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Article

Evolutive Follow-up of the Photocatalytic Degradation of Real Textile Effluents in TiO_2 and TiO_2/H_2O_2 Systems and their Toxic Effects on *Lactuca sativa* Seedlings

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Dentre os resíduos industriais, um dos mais preocupantes é o do setor têxtil, por apresentar forte coloração e toxicidade. O objetivo do presente trabalho foi caracterizar o comportamento de degradação e mineralização de efluentes têxteis reais através de processos oxidativos avançados utilizando TiO_2 ou associação de TiO_2/H_2O_2, e monitorar a toxicidade dos produtos formados em relação ao efluente bruto durante 6 h de irradiação. Os resultados demonstraram que a associação TiO_2/H_2O_2 é mais eficiente na mineralização destes resíduos alcançando taxas representativas de redução de matéria orgânica (representada pela coloração, DQO e COT) e, ainda, altas concentrações de íons mineralizados (NH_4^+, NO_3^- e SO_4^{2-}). Em relação à toxicidade apresentada pelos produtos formados durante a degradação perante as sementes de alface (*Lactuca sativa*) os dados sugerem que não foi apresentada toxicidade considerável, uma vez que não houve redução significativa da porcentagem de germinação nem influência na porcentagem de crescimento das raízes e radículas, contudo, a associação TiO_2/H_2O_2 apresenta maior toxicidade nas primeiras horas de irradiação e posterior redução da mesma ao final de seis horas, enquanto que o TiO_2 somente aumenta um pouco sua toxicidade no final dos experimentos. Porém, comparados ao efluente bruto, ambos apresentaram redução de toxicidade, ou seja, os produtos fotogerados apresentam-se menos tóxicos que o efluente inicial.

Textile industry wastes raise a great concern due to their strong coloration and toxicity. The objective of the present work was to characterize the degradation and mineralization of textile effluents by advanced oxidative processes using either TiO_2 or TiO_2/H_2O_2 association and to monitor the toxicity of the products formed during 6 h irradiation in relation to that of the *in natura* effluent. The results obtained demonstrated that the TiO_2/H_2O_2 association was more efficient in the mineralization of textile effluents than TiO_2 alone, with high mineralized ion concentrations (NH_4^+, NO_3^-, and SO_4^{2-}) and significant organic matter reduction rates (represented by the COD and TOC). The toxicity of the degradation products to lettuce seeds (*Lactuca sativa*) was not significant, since percent germination was not significantly affected and neither was root and sprout percent growth. However, while the TiO_2/H_2O_2 association was more toxic in the first hours of irradiation and less so in the end of the 6 h irradiation, the toxicity of TiO_2 increased only slightly in the end of the experiments. Comparatively, the photogenerated products of both the TiO_2 and the TiO_2/H_2O_2 association were less toxic than the *in natura* effluent.

Keywords: TiO_2, textile effluents, photodegradation, toxicity, *Lactuca sativa*

Introduction

Among the industrial chemical wastes, those of the textile industry raise great concern because of their diverse environmental hazards. Additionally, their aromatic amines, dye by-products, are mutagenic and carcinogenic.[1]

The azo dye family, characterized by one or more –N=N– groups bounded to aromatic systems, is the most representative and most used group of dyes in the textile industry. They represent about 60% of the dyes currently used in the world.[2]

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The removal of dyes from textile effluents has been studied by several techniques such as adsorption, precipitation, filtration, biological degradation,[3] biosorption[4] and chemical degradation.[5] Each of the mentioned techniques has some advantages and disadvantages; however, their main disadvantage is that they only transfer the pollutants from one phase to another, without effectively destroying the polluting load. Chemical degradation is a more viable alternative, mainly because it does not produce secondary solid wastes. As advanced oxidative processes (AOP) have gained importance recently, the chemical oxidation of dyes has been carried out by several techniques such as with hydrogen peroxide,[6] ozone,[7] some metal oxides such as those of titanium and zinc,[8] Fenton reactions,[9] and also by the association of some techniques to ultraviolet,[10,11] visible[12] and even sun light irradiation.[13,14] Heterogeneous photocatalysis in the presence of TiO_2 presents several advantages, as it is inexpensive, thermally and photochemically stable, atoxic to microorganisms, and works in the whole pH range.

