



Simultaneous removal of chromium and leather dye from simulated tannery effluent by photoelectrochemistry

Fabiana Maria Monteiro Paschoal^a, Marc A. Anderson^b, Maria Valnice B. Zanoni^{a,*}

^a Departamento de Química Analítica, Instituto de Química, Universidade Estadual Paulista, Av. Prof. Francisco de G. Degni, s/n, C. P. 355 14801-970 Araraquara, SP, Brazil

^b Environmental Chemistry and Technology Program, University of Wisconsin-Madison, 660N. Park Street, Madison, WI 53706, USA

ARTICLE INFO

Article history:

Received 8 August 2008

Received in revised form

18 November 2008

Accepted 19 November 2008

Available online 27 November 2008

Keywords:

Photoelectrocatalysis

Leather dye

TiO₂ electrode

Chromium reduction

Photoelectrochemistry

ABSTRACT

The feasibility of the photobleaching of a leather acid dye, acid red 151, simultaneously to degradation of anionic surfactant, Tamol[®], and reduction of Cr(VI) to the less toxic Cr(III) was investigated by photoelectrocatalytic oxidation. The best experimental conditions were found to be pH 2.0 and 0.1 mol L⁻¹ sodium sulfate when the nanoporous Ti/TiO₂ photo anode was biased at +1.0 V and submitted to UV-irradiation. The photoelectrocatalytic oxidation promotes 100% discoloration, reducing around 98–100% of Cr(VI) and achieving an abatement of 95% of the original total organic carbon. The effect of pH, the applied potential, the Cr(VI) concentration and the complexation reaction between Cr(VI) and acid red dye were evaluated as to their effect on the kinetics of the reaction.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The transformation of raw skin into manufactured products requires a series of complex treatments [1]. This process of tanning is one of the oldest procedures in the world, and currently these industrial activities are based on chemical processes involving several organic and inorganic compounds, such as: acids, chromium salts, dyes, auxiliaries and other chemical additives [2]. Therefore, tannery wastewaters constitute a substantial pollutant. These wastewaters can cause severe environmental problems related to their high chemical oxygen demand, elevated chrome concentrations and deep color content. While the tanning industry has been in existence for centuries, the significant deterioration of water bodies due to these improperly managed wastewaters has received serious consideration only in the last few years [3,4].

Although the majority of operations in the leather industry are based on the use of Cr(III), attention is being expressed about the possible hazards arising from the presence of chromium(VI) in the effluent due to its generation by oxidation steps or natural bio-transformations in the environment [5,6]. The environmental importance of these species is derived from the difference in toxicity of the different valence states of chromium. Hexavalent chromium is highly soluble, remarkably toxic and is a suspected

carcinogen and mutagen. Cr(III), in contrast, is readily precipitated at a certain pH and exhibits no toxicity, even being considered an essential element to human metabolism at controlled levels [7].

In addition, the dyeing of leather is one of the most important steps in post-tanning operations in leather production. The use of acid dyes bearing azo groups is very popular in the leather industry. This process typically requires surfactants or other dispersing agents to overcome the complexity of leather as a substrate. Therefore, as a consequence a very complex effluent is generated containing organic and inorganic compounds that can be lost to superficial water due to inefficient operations of the treatment. In addition, another complication is the possible complexation between chromium and some azo dyes [8] that can lead to very stable complex, which is harder to destroy.

Over the last few years, a number of studies have been proposed to remove organic waste materials and others have been aimed at removing inorganic pollutants. One of the most promising methods to treat such complex systems has been the photocatalytic system due to their ability to treat low levels of contaminants [9]. Several authors have indicated the possibility to reduce Cr(VI) using semiconducting materials such as TiO₂ [10,11]; ZnO [12,13]; WO₃ [14]; among others. On the other hand, the application of photocatalytic methods for the oxidation of dyes in wastewater using TiO₂ and UV-irradiation is a well-known process [15–17]. Although, the reduction of chromium simultaneously to oxidation of organics has been previously explored in the literature [18–20] the high rate of

* Corresponding author. Fax: +55 16 33227932.

E-mail address: boldrinv@iq.unesp.br (M.V.B. Zanoni).

electron/hole pair recombination reduces the quantum yield of the TiO_2 process and represents a major drawback to its application.

Photoelectrocatalytic oxidation has been proposed as an attractive way to increase photocatalytic efficiency in general, especially for degrading textile dyes [21,22]. In this system, a biasing potential is applied across a photoanode on which the catalyst is supported. While the method has been presented higher efficiency for the successful conversion of some textile organic compounds, few studies have been conducted on the application of photoelectrochemistry to promote the simultaneous reduction of chromium and the oxidation of textile dye.

In the present work, we report the simultaneous reduction of Cr(VI) and also the degradation of the acid dye 151 in the presence of a surfactant agent (currently used in tanning/dyeing operations involving leather production to stabilize the color, to improve the dye solubility and also to improve fixation onto the leather fibers), by photoelectrocatalysis on nanoporous Ti/TiO_2 electrodes, simulating leather wastewater. The photoelectrocatalytic reduction of Cr(VI) was systematically compared to the photocatalytic process and the degradation of the azo dye with and without surfactants followed by measuring the kinetic parameters, assessing the total organic carbon (TOC) removal and the solution discoloration to verify the effectiveness of this method.

