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Article

Dye Degradation Enhanced by Coupling Electrochemical Process and Heterogeneous Photocatalysis

Lidiaine M. Santos,[a] Kamila P. de Amorim,[b] Leonardo S. Andrade,[b] Paulo S. Batista,[c] Alam G. Trovó[a] and Antonio E. H. Machado*,[a,b]

[a]Laboratório de Fotoquímica e Ciência de Materiais, Instituto de Química,
Universidade Federal de Uberlândia, P.O. Box 593, 38400-902 Uberlândia-MG, Brazil

[b]Departamento de Química - Regional Catalão, Universidade Federal de Goiás,
Av. Dr. Lamartine Pinto de Avelar, 1120, 75704-020 Catalão-GO, Brazil

[c]Coordenação de Ciências Exatas e Naturais, Instituto Federal do Tocantins, AE310 Sul,
Av. LO 05, S/N, Plano Diretor Sul, 77021-090 Palmas-TO, Brazil

In this study, we evaluated the combination between an electrochemical process, occurring in the dark, and a heterogeneous photocatalytic process for dye degradation, using the azo dye tartrazine as model of oxidizable substrate. TiO_2 P25 and an Ag-doped TiO_2 were used as photocatalysts in suspensions containing 50 mg L^{-1} of tartrazine. The best result, 74% of dye mineralization in 120 min of reaction, was obtained using TiO_2 P25 as photocatalyst and a current density of 10 mA cm^{-2} in the electrochemical cell, a value 30% higher than the sum of the results obtained by heterogeneous photocatalysis (44%) and electrochemical oxidation (13%). The use of Ag-doped TiO_2 did not result in significant improvement on tartrazine mineralization, due to the aggregation of these nanoparticles. Our results suggest that this process can be an alternative for a complete treatment (discoloration and mineralization) of tartrazine and most likely other azo dyes.

Keywords: azo dyes, advanced oxidation processes, discoloration, mineralization, titanium dioxide

Introduction

The environmental impact caused by the discharge of untreated wastewaters, or even partially treated in sewage stations, is an increasingly worrying problem, considering the damage caused to the environment.[1,2] In general, the discharge of effluents containing synthetic dyes tends to cause serious damage to aquatic biota, since the dye impedes the passage of light, compromising the photosynthesis and water oxygenation.[3] In view of this, a great effort has been made to develop new technologies aiming the treatment of persistent substances in the environment such as heterogeneous photocatalysis,[4-6] electrochemical techniques[7,8] and photoelectrochemical processes.[9-12]

Heterogeneous photocatalysis belongs to the class of the advanced oxidation processes (AOP),[13] promising in the treatment of industrial effluents and environmental decontamination. AOPs have received much attention because they are viable alternatives when compared to the processes commonly used to minimize the impact caused by suspended residues or dissolved in wastewaters. In the heterogeneous photocatalytic processes, reactive oxygen species (hydroxyl radicals, superoxide, etc.) are efficiently generated and act in a non-selective way, converting toxic compounds into carbon dioxide, water and eventually inorganic ions.[14] The process begins by the electronic excitation of semiconductor oxide.[4,6,13,15,16] In the electrochemical processes, aromatic compounds can be converted into biodegradable products or eventually into CO_2 and H_2O, by the generation of strong oxidizing agents, mainly the hydroxyl radical (HO•), formed by the electrochemical oxidation of water.[17,18]

Studies evaluating the use of AOPs,[19-22] electrochemical degradation[23] and coupling of electrocoagulation with electrochemical advanced oxidation processes,[24] as alternatives for wastewater treatment to remove tartrazine (TTZ), have been assessed. Although the coupling of photocatalytic and electrochemical processes has been

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*e-mail: aehmachado@gmail.com, aeduardo@ufu.br

more and more evident in the last years,[12,25] there are no studies evaluating the coupling of electrochemical and heterogeneous photocatalysis processes to TTZ degradation. In addition, it should be emphasized that most of the published studies involving photoelectrocatalysis in the treatment of toxic substances is restricted to the use of semiconductors immobilized on suitable supports, which in turn decreases significantly the active area of these materials when exposed to light. Thus, studies aiming the degradation of toxic substances involving photocatalysis coupled to electrochemical process using the photocatalyst in suspension are very attractive, especially as a function of the large margin of investigative exploration offered.

