH on the photodegradation rate of BCPD dye was investigated by testing treatment solutions of 100 ppm of BCPD dye in NaCl 0.1 mol L^{-1} at pH values from 2.0 to 12 and applied potential of +1.0 V. Aliquots removed during photoelectrocatalytic oxidation and the degradation rate followed during 60 min recording chromatograms for sample collected at each 5 min were analyzed. The oxidation of each component of BCPD dye reaches 100% of degradation after 60 min, following a process controlled by a pseudo first-order reaction, showing a linear relationship of ln C_t/C_0 versus time, whose degradation rate constants are presented in Table 1. These results show that dye removal is to a great extent faster at acidic medium with preponderant degradation rate constant at pH $\leq$ 4. In all further investigations, pH 4.0 was selected as the optimum pH to investigate the dye degradation using chlorine medium.

The effect of applied potential on rate constants was also estimated from the degradation measurements obtained during photoelectrocatalytic oxidation of 10 mg L^{-1} of BCPD dye in NaCl 0.1 mol L^{-1} at pH values from 4.0. The results indicate a linear relationship between ln[C_t/C_0] and treatment time for all potential higher than flat band potential of TiO_2, that in this condition presented values around –0.25 V versus SCE. The rate degradation constant (k) values obtained after 60 min of treatment for all components of BCPD dye are shown in Table 1.

Clearly, the data in Table 1 underline the fact that degradation on Ti/TiO_2 electrodes performed at +1.0 V and UV irradiation is significantly faster when only higher applied potential is adopted. The chemical structure of each dye is also seen to influence its chemical degradation. Faster removal is observed for DV93, where unsaturated amine facilitates the attack of chlorine/hydroxyl radicals. The lower degradation rate is observed for DO37, where the chlorine substituent compromises the electron density influence on the chemical structure.

Table 1 Influence of applied potential and pH of solution on the degradation rate constant values, k (min^{-1}), obtained from plots of [$\ln(C_t/C_0)$] versus treatment time, for the photoelectrocatalytic oxidation of 10 mg L^{-1} of CVS dye in 0.1 mol L^{-1} NaCl

Components of CVS dye	Influence of potential[a]		Influence of pH[b]	
	Applied potential (V)	k (min^{-1})	pH	k (min^{-1})
DB373	+0.8	0.01720	2	0.02103
	+1.0	0.02103	4	0.02860
	+1.2	0.00565	7	0.01980
	+1.4	0.00219	12	0.00191
DO37	+0.8	0.00538	2	0.00327
	+1.0	0.00560	4	0.00343
	+1.2	0.00339	7	0.00227
	+1.4	0.00344	12	0.0083
DV93	+0.8	0.0169	2	0.0208
	+1.0	0.0208	4	0.0560
	+1.2	0.0232	7	0.0290
	+1.4	0.0049	12	0.0263

Values monitored by peaks obtained for C.I. Disperse blue 373 (DB373), C.I. Disperse orange 37 (DO37), and C.I. Disperse violet 93 (DV93) separated on chromatographic conditions CLAE/DAD

[a] pH = 4

[b] Applied potential = 1 V versus SCE

Finally, the potentiality of photoelectrocatalytic process to mineralize all the components of BCPD dye was evaluated using TOC measurements. The results obtained from TOC experiments after 60 min of photoelectrocatalysis of 10 mg L^{-1} of BCPD dye in 0.1 mol L^{-1} NaCl pH 4.0 is shown in Fig. 5 (curve A). A maximum reduction of 67% was obtained, respectively. Reduction of TOC concentration can be a good parameter for assessing the energy consumption of the process [23]. This can be described by the equation: Energy consumption/TOC removed/h/A/m^2 = I (A) × V (L) × time (h)/kg ($TOC_{t=0} - TOC_t$). The values obtained for TOC pollutant was of 0.040 kWh/kg. While one cannot totally mineralize the BCPD dye to CO_2 in either of these solutions, these degradation results are much better than in chlorination processes as shown above.

3.2 Chlorination of BCPD dye

Further evidence of the importance to generate $Cl^{\bullet}$, $Cl_2^{\bullet}$ radicals as the primary oxidant in the dye degradation was investigated comparing the previous results with treatment of 2.5 mg L^{-1} of BCPD dye at pH 4.0 by conventional chemical chlorination, as described in Sect. 2. HPLC chromatograms of the BCPD dye after chlorination is shown in Fig. 3, curve C, where the response obtained for original dye (curve A) and photoelectrocatalytic treated samples (curve B) are also compared. After 2 h of chlorination complete removal of the original dye is observed. In addition, the UV–vis absorbance spectra obtained for each component monitored at specific retention time reaches a maximum discoloration of 100% after 2 h of oxidation reaction. Nevertheless, the chromatograms presented four new peaks rising at $t_{r1} = 3.2$ min, $t_{r2} = 3.5$ min, $t_{r3} = 8$ min, and $t_{r4} = 4$ min indicating that new byproducts are generated in this experimental conditions, which were not detected in the product treated by photoelectrocatalytic oxidation.