2. Experimental

2.1. Preparation of Ti/TiO_2 thin-film electrodes

Titanium(IV) isopropoxide (Aldrich) was used as a precursor for preparing TiO_2 colloidal suspensions. Typically, 20 mL of titanium isopropoxide was added to a nitric acid solution keeping the ratio of $\text{Ti/H}^+/\text{H}_2\text{O}$ at 1/1.5/200. The resulting precipitate was continuously stirred until completely peptized to a stable colloidal suspension. This suspension was dialyzed against ultrapure water (Milli-Q Millipore) to a pH of 3.5 using a Micropore 3500 MW membrane. Thin-film photoelectrodes were dip-coated onto a titanium-foil backed contact (0.05 or 0.5 mm thick, Goodfellow Cambridge Ltd.) after heating the Ti foils to 350°C . A sequence of dipping, drying and firing at 350°C for 3 h was used after each coating (five repetitions) according to a procedure described earlier [23]. A detailed

description of the characterization of these thin-film electrodes is presented elsewhere [24].

2.2. Apparatus and procedure

The photoelectrocatalytic oxidation experiments were performed in a 250 mL single compartment reactor maintained at 25°C using a thermostatically controlled water bath (Nova Técnica, Brazil). A working electrode of (TiO_2) acting as anode (12 cm^2), an auxiliary electrode of pt gauze and an Ag/AgCl reference electrode were arranged within the cell. The photoactive area of the anode (TiO_2) was 12 cm^2 and was illuminated using a UV light source (315–400 nm) from a 125 W Philips medium pressure mercury lamp ($I=9.23\text{ W/m}^2$) without the glass, inserted into a quartz bulb separated by a distance of 2.5 cm from the photoanode. The surfactant and dye in 0.1 mol L^{-1} sodium sulfate (Na_2SO_4) solutions were placed into the reactor without any pretreatment and the photoelectrochemical process was carried out using bubbling compressed air.

A potentiostat/galvanostat EG & G PARC Model 283 controlled by the software electrochemical 270 was used to bias the photoanode in the photoelectrocatalytic oxidation experiments. All pH measurements were made using a Corning 555 pH meter. In experiments where the pH was to be kept constant, 0.1 mol L^{-1} NaOH solution or H_2SO_4 solution was added to the cell in order to control the pH.

The concentrations of both surfactant and dye in solutions were analyzed using a Hewlett Packard 8453 spectrophotometer operating from 190 to 1000 nm in a quartz cell. The total organic carbon was monitored using a total organic carbon analyzer (a Shimadzu 5000A).

The Cr(VI) content was determined using the official colorimetric method [25], which employs the reaction with diphenylcarbazide (DPC), calibrated previously to a minimum detectable concentration of Cr(VI) of $10\text{ }\mu\text{g L}^{-1}$. Aliquots of $200\text{ }\mu\text{L}$ of the photoelectrolyzed solution were collected in a tube containing DPC solution in acidic medium. The product of the instantaneous reaction produced a red color ($\lambda=540\text{ nm}$), which was analyzed immediately by measuring the absorption spectra in the visible range of 400–800 nm. The complex formation was carried out fol-

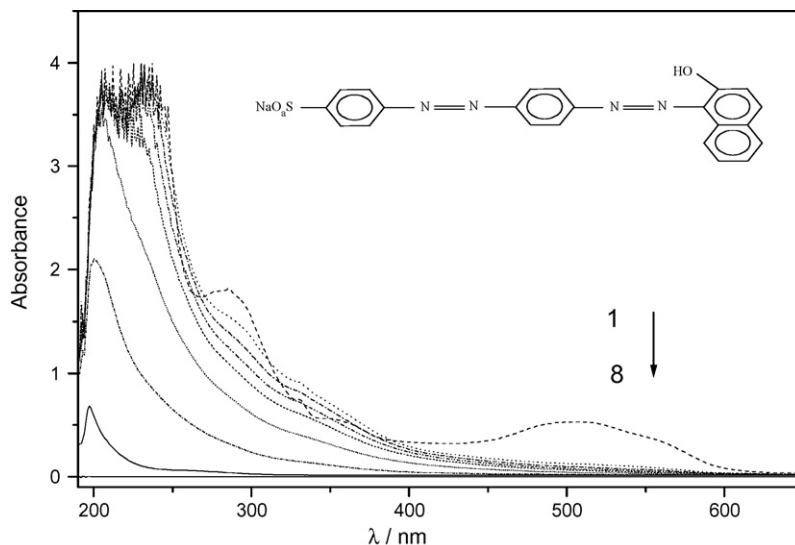


Fig. 1. UV-Vis spectra recorded before and after photoelectrocatalytic oxidation on Ti/TiO_2 thin-film anode of 0.005% (m/v) acid 151 dye + 0.009% surfactant + 14.12 mg L^{-1} Cr(VI) in 0.1 mol L^{-1} Na_2SO_4 at pH 2.0 under applied potential of 1.0 V and UV-irradiation. Treatment times: (1) 0, (2) 5, (3) 10, (4) 15, (5) 20, (6) 30, (7) 45 and (8) 60 min. Inlet: Chemical structure of acid red 151 dye.