In this study the performance of three different methodologies (heterogeneous photocatalysis mediated by two different TiO_2 photocatalysts, electrochemical, using a TiO_2-RuO_2 electrode (DSA®) and the combination of the two first processes) was evaluated in the degradation of TTZ (Figure 1), an azo dye, known to be resistant to degradation by photolysis.[20,26]

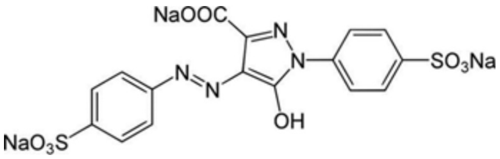


Figure 1. Chemical structure of TTZ ($C_{16}H_9N_4Na_3O_9S_2$; MW = 534.3 g mol^{-1}) in the neutral form.

Experimental

Chemicals

The solutions were prepared using deionized water. All chemicals, including Na_2SO_4 (PA, Vetec), TTZ (Sigma-Aldrich, dye content 85%) and TiO_2 (P25, Degussa) were used as received. TiO_2 silver-doped (LAFOT-Ag 5%) was prepared according to Machado *et al.*[16]

Diffuse reflectance spectra were taken for TiO_2 P25 and LAFOT-Ag 5%. The measurements were done at room temperature using a Shimadzu UV-1650PC spectrophotometer equipped with an integrating sphere, in the range between 190 and 800 nm. These plots were converted to plots of the Kubelka-Munk function F(R) against photon energy (eV).

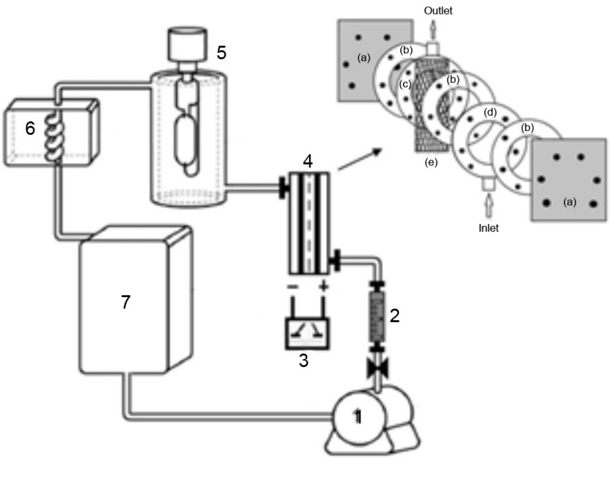
Monitoring the discoloration and mineralization of TTZ

In all assays, 3.0 L of an aqueous solution containing 50 mg L^{-1} TTZ (dissolved organic carbon (DOC) = 18 mg C L^{-1}) and 71 mg L^{-1} of Na_2SO_4, without pH adjustment (initial pH 6.9). Na_2SO_4 was added to standardize the assays since it is used as support electrolyte in the electrochemical and photocatalysis coupled to an electrochemical process.

TTZ discoloration was carried out at 25 °C and investigated for four different conditions: (*i*) photolysis; (*ii*) photocatalysis (PC); (*iii*) electrochemical oxidation (EO) and (*iv*) photocatalysis coupled to electrochemical oxidation (PCE). All these experiments were carried out using 100 mg L^{-1} of the photocatalysts, a concentration defined in previous studies,[27,28] dispersed in the solution containing the dye and performed in a batch recirculation system at a flow rate of 100 L h^{-1}.