However, chemically degraded wastes may be toxic due to the presence of products generated during the photodegradation. Biological tests, along with chemical tests, are necessary to evaluate the inherent risks of their disposal and to verify the environmental quality and the viability of their disposal to aquatic environments. As industrial effluents are a mixture of toxic components, the contribution of each component to toxicity varies with its dilution and dispersion in water and is also affected by the diversity of the discharge environments.[15]

Biological and microbiological tests allow evaluating water pollution nearly as accurately as chemical ones do. However, chemical estimates have limitations as well and most of techniques are unable to evaluate the bioavailability of contaminants to the biota. Chemical evaluations, associated with toxicological studies, may be applied to several processes.[16,17] Due to the complexity of the aquatic ecosystems and the multifunctionality of toxicity tests, they may be carried out with a large variety of biological species at different trophic levels. Living organisms are almost always exposed to possibly genotoxic environmental agents both at cellular and molecular levels. Genotoxic potential studies are important to predict the impact of certain agents on animals, vegetables, and consequently on human beings.[18]

Lettuce seeds (*Lactuca sativa*) were used in phytotoxicity study in this work. Among the environmental factors, water influences germination the most. Respiration and other metabolic activities are intensified in rehydrated tissues and result in the supply of energy and nutrients necessary for the embryo axle growth.[19] As contaminated water is hazardous to germination, the evaluation of toxic effects of wastes on the germination of sensitive species is highly valuable. *Lactuca sativa* is largely used in the evaluation of germination as it is easily obtainable and the fast results are easy to evaluate.[20] Although lettuce is not representative of aquatic system species, the data afforded by its toxicity test are informative on the possible effect of contaminants on vegetable communities. Several researchers have used this species in their works.[21-24] Lettuce seed bioassays are static acute toxicity tests (120 h exposure) that allow evaluating the phytotoxic effects of pure compounds and complex mixtures on plant germination and seedling development during the first days of growth. The germination and the growth inhibition of the root and sprout are used as evaluation endpoints of phytotoxic effects.

Experimental

Reagents

The textile effluents studied were obtained from a clothing manufacturer of Northwest Paraná State (PR), Brazil. TiO_2 (P-25, 80% anatase, 20% rutile with a specific surface of 50 $m^2 g^{-1}$) was kindly provided by Evonik-Degussa-Brazil and used without previous purification. H_2O_2 (30%, analytical grade) was purchased from Synth. The other reagents employed had analytical grade and were used without previous purification.

Photodegradation

Irradiation was performed with a mercury lamp (250 W) without protective glass at room temperature in three open cylindrical borosilicate reactors. The suspensions contained TiO_2 (0.25 g L^{-1}) and H_2O_2 (1.0×10^{-2} mol L^{-1}) in concentrations established according to previous studies.[25,26] Textile effluent was collected at the dying machine output after pH neutralization. Degradation evolution was evaluated under 6 h irradiation. Table 1 gives the raw textile effluent characteristics.

Before irradiation, 500 mL of suspensions containing 0.25 g L^{-1} of TiO_2 were sonicated for 20 min in the dark at pH 3.5 for obtaining optimal adsorption level.[26] After adsorption, 1.0×10^{-2} mol L^{-1} of H_2O_2 was added to the suspensions. In the reactors, the suspension surface was at a fixed distance of 30 cm from the mercury lamp (250 W) without glass filter. The suspension was continuously magnetically agitated. The irradiation sources were fixed vertically to the top side of a wooden box (80 cm × 80 cm × 50 cm) height, length, and width, respectively. Four fans were positioned at different

Table 1. Real textile effluent characterization before irradiation

pH	Abs / nm						
	228	254	284	310	390	500	600
7.5	2.4479	1.5937	1.071	0.7501	0.3204	0.1950	0.1697
H_2O_2 / (mol L^{-1})	COD / (mgO_2 L^{-1})	Cond. / (mS cm^{-1})	TOC / (mg L^{-1})	Norg / (mg L^{-1})	NH_4^+ / (mg L^{-1})	NO_3^- / (mg L^{-1})	SO_4^{2-} / (mg L^{-1})
n.a.	430	4.06	173	33.04	28.35	n.d.	n.d.

n.a.: not added to *in natura* effluent; n.d.: neither detected nor added as a salt to *in natura* effluent.

heights on the sides of the box to minimize the effect of the lamp-generated heat.[25] The temperature during irradiation oscillated around 35 ºC.

Analytical determination

The changes in effluent composition as a function of irradiation time were studied by UV-Vis (Shimadzu 1240 spectrophotometer) after filtration with 25 μm millipore membrane. Mineralization rates were investigated through the decrease in Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC-5000 Analyser), and nitrate (NO_3^-), ammonium (NH_4^+), and sulfate (SO_4^{2-}) ion formation. The analytical techniques were used according to the Standard Methods.[27] Residual peroxide was determined according to Silva *et al*.[28]

Lettuce seed toxicity test

Lettuce seed bioassays were carried out according to Sobrero and Ronco.[20]

Dilution preparation

The effluent samples (*in natura* and irradiated for 1, 2, 3, 4, 5, and 6 h in the presence of either TiO_2 0.25 g L^{-1} or the TiO_2 0.25 g L^{-1} + H_2O_2 1.0 $\times 10^{-2}$ mol L^{-1} association were diluted five-fold with distilled water to 100%, 80%, 50%, 20%, and 10% v/v.