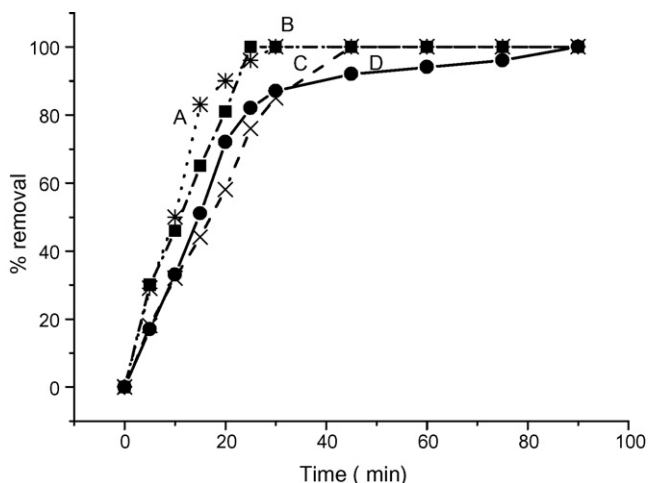


Fig. 2. Percentage of color removal during photoelectrocatalytic oxidation for (A) 0.003% acid 151 dye in Na_2SO_4 0.1 mol L^{-1} at pH 2.0 ($\lambda = 500 \text{ nm}$); (B) 0.009% of Tamol[®] surfactant in Na_2SO_4 0.1 mol L^{-1} at pH 2.0 ($\lambda = 285 \text{ nm}$); (C) 0.003% acid 151 dye + 0.009% of Tamol[®] surfactant in Na_2SO_4 0.1 mol L^{-1} at pH 2.0 ($\lambda = 500 \text{ nm}$); (D) 0.003% acid 151 dye + 0.009% of Tamol[®] surfactant in Na_2SO_4 0.1 mol L^{-1} at pH 2.0 + 14.12 mg L^{-1} Cr(VI). Photoelectrocatalysis operating with Ti/TiO₂ anode at $E_{\text{app}} = +1 \text{ V}$ under UV-irradiation.

lowing the UV-Vis spectra for 0.003% (m/v) acid 151 dye solution containing 0.009% (m/v) Tamol[®] in Na_2SO_4 0.01 mol L^{-1} solution at pHs of 2.0, 6.0 and 12.0.

3. Results and discussion

3.1. Photoelectrocatalytic oxidation

Fig. 1 illustrates the efficiency of the system to decolorize a solution containing 0.005% (m/v) acid 151 dye + 0.009% surfactant + 14.12 mg L^{-1} Cr(VI) in 0.1 mol L^{-1} Na_2SO_4 at pH 2.0 under applied potential of 1.0V and UV-irradiation. The photoelectrocatalytic treatment leads to complete vanish of the color and bands of the UV region.

The performance of photoelectrocatalytic treatment on each individual component can be better analyzed on Fig. 2. 100% of discoloration was observed by monitoring the bands at 500 nm after 30 min, as shown Curve A. Fig. 2B indicates the decay obtained for a 0.009% Tamol[®] surfactant (monitored at a typical absorption on 285 nm). Fig. 2C shows the results for 0.003% acid 151 dye + 0.009% of Tamol[®] surfactant (monitored at 500 nm) and Fig. 2D illustrates the degradation for a solution containing 0.003% acid 151 dye + 0.009% of Tamol[®] surfactant in Na_2SO_4 0.1 mol L^{-1} at pH 2.0 + 14.12 mg L^{-1} Cr(VI) (monitored at 500 nm) under the same experimental conditions. All solutions showed 100% removal after 90 min of treatment.

The photodegradation rate of solution of dye and surfactant can be represented by linear plot of $\ln C/C^\circ$ vs t with a slope of 0.076 and 0.070 min^{-1} . However, this value is at least 32% lower than when the dye is treated in the presence of surfactant. This value is expected since the occurrence of surfactant micelles plays an important role in the solubility of the dye [26]. Since acid dye 151 is always used in the leather industry in the presence of Tamol[®] surfactants, all further studies were carried out under these conditions.

In contrast to the previous results, the decrease in concentration as a function of time plotted as $\ln[A]t/[A]$ vs t shows a deviation when Cr(VI) is present in the solution containing dye + surfactant. Degradation of the dye fits a second-order kinetic law, whose relationship of $1/A$ vs t , which yields a slope of $1.38 \text{ mol}^{-1} \text{ L min}^{-1}$. The time required for complete

degradation given in comparative order is represented by: dye solution < surfactant < dye + surfactant < dye + surfactant + Cr(VI). The decreases in the presence of Cr(VI) could be attributed to the reduction in the light intensity reaching the TiO₂ film surface due to the lower transparency of the solution, but the complexation reaction between the Cr(VI) and the acid dye 151 cannot be discarded.

3.2. Complexation of acid red dye and Cr(VI)

In order to help interpret a suspected interaction of the acid red dye and Cr(VI), UV-Vis spectra were recorded for 25 h for samples of 0.003% acid dye + 0.009% Tamol[®] surfactant in Na_2SO_4 at pH 2.0, 6.0 and 12 monitoring absorbance decay in the presence of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ Cr(VI), as shown Fig. 3. There is no alteration without Cr(VI) (Curve A), but a marked reduction in the absorbance of the dye of up to 80% is observed in the presence of Cr(VI) after 24 h at pH 2.0. The system also pointed a diminution of 30% in alkaline medium (Curve C) and 15% at 6.0 (Curve B). The same effect is observed when Cr(VI) is increased in a solution containing the acid red 151 dye (not shown here). These results indicate that acid dye 151 could be acting as a powerful ligand particularly in acidic medium, which is able to form complexes with Cr(VI). This phenomenon has been previously verified in studies of the complexation of Cr(VI) with citrate, and EDTA ligands [27,28]. These results indicate that the complex formation between Cr(VI) and acid dye 151 could substantially affect the rate of degradation in relation to the color change promoted by Cr(VI) in the photoelectrocatalytic process.

All of the further studies below were carried out using a synthetic sample of a tanning effluent containing acid dye 151, a surfactant and Cr(VI).