Total organic carbon removal of the chlorinated solution was also monitored and presented only maximum of 8% of TOC removal. These results suggest that the chlorination process involves only partial cleavage of the dyes molecules.

Therefore, it appears that, as chlorine radicals are better oxidants than only active chlorine species, mineralization of the original dye is more efficient when a photoelectrocatalytic oxidation process is used under conditions that can generate chlorine radicals. The rapid discoloration and mineralization observed in the photoelectrocatalytic oxidation probably justify the absence of sub-products detected during oxidation reaction by chlorination reaction, where active chlorine is the preponderant species.

3.3 Evaluation of mutagenic activity

According to Umbuzeiro et al. [11, 23], the BCPD dye is mutagenic with a potency of 9,300 and 119,000 revertants L^{-1} for YG1041; 1,100 and 3,100 revertants L^{-1} for TA98 assay without and with S9, respectively [14]. The results are illustrated in Fig. 6.

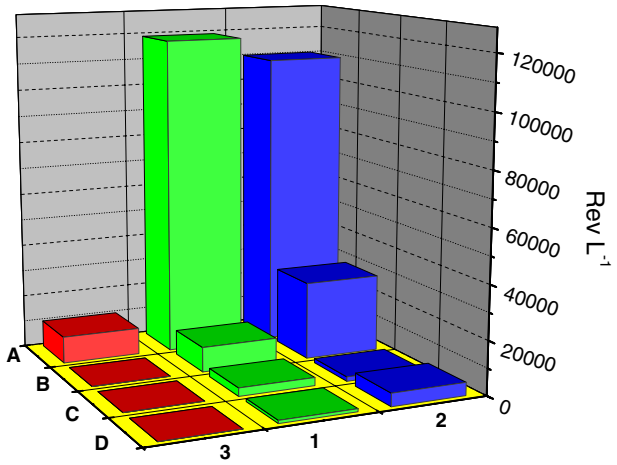

Fig. 6 Mutagenic profile of the BDCP dye (1), chlorinated BDCP dye (2), BDCP dye after 60 min of photolectrocatalytic oxidation at +1.0 V + UV irradiation on Ti/TiO_2 (3) using different strains of *Salmonela* (*A*, *B*) TA98 and (*C*, *D*) YG1041 in the presence and absence of S9

The mutagenic response of the chlorinated sample of BCPD dye was evaluated following the procedure described in Sect. 2 in agreement with methodology adopted in DWTP. Although we did not detect the dyes in the chlorinated solution, mutagenic activity was still detected, both with TA98 and YG1041 in the absence and presence of S9 (Fig. 6) in solutions of BCPD chlorinated at the same experimental conditions described previously. Potency of 29,000 and 110,000 revertants L^{-1} for YG1041; 4,800 and 1,600 revertants L^{-1} for TA98 assay without and with S9, respectively, was obtained. The values are dramatically increased for TA98 and YG1041 without S9. Considering the great increase of the potency obtained with the YG1041 in relation to the parental strain TA98, it is possible to conclude that the non-colored generated compound(s) generate a more harmful compound [10, 11]. Thus, these results are great environmental concern since this kind of product could be generated during conventional water treatment, which is usually employed during chlorination as disinfections process [11].

Mutagenic potency of BCPD dye before and after 2 h of photoelectrocatalytic treatment, operating at 1 V and UV irradiation was assessed in the same experimental condition of original dye and chlorinated dye, as elaborated in Sect. 2. There was 100% removal of potency for TA98 in the absence and presence of S9. The tested samples involving YG1041 pointed 100% and 92% of removal with and without S9 strains, respectively. These results lead to the inevitable conclusion that the photoelectrocatalytic oxidation is efficient to decrease the mutagenicity of the sample detected previously for the untreated and treated BCPD dye by chlorination process.

4 Conclusion

In summary, this study demonstrates that a photoeletrocatalytic procedure leads to a fast and complete degradation of BCPD dye, promotes significant mineralization of the dye (around 72%) and high removal of mutagenic activity can be achieved. The highest BCPD degradation rate was found to occur in chloride solution, which in turn seems to account for generation of powerful oxidants such as $Cl_2^{\bullet}$, $Cl^{\bullet}$, and $OH^{\bullet}$ radicals that are directly responsible for fast dye degradation and no formation of more mutagenic compounds. The photodegradation was very effective and could be appropriate to treat wastewater effluents reaching the public sewage treatment plants, where the dye concentration is usually diluted and the dye could be present at low concentration.

Despite the fact that chlorine has been used extensively as a disinfectant for water purification systems, chlorinated compounds could result in this process, which could increase the mutagenicity potency detected for BCPD samples treated with active chlorine.

Although, our method warrants further studies to clarify the generated product, the suppression of mutagenic response indicates that the formation of chlorine radicals can be more efficient than only treatment by active chlorine. Despite, the chlorination of textile waste is based on optimal solution acceptable in treatment plants, analysis of our results have shown that the generated products can be more harmful than the original dye. Future efforts should identify the structures of those new compounds, then a toxicological characterization could establish the risks involved in the consumption of the contaminated drinking water.

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