Assay protocol

A paper filter disk (Whatman No. 3, 90 mm diameter) was placed on a Petri dish (100 mm diameter) previously marked with the corresponding dilution and the bioassay start and end dates. The paper filter disk was then saturated with 4 mL of diluted sample with care to avoid bubble formation. Twenty seeds were placed on the filter paper with a pair of tweezers with enough room to allow root growth.

The plates were covered and placed in plastic bags to prevent moisture loss and incubated for 5 days (120 h) at 22.2 ± 2 ºC, as shown in Figure 1. Each assay was done in triplicate.

Measurement of phytotoxicity evaluation end points

The endpoint effect of sample exposure was evaluated by comparing the response of experimental and negative control organisms (exposed to pure water). Experimental conditions were the same as the assay conditions, except for the absence of effluent sample. After exposure, the effect on the germination and the growth inhibition of the root and sprout were quantified.

Effect on germination

It was counted the number of seeds that germinated normally, considering the germination criterion and the effective root growth, according to equation 1.

$$\% \text{ absolute germination} = \frac{\text{number of germinated seeds}}{\text{total number of seeds}} \text{ x100} \quad (1)$$

Effect on both dilution and control root and sprout length (equation 2)

Seedling root and sprout were carefully measured with either a ruler or cross section paper. Roots were measured from the knot region (thicker transition from root to sprout) to the root apex. Sprout growth was measured from the knot to the cotyledon insertion.

$$\% \text{ relative root growth inhibition} = \frac{\text{MCRG} - \text{MSRG}}{\text{MCRG}} \text{ x100} \quad (2)$$

where MCRG = Mean control root growth and MSRG = Mean sample root growth.

Results and Discussion

Photodegradation

The actual textile effluents and catalyst mass values, oxidizer, and pH (TiO_2 = 0.25 g L^{-1}, H_2O_2 = 1.0 $\times 10^{-2}$ mol L^{-1}, and pH 3.5) used in the experiments were optimized in previous experiments.[26]

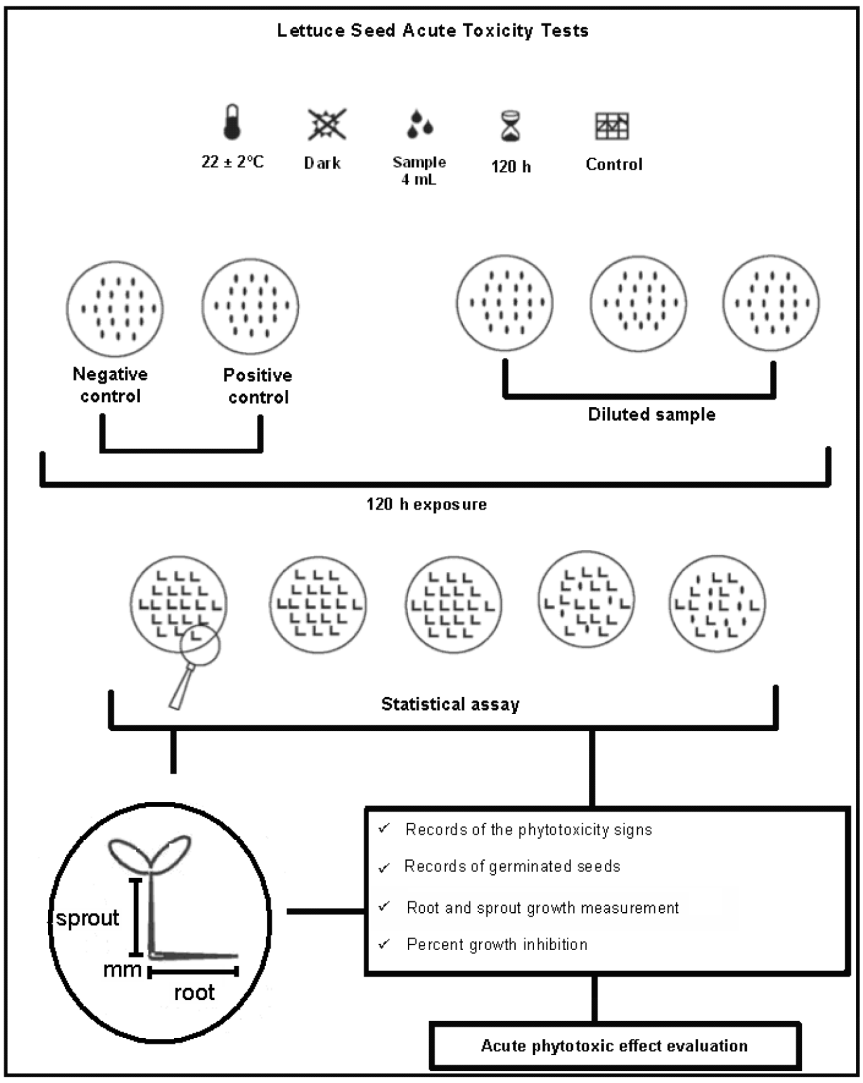

Figure 1. Summary of the lettuce seed bioassay technique. Adapted from reference 20.