3.3. Comparison of the efficiency of photolysis, photocatalysis and photoelectrocatalysis to treat simulated leather effluent

Fig. 4 presents the effect of photoelectrocatalytic process, photolytic and photocatalytic on the discoloration of a 250 mL of a 0.003% (m/v) acid dye 151 + 0.009% surfactant and 14.12 mg L^{-1} Cr(VI) in 0.1 mol L^{-1} Na_2SO_4 . Three distinct conditions were investigated: the photolysis operating only with UV-irradiation (A); the photocatalytic treatment using UV light without a bias potential (B) and the photoelectrocatalytic treatment (C), i.e., using both UV

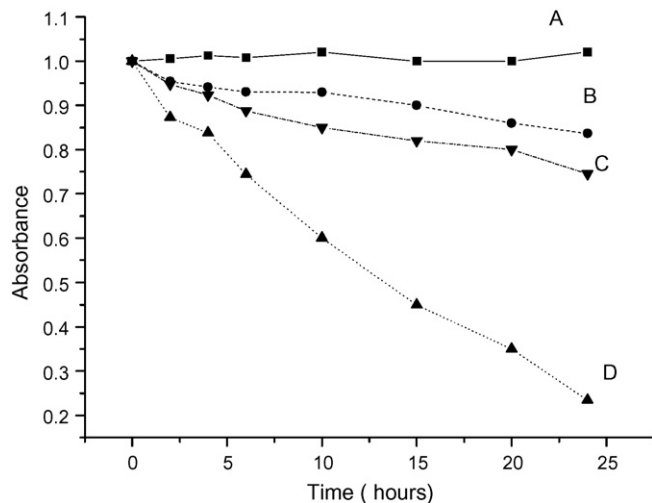


Fig. 3. Influence of time on the absorbance reduction recorded for a solution of 0.003% (m/v) acid dye 151 in Na_2SO_4 0.1 mol L^{-1} + 0.009% surfactant before (A) and after addition of $5 \times 10^{-4} \text{ mol L}^{-1}$ Cr(VI) at pH 6.0 (B), pH 12 (C) and pH 2.0 (D).

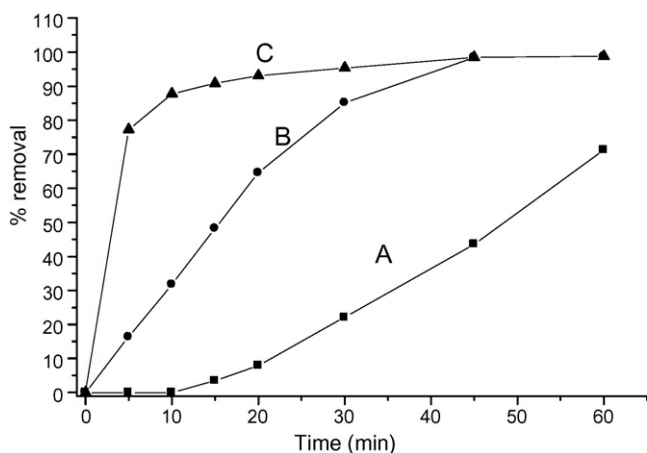


Fig. 4. Percentage of removal of acid dye 151 during: (A) photolytic; (B) photocatalytic and (C) photoelectrocatalytic treatments.

light and 1.0 V (SCE) of biasing potential. The percentage conversion obtained indicates complete color removal after 20 min of photoelectrolysis. But, the color removal is lower under photocatalytic or photolytic treatment.

The results were also analyzed by comparing its mineralization. Dissolved total organic carbon measurements were conducted by treatment using photolysis, photocatalysis and photoelectrocatalysis, which results are shown in Fig. 5A–C, respectively. While photoelectrocatalysis promotes a TOC reduction of 94.6%, photolysis and photocatalysis promote only 35% and 61% respectively. These results suggest that the photoelectrocatalytic treatment is very effective not only to promote the rupture of the chromophore and some aromatic centers but also results in the complete oxidizing of a portion of the organic matter to CO_2 .

3.4. Effect of Cr(VI)

The reduction of Cr(VI) in a solution containing 0.003% (m/v) acid 151 dye + 0.009% surfactant and 14.12 mg L^{-1} Cr(VI) in 0.1 mol L^{-1} Na_2SO_4 was monitored by aliquots removal and the percentage reduced during treatment is shown in Fig. 6. The process reaches a level of 100% Cr(VI) reduction after 10 min of photoelectrocatalytic oxidation. This can be explained by the following equation representing the process operating on the TiO_2 photoanode under UV-irradiation and cathode respectively:

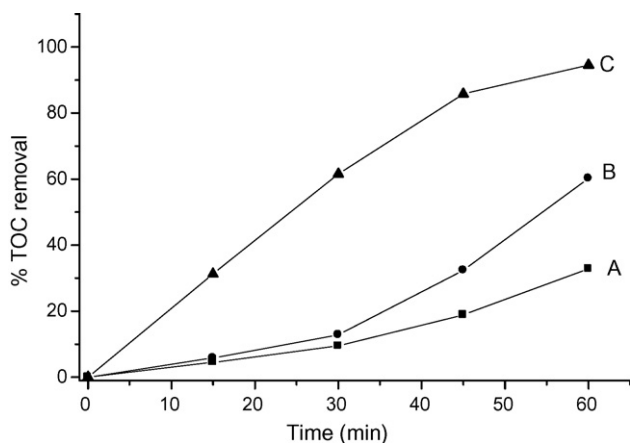


Fig. 5. Percentage of TOC removal of acid dye 151 during photolytic (A); photocatalytic (B) and (C) photoelectrocatalytic treatment.

