Kinetic study of dye removal using TiO$_2$ supported on polyethylene terephthalate by advanced oxidation processes through neural networks

Ada Azevedo Barbosa, Ramon Vinicius Santos de Aquino, Naiana Santos da Cruz Santana Neves, Renato Falcão Dantas, Marta Maria Menezes Bezerra Duarte and Otidene Rossiter Sá da Rocha

ABSTRACT

This work investigated the efficiency of polyethylene terephthalate (PET) as support material for TiO$_2$ films in the photocatalytic degradation of red Bordeaux and yellow tartrazine dyes. The optimum operating conditions were determined by a factorial design, which resulted after 180 min of treatment in degradations of 99.5% and 99.1% for the UVC/H$_2$O$_2$/TiO$_{2Sup}$ and solar/H$_2$O$_2$/TiO$_{2Sup}$ systems, respectively. For the kinetic study, the experimental data fitted to the pseudo-first-order model and the calculated kinetic constants (k) values were 0.03 min^{-1} for the UVC/H$_2$O$_2$/TiO$_{2Sup}$ system and 0.0213 min^{-1} for the system solar/H$_2$O$_2$/TiO$_{2Sup}$. It was verified that TiO$_2$ supported in the PET remained with high degradation efficiency even after five cycles of reuse, indicating a good stability of the photocatalyst in the support. A significant reduction of TOC content was also observed along the reaction time. The phytotoxicity bioassay with *Lactuca sativa* demonstrated that after treatment with UVC/H$_2$O$_2$/TiO$_{2Sup}$ and solar/H$_2$O$_2$/TiO$_{2SUP}$, an increase in IC50 and consequently lower toxicity was observed.

Key words | advanced oxidation processes, artificial neural networks, effluent treatment, food dye, polyethylene terephthalate, supported titanium dioxide

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INTRODUCTION

The water pollution by industrial wastes has become an environmental problem. Part of that pollution comes from the discharge of effluents containing a series of substances, including synthetic dyes (Nidheesh *et al.* 2018; Santos *et al.* 2018). The dyes have their removal hindered by their resistance to biodegradation and high chemical stability (Nidheesh *et al.* 2018), thus effective techniques are necessary for their degradation. Due to this difficulty, several methods have been studied for the treatment of dyes in wastewater. However, in the majority of the cases, these processes do not effectively remove the dye molecule (Zangeneh *et al.* 2015).

Advanced oxidation processes (AOP) have shown good results in the treatment of these compounds, in which it is possible to observe high degradation rates and even mineralization, occurring the formation of CO$_2$ and water (Zangeneh *et al.* 2015). AOP can be divided into some classes such as photocatalytic methods, hydrodynamic cavitation and the use of chemical oxidants such as Fenton and photo-Fenton (Kumar *et al.* 2018). They are based on the generation of highly oxidizing agents, such as hydroxyl radical (HO•) (Nascimento Júnior *et al.* 2018).

The use of semiconductors such as TiO$_2$, ZnO, Fe$_2$O$_3$, WO$_3$, ZrO$_2$ and V$_2$O$_5$ to generate hydroxyl radicals has been a widely used alternative in the photodegradation of dyes (Zangeneh *et al.* 2015). Special attention is given to titanium dioxide (TiO$_2$) due to its photocatalytic properties, light stability, good availability and low toxicity (Sridewi *et al.* 2011). TiO$_2$, when exposed to UV radiation, has its electrons excited from the valence band to the conduction band, which generates electron/lacuna pairs responsible for the formation of oxygen radicals, which interact with the molecules of pollutants adsorbed on the surface of the semiconductor (Li *et al.* 2013).