A total of six degradations of the same effluent (1, 2, 3, 4, 5, and 6 h irradiation) were carried out for a complete and coherent study of degradation and a complete evolution profile of degradation (decrease in coloration, COD, TOC) and mineralization. The experiments in the presence of only TiO_2 and of the association TiO_2/H_2O_2 allowed evaluating the toxic potential of the effluents before and after different irradiation times and the influence of the presence or not of peroxide in the medium. Although peroxide certainly improves the process efficiency, it may affect toxicity. Due to the instability of solar radiation and as this study required constant radiation for later comparison, the experiments were carried out only in an artificial radiation reactor.

Figure 2 shows the typical absorbance decay of the textile effluent during photodegradation in the presence of TiO_2. The decay is more intense in A due to the presence of H_2O_2, a strong oxidant. It accelerates the decrease of VIS and UV light peaks, which indicates a rupture of the characteristic organic structures, mainly dyes such as the azo groups and aromatic rings[29] of the effluents, due to the large number of hydroxyl radicals in the medium, which makes degradation rather easy. The large quantity of these radicals in the TiO_2/H_2O_2 association is attributed to the reactions illustrated in Scheme 1. It is not observed the formation of new UV peaks, which suggests that the intermediate products are consumed during the process without the formation of any refractory product. This fact is also demonstrated by the large reduction of COD and TOC, parameters that indicate the presence of organic matter in the medium.

Table 2 gives the degradation evolution data of textile effluents in the presence of either TiO_2 or the TiO_2+H_2O_2 association as a reducer of TOC and COD, and conductivity evolution and inorganic ion formation (mineralization),

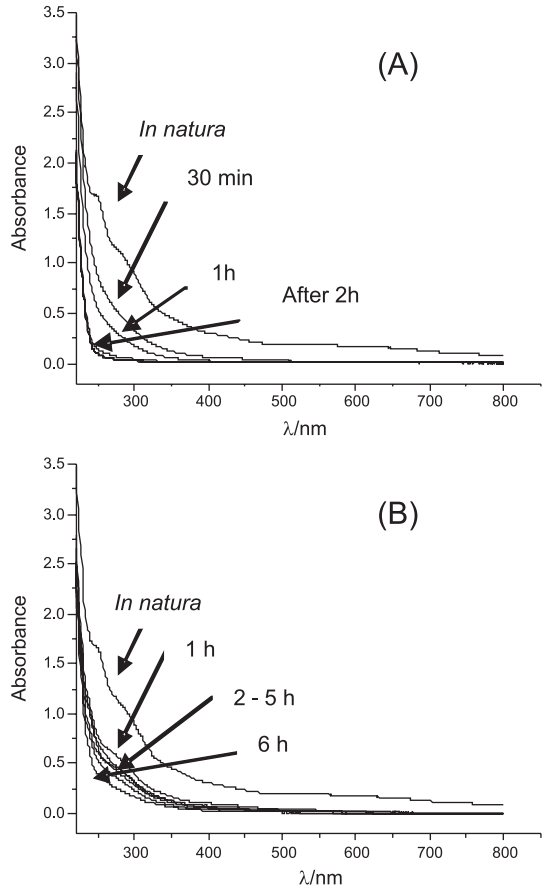

Figure 2. Decay in the absorbance spectrum of textile effluent EF in conditions: (A) TiO_2 0.25 g L^{-1}/ H_2O_2 1.0 $\times 10^{-2}$ mol L^{-1}, (B) TiO_2 0.25 g L^{-1}.

UV/TiO_2 (A)

$$TiO_2 + h\nu \rightarrow TiO_2\ (e^- + h^+)$$
$$TiO_2h^+ + OH^-_{ad} \rightarrow TiO_2 + OH^\bullet$$

UV/H_2O_2/TiO_2 (B)

$$TiO_2 + h\nu \rightarrow TiO_2\ (e^- + h^+)$$
$$TiO_2h^+ + OH^-_{ad} \rightarrow TiO_2 + OH^\bullet$$
$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^-$$

Scheme 1. Probable mechanisms of formation of hydroxyl radicals in different AOPs.[30]

which are fundamental parameters of photocatalytic process efficiency.