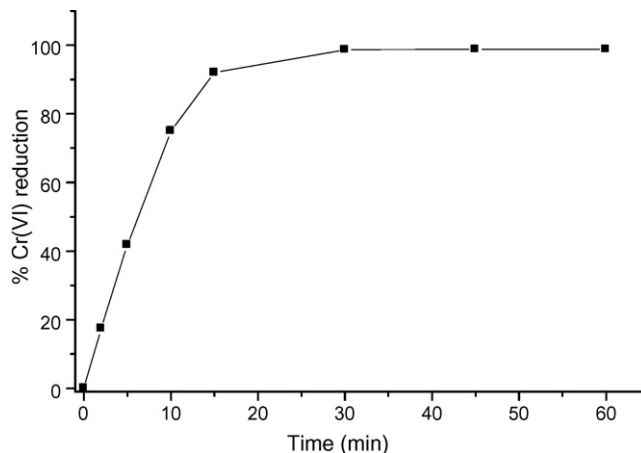
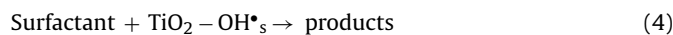
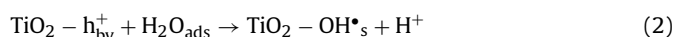
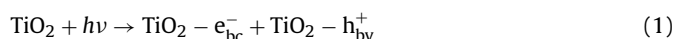
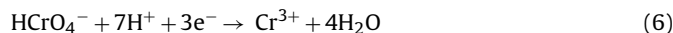


Fig. 6. Percentage of Cr(VI) reduction during photoelectrocatalytic degradation: solution containing 0.003% (m/v) acid red 151 dye + 0.009% (m/v) of Tamol® + 14.12 mg L^{-1} of Cr(VI) in Na_2SO_4 0.1 mol L^{-1} pH 2.0.

Photoanode:



Cathode:



where, $h\nu$ is the UV-irradiation, bv is the valence band and bc is the conduction band. When TiO_2 is irradiated with light less than 380 nm, electron–hole pairs are generated when electrons are excited from their resting valence band to the conduction band (Eq. (1)). The photocatalytically generated electrons and holes can then reduce or oxidize other species, respectively. However, if these electrons and holes immediately recombine, they simply generate heat, and any opportunity to initiate desired oxidation–reduction reactions is lost. Electron–hole recombination is reduced by charge separation, which can be achieved by applying a potential to an irradiated TiO_2 electrode. In addition, the movement of the electrons along the external circuit increases the likelihood of reactions occurring at either the working or counter electrode. This more efficient use of electrons and holes is the added benefit of photoelectrocatalysis over photocatalysis, and the reason for the applied potential in this study. The hole–electron pairs generated at the surface of the TiO_2 photoanode are responsible for the production of the powerful hydroxyl radical (OH^{\bullet}) oxidizing agent, which promotes the oxidation of the dye and surfactant to CO_2 + products. In a similar manner, Cr(VI) is simultaneously reduced by electron driven to the Pt cathode during photoelectrocatalytic experiments.

We also observed one other interesting phenomenon when photolytic and photocatalytic experiments were carried out under the same experimental conditions. The reduction of Cr(VI)/Cr(III) was negligible (2.64%) after 60 min of photolytic treatment. However, a 95.8% conversion was obtained for the photocatalytic process after 30 min of treatment, illustrating that photocatalysis alone can be used to reduce Cr(VI)/Cr(III). But, under this system is observed only 34.8% of TOC removal from the initial solution, indicating that simultaneously the method is not so efficient to remove organic matters, as it is the photoelectrocatalysis that leads to high removal of both organic and inorganic compounds.

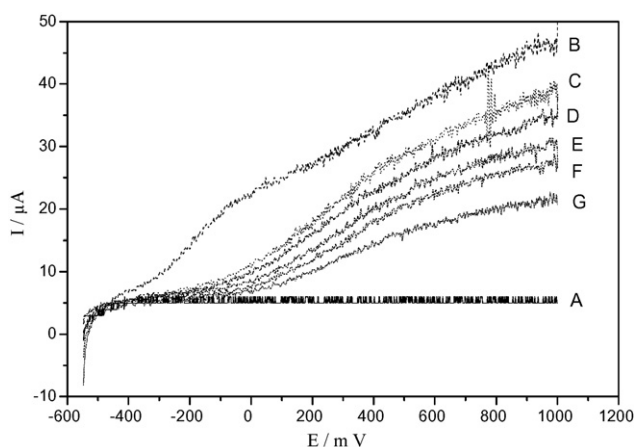


Fig. 7. Linear scan voltammograms recording photocurrent vs potential for Ti/TiO₂ anode in Na₂SO₄ 0.1 mol L⁻¹, without (A) and with irradiation (B) and the effect of addition: (C) 1.47 mg L⁻¹, (D) 2.94 mg L⁻¹, (E) 14.7 mg L⁻¹, (F) 29.1 mg L⁻¹ and (G) 88.2 mg L⁻¹ of Cr(VI). Scan rate 10 mV s⁻¹.