Despite the TiO$_2$ having a high catalytic activity, its use to treat wastewater presents disadvantages due to its hard separation from aqueous solution, needing a posterior filtration step (Sridewi *et al.* 2011). In order to avoid this disadvantage, recent studies have used a series of materials to immobilize TiO$_2$ such as glass (Xing *et al.* 2018), polyethersulfone (Hir *et al.* 2017), polystyrene (Santos *et al.* 2018) and metallic supports (Alijani *et al.* 2014). These support materials need to have roughness for the fixation of the catalyst particles and good adhesion to avoid leaching after immobilization (Borges *et al.* 2016). Polyethylene terephthalate (PET) is a recyclable, biodegradable and flexible material (De Barros *et al.* 2014) that allows various shapes and geometries for the immobilization of TiO$_2$.

The objective of this work was to evaluate the use of PET, recycled after consumption, as a support material for titanium dioxide (TiO$_2$) films. The supported TiO$_2$ was used in the degradation of the aqueous mixture of red Bordeaux (RB) and yellow tartrazine (YT) dyes, which are dyes largely used in the food industry.

MATERIAL AND METHODS

An aqueous solution of the RB and YT mixtures (provided by F. Trajano Ltda, Brazil) of 35 mg.L^{-1} of each dye was prepared from the individual solutions using distilled water. The concentration of the dyes before and after each experiment were quantified using the UV-visible spectrometric technique (Thermo Scientific Genesys 10S). The measurements were performed using an analytical curve constructed at the wavelength (λ) of maximum absorbance: 427 and 521 nm for YT and RB, respectively. The detection limit (DL) and quantification limit (QL) were 0.037 mg.L^{-1} and 0.164 mg.L^{-1} while the coefficient of variance (CV) was 0.327% for λ of 427 nm. For λ of 521 nm the DL was 0.064 mg.L^{-1}, QL was 0.283 mg.L^{-1} and the CV was 0.566%.

Tio$_2$ immobilization

PET films were obtained from cut-outs of transparent mineral water bottle purchased after local consumption. The photocatalyst was immobilized on PET surfaces according to the procedure described by De Barros *et al.* (2014). The impregnation procedure was repeated in order to achieve the required mass of TiO$_2$ on the surface of the PET according to each experiment.

Characterization of supported TiO$_2$

Surface analyses were carried out in order to identify chemical groups over the material surface as well as characterize its morphology. In order to obtain details about the morphology of the material, mesh samples before and after the titanium immobilization were analyzed by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDX) in a Shimadzu SS-550 microscope. In addition, X-ray diffraction (XRD-6000, SHIMADZU) was determined using Cu-Kα radiation ($\lambda = 1.5406$ Å) with scans in the range of $20° < 2\theta < 80°$, step of 0.02° and speed of 2° s^{-1}; the crystallographic charts of the international center for diffraction data (nos. 21–1,272 and 21–1,276) were used to evaluate the structure of the material.

Fourier transform-infrared spectrometry (FT-IR) analysis was used to determine the major functional groups on the surface of the solid and to verify the presence of TiO$_2$ in the studied supports, which were recorded in the range of 500 to 4,000 cm^{-1}, with a 4 cm^{-1} resolution, using a Bruker Tensor 27 spectrometer with DLaTGS detector and an ATR probe (attenuated total reflectance). The spectra were recorded at room temperature (23 ± 2 °C) at a spectral resolution of 4 cm^{-1} and 128 scans on average.

Preliminary tests

Preliminary experiments were carried out on the degradation of RB and YT dyes in a batch reactor for the selection of the advanced oxidative process. A UV-254 germicidal lamp (UVC, tovalight, 20 W) was used as radiation source, which had an irradiation intensity of 8.3 W/m², measured with a MRUR-203 radiometer from Instrutherm Ltda. The experiments with solar radiation were performed in Recife-Brazil (8°04′03″S; 34°55′00″W). Experiments were also performed without exposure to radiation. The overall intensity of solar radiation was in the range of 16.28–16.51 W.cm^{-2}.