The efficiency of the techniques tested was satisfactory. For COD removal, when TiO_2 was associated to H_2O_2 the efficiency was higher (100%) than TiO_2 alone (88%) after 6 h irradiation time. TOC yields under 6 h reaction were 80 and 66% for TiO_2/H_2O_2 and TiO_2, respectively.

Discoloration and organic matter reduction results are essential for the good development of the photodegradation technique. However, it must be pointed out that mineralization is the most important process characteristic, since it shows the real process efficiency. Breaking up organic structures is relatively easy; the difficult is mineralizing them to CO_2, H_2O, and inorganic ions (NO_3^-, NH_4^+, SO_4^{2-}, etc). Table 2 shows the evolution of conductivity values of the irradiated solution. It starts high as the solution presents a large sodium chloride concentration, which is necessary for the textile dying process and for the pH adjustment at the beginning of the reaction. However, this value changes during the photocatalytic process due to the formation of new ions in the reaction medium. As the correct effluent sample composition is unknown, it is inferred that such ions result from the degradation of dyes present in large concentration in this type of effluent. Previous studies with standard factory dyes[26] showed that large amounts of dye may be mineralized to NO_3^-, NH_4^+, SO_4^{2-} due to the structure type, procion HE (diaminochlorotriazine) and remazol (sulfate ethyl solfones) dyes, both sulfonated to increase compound solubility. Therefore, for these effluents, mineralization was analyzed in terms of formation of these types of ions.

Table 2 also shows that the evolution of nitrogenated species is a little more pronounced for the TiO_2/H_2O_2 association (about 18%), because NO_3^- is the most oxidized nitrogen form. In a more oxidizing medium, it is predicable that a large amount of NO_3^- be formed, drastically reducing the amount of NH_4^+, the most reduced form. In relation to the mass balance, a more specific calculation is complicated due to the catalyst positive surface charge, since adsorption of anionic species occurs in acidic medium.[31]

In relation to sulfur in the medium, the only form present is sulfate. Its amount is about 82% larger for the TiO_2/H_2O_2 association than for TiO_2 alone. This may also be explained by the larger oxidizing power of the medium, mainly in the beginning of the reaction, when excess hydroxyl radicals are formed by the consumption of peroxide. Later, the concentration stabilizes at its peak. One must also consider that the final concentration of SO_4^{2-} may not represent the real concentration formed for the same reasons of the nitrogenated species, adsorption on the catalyst surface in acidic medium.[32]

The chemical analyses show a good mineralization rate; however, the complementation with biological data adds to the data reliability, since the degraded products may still present residual toxicity. This is the reason why the lettuce (*Lactuca sativa*) seed toxicity test was carried out.

Lettuce seed (Lactuca sativa) phytotoxicity evolution

The evaluation of lettuce (*Lactuca sativa*) germination and root and sprout development are representative indicators of the capacity of plant establishment and development in potentially toxic media. It is important to point out that plants are largely sensitive to adverse external factors in the first days of development and that several

Table 2. Evolutive follow-up of degradation and mineralization of textile effluents in the presence of either TiO_2 or TiO_2/H_2O_2

Samples	COD / (mgO_2 L^{-1})	TOC / (mg L^{-1})	N_{org} / (mg L^{-1})	NH_4^+ / (mg L^{-1})	NO_3^- / (mg L^{-1})	SO_4^{2-} / (mg L^{-1})	Conductivity / (mS cm^{-1})
EF	430.20	173.2	33.04	28.35	0	0	4.06
T 1 h	225.0	92.55	30.07	30.24	26.06	59.08	4.20
T 2 h	205.3	90.21	25.22	34.77	27.03	59.72	4.25
T 3 h	160.5	87.90	0	34.53	29.12	60.22	4.25
T 4 h	150.0	84.00	0	26.26	30.09	61.86	4.32
T 6 h	50.20	57.60	0	17.81	39.92	66.31	4.86
TH 1 h	205.6	75.20	28.03	35.32	30.56	92.83	4.37
TH 2 h	155.2	56.11	15.25	30.36	30.59	117.8	4.38
TH 3 h	85.40	48.02	0	28.42	30.89	120.3	4.50
TH 4 h	50.60	37.05	0	13.36	45.43	120.5	4.60
TH 5 h	0	35.00	0	6.35	49.08	121.7	4.95

T = effluent irradiation in the presence of TiO_2 0.25 g L^{-1}; TH = effluent irradiation in the presence of TiO_2 0.25 g L^{-1} and H_2O_2 1.0 $\times 10^{-2}$ mol L^{-1}. Results expressed as means of triplicate experiments. Same letters (a) in the same line indicate that differences are not significant ($P < 0.05$) by Tukey test.[33]

physiological processes may be affected by toxic substances and thus alter the normal plant survival and development. It is accepted that the toxicity of organic load effluents is due to the presence of phenolic compounds. However, other constituents such as aldehydes and alcohols also have a phytotoxic effect.[21]

In this study, besides germination, roots and sprouts were also studied during the exposure period, as shown in Figure 1.