In order to investigate the effect of Cr(VI) concentration on the photoelectrocatalytic efficiency curves of photocurrent vs potential were recorded using linear sweep voltammetry (LSV) experiments for Ti/TiO₂ thin-film electrode in Na₂SO₄ 0.1 mol L⁻¹ electrolyte, scan rate of 10 mV s⁻¹, in the absence and presence of different concentration of Cr(VI). The results are shown in Fig. 7. The photocurrent decreases markedly when Cr(VI) is increased in solution, indicating that under this condition there is a small constant photocurrent flux, attesting to the competitive process of the complex involving the Cr(VI) and the dye. This effect could be responsible for the lower efficiency in separating photogenerated charged species, which in turn are responsible for the reduction of the chrome and the oxidation of the dye. The strong adsorption of the Cr(VI) complex dye onto the TiO₂ surface and/or the solution's lack of transparency are the limiting factors that control the reaction rate of dye degradation and Cr(VI) reduction. This problem could interfere in the Cr(VI) reduction at higher concentrations. Therefore, photoelectrocatalysis could be an efficient means of treating dye wastewater containing Cr(VI) under dilute solution conditions or the method could be coupled with another preceding treatment to reduce the discharge of organic contaminants.

In order to confirm this behavior, photoelectrocatalysis were carried out for solutions containing: 0.003% acid red 151 dye + 0.009% surfactant in Na₂SO₄ 0.1 mol L⁻¹ at pH 2 and concentrations of Cr(VI) from: 1.47, 2.94, 14.7, 29.1 up to 88.2 mg L⁻¹. Samples of the yielded solution were analyzed testing the color removal at 500 nm (monitoring dye discoloration), surfactant removal at 285 nm and the Cr(VI) concentration by chemical analysis. The surfactant degradation reaches 100%, following a process controlled by a first order reaction, showing a linear relationship of ln A_t/A₀ vs time, whose pseudo-first-order degradation rate constants are also presented in Table 1. The dye degradation process presents a straight line only for the relationship of 1/[dye] vs time, suggesting a process controlled by a second-order reaction. The degradation rate constants

Table 1
Effect of chrome on the rate degradation constant for 0.003% acid red 151 and 0.009% Tamol® surfactant and Cr(VI) reduction in Na₂SO₄ 0.1 mol L⁻¹ at pH 2.0.

[Cr(VI)] mg L ⁻¹	K (min ⁻¹) Tamol®	K (M ⁻¹ min ⁻¹) acid red 151	% Cr(VI) reduction
1.47	0.0466	2.5394	100.00
14.7	0.0419	1.3766	99.44
29.1	0.0399	0.9314	98.35
88.2	0.0371	0.5792	97.77

Table 2
Influence of pH on the degradation rate obtained of 0.003% (m/v) acid dye 151 + 0.009% (m/v) de Tamol® in Na₂SO₄ 0.1 mol L⁻¹ containing 14.8 mg L⁻¹ of Cr(VI).

pH	Cr(VI) % removal	k (min ⁻¹) Tamol®	k (M ⁻¹ min ⁻¹) acid red dye	R	
2.0	100.0	0.0420	1.3766	0.996	0.999
6.0	98.5	0.0124	0.1993	0.950	0.997
12.0	40.0	0.0083	0.3589	0.974	0.997

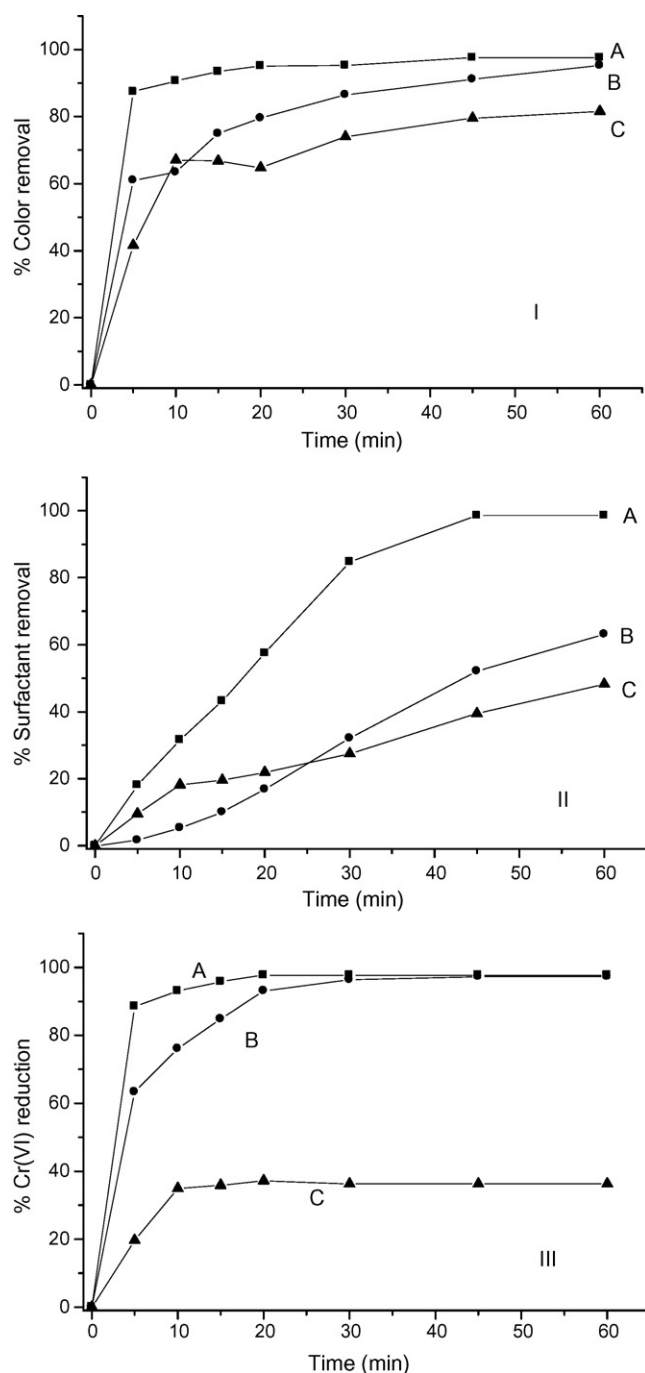


Fig. 8. Effect of pH on the photoelectrocatalytic oxidation of 0.003% (m/v) acid red 151 dye (Curve I), 0.009% (m/v) surfactant (Curve II) and reduction of 14.12 mg L⁻¹ Cr(VI) (Curve III) in Na₂SO₄ 0.1 mol L⁻¹ at pH 2.0 (A), pH 6.0 (B) and pH 12 (C) under E_{app} = 1.0 V and UV-irradiation.