All experiments were conducted at lab-scale. The assays based on the irradiation of the oxidizable substrate (*i*, *ii* and *iv*) were carried out using a photocatalytic reactor described previously.[5,29] This reactor consists of a cylindrical borosilicate glass jacket with a path length of 2 cm and a 400 W high pressure mercury lamp positioned at the center (coaxial to it). This lamp furnishes a mean photonic flux of 3.3×10^{-6} einstein s^{-1} in the spectral range between 292 and 815 nm.[30] The suspension containing the photocatalyst and the TTZ solution was pumped into the jacket, being circulated in front of the lamp. A thermostatic bath was used to control the temperature of the reaction medium.

The assays involving the combination of EO and PC (*iv*) were carried out using the setup presented in the diagram below (Scheme 1), consisting of the combination of a one-compartment filter-press electrochemical reactor[31] and a photochemical reactor.[5] The electrochemical reactions



Scheme 1. Illustration of the setup used in the assays involving the coupling of an electrochemical process and heterogeneous photocatalysis, composed of: (1) magnetic drag pump; (2) rotameter; (3) voltage and current source; (4) electrochemical reactor (and expanded and detailed view)[a]; (5) photocatalytic reactor and radiation font (Philips HPL-N Hg lamp); (6) heat exchanger and (7) reservoir. The setup for the assays involving the electrochemical process involves the first four components presented in the scheme. [a](a) End plates and counter electrodes (cathode-stainless steel); (b) silicone gaskets; (c) solution outlet compartment; (d) solution inlet compartment; (e) working electrode (DSA®).

were conducted in the absence of light. In the combined process the suspension containing the catalyst and the target-compound was firstly submitted to EO in the absence of light, to then be treated by PC.

In the EO and PCE, different current densities (10, 30 and 50 mA cm^{-2}) were applied. A DSA® electrode was used as anode (70 cm^2). Two stainless steel plates were used as counter electrodes.

During the assays, TTZ discoloration was continuously monitored by visible spectroscopy through measurement of the absorbance at 428 nm, attributed to TTZ.

TTZ mineralization, given by conversion of organic carbon to carbon dioxide and water, was monitored by decay of DOC using a total organic carbon (TOC) analyzer (TOC 5000, Shimadzu). Due to practical limitations, only the measurements for the initial and final point during the reaction were done. Before spectrophotometric and DOC analyses the photocatalysts were removed by filtration by the use of 0.45 µm pore size polytetrafluoroethylene (PTFE) membranes. Aliquots of 30 mL were withdrawn every 20 min up to the end of the reaction.

It should be emphasized that TTZ is highly soluble in water (> 100 g L^{-1}). During its degradation, the formation of short carbonic chain oxidized degradation products occurs and therefore with a high solubility in water. Thus, is not expected that the TTZ or degradation products are retained by the PTFE membranes. It is worth mentioning that, except in the EO, any other processes (PC and PCE) require mandatorily the filtration in membranes for removal of the photocatalyst (TiO_2) before the analyses.

Results and Discussion

Direct photolysis and adsorption of TTZ by photocatalysts

Figure 2 shows the results obtained for TTZ photolysis. As expected[26] an extremely low mineralization (2.4% of the initial DOC content) was reached for TTZ mineralization, after 120 min of irradiation. Besides, at the end of this interval less than 4% of discoloration was achieved (Figure 2, inset).

These results confirm the assertion that TTZ is difficult to be degraded only by photolysis using UVA-Vis radiation without the aid of any additive or catalyst,[20,26] which hinders the degradation of effluents containing dyes, dumped in aquatic environments. It should be emphasized that under our experimental conditions only radiation with wavelengths higher than 290 nm (energy lower than 4.27 eV) reaches the reaction medium, since the photocatalytic reactor was built with borosilicate glass.[30]