The degradation experiments of dyes RB and YT mixture in aqueous solution were carried out using cylindrical Pyrex glass cells, 5.5 cm high, 9.0 cm in diameter and volumetric capacity of 400 mL. All the experiments described in Table 1 were performed in batch system. The volume of the solution used for the treatment was 300 mL for each glass cell. The stirring rate for all experiments was 1,000 rpm.

The AOP treatment systems used for the degradation of aqueous solutions of dyes RB and YT mixture are described in Table 1.

Table 1 │ Processes used for preliminary experiments

Without radiation	UVc radiation	Solar radiation
• H_2O_2	• UVc	• Solar
• TiO_2	• UVc/H_2O_2	• Solar/H_2O_2
• TiO_{2Sup}	• UVc/TiO_2	• Solar/TiO_2
• H_2O_2/TiO_2	• UVc/TiO_{2Sup}	• Solar/TiO_{2Sup}
• H_2O_2/TiO_{2Sup}	• UVc/H_2O_2/TiO_2	• Solar/H_2O_2/TiO_2
	• UVc/H_2O_2/TiO_{2Sup}	• Solar/H_2O_2/TiO_{2Sup}

The amount of H_2O_2 added to the systems was calculated according to the stoichiometric balance for degradation reaction of RB and YT, which was found to be 5.79 mmol.L^{-1}. Standardization of the H_2O_2 solution (50% v/v, P.A.) was performed with $KMnO_4$ (1N) in acidified medium (H_2SO_4 at 10%).

For the systems containing TiO_2, 100 mg of the photocatalyst was used for 300 mL of solution, which means 333 mg.L^{-1}, calculated to reduce the turbidity of the solution in the system with TiO_2 in suspension (Santos *et al.* 2018). It was necessary to wait 30 min in the dark, under stirring 1,000 rpm, in order to stabilize the adsorptive process before the start of aliquot withdrawal (Nascimento Júnior *et al.* 2018). To eliminate the possibility of interference in the analyses, sample was taken from the supernatant.

During the experiments, samples were collected and quantified to monitor the degradation process at times of 1, 5, 10, 30, 60, 120, 240, 300 and 360 min, thus samples were analyzed with a UV-visible spectrophotometer.

Factorial planning

After the selection of the processes which presented the highest efficiency in dyes degradation in the preliminary test, the variables of greatest influence for each process were identified. The limits of each variable were selected from previous experiments.

The operating conditions were defined using a factorial planning 2^3 (FP 2^3) for the system using UVC radiation and a factorial planning 2^2 (FP 2^2) for solar radiation. For FP 2^2, the selected variables were: TiO_2 (50 mg and 150 mg) and H_2O_2 (3.86 and 5.79 mmol.L^{-1}); for the FP 2^3 the selected variable were TiO_2 (50 mg and 150 mg), H_2O_2 (3.86 and 5.79 mmol.L^{-1}) and radiation power (20 and 40 W). The tests were performed in duplicate to allow the test of lack of fit of the empirical model. From the obtained data, the effects of the factors and the interactions between them

were estimated according to the work of Barros Neto & Scarminio (2010), using the Statistical 6.0 program.

Kinetics

From the data obtained in the factorial planning, the best conditions were used in the kinetic study. The kinetic model of pseudo-first-order was adjusted to the experimental data through the program Sigma Plot 11.0 © (Hir *et al.* 2017; Aoudjit *et al.* 2018).

The data were adjusted to pseudo-first-order models according to Equation (1) by regression analysis. Half-life reaction time ($t_{1/2}$) was estimated by Equation (2).

$$\ln\left(\frac{(C_t)}{C_0}\right) = -kt \tag{1}$$

$$t_{\frac{1}{2}} = \ln\frac{2}{k} \tag{2}$$

where C_t is the total dyes concentration at time t, C_0 is the initial concentration of dyes and k is the reaction rate.

A study was also carried out to evaluate the possibility of the supported TiO_2, used in the kinetic study with UVC radiation, being used in successive cycles monitoring the percentage of degradation along the cycles according to Hir *et al.* (2017).