were calculated and they decrease at high concentration of Cr(VI), which are presented in Table 1. This is possibly due to a reduction in the light intensity. Once again, this process is most useful for dilute solutions as was noted in the introduction to this paper. Nevertheless, maximum values around 100% of Cr(VI) are obtained in all experiments, showing that it is possible to remove Cr(VI) even at concentration around 88 mg L⁻¹.

3.5. Influence of pH

In order to obtain more information about the photoelectrocatalytic process of wastewater containing acid dye, surfactant and Cr(VI) and to optimize the method for reducing organic and inorganic contaminants in general, we also investigated other parameters controlling this process such as the pH of the solution. For this, solutions of 0.003% acid red dye 151 + 0.009% Tamol® + 14.12 mg L⁻¹ Cr(VI) in Na₂SO₄ 0.1 mol L⁻¹ were tested for initial pH values of 2.0, 6.0 and 12. Aliquots removed during photoelectrocatalytic oxidation were analyzed and the color removal ($\lambda = 500$ nm), surfactant degradation ($\lambda = 285$ nm) and Cr(VI) reduction are compared in Curves I, II and III of Fig. 8, respectively. All the curves obtained at pH 2 presents 100% of the color removal, indicates 100% of Cr(VI) reduction and also 100% of surfactant degradation. These values are significantly decreased to neutral and alkaline conditions.

A linear fit between $\ln(C/C^0)$ and photoelectrocatalysis time is obtained for surfactant degradation, suggesting that the process follows pseudo-first-order kinetics for all of the pH values evaluated. As verified previously the discoloration measurement of the acid red 151 dye followed a second-order kinetics. The dependence of the initial degradation rate (k) evaluated from slopes of the curves obtained for dye consumption (mol L⁻¹), surfactant removal and total reduction of Cr(VI) as function of time at different pH values is presented in Table 2. The rate constant is at least 5 times greater (faster) at pH 2 as to color removal as surfactant degradation than at pH 12. This behavior is also observed for Cr(VI) reduction, indicating that the photoelectrocatalytic treatment performs is best in acidic medium.

It is well known [29,30] that pH affects the chemical equilibrium involving species of CrO₄²⁻, HCrO₄⁻ and Cr₂O₇²⁻ formed for chromium(VI) in aqueous medium. The relative amounts of the species derivative species vary as a function of pH. At pH < 7 the chemical equilibrium involves hydrogenchromate and its polynuclear structure of dichromate (2HCrO₄⁻ \rightleftharpoons Cr₂O₇²⁻ + H₂O; $K = 3.58 \times 10^1$), and both species are reduced on Vitreous carbon or Platinum electrodes. However, at pH > 7.5, the new chemical equilibrium involving the generation of the chromate anion (HCrO₄⁻ \rightleftharpoons CrO₄²⁻ + H⁺; $K_{a1} = 3.09 \times 10^{-7}$) takes part in the reaction, but the specie is not electroactive. Therefore its reduction is hindered on the auxiliary electrode, and the efficiency of converting Cr(VI) to Cr(III) is minimized under conditions where the pH of the solution is higher than the pH of the isoelectric point (pH 5.6), which unflavored adsorption of dye on working electrode and also the reduction of inorganic specie on counter electrode. As a consequence, both the percentage of Cr(VI) reduction and dye degradation are decreased on neutral and alkaline medium.

4. Conclusions

Our findings illustrate that photoelectrocatalytic oxidation may be an excellent alternative to promote fast removal of acid dye, surfactant and also simultaneous reduction of toxic hexavalent chrome. Using optimized conditions of pH 2.0 and low concentrations of dye, surfactants and Cr(VI), it is possible to reach 100% discoloration, 100% surfactant removal and around 100% Cr(VI)

reduction. The results are dramatically improved in relation to photocatalytic treatment of wastewater containing both organic and inorganic pollutants.

Acknowledgement

The authors are grateful for the financial support from Brazilian funding agencies FAPESP (Proc: 04/07353-7), Capes and CNPq.