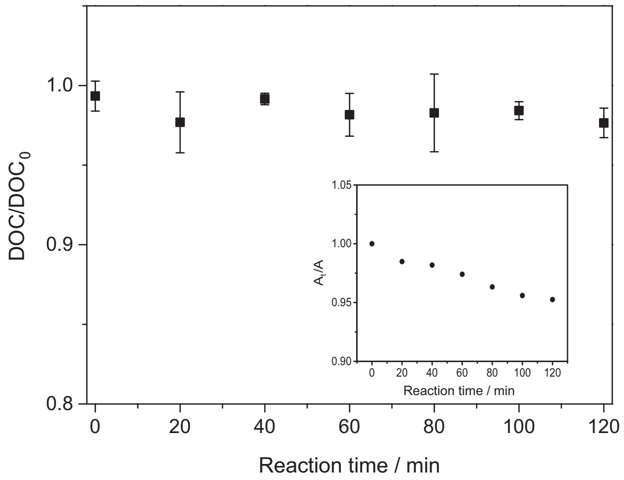


Figure 2. Normalized DOC *vs.* irradiation time for TTZ photolysis. Inset: normalized absorbance of TTZ *vs.* irradiation time. Initial conditions: $[TTZ]_0$ = 50 mg L^{-1} (DOC = 18 mg C L^{-1}); pH 6.90.

A fast adsorption/desorption equilibrium between TTZ and the surface of the photocatalysts occurs during the process, with less than 3% of TTZ (data not shown) adsorbed at the equilibrium. These assays were conducted at three different pH (3.0, 6.9 and 8.0) in the absence of light, under similar conditions used in the degradation assays.

Photocatalytic TTZ degradation

Figure 3 presents the changes in the absorption spectra of solutions containing TTZ during its discoloration mediated by PC using LAFOT-Ag 5%. The behavior for P25-mediated discoloration is very similar.

Analyzing the spectra presented in Figure 3, it can be observed, at the end of the process, that the bands located

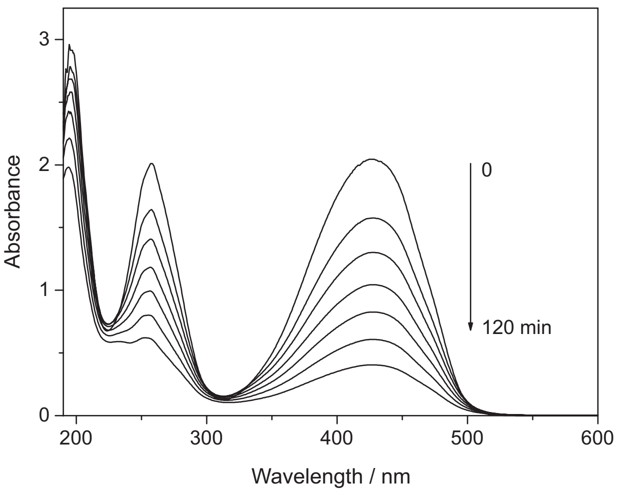


Figure 3. Typical TTZ UV-Vis spectrum decay obtained for different reaction times, using LAFOT-Ag 5% as photocatalyst. Initial conditions: $[TTZ]_0$ = 50 mg L^{-1} (DOC = 18 mg C L^{-1}); [TiO_2 P25 or LAFOT-Ag 5%] = 100 mg L^{-1}; pH 6.90.

in the spectral region between 200 and 400 nm, referred to as π → π* aromatic transitions, decrease significantly. Thus, the results demonstrate that the photocatalytic discoloration of TTZ did not result in new absorption bands, suggesting that the compounds formed do not absorb significantly in the range monitored of the electromagnetic spectrum. In addition, the band with a maximum at 428 nm decreases significantly, suggesting a good efficiency in the discoloration of TTZ.