According to Table 3, none of the experiments carried out showed significant differences ($P < 0.05$) in lettuce seed absolute percent germination, that is, the treatments using only either TiO_2 or TiO_2/H_2O_2 association with different irradiation times do not affect the germination process negatively comparatively to the *in natura* effluent and negative control. This fact may be related to the low concentrations of toxic compounds, which were insufficient to affect the germination process. Other authors obtained similar results for lettuce seeds.[22,24] It is worth pointing out that these results are for undiluted effluents. Even the 100% effluent sample was not so toxic (inhibition larger than 50%), considering that dilution would further reduce the effluent toxicity.[24]

Differently from the traditional seed germination test, the evaluation of seedling root and sprout growth allows evaluating the toxic effect of soluble compounds present at concentration levels insufficiently low to inhibit germination, but high enough to possibly slow down or inhibit root and sprout growth completely, depending on the compound site and mode of action. Thus, the inhibition of root and sprout growth is a very sensitive sub-lethal indicator of toxic effects of effluents on vegetables that provides complementary information on their effect on germination.[34,35] The difference between the seed bioassay and other evidences based on algae and submersed aquatic plants as diagnose organisms is that it allows evaluating phytotoxicity in colored samples, such as textile effluents, and in high turbidity samples directly without the need of previous filtration, thus reducing pre-treatment interferences and simplifying the test procedure.[20]

Table 4 gives the root growth results obtained with TiO_2 alone and TiO_2/H_2O_2 association. The data suggest that the chemical mineralization obtained with TiO_2/H_2O_2 association is more efficient to removes organic pollutants; thus yielding a larger final ion concentration. However, the

Table 3. Absolute (mean) percent germination of lettuce seeds for different textile effluent treatment conditions (only TiO_2 and TiO_2/H_2O_2 association) and different irradiation times

Negative	*In natura*					
Control	EF	T 1 h	T 2 h	T 3 h	T 4 h	T 6 h
90	90[a]	85[a]	85[a]	95[a]	75[a]	80[a]
		TH 1 h	TH 2 h	TH 3 h	TH 4 h	TH 6 h
90	90[a]	95[a]	90[a]	85[a]	90[a]	85[a]

T = effluent irradiation in the presence of TiO_2 0.25 g L^{-1}. TH = effluent irradiation in the presence of TiO_2 0.25 g L^{-1} and H_2O_2 1.0 $\times 10^{-2}$ mol L^{-1}. Results expressed as means of triplicate experiments. Same letters (a) in the same line indicate that differences are not significant ($P < 0.05$) by Tukey test.[33]

statistical comparison of the two treatments shows that TiO_2 alone affects sample root development less up to 3 h irradiation and the development of samples irradiated for 4 and 6 h far more, which shows that the irradiated sample is still better than the *in natura* effluent, despite its high toxicity.

The TiO_2/H_2O_2 association samples irradiated for 4 and 6 h presented a significant improvement ($P < 0.05$) in growth rate. This improvement may be attributed to the fact that in the first hours of irradiation (2-3 h) under catalyst/oxidizer association there is a larger number of $OH^{\bullet}$ radicals, which may affect seedling development, as it is a highly oxidizing compound, mainly when it is considered it was not detected the presence of residual peroxide. However, after its consumption during the reaction (4-6 h), this effect was reduced, with and an improvement in root growth, which shows that mineralized samples without the presence of radicals results in minor toxicity.[21] The increased root growth shows that the phytotoxic effect was reduced after 4 h irradiation of the textile effluent in the presence of the TiO_2/H_2O_2 association comparatively to that of the *in natura* effluent. Similar results were obtained by other researchers for a similar treatment with distinct effluents and organisms.[35]

These results shows that the *in natura* effluent exerts a rather negative influence on lettuce seedling root growth despite the improvement in the first hour of irradiation in the two types of experiments. A closer look at the evolution of the experiments during the 6 h effluent irradiation makes it clear that the longer the irradiation with TiO_2 alone is, the larger the percent root growth inhibition. It shows that the concentration of partially mineralized intermediate toxic compounds increases, as confirmed by chemical analysis. The influence of peroxide is high in the beginning of the experiment and falls along the 6 h of irradiation.

