Degradation of leather dye on TiO$_2$: A study of applied experimental parameters on photoelectrocatalysis

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Abstract

TiO$_2$ supported on ITO (indium tin oxide coated glass) was prepared and its photocatalytic activity was determined by photo-oxidation of commercial leather dye in aqueous solution illuminated with UV light. A vision of the use of the heterogeneous photocatalysis/electrochemically assisted degradation is discussed. Several operational parameters to achieve optimum efficiency of this photodegradation system are presented, such as the influence of temperature, applied potential, pH, initial dye concentration and choice of a UV source. The results indicate that the dye can be degraded totally and mineralized into inorganic products such as NH$_4^+$ ions. Decolorization ratios higher than 90% were observed during a period of 480 min. Relating the initial concentration with the approximate azo dye molar mass the formation of $\approx$96.79% NH$_4^+$ was calculated. FT-Raman and FT-IR spectroscopies indicated the influence the supporting electrolyte had on the process.
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1. Introduction

A number of synthetic dyes that are continuously emitted into the environment accompanying industrial development have caused great damage to biodiversity, principally due to the release of large volumes of wastewaters containing a high content of organic discharge and strong coloration. Unfortunately, these post-industrial residues find their way into river causeways because the traditional processes used to treat wastewater do not remove these compounds efficiently. Many dyes used in leather treatment can biologically transform to toxic species and cause interference in natural photosynthetic processes [1,2]. We should also take into consideration the fact that finding better ways of treating and recycling effluents is a topic of timely interest because of the increased shortages and escalating costs of water in many countries.

Several pollutants, such as azo dyes [3,4], have been degraded by advanced oxidative processes that produce hydroxyl radicals as the primary oxidant. Hydroxyl radicals are very efficient oxidizers; the oxidation potential of OH$^\bullet$ is as high as 2.80 V. Therefore, photoelectrocatalytic degradation has been widely established as an alternative electrochemical process for environmental remediation [5,6]. The use of UV light and semiconductor photocatalysts such as TiO$_2$ immobilized films [7–9] can degrade and even mineralize these dyes.

The photocatalytic activity of the supported TiO$_2$ was tested via degradation of an aqueous leather dye (its structure is shown in Scheme 1).

The objective of the present paper was to examine some of the photoelectrocatalytic factors that could affect the efficiency of the decomposition of leather dye in an ITO/TiO$_2$/KCl system.

2. Experimental details

2.1. Chemicals

Leather dye was kindly supplied by Clariant Brasil (Resende, Rio de Janeiro, Brazil) and was used as a model pollutant. Titanium dioxide (P-25$^\circledR$, 70% anatase, 30% rutile, density = 3.8 g/cm^3) was a gift from Degussa and was used without further purification. All other chemicals were analytical grade and employed without purification. The water used in all the

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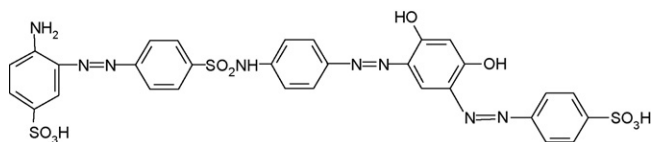
Scheme 1. Molecular structure of dye.

experiments was purified with a Milli-Q-Plus water purification system.

2.2. Electrodes

The TiO$_2$ sol was synthesized using a method described by Hoffmann et al. [10]. A solution with a ratio of 0.39 mL NH$_4$OH:0.34 mL H$_2$O$_2$:10 mL H$_2$O:0.70 g TiO$_2$ was dispersed in a 25 mL beaker and the gel formation was heated to 75 °C under magnetic agitation for 2 h. To increase the gel fluidity, three drops of Triton X-100 and seven drops of acetylacetone were added to the solution as described by Nazeeruddin et al. [11]. The TiO$_2$ thin film was prepared using a painter method on 2.41 cm^2 of ITO (sheet resistance $20 \pm 5 \, \Omega$); it was dried at 70 °C for 20 min and fired to 400 °C for 4 h. After this process, the films were left until reaching ambient temperature and then masses of TiO$_2$ composite deposited on ITO were obtained. Through the volume/area relationship of the films an estimate of the thickness of the TiO$_2$ films on ITO were made, similarly to the method described by Lipp and Pletcher [12].

2.3. Reactor system

The reactor system has been described in detail previously [13]. The system for the photoelectrodegradation reaction contained a 70 mL cylindrical glass vessel with a quartz window (thickness of 1.0 mm) surrounded by a circulating water-jacket; a UV light (the source was mercury vapor with or without a bulb; General Electric and Philips, respectively; both 125 W) and a potentiostat (Microquímica, MQBTC99-20). The reactor contained a 50 mL sample solution that was agitated with a mechanical stirrer while the temperature was measured using a thermocouple equipped with a digital reader. Photoelectrodegradation was performed in a single compartment cell fitted with ITO/TiO$_2$ as the working electrode, a large Pt sheet as the auxiliary electrode and Ag/AgCl as the reference electrode. The electrolyte solutions were 0.1 mol L^{-1} KCl in H$_2$O.

2.4. Electrochemical measurement

The open-circuit potential (E_{oc}) was measured between the electrodes, ITO/TiO$_2$ and Ag/AgCl, using a potentiostat during UV light illumination.