Kinetics

The kinetic models using ANN were established for the degradation systems via solar and UVC radiation. The ANN was developed with the time and wavelength absorption as input variables to generate a curve of concentration over time, as used by Giroto *et al.* (2006). For this purpose, a software was created based on C# language in Unity 3D©. The ANN is composed of input, hidden and output layers with a different number of neurons. A group of procedures was set to turn the adjustment possible. The type of ANN used was 2:3:1 (two input variables, three hidden layers, and one output variable). The training method was based on particle swarm optimization (PSO) as exposed by Kennedy & Eberhart (1995), in which a small disturbance was induced in the weights and biases to verify if the resultant network is a better adjustment according to the experimental data.

Physical-chemical analysis and toxicity

A sample of the experiment providing the best degradation result was evaluated before and after the AOP by total

organic carbon (TOC) analyses, according to the methodologies established by APHA (2012). The results obtained from the analyses were used to evaluate the effectiveness of the process. Phytotoxicity tests were conducted according to the procedure adopted by Sobrero & Ronco (2004).

RESULTS AND DISCUSSION

Support characterization

The TiO$_2$ supported in PET was characterized by FT-IR, XRD and SEM analyses (Figure 1).

FT-IR analysis of the samples was conducted in the range of 500–4,000 cm^{-1} wave numbers. Figure 1(a) shows the spectra with the identification of the chemical groups in the PET Support without TiO$_2$, PET Support with immobilized TiO$_2$ and PET Support with immobilized TiO$_2$ after its use