Table 5 shows that the lettuce seedling sprout length in the presence of treated effluents, both for the TiO_2/H_2O_2 association and for TiO_2 alone, increased rather than decreased as expected, likewise for the *in natura* effluent. There were not observed significant differences among the irradiated samples, control and *in nature* effluent. This is characteristic of samples with low phenolic compound concentrations, which stimulate sprout growth. As lettuce seeds are extremely sensitive, they always present a positive sprout growth response when exposed to low concentrations of phenolic acid.[24]

Conclusions

The effluent analyzed presented good organic matter reduction and mineralization rates as demonstrated by the high concentrations of NH_4^+, NO_3^-, and SO_4^{2-}. The chemical and toxicological analyses confirmed the mineralization data. The products formed during 6 h effluent irradiation under TiO_2 alone or TiO_2/H_2O_2 association were not statistically significantly more toxic than the *in natura* effluent was, since samples with 100% concentration did not inhibit percent germination significantly.

The toxicity found (root and sprout development) in the samples irradiated during 6 h in the presence of TiO_2/H_2O_2 was lower than that observed for samples irradiated with only TiO_2, fact which indicates that more intense oxidation creates products less toxic, especially after 4 h of irradiation.

Other toxicity tests with other species of interest may yield better results and clarify if the increase in sprout growth is due to either low toxicity or the presence of micronutrients in the medium.

Table 4. Root length in cm for the three Petri dishes for different textile effluent treatment conditions (only TiO_2 and TiO_2/H_2O_2 association) and different irradiation times

Replicates	NC	InE	2 h	3 h	4 h	6 h
			T			
Dish 1	2.05	0.91	1.15	1.79	1.40	1.14
Dish 2	2.29	1.14	1.33	2.03	1.65	1.23
Dish 3	1.99	1.17	1.77	2.11	1.35	1.11
Mean	2.11^{c}	1.07^{a}	1.42^{ab}	1.98^{c}	1.47^{ab}	1.16^{a}
			TH			
Dish 1	2.05	0.91	1.18	1.40	1.71	1.52
Dish 2	2.29	1.14	1.07	1.07	1.65	1.55
Dish 3	1.99	1.17	1.07	1.20	1.40	1.67
Mean	2.11^{d}	1.07^{a}	1.11^{a}	1.23^{ab}	1.59^{bc}	1.58^{bc}

NC = Negative control. InE = *In natura* effluent. T = Samples irradiated in the presence of TiO_2 0.25 g L^{-1}. TH = Samples irradiated in the presence of TiO_2 0.25 g L^{-1} and H_2O_2 1.0×10^{-2} mol L^{-1}. Results expressed as means of triplicate experiments. Different letters (a, b, c) in the same line indicate significant differences between samples ($P < 0.05$) by Tukey test.[33]

Table 5. Sprout length (cm) in the three Petri dishes for different textile effluent treatment conditions (only TiO_2 and TiO_2/H_2O_2 association) and different irradiation times

Replicates	NC	InE	2 h	3 h	4 h	6 h
			T			
Dish 1	2.19	2.77	2.41	1.79	1.94	1.98
Dish 2	2.35	2.46	2.53	1.85	2.13	2.10
Dish 3	2.23	2.23	2.83	2.03	2.11	2.04
Mean	2.25^{bcd}	2.48^{cd}	2.59^{d}	1.94^{b}	2.06^{bc}	2.04^{b}
			TH			
Dish 1	2.19	2.77	2.07	2.32	2.90	2.39
Dish 2	2.35	2.46	2.06	2.64	2.61	2.59
Dish 3	2.23	2.23	2.27	2.59	2.44	2.63
Mean	2.25^{ab}	2.48^{ab}	2.13^{a}	2.52^{ab}	2.65^{b}	2.54^{ab}

NC = Negative control; InE = *In natura* effluent. T = Samples irradiated in the presence of TiO_2 0.25 g L^{-1}. TH = Samples irradiated in the presence of TiO_2 0.25 g L^{-1} and H_2O_2 1.0 $\times 10^{-2}$ mol L^{-1}. Results expressed as means of triplicate experiments. Different letters (a, b, c, d) in the same line indicate significant differences between samples ($P < 0.05$) by Tukey test.[33]