2.5. Dye decolorization

Changes in dye concentration were determined spectrophotometrically at the maximum absorption wavelength of 430 nm with a Genesys^{TM} 2 spectrophotometer. The calibra-

tion curves were prepared for a concentration range of (10^{-4} to 0.02) mg/mL, using solutions having a constant concentration of 0.1 mol L^{-1} KCl, and performed twice, once for pH 6.13 and again for 3.35. The correlation factors (R^2) of the calibration curves were greater than 0.999.

2.6. Analytical determination

The ammonium ion was determined spectrophotometrically at 694 nm by the modified Berthelot method [14,15]. The calibration curves were prepared for a concentration range of $(1.5–28.0) \times 10^{-6}$ mol L^{-1}, and had correlation factors greater than 0.999 and a detection limit (DL) = 7.1×10^{-7} mol L^{-1} [16]. This procedure was repeated whenever this ion was determined.

2.7. Statistical analysis

Comparisons between means were assessed by using: Student's t-test, ANOVA and Student–Newman–Keuls (SNK) test all providing a significance level of $p < 0.05$.

2.8. Spectroscopic techniques

After photoelectrodegradation the liquid sample was dried by dehydration and then FT-Raman and FT-IR spectra were obtained. For comparison, the spectra of the leather dye and sulfanilic acid were also obtained. FT-Raman spectra were acquired on a Bomen DA 3.16. The excitation wavelength was provided by a 1064 nm Nd–YAG laser. IR spectra of pressed KBr disks were recorded on a Shimadzu 8300 FT-IR.

3. Results and discussion

3.1. Experimental conditions for irradiation

The Hg vapor lamp (high pressure), used as the source, presents emission lines between 185 and 580 nm [17]. As observed in the absorption spectrum of dye (spectrum not shown), the dye absorbs radiation at 256 nm. Therefore, the use of the source with irradiation close to $\lambda = 256$ nm can propagate a photochemical degradation of dye. Consequently, the experimental conditions intended to minimize that process will be discussed here now.

This problem pertaining to the unwanted wavelength exposure was addressed using a Pyrex® glass plate to filter the radiation in the range of dye absorption, from 200 to 300 nm. Alternatively, radiation 300–386 nm is enough to achieve the photocatalytic process on the TiO$_2$ surface. The glass does not absorb this radiation.

In a cell protected with the Pyrex® plate, the solution containing the dye was irradiated and solution aliquots were collected at specific periods (0, 3, 7 and 8 h). In Fig. 1 it shows the absorbance spectra of 0.01 mg/mL dye concentration in 0.1 mol L^{-1} KCl (pH 6.14) during 8 h of irradiation. The band at 430 nm, characteristic of the azo group conjugated with the chromophoric part of the dye by charge transfer [18], remained very stable for 480 min of irradiation leading to a measured decolorization of
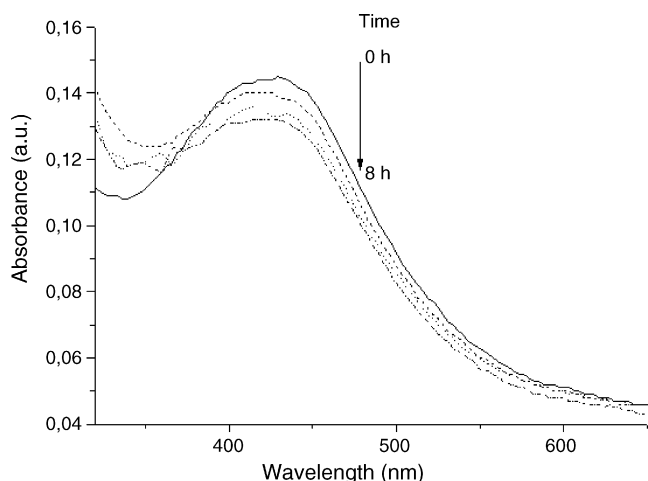
Fig. 1. Absorbance spectra of 0.01 mg/mL dye concentration in KCl 0.1 mol L^{-1} (pH 6.14) during 0, 3, 7 and 8 h of irradiation of the solution in the cell filtering with a Pyrex® plate.

14.87%. At pH 3.35 the results were similar to those obtained at pH 6.14, only the absorbencies were weaker.

3.2. Open-circuit potential of an irradiated ITO/TiO$_2$/dye-KCl system

In Fig. 2(a) and (b) are shown the measurements of E_{oc} at different temperatures of an initial dye concentration of 0.01 mg/mL/0.1 mol L^{-1} KCl solution at pH 6.14 and 3.35, respectively, on ITO/TiO$_2$ thin film electrodes over an 8 h experiment. The effect of temperature was studied in the range of 21–35 °C with temperatures kept constant ($\pm$0.5 °C).

In Fig. 2(a), the effects of temperature on the anodic E_{oc} values of the ITO/TiO$_2$/KCl-dye system (approximately 0–1.2 V versus Ag/AgCl) were observed, in other words, the ITO glass system behaved as the oxidizer. The most important property of the double layer, formed between the electrolyte ions and ITO/TiO$_2$ surface, was the effect it had on the electric potential near the electrode. This surface is a semiconductor and conductivity increases with temperature, and this effect is seen by the increasing E_{oc} between the semiconductor and the solution as the temperature was increased.