A complex mechanism is expected to occur in heterogeneous photocatalytic processes, where the reactions tend to occur initially in the solid-liquid interface, involving reactive species generated in the active sites of the excited photocatalyst, or the direct interaction between the excited photocatalyst and the oxidizable substrate.[5,27-29]

The discoloration of TTZ should be directly related to the N=N (azo) homolytic scission. The desorbed hydroxyl radicals, formed in the interface TiO_2/solution should to be one of the responsible for this process.[5]

Figure 4 shows that the ratio between absorbance and reaction time has a profile of first order decay for TTZ discoloration mediated by both photocatalysts. It has been suggested that the degradation of organic matter by heterogeneous photocatalysis follows a Langmuir-Hinschelwood kinetics.[30,32] The rate of production of reactive species during the adsorption-desorption process in the surface of the excited photocatalyst can reach quickly a stationary state regimen with characteristics of a pseudo 1st order decay. Considering this, the apparent rate constants for TTZ discoloration obtained using P25 and LAFOT-Ag 5% (Figure 4, inset) are equal to 0.0340 min^{-1} (R = 0.9530) and 0.0183 min^{-1} (R = 0.9897), respectively. At the end of the PC, the efficiencies are approximately similar, since for LAFOT-Ag 5% about 90% of the color and 40% of mineralization were reached after 120 min of reaction, while for TiO_2 P25 the discoloration and mineralization reached values of 97% and 44%, respectively. It has been reported that photocatalytic processes promoted Ag-doped TiO_2 tend to be favored by the silver incorporated into the crystal structure of TiO_2, generally in proportions between 2.0 and 5.0% m/m,[33] reducing the band gap energy and introducing structural defects that should influence favorably on the photocatalytic action by minimizing the electron/hole recombination.[13,16]

It should be emphasized that the band gap energies for P25 and TiO_2-5% Ag are respectively 3.20 eV (387 nm)[34] and 3.04 eV (408 nm). The analysis of the spectral irradiance of a high pressure mercury lamp[35] shows that the difference of absorption of radiation between the two catalysts is in a line of low to medium intensity at 404.6 nm that can be absorbed only by the Ag-doped catalyst.

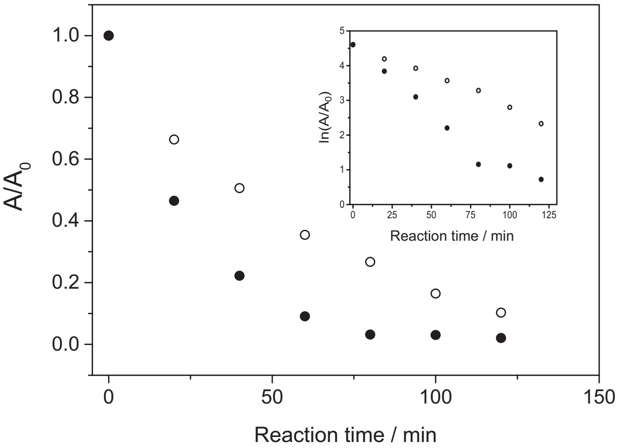


Figure 4. Normalized absorbance *vs.* reaction time for the photocatalytic discoloration of TTZ, using the photocatalysts P25 (●) and LAFOT-Ag 5% (○). Inset: natural logarithm of the normalized absorbance of TTZ, using TiO_2 P25 (R = 0.9530) and TiO_2 LAFOT-Ag 5% (R = 0.9897), *vs.* reaction time. Initial conditions: $[TTZ]_0$ = 50 mg L^{-1} (DOC = 18 mg C L^{-1}); [TiO_2 P25 and LAFOT-Ag 5%] = 100 mg L^{-1}; pH 6.90.

Besides, it deserves to be highlighted that the plot of F(R) *vs.* energy (eV) shows that P25 absorbs at least six times more photons than our Ag-doped photocatalyst in almost all the spectral range between 290 and 408 nm (Figure 5), which can be considered, combined with the structural defects caused by the coexistence of anatase and rutile as crystalline phases of P25, as reasons for the high photocatalytic efficiency of this material compared to the doped photocatalyst.