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References

1. Pinheiro, H. M.; Touraud, E.; Thomas, O.; *Dyes Pigm.* **2004**, *61*, 121.
2. Zollinger, H.; *Colour Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments*, VCH: Weinheim, Germany, 1991.
3. Frijters, C. T. M. J.; Vos, R. H.; Scheffer, G.; Mulder, R.; *Water Res*. **2006**, *40*, 1249.
4. Prigione, V.; Tigini, V.; Pezzella, C.; Anastasi, A.; Sannia, G.; Varese, G. C.; *Water Res*. **2008**, *42*, 2911.
5. Malpass, G. R. P.; Miwa, D. W.; Mortari, D. A.; Machado S. A. S.; Motheo A. J.; *Water Res*. **2007**, *41*, 2969.
6. Costa, F. A. P.; Reis, E. M.; Azevedo, J. C. R.; Nozaki, J.; *Sol. Energy Mater. Sol. Cells* **2004**, *77*, 29.
7. Oguz, E.; Keskinler, B.; Çelik, Z.; *Dyes Pigm.* **2006**, *64*, 101.
8. Lizama, C.; Freer, J.; Baeza, J.; Mansilla, H. D.; *Catal. Today* **2002**, *76*, 235.
9. Muruganandham, M.; Swaminathan, M.; *Dyes Pigm.* **2004**, *63*, 315.
10. Pekakis, A. P.; Xekoukoulotakis, N. P.; Mantzavinos, D.; *Water Res*. **2006**, *40*, 1276.
11. Daneshvar, N.; Rabbani, M.; Modirshahla, N.; Behnajady, M. A.; *J. Photochem. Photobiol., A* **2004**, *168*, 39.
12. Yu, Y.; Zhuang, Y-Y.; Wang Z-H.; Qiu M-Q.; *Chemosphere* **2004**, *54*, 425.
13. Neppolian, B.; Choi, H. C.; Sakthivel, S.; Arabindoo, B.; Murugesan, V.; *Chemosphere* **2002**, *46*, 1173.
14. Garcia, J. C.; Simionato, J. I.; Silva, A. E. C.; Nozaki, J.; Souza, N. E.; *Sol. Energy* **2009**, *83*, 316.
15. Reemtsma, T.; *Anal. Chim. Acta* **2001**, *426*, 279.
16. Manusadzianas, L.; Balkelyte, L.; Sadauskas, K.; Blinova, I.; Pollumaa, L.; Kahru, A.; *Aquat. Toxicol*. **2003**, *63*, 27.
17. Moraes, S. G.; Freire, R. S.; Duran, N.; *Chemosphere* **2000**, *40*, 369.
18. Kim, H. J.; Rakwal, R.; Shibato, J.; Iwahashi, H.; Choi, J-S.; Kim, D-H.; *Water Res*. **2006**, *40*, 1773.
19. Souza, S. A. M.; *PhD Thesis*, Universidade Federal de Pelotas, Brasil, 2005.
20. Sobrero M. C.; Ronco, A.; *Toxicologic Assay and Evaluation Methods of the Water Quality: Standardization, Intercalibration and Applications*; Universidad do Chile: Santiago, 2004.
21. Ginos, A.; Manios, T.; Mantzavinos, D.; *J. Hazard. Mater*. **2006**, *133*, 135.
22. Kummerová, M.; Kmentová, E.; *Chemosphere* **2004**, *56*, 387.
23. Beltrami, M.; Rossi, D.; Baudo, R.; *Aquat. Ecosyst. Health Manag*. **1999**, *2*, 391.
24. Ortega, M. C.; Moreno, M. T.; Ordovás, J.; Aguado, M. T.; *Sci. Hortic*. **1996**, *66*, 125.
25. Garcia, J. C.; Oliveira, J. L.; Silva, A. E. C.; Oliveira, C. C.; Nozaki, J.; Souza, N.E.; *J. Hazard. Mater*. **2007**, *147*, 105.
26. Garcia, J. C.; Boroski, M.; Oliveira, J. L.; Silva, A. E. C.; Nozaki, J. In *Trends in Solar Energy Research*, Nova Publishers: New York, 2006.
27. APHA-American Public Health Association; *Standard Methods for the Examination of Water and Wastewater*, AWWA, WPCF: Washington, D.C., 1998.
28. Silva, M. R. A.; Oliveira, M. C.; Nogueira, R. F. P.; *Eclet. Quim*. **2004**, *29*, 19.
29. Akyol, A.; Yatmaz, H. C.; Bayramoglu, M.; *Appl. Catal., B* **2004**, *54*, 19.

30. Malato, S.; Blanco, J.; Campos, A.; Cáceres, J.; Guillard, C.; Herrmann, J. M.; Fernández-Alba, A. R.; *Appl. Catal., B* **2003**, *42*, 349.
31. Wang, K-H.; Hsieh, Y-H.; Chou, M. Y.; Chang, C-H.; *Appl. Catal., B* **1999**, *21*, 1.
32. Karkmaz, M.; Puzenat, E.; Guillard, C.; Herrmann, J. M.; *Appl. Catal., B* **2004**, *51*, 183.
33. Statsoft; *Statistica 5.1 Software*,Tucksa, USA, 1996.
34. Bowers, N.; Pratt, J. R.; Beeson D.; Lewis M.; *Environ. Toxicol. Chem*. **1997**, *16*, 207.
35. Cheung, Y. H.; Wong, M. H.; Tam, N. F. Y.; *Hydrobiologia* **1989**, *188*, 377.
36. Casa, R.; Annibale, A. D.; Pieruccetti, F.; Stazi, S. R.; Sermanni, G. G.; Cascio, B. L.; *Chemosphere* **2003**, *50*, 959.

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