In Fig. 2(b) the effect of temperature on the E_{oc} of the ITO/TiO$_2$/KCl-dye system was observed in the range between 0.5 and 0.3 V, demonstrating an effect different from that observed when the pH was 6.14. In this case the dye molecules appear more strongly attached to the surface indicating that the experimental conditions are favoring the dye adsorption.

These results prompted a more detailed study of the experimental parameters involved in enhancing the electrode surface to receive electrons from dye species either in solution or strongly linked to the surface.

3.3. Decolorization study

In Table 1 are presented the parameters varied for the dye decolorization experiments, which was determined by UV–vis
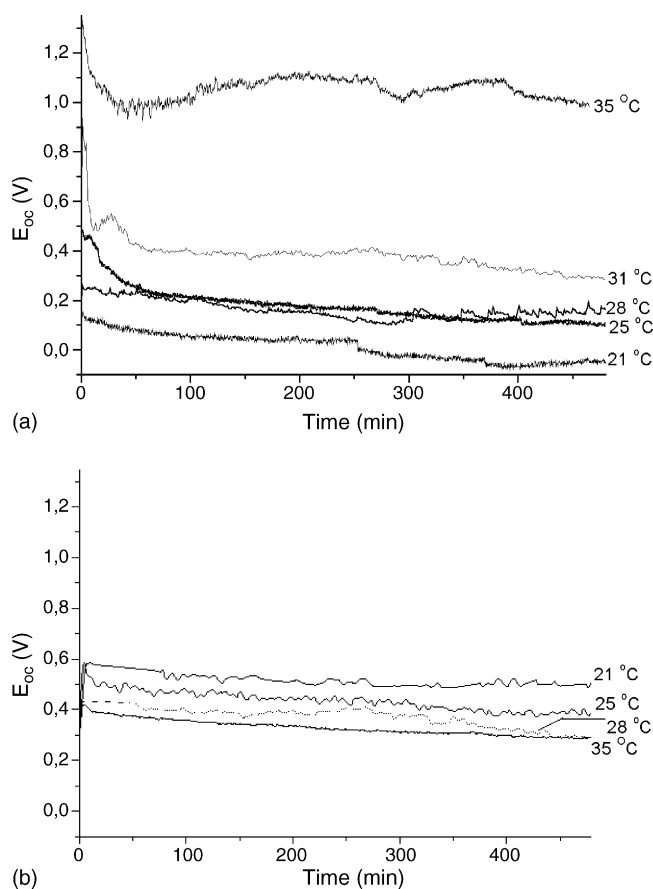

Fig. 2. Measurement of open-circuit potential (E_{oc}) at different temperatures of an initial dye concentration of 0.01 mg/mL in KCl 0.1 mol L^{-1} solution at pH 6.14[a] and 3.35[b] on ITO/TiO$_2$ thin film electrodes over an 8 h experiment (mass of TiO$_2$ = 3.5 ($\pm$0.8) mg).

Table 1

Decolorization (D) by photoelectrocatalytic oxidation at different temperatures (T) and applied potentials (E) using an initial dye concentration of 0.01 mg/mL in KCl 0.1 mol L^{-1} solution at pH 6.14[a] and 3.35[b] on ITO/TiO$_2$ thin film electrodes over an 8 h experiment (mass of TiO$_2$ = 3.5 ($\pm$0.8) mg; thickness = 6.3 ($\pm$1.7) μm)

T (°C)	E (V)	D^a (%)	D^b (%)
21	–	21.5	28.4
25	–	26.9	30.6
28	–	26.2	30.6
35	–	29.6	28.4
21	0.2	57.0	60.7
25	0.2	59.8	58.8
28	0.2	51.0	54.0
35	0.2	60.8	34.8
21	0.8	48.5	55.1
25	0.8	54.5	59.2
28	0.8	85.6	72.5
35	0.8	98.5	72.5
21	1.2	89.0	50.05
25	1.2	97.1	80.94
28	1.2	98.0	76.02
35	1.2	98.0	66.09

spectrometry at a wavelength of 430 nm. In the interest of optimizing the photoelectrocatalysis experiments, in a way to obtain meaningful results using the smallest number of experiments, the following variables were considered: temperature, open-circuit potential and the potential applied to ITO/TiO$_2$. Results obtained of the dye decolorization in pH 6.14[a] and 3.35[b], during 8 h of irradiation of a 0.01 mg/mL dye solution in 0.1 mol L^{-1} KCl, on a fixed mass of TiO$_2$ deposited on the ITO electrode in an electrochemical cell are presented in Table 1.

The results of dye decolorization at the different temperatures (21, 25, 28 and 35 °C) without applied potential (open-circuit potential), were lower than those obtained upon applying potentials (0.2, 0.8 and 1.2 V). To justify the results the discussion of Vinodgopal et al. [19] was employed. It was considered that during the processes of irradiation on ITO/TiO$_2$, leading to oxidation, the phenomenon of recombination between photogenerated electrons and holes could be occurring. This is a major limiting factor for a photodegradation process. In the experiments performed using an open-circuit potential this recombination phenomenon is more likely to occur, and therefore to avoid that problem the application of an oxidation potential on ITO/TiO$_2$ is favorable for an efficient process. The thin composite films comprised of particulates had the ability to conserve the photochemical properties of the individual semiconductor particles and react similarly photocatalytically, with the same efficiency as the particles of semiconductors in suspension. This implies that the potential gradient at the interface promotes the electrons and holes to flow in opposite directions, and the photogenerated holes migrate towards the interface while the electrons migrate towards ITO, making the behavior of the film analogous to that of a n-type semiconductor [20].