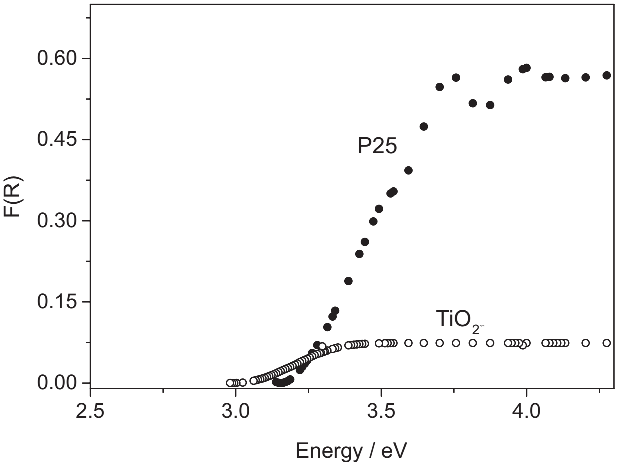


Figure 5. Plot of F(R) *vs.* energy (eV) for the photocatalysts P25 and TiO_2-Ag 5%.

TTZ degradation mediated by electrochemical oxidation

In the EO (Figure 6) the discoloration obtained for current densities of 10 and 30 mA cm^{-2} followed zero-order kinetics (i.e., a linear dependence between absorbance and time, with R = 0.997 and 0.992, respectively), typical of processes controlled by charge transport, while for 50 mA cm^{-2} of current density the color disappearance followed an exponential pattern of 1st order, typical of processes controlled by mass transport. Although unhappily we do not have the value of the current limit of the reactor, these different kinetic profiles should be related to the value of the applied current relative to the limiting current for the system studied, since it is known that when the electrochemical process operates with an applied current (I_{appl}) lower than the current-limit typical of the reactor (I_{lim}), the process tends to be predominantly controlled by charge transport. On the other hand, if $I_{appl} > I_{lim}$ the process tends to be predominantly controlled by the diffusion of oxidizable substrate towards the surface of the electrode.[31,36,37] In this case, it is expected that an increase in I_{appl} results in a minimal influence on the rate of discoloration.

In this study, at the end of the EOs, the percentages of TTZ color elimination were 27, 36 and 88% for the applied current densities of, respectively, 10, 30 and 50 mA cm^{-2} (Figure 6).

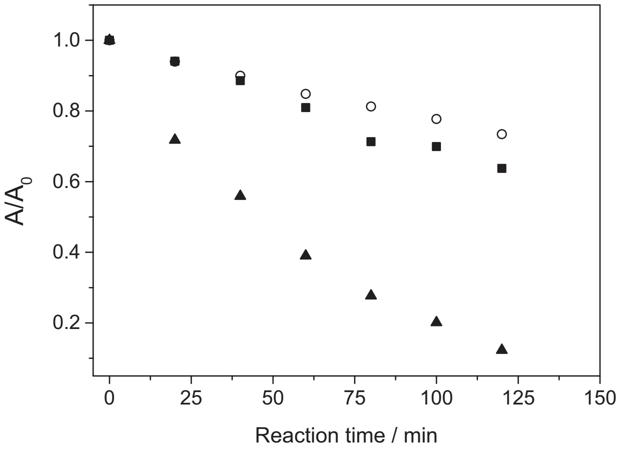


Figure 6. Graphs of normalized absorbance as function of the reaction time for electrochemical TTZ discoloration using the DSA® electrode at current densities of 10 mA cm^{-2} (○), 30 mA cm^{-2} (■) and 50 mA cm^{-2} (▲). Initial conditions: $[TTZ]_0$ = 50 mg L^{-1} (DOC = 18 mg C L^{-1}); pH 6.90.

Although the results obtained by the application of a current density equal to 50 mA cm^{-2} have presented the highest color removal, from the economical point of view this condition does not reflects the most advantageous result.