References

- [1] K.H. Gustavson, The Chemistry and Reactivity of Collagen, Academic Press Inc., New York, 1992.
- [2] L.M. Ortega, R. Lebrun, I.M. Noél, R. Hunsler, Application of nanofiltration in the recovery of chromium (III) from tannery effluents, Sep. Purif. Technol. 44 (2005) 45–52.
- [3] A. Cassano, R. Molinari, M. Romano, E. Drioli, Treatment of aqueous effluents of the leather industry by membrane process, J. Membr. Sci. 181 (2001) 111–126.
- [4] R. Oral, S. Meric, E. Nicola, D. Petruzzelli, C.D. Rocca, G. Pagano, Multi-species toxicity evaluation of a chromium-based leather tannery wastewater, Desalination 211 (2007) 48–57.
- [5] J.O. Nriegen, E. Nieboer, Chromium in the Natural and Human Environments, Wiley, New York, 1988.
- [6] J. Kotas, Z. Stasicka, Chromium occurrence in the environmental and methods of its speciation, Environ. Pollut. 107 (2000) 263–283.
- [7] J.M. Figueiredo, C.A. Nogueira, F. Pedrosa, J. Guimarães, Setor dos Curtumes – Guia Técnico. Lisboa: INETE (Instituto Nacional de Engenharia e Tecnologia Industrial), 2000.
- [8] W. Delee, C. O'Neil, F.R. Hawkes, H.M. Pinheiro, Anaerobic treatment of textile effluents: a review, J. Chem. Technol. Biotechnol. 73 (1998) 323–327.
- [9] H.O. Finklea, Semiconductor Electrodes, Elsevier, New York, 1988.
- [10] M.I. Litter, Heterogeneous photocatalysis. Transition metal ions in photocatalytic systems, Appl. Catal. B Environ. 23 (1999) 89–114.
- [11] C.R. Chenthamarakshan, K. Rajeshwar, Heterogeneous photocatalytic reduction of Cr (VI) in UV-irradiated titania suspensions: effect of protons, ammonium ions and other interfacial aspects, Langmuir 16 (2000) 2715–2721.
- [12] J. Domenech, J. Munoz, Photocatalytic reduction of Cr (VI) over ZnO powder, Electrochim. Acta 32 (1987) 1383–1388.
- [13] L.B. Khalil, W.E. Mourad, M.W. Rophael, Photocatalytic reduction of environmental pollutant Cr (VI) over some semiconductors under UV/visible light illumination, Appl. Catal. B: Environ. 17 (1998) 267–273.
- [14] S. Wang, Z. Wang, Q. Zhuang, Photocatalytic reduction of the environmental pollutant Cr (VI) over a cadmium sulphide powder under visible light illumination, Appl. Catal. B: Environ. 1 (1992) 257–263.
- [15] L.B. Reutergerdh, M. langphasuk, Photocatalytic decolorization of reactive azo dye: a comparison between TiO₂ and us photocatalysis, Chemosphere 35 (1997) 585–596.
- [16] F. Kiriakidou, D.I. Kondarides, X.E. Verykios, The effect of operational parameters and TiO₂-doping on the photocatalytic degradation of azo-dyes, Catal. Today 54 (1999) 119–130.
- [17] Y. Wang, Solar photocatalytic degradation of eight commercial dyes in TiO₂ suspension, Water Res. 34 (2000) 990–996.
- [18] S.G. Schrnk, H.J. José, R.F.P.M. Moreira, Simultaneous photocatalytic Cr (VI) reduction and dye oxidation in a TiO₂ slurry reactor, J. Photochem. Photobiol. A: Chem. 147 (2002) 71–76.
- [19] R. Gkika, A. Troupis, A. Hiskia, E. Papaconstantinou, Photocatalytic reduction of chromium and oxidation of organics by polyoxometalates, Appl. Catal. B: Environ. 62 (2006) 28–34.
- [20] X.R. Xu, H.B. Li, J.D. Gu, Simultaneous decontamination of hexavalent chromium and methyl tert-butyl ether by UV/TiO₂ process, Chemosphere 63 (2006) 254–263.
- [21] M.V.B. Zanoni, J.J. Sene, M.A. Anderson, Photoelectrocatalytic degradation of Remazol Brilliant Orange 3R on titanium dioxide thin-film electrodes, J. Photochem. Photobiol. A: Chem. 157 (2003) 55–63.
- [22] P.A. Carneiro, M.E. Osugi, J.J. Sene, M.A. Anderson, M.V.B. Zanoni, Evaluation of color removal and degradation of a reactive textile azo dye on nanoporous TiO₂ thin-film electrodes, Electrochim. Acta 49 (2004) 3807–3820.
- [23] H. Selcuk, J.J. Sene, M.V.B. Zanoni, H.Z. Sarikaya, M.A. Anderson, Behavior of bromide in photoelectrocatalytic process and bromide generation using nanoporous titanium dioxide thin-film electrodes, Chemosphere 54 (2004) 969–974.
- [24] M.E. Osugi, G.A. Umbuzeiro, M.A. Anderson, M.V.B. Zanoni, Degradation of metallophthalocyanine dye by combined processes of electrochemistry and photoelectrochemistry, Electrochim. Acta 50 (2005) 5261–5269.
- [25] L.S. Clescer, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, 17th ed., APNA, Washington, 1989.
- [26] J.M. Meichtry, M. Brusa, G. Mailhot, M.A. Grela, M.I. Litter, Heterogeneous photocatalysis of Cr (VI) in the presence of citric acid over TiO₂ particles: relevance of Cr (V)-citrate complexes, Catal. B: Environ. 71 (2007) 101–107.

- [27] J. Testa, M.A. Grela, M.I. Litter, Heterogeneous photocatalytic reduction of chromium (VI) over TiO₂ particles in the presence of oxalate: Involvement of Cr (V) species, *Environ. Sci. Technol.* 38 (2004) 1589–1594.
- [28] T. Papadam, N.P. Xekoukoulotakis, I. Poullos, D. Mantzavinos, Photocatalytic transformation of acid orange 20 and Cr (VI) in aqueous TiO₂ suspensions, *J. Photochem. Photobiol. A: Chem.* 186 (2007) 308–315.
- [29] I. Svancara, P. Foret, K. Vytras, A study on the determination of chromium as chromate at a carbon paste electrode modified with surfactants, *Talanta* 64 (2004) 844–852.
- [30] M.F. Bergamini, D.P. Santos, M.V.B. Zanoni, Development of a voltammetric sensor for chromium (VI) determination in wastewater sample, *Sens. Actuators B* 123 (2007) 902–908.