This hypothesis was verified by the experiments having an electrochemical potential applied to the ITO/TiO$_2$. The charged surface acted as a positive carrier and displaced the electron/hole pairs or attracted the dye species onto the catalyst surface [21,22].

Observed in the results of Table 1, there is better decolorization with the applied potential of 1.2 V at the different temperatures for a sample at pH 6.14[a] than when at pH 3.35[b]. When the applied voltage was 0.8 V only at the temperatures of 28 and 35 °C, at pH 6.14[a], were the results comparable to those observed at 1.2 V. These results demonstrated that the effect of temperature was important to favor the dye decolorization when the potential of 0.8 V was applied, and with the relative increase of the temperature an increase in the decolorization of the solution was obtained. With the applied potential of 0.2 V a decolorization between 51 and 60.8% was obtained, demonstrating that the applied potential was not enough to attract the species of the solution onto the ITO/TiO$_2$ surface.

These facts can be understood according to Zainal et al. [23], whose results indicated that the irradiation is the primary source of propagation of the electron/hole pairs. The bandgap energy is too large to be excited by thermal activation. Therefore, the results show a synergistic effect of the temperature increasing the collision frequencies between the dye molecules and the radical hydroxyl [24]. After being initiated by the UV irradiation thermal energy allows the reaction to compete with

the electron-hole recombination, leading to a notably efficient reaction.

In the decolorization results of Table 1 for the solutions at pH 3.35[b], it was observed that samples analyzed at open-circuit potential at the different temperatures were inferior to the results obtained with the application of the different potentials. For the tests run using open-circuit potential it was observed that the decolorization increased initially with increasing temperature and then became constant.

For the test at 0.2 V, pH 3.35[b], increasing the temperature had an inverse effect on decolorization. At 0.8 V increasing the temperature led to an increase of decolorization up to 28 °C at which point it remained constant. The results of 1.2 V applied potential were interesting in that a decolorization maximum at 25 °C was observed, followed by a decrease. Among the potentials that were applied, the largest decolorization was obtained for an applied potential of 1.2 V at 25 °C. Thus, the experiments at pH 3.35 were dependent on the dye adsorption, a different behavior compared to the other experiment at pH 6.14 where an oxidation potential caused the decolorization.

3.4. Mineralization

After irradiation for 8 h of the ITO/TiO$_2$/KCl-dye system for pH 6.14[a] and 3.35[b] solutions the partial dye mineralization was confirmed by analysis of the inorganic ion (NH$_4$$^+$) in solution. It should be considered that the nitrogen heteroatoms in the dye structure were converted into inorganic ions such as ammonium during photodegradation of the dye solution. In Table 2 the results are presented in view of the different experimental parameters.

As observed in Table 2, for the open-circuit potential and 0.2 V applied potential samples, the temperature did not influence the production of ammonium for samples at both pH 6.14[a] and 3.35[b]. For the case of the samples exposed to 0.8 and 1.2 V applied potential, the production of the ammonium ion was similar at the temperatures that were investigated for both pH levels. For pH 6.14[a] and 3.35[b], and an applied potential of 0.8 V, an increase in the production of ammonium was seen from 21 to 25 °C, and the results at 28 °C remained statistically the same. But for both pHs the production of ammonium decreased at 35 °C. For the samples having an applied potential of 1.2 V the production of ammonium initially declined at temperatures of 25 and 28 °C, however, the samples at 35 °C demonstrated a small increase. This was true for the samples at both pH 3.35 and 6.14.

Table 2 also shows the effect of the applied potential on the production of ammonium while keeping the temperature constant. At 21 °C for both pHs, an increase of potential from open-circuit potential to 0.2 V led to an increase in the production of ammonium. For the sample pH 6.14[a], when the potential was changed from 0.2 to 0.8 V the production of the ammonium stayed approximately constant, and increasing the potential from 0.8 to 1.2 V led to an increase in the production of ammonium for both pHs. At 25 °C changing the potential from open-circuit to 0.2 V led to an increase in the production of ammonium for both pHs, and when the potential was increased from 0.2 to

Table 2
Mineralization: concentration of ammonium formed ($[NH_4^+]$) by photoelectrocatalytic oxidation at different temperatures (T) and applied potentials (E) using an initial dye concentration of 0.01 mg/mL in KCl 0.1 mol L^{-1} solution at pH 6.14[a] and 3.35[b] on ITO/TiO$_2$ thin film electrodes during an 8 h experiment (mass of TiO$_2$ = 3.5 ($\pm$0.8) mg; thickness = 6.3 ($\pm$1.7) μm)