The total energy consumption (TEC) for the removal of 1 kg of TTZ (measured in kWh kg$^{-1}_{TTZ}$) was calculated using equation 1:

$$TEC = \frac{t \times U \times I}{V \times \Delta TTZ} \times 1000 \qquad (1)$$

where t is the electrolysis time (h), U the average electrolysis cell voltage (V), I the applied electrolysis current (A), V the wastewater volume (L), and ΔTTZ the difference in TTZ concentration (mg L^{-1}).

The average electrolysis cell voltage values measured at 10, 30 and 50 mA cm^{-2} were respectively 3.7, 6.2 and 7.7 V. The corresponding TEC values for these current densities were 0.132, 0.479 and 0.409 kW h g^{-1}. Based on these values, the most advantageous result from the economical point of view was the one obtained by applying 10 mA cm^{-2}. However, even though only 27% of the color was removed under this condition, this parameter does not seem to be the main parameter to be improved considering the conjugation between photocatalysis and electrochemical process, since the former is capable to remove efficiently the color but not totally the organic load. In this sense, we decided to choose a condition of electrolysis with energy consumption as small as possible for TTZ degradation, but considering a possible synergy between both processes.

TTZ degradation mediated by the combined use of electrochemical process and heterogeneous photocatalysis

The use of PCE for degradation of pollutants requires first an individual assessment of the contribution of each process, and subsequently the synergy between them. For example, in TTZ photocatalytic degradation, at the end of the process the color was almost completely eliminated, while the destruction of the organic load varied depending on the photocatalyst used (Table 1).

Figure 7 presents the kinetic profiles related to the discoloration promoted by PC, EO and PCE processes, in the presence of TiO_2 P25 (Figure 7a) and of LAFOT-Ag 5% (Figure 7b).

Regardless of the type of photocatalyst, the kinetics of color removal by PCE shows a first-order exponential profile, with apparent rate constants equal to 0.0351 and 0.0213 min^{-1}, using, respectively, TiO_2 P25 and LAFOT-Ag 5%, being similar to the one reached when using only PC (Table 1). On the other hand, considering the TTZ mineralization mediated by TiO_2 P25 in the PCE, at the end of 120 min of reaction 74% of the dye was mineralized, a value 30% higher than the sum of the results obtained separately by PC (44%) and EO (13%). Comparing to the mineralization reached by EO, the improvement achieved was of about 470%. It is probable that the electrochemical step contributed to the combined process with degradation products more easily mineralized in the photocatalytic step, due to complementary action of the oxygen evolved on the anode during the electrochemical process.

Table 1. Mineralization and discoloration of TTZ in 120 min of reaction, and the apparent first order rate, k_{app}, for TTZ degradation, mediated by TiO_2 P25 or LAFOT-Ag 5% in the PC, PCE and in the EO

Process	Catalyst	Mineralization / %	Discoloration / %	k_{app} / ($\times 10^3$ min^{-1})
PC	TiO_2 P25	44	97	34.0
	LAFOT-Ag 5%	40	90	18.3
EO	DSA® electrode	13	27	[a]
PCE	TiO_2 P25	74	99	35.1
	LAFOT-Ag 5%	44	92	21.3

[a] 2.02×10^{-7} mol L^{-1} min^{-1}.