Group$^\Omega$	T ($^\circ$C)	E (V)	$[NH_4^+]^{\#a}$ ($\times 10^{-6}$ mol L^{-1})	$[NH_4^+]^{\#b}$ ($\times 10^{-6}$ mol L^{-1})	Group$^\$$
A1	21	–	2.05 ± 0.095 (2)	5.50 ± 0.360 (2)	
B1	25	–	1.72 ± 0.045 (2)	5.17 ± 0.090 (2)	
C1	28	–	1.86 ± 0.095 (2)	5.69 ± 0.390 (2)	1
D1	35	–	1.84 ± 0.045 (2)	6.13 ± 0.530 (2)	
A2	21	0.2	2.43 ± 0.095 (2)	7.67 ± 0.305 (2)	
B2	25	0.2	3.70 ± 0.520 (2)	8.62 ± 0.095 (2)	
C2	28	0.2	2.44 ± 0.190 (2)	8.05 ± 0.290 (2)	2
D2	35	0.2	2.15 ± 0.190 (2)	8.55 ± 0.215 (2)	
A3	21	0.8	2.65 ± 0.080 (2)	4.16 ± 0.135 (2)	
B3	25	0.8	3.34 ± 0.040 (2)	5.57 ± 0.095 (2)	
C3	28	0.8	3.31 ± 0.090 (2)	5.43 ± 0.050 (2)	3
D3	35	0.8	1.77 ± 0.095 (2)	5.07 ± 0.335 (2)	
A4	21	1.2	3.18 ± 0.001 (2)	6.23 ± 0.195 (2)	
B4	25	1.2	1.49 ± 0.001 (2)	4.96 ± 0.095 (2)	
C4	28	1.2	1.34 ± 0.140 (2)	4.97 ± 0.090 (2)	4
D4	35	1.2	2.01 ± 0.050 (2)	6.68 ± 0.450 (2)	

[#]The results are presented as mean ± standard error of the mean. The number of sets is given in parentheses. For comparison groups were formed among the results for statistical treatment (ANOVA test). [#a]Values listed for the group$^\$$: group 1 ($F = 3.37$ and $p = 0.136$), group 2 ($F = 5.47$ and $p = 0.067$), group 3 ($F = 86.55$ and $p = 0.000$), with the values of the lines 2 and 3 statistically the same ($p > 0.05$). Group 4's statistics are $F = 125.97$ and $p = 0.000$, with the values of the lines 2 and 3 statistically the same ($p > 0.05$). The other observed values for the group were statistically different ($p < 0.05$). [#a]Values observed for the group$^\Omega$: group A ($F = 36.44$ and $p = 0.002$), has the values between A2 and A3 statistically the same ($p > 0.05$); group B ($F = 18.29$ and $p = 0.008$), the values between B2 and B3, and B1 and B4 are statistically the same ($p > 0.05$); group C ($F = 39.17$ and $p = 0.002$), the values between C1 and C4 are statistically the same ($p > 0.05$). The group D was $F = 2.36$ and $p = 0.213$, with all the values statistically the same ($p > 0.05$). The other observed values for the group were statistically different ($p < 0.05$). [#b]Values observed for the group$^\$$: group 1 ($F = 1.09$ and $p = 0.451$), group 2 ($F = 3.44$ and $p = 0.132$), group 3 ($F = 11.34$ and $p = 0.020$), with statistically similar values for lines 2 and 4, and 3 and 4 ($p > 0.05$). Group 4's statistics are $F = 12.01$ and $p = 0.018$, the lines 4 and 1, and 1 and 2 are statistically the same ($p > 0.05$) and the values of the lines 1 and 3 were not tested. The other observed values for the group were statistically different ($p < 0.05$). [#b]Values observed for the group$^\Omega$: group A ($F = 30.74$ and $p = 0.003$), with the values of A4 and A1 being statistically the same ($p > 0.05$). Group B ($F = 333.25$ and $p = 0.000$), had the values between B1 and B4 statistically the same ($p > 0.05$). Group C ($F = 30.68$ and $p = 0.003$), the values between C1 and C4 are statistically the same ($p > 0.05$) and the values between C1 and C3, and C3 and C4 were not tested. Group D was $F = 13.23$ and $p = 0.015$, with the values between D4 and D3 statistically the same ($p > 0.05$) and the values between D4 and D1, and D1 and D3 were not tested. The other observed values for the group were statistically different ($p < 0.05$).

0.8 V the formation of ammonium stayed approximately constant at pH 6.14[a], and decreased for pH 3.35[b]. For both pHs at 25 °C, increasing the potential from 0.8 to 1.2 V led to a decrease in the formation of ammonium. At 28 °C varying the potential from open-circuit to 0.2 V led to an increase in the production of ammonium for both pHs and this increase continued as the potential was increased from 0.2 to 0.8 V. Increasing the potential from 0.8 to 1.2 V led to a decrease in the formation of the ammonium in the pH 6.14[a] samples, and the formation of ammonium stayed approximately constant for pH 3.35[b]. At 35 °C for pH 6.14[a], the influence of going from open-circuit potential to 1.2 V in relation to formation of the ammonium is not evident. For pH 3.35[b], changing from open-circuit potential to 0.2 V increased the formation of ammonium. Going from 0.2 to 0.8 V led to a decrease, and when going from 0.8 to 1.2 V the formation of ammonium became approximately constant.

To better express the photodegradation process just described the data in Table 2 was converted into chemical equivalence. Chemical equivalence allows the values in Table 2 to be expressed in terms of dye mineralization efficiency, which was the goal of determining in this research. To demonstrate this conversion, the data for the optimal results at pH 6.14 (from Table 2) will be used. This test run at 25 °C, with an applied potential

of 0.2 V, led to a concentration of 3.70×10^{-6} mol L^{-1} NH_4^+. Relating the concentration of 0.01 mg/mL with the approximate molecular mass of the dye, 753 g/mol, implies that a solution 0.01 mg/mL corresponds to 1.33×10^{-5} mol L^{-1} of NH_4^+. As there are eight atoms of nitrogen, the concentration of NH_4^+ would be 1.06×10^{-4} mol L^{-1}. A measured value of 3.70×10^{-6} mol L^{-1} of NH_4^+ produced from the photoelectrodegradation process implies that the yield was only 3.49%.