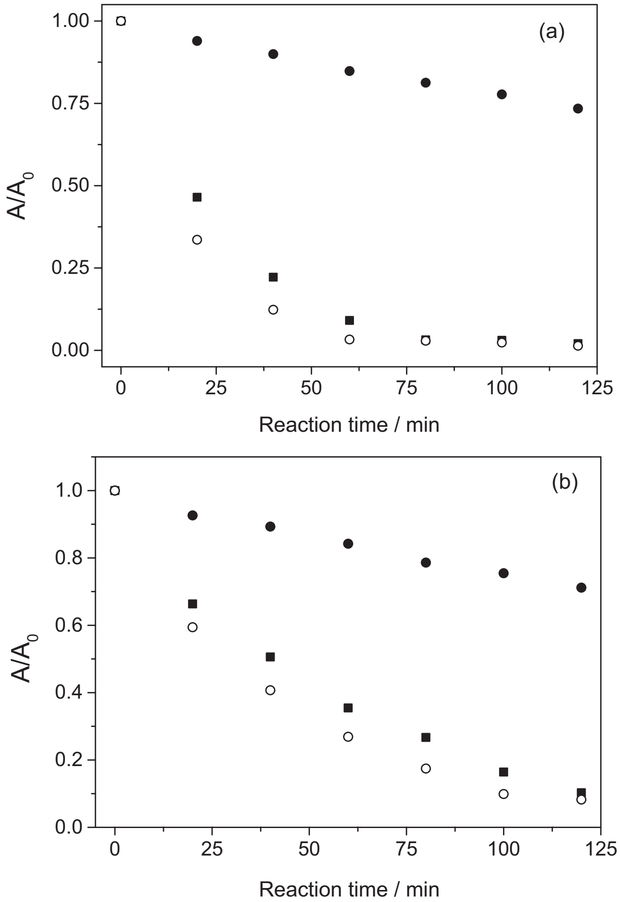


Figure 7. Normalized absorbance *vs.* reaction time for TTZ color removal by EO (●), PC (■) and by PCE (○) in the presence of (a) TiO_2 P25, or (b) LAFOT-Ag 5%. Initial conditions: $[TTZ]_0 = 50$ mg L^{-1} (DOC = 18 mg C L^{-1}); [TiO_2 P25 or LAFOT-Ag 5%] = 50 mg L^{-1}; DSA® electrode at 10 mA cm^{-2}; pH 6.90.

Thus, we can conclude that there is in fact a significant synergistic effect when both processes are coupled in the presence of TiO_2 P25. On the other hand, the significantly lower mineralization obtained when using LAFOT-Ag 5% in the PCE was probably harmed because the TiO_2 P25 is more efficient in absorbing photons in the spectral range between 290 and 408 nm combined with the structural defects caused by the coexistence of anatase and rutile as crystalline phases in P25 and the high aggregation of nanoparticles in LAFOT-Ag 5%, which hindered a higher dispersion of this photocatalyst, even though this Ag-doped photocatalyst has a surface area twice that of TiO_2 P25 (unpublished results).

Conclusions

The synergetic effect observed by the coupling between the electrochemical and photocatalytic processes could be evidenced by the increase in the percentage of TTZ mineralization when TiO_2 P25 was employed. With 120 min of reaction 74% of mineralization was reached in the combined process, a value 30% higher than the sum of the results obtained separately by heterogeneous photocatalysis (44%) and electrochemical process (13%). The influence of the electrochemical process seems to be mainly due to the degradation products being easier to be mineralized in the step involving heterogeneous photocatalysis, and by the dispersion of the photocatalyst in solution, improved by the generation of extremely small-sized micro-bubbles of oxygen at the anode from the electrochemical oxidation of water and by additional production of hydroxyl radicals. From the point of view of color removal, both photocatalysts led to similar results, with almost complete color removal after 120 min of reaction.

The low increase of mineralization observed when using LAFOT-Ag 5% when the combined process is compared to photocatalysis is likely to be exclusively due to the more degraded species produced in the electrochemical stage, since for the Ag-doped photocatalyst the dispersion induced by the O_2 produced in the anode should be minimal, considering that these nanoparticles are more aggregated.

In this context, it is clear that depending on the type of matrix and oxidizable substrates present, to obtain a high efficiency of mineralization using the combination of processes, it is firstly necessary to know the limitations inherent to each one.

It should be emphasized that, although they are combined, the two processes occur independently, with the electrochemical process occurring in the absence of light and, therefore, in no time the electrodes are irradiated.

Finally, it is concluded that the coupling between the heterogeneous photocatalysis and electrochemical process can be used as an alternative for the treatment of this kind of effluent and probably containing other azo dyes.

Acknowledgements

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