This result demonstrates that only 3.49% of the total possible ammonium that could have formed, did form when the initial dye concentration was 0.01 mg/mL and the pH was 6.14[a]. Better conditions were demonstrated at similar temperature and applied potential when the pH was 3.35[b]. These conditions led to the formation of 8.62×10^{-6} mol L^{-1} NH_4^+, which corresponds to an 8.13% yield.

The adsorption effect in pH 3.35 creates a strong interaction between the dye molecules and the surface, resulting in mineralization. On the other hand, intermediate species should be formed in conditions in which decolorization is favorable. The strong influence of applied potential on decolorization was shown in Table 1, it minimizes the recombination phenomenon. At 0.2 V (pH 3.35) better mineralization was observed than at the other potentials. This is due to a greater attraction of the

molecules towards the surface, which is dependent on the applied potential. For the potentials of 0.8 and 1.2 V a saturation of the surface is likely occurring.

Comparing the results of ammonium formed for the open-circuit potential at different pHs, it can be considered that the process of adsorption plays an important part in the dye mineralization. The adsorption was favored, according to that data, in more acidic pH. To explain this fact the pH of the point of zero charge of TiO_2 (pH pcz) should be considered, that is 6.3 [25]. This means that the TiO_2 surface is a positive carrier when the pH is lower than 6.3, as shown in the following amphoteric relationship of TiO_2 species: $Ti–OH_2^+ \leftrightarrow Ti–OH \leftrightarrow Ti–O^-$. Since the dye studied is anionic, as should be expected there appears to be a strong interaction between the species $Ti–OH_2^+$ and the anionic dye (D^-).

3.5. Effect of initial concentration on the photoeletrocatalytic process initiated by the lamp with and without a bulb

With the objective of understanding the efficiency of the photoelectrocatalytic process on ITO/TiO_2 some experiments were performed. One, the initial dye concentrations were varied, and two, a lamp with and without a bulb was used. The results of dye decolorization and mineralization following irradiation are presented in Table 3.

The results for different initial dye concentrations excited by the lamp without the bulb showed an increasing decolorization behavior relative to a decrease of the concentration. For the experiments performed using the lamp that had a bulb the results were similar with regards to a decrease of decolorization around 90%, but the yield when using the bulb was greater. These results present the effect of the exciting radiation on the nature of ITO/TiO_2 film. An explanation of this behavior is the presence of the rutile form of TiO_2 that presents a bandgap of 410 nm. With the use of the lamp having a bulb, the fluorescence of phosphor powder causes the source to emit radiation above 400 nm with more intensity. The largest decolorization observed was due to a greater number of the electron-hole pairs forming in the system.

In Table 3 the amounts of the ammonium that formed are presented with statistics and stoichiometric analyses, which demonstrate the effect of the initial dye concentration in relation to formation of the ammonium.

Using the mercury vapor lamp without a bulb (L), for the irradiation source and dye concentrations of 0.01, 0.002 and 0.001 mg/mL, similar amounts of ammonium ions were produced. But analyzing the efficiency of conversion results based on initial dye concentration one can see a much greater efficiency for the lower initial concentrations. The results were 81.79% for the initial 0.001 mg/mL sample, 40.89% for the 0.002 mg/mL sample and 8.13% for the 0.01 mg/mL sample. Therefore, this implies that with the decrease of the dye concentration the formation of the ammonium is favored. This means that the process is less efficient in dye concentrations above 0.002 mg/mL due to the saturation of the semiconductor surface, which hinders the photoeletrocatalytic process.

For the results presented in Table 3, when using the lamp with a bulb (L*) and initial dye concentrations of 0.01, 0.002 and 0.001 mg/mL there was an increasing amount of ammonium formed relative to the increasing concentration. This data is statistically different from the data collected without a bulb. The corresponding efficiency data was as follows: for 0.01 mg/mL an efficiency of 14.11%; for 0.002 mg/mL it was 63.86% and for 0.001 mg/mL it was 96.79%. These results demonstrate the effect of the irradiation on the crystalline phases of TiO_2 that contribute to the formation of electron-hole pairs.

3.6. Characterization of photodegraded samples by spectroscopic techniques

The FT-IR spectrum of the sample produced by photoelectrodegradation after being irradiated for 8 h, at 0.2 V and 25 °C, and pH 3.35 is displayed in Fig. 3(c). A tentative attribution of the main bands of the sample spectrum based on the characteristic bands of the benzene ring, and benzene derivatives, aided in interpreting the FT-IR spectra of the dye and of a possible intermediate, sulfanilic acid (Fig. 3a and b, respectively).

The band observed at 1499 cm^{-1} in the sulfanilic acid spectrum, Fig. 3(b), and the bands at 1509 and 1479 cm^{-1} in the dye spectrum, Fig. 3(a), were assigned to ν19a and ν19b benzene modes, respectively, as Varsànyi [26]. The β(NH) mode of secondary aromatic amines was assigned the band at 1421 cm^{-1} in the sulfanilic acid spectrum and at 1411 cm^{-1} in the dye

Table 3
Decolorization and mineralization by photoelectrocatalytic oxidation in different dye concentrations in KCl 0.1 mol L^{-1} solution at pH 3.25($\pm$0.1) and +0.2 V (Ag/AgCl) on ITO/TiO_2 thin film electrodes over a 8 h experiment (mass of TiO_2 = 3.5 ($\pm$0.8) mg; thickness = 6.3 ($\pm$1.4) μm; temperature = 25 ($\pm$0.6) °C)

$[C]_0$ (mg/mL)	D (%)		$[NH_4^+]^\#$ ($\times 10^{-6}$ mol L^{-1})		%E (NH_4^+)	
	L	L*	L(a)	L*(b)	L	L*
0.01	58.8	91.3	8.62 $\pm$ 0.095 (2)	14.96 $\pm$ 0.410 (2)	8.13	14.11
0.002	72.0	94.0	8.67 $\pm$ 0.330 (2)	13.54 $\pm$ 0.100 (2)	40.89	63.86
0.001	88.4	94.3	8.67 $\pm$ 0.045 (2)	10.26 $\pm$ 0.045 (2)	81.79	96.79

$[C]_0$, initial concentration of dye; D, decolorization of dye (in %); $[NH_4^+]$, concentration of ammonium formed and %E (NH_4^+), % yield of ammonium formed. Lamp without bulb (L) and with bulb (L*). $^\#$The results are presented as mean $\pm$ standard error of the mean. The number of sets is given in parentheses. For comparison, groups were formed among the results for the statistical treatment (ANOVA test). The values listed in column (a) were: $F = 0.02$ and $p = 0.980$, implying that the values of the lines 2 and 1 are statistically the same ($p > 0.05$). The values of the lines 2 and 3, and 3 and 1, were not tested. The values listed for column (b) were: $F = 96.78$ and $p = 0.002$, implying the values of the lines are statistically different ($p < 0.05$). The values listed for the column (a) vs. column (b) for the Student's t-test were: line 1, $p = 0.004$; line 2, $p = 0.005$ and line 3, $p = 0.002$.

spectrum. The vibrational mode relative to C–N(benzene ring) was assigned to the band at $1317 \, cm^{-1}$ in the dye spectrum and to 1317 and $1245 \, cm^{-1}$ in the sulfanilic acid spectrum. The $\nu 9a$ (βCH) *para* disubstituted benzene mode corresponds to the frequency at $1123 \, cm^{-1}$ in the dye spectrum and at 1125 and $1167 \, cm^{-1}$ in the sulfanilic acid spectrum. The $\nu 18b$ (βCH) mode was assigned to the bands at 1011 and $1037 \, cm^{-1}$ in the sulfanilic acid spectrum and at 1008 and $1034 \, cm^{-1}$ in the dye spectrum. The 10a (βCH) mode was observed at $832 \, cm^{-1}$ in both of the spectra.

The FT-IR features related to the product, Fig. 3(c), observed at 1405, 1131, 1099, 977 and $939 \, cm^{-1}$, were different from those bands observed in the dye and sulfanilic acid spectra. The band at $1405 \, cm^{-1}$ is characteristic of the N=N stretching mode of the azo group of asymmetric aromatic substances. For the azo group of symmetrical aromatic substances with a symmetry center, this frequency is not IR active, however, it is active in the Raman spectrum [27]. Therefore, to understand the nature of the sample produced by the photoelectrodegradation and to attribute the bands at 1405, 1131, 1099, 977 and $939 \, cm^{-1}$ a spectrum using Raman spectroscopy was obtained.

From the FT-Raman spectra displayed in Fig. 4 it was observed that the bands at 1600 and $1503 \, cm^{-1}$, characteristics found in the Raman spectrum of the dye shown in Fig. 4(a), were similar to those observed in the photodegradation sample spectrum in Fig. 4(c). The bands at 1600 and $1503 \, cm^{-1}$ in the sample spectrum, characteristics of ν(C=C) and ν(N–C) (benzene ring), respectively, can be an indication that the aromatic dye structure was not totally degraded in those samples. It was ruled out though that sulfanilic acid had formed in the sample due to the absence of a band at $1630 \, cm^{-1}$, which is a characteristic in the Raman spectrum of sulfanilic acid (Fig. 4(b)). Due to this result, it was concluded that the bands at 1405, 1131 and $1099 \, cm^{-1}$ in the FT-IR spectrum, Fig. 3(c), are characteristic of the formation of an exceptionally stable azo substance.

Fig. 4. FT-Raman spectra between 850 and $1700 \, cm^{-1}$ of the solid samples of: (a) azo dye; (b) intermediate (sulfanilic acid) and (c) sample obtained by dehydration of photodegraded solution (initial concentration of 0.01 mg/mL) in KCl $0.1 \, mol \, L^{-1}$, pH 3.35 and irradiation for 8 h at 0.2 V and 25 °C. Radiation laser = 1064 nm.

The bands observed at 939 and $982 \, cm^{-1}$ in the FT-Raman spectrum of the prepared sample, that were also observed previously in the FT-IR spectrum at 977 and $939 \, cm^{-1}$, can be attributed to the formation of $KClO_3$ species, probably by oxidation of Cl^- ions. The results indicate this phenomenon could be occurring due to Cl^- ions adsorbed on the semiconductor surface. According to Zanoni et al. [22], it was observed that the Cl^- ions are oxidized in less positive potential under photoelectrocatalytic conditions, according to the reaction: $TiO_2 - h_{vb}{}^+ + Cl^- \rightarrow TiO_2 - Cl_s{}^\bullet$. Carneiro et al. [28] considered this reaction and suggested that the formation of $Cl^\bullet$, $Cl_2{}^\bullet$, active chlorine (Cl_2, HClO, ClO^-), all powerful oxidizing agents capable of degrading the dye, could occur but they stated that it would require special conditions of pH.

4. Conclusions

The photoeletrocatalytic activity of the ITO/TiO_2 electrode was confirmed in this work by varying the experimental decolorization and mineralization parameters and studying spectroscopic data resulting from a pollutant model (leather dye). The following points have been demonstrated.

The photoelectrocatalytic process of the ITO/TiO_2/KCl-dye system was efficient due to filtering UV-C irradiation with a Pyrex® plate. The presence of photon energy in the UV-A and Vis range contributes to the formation of electron-hole pairs when using crystalline forms of TiO_2 (anatase and rutile). The UV-photons reaching the electrode surface during electrochemical reaction steps, form radicals, which can enhance the dye degradation. The effect of recombination of the electron-hole pairs was dominant in the experiments when there was an open-circuit potential regardless of varying the temperature.

The results of this investigation clearly indicate that the temperature, pH and applied potential markedly influences the overall efficiency of the degradation process (decolorization or mineralization) which correlates with the adsorption behavior
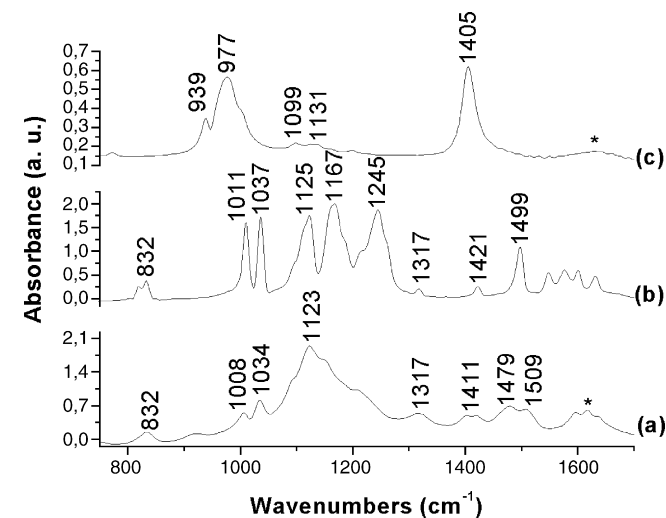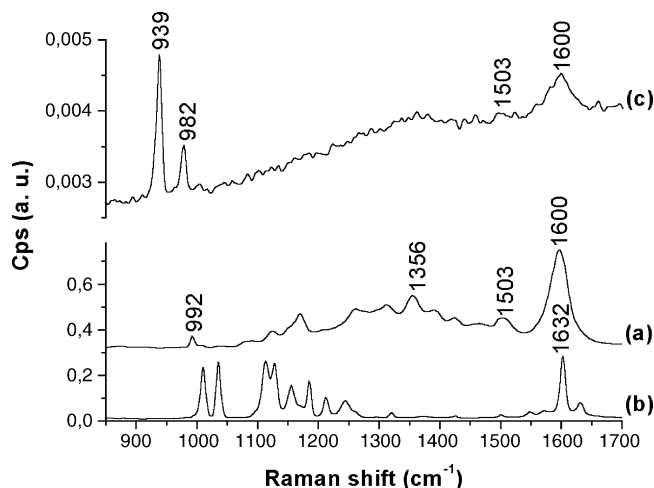

Fig. 3. FT-IR spectra of solid samples of: (a) azo dye; (b) an intermediate phase (sulfanilic acid) and (c) a sample obtained by dehydration of photodegraded solution (initial concentration of 0.01 mg/mL) in KCl $0.1 \, mol \, L^{-1}$, pH 3.35 and after irradiation for 8 h at 0.2 V and 25 °C. Obs: asterisk (*) indicates water band.

of dye on the ITO/TiO$_2$/KCl system. The highest degradation was observed for ITO/TiO$_2$ at 0.2 V when the pH was 3.35 and at 0.8 V when the pH was 6.14. The possible reason for this behavior is that the dye molecules are predominantly located at the adsorbent sites creating a highly concentrated environment around the loaded TiO$_2$. This enhances the photodegradation efficiency.

The saturation of the semiconductor surface hindered the photoeletrocatalytic process, but this effect was minimized by the choice of an irradiation source having a greater intensity in the range of 300–546 nm. The mercury vapor lamp consisting of a bulb had the ability to activate the crystalline structures of TiO$_2$, anatase and rutile, providing the best mineralization.

The temperature and the applied potential were important in decolorization, increasing the collision frequencies between the dye molecules and the oxidizing species and reducing the recombination of electron-hole pairs.

The supporting electrolyte influenced the photoelectrocatalytic process according to the half reaction:

$$\text{ClO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{Cl}^- + 3\text{H}_2\text{O} \quad E^0 = 1.451 \text{ V}$$
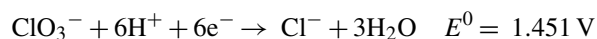
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