in the treatment of aqueous dye mixture solution. In the spectrum of the PET Support the main characteristic peaks of the bonds present in the PET molecule such as 1,712 cm^{-1}, the strong intensity peak associated with the stretching of the carboxyl group (C = O) and in 1,500 cm^{-1} were identified peaks of average intensity associated with C = C stretching in vibration in the aromatic ring, according to Solomons & Fryhle (2012). The peak at 1,340 cm^{-1} refers to the folds and balances of the trans-ethylene glycol-segment vibration, according to Solomons & Fryhle (2012). Regarding to 1,245, 1,095 and 1,017 cm^{-1}, they are peaks of high intensity and associated with the stretching of the ester group (C-O-C). The peaks 870 and 724 cm^{-1} are associated with aromatic (C-H) and benzene ring vibration, respectively. It was observed in Figure 1(a) that the disappearance of the peaks observed in the support when TiO$_2$ was supported, noting the efficiency of the immobilization process due to deposition of TiO$_2$ on the surface of the plate. The typical
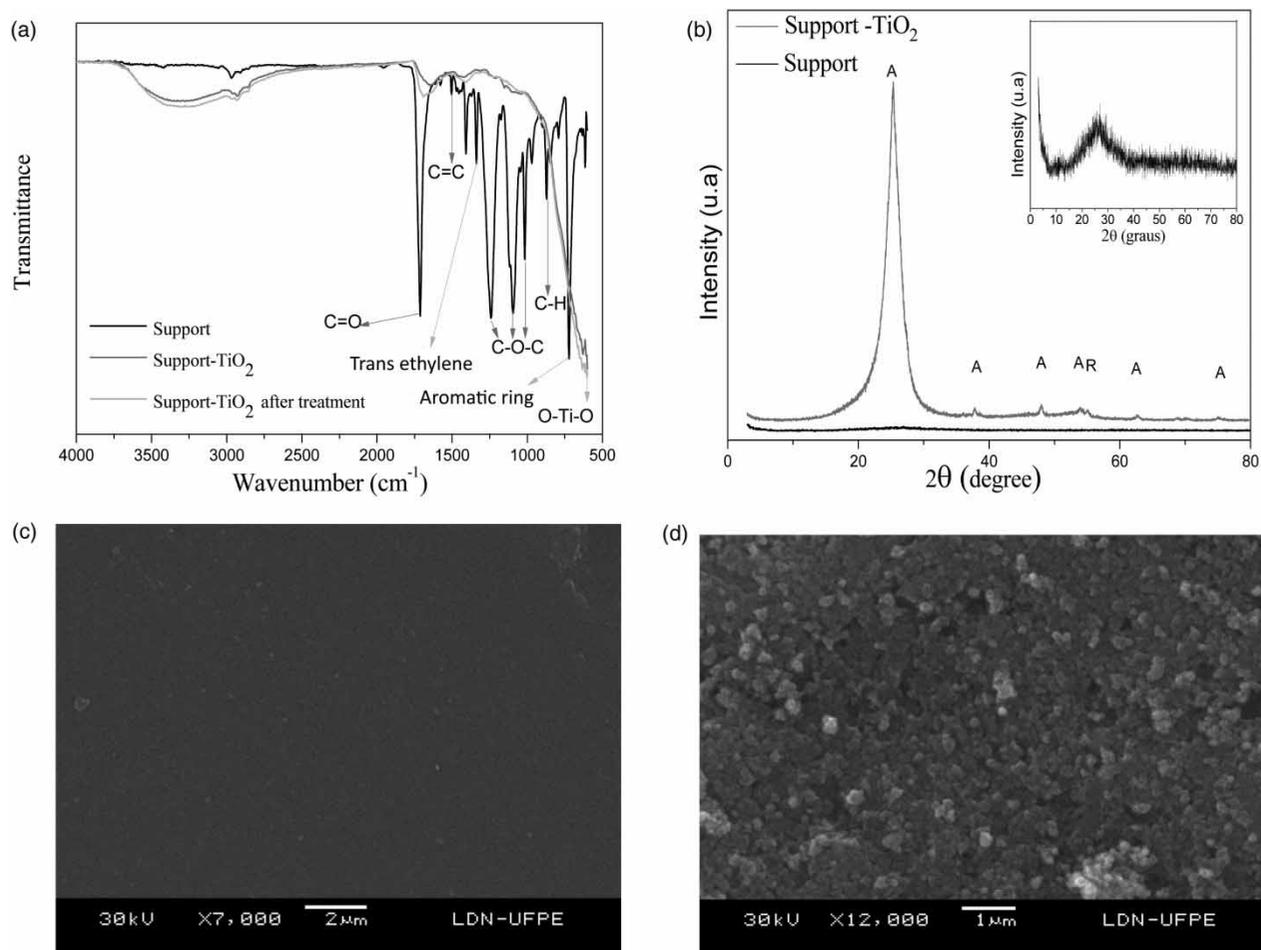
Figure 1 │ (a) FT-IR of PET Support without TiO$_2$ and PET with immobilized TiO$_2$ before and after the treatment. (b) X-ray diffraction patterns of PET-TiO$_2$ and SEM analysis obtained for (c) PET and (d) PET with immobilized TiO$_2$.

absorption band for the O-Ti-O bond was around 600 cm^{-1}, which is in accordance with Santos *et al.* (2018). In addition, no differences were observed between the spectra of supported TiO_2 before and after treatment.

The XRD pattern of the PET and PET-TiO_2 samples can be seen in Figure 1(b). The PET-TiO_2 diffractogram shows an evident peak at $2\theta = 25.31$, which is characteristic of anatase. However, the diffraction pattern of the PET compound at $2\theta = 25.58$ observed, close to this angle, coincides with that of TiO_2.

After addition of TiO_2 in the polymer, several characteristic peaks of the anatase TiO_2 (JCPDS 00-021-1272) at 2θ of $25.24°$ (101), $37.84°$ (004), $48.13°$ (200), $53.88°$ (105), $55.02°$ (211), $62.82°$ (204) and $75.29°$ (215) and a Rutile Attributed Peak TiO_2 (JCPDS 00-021-1276) at 2θ of $56°$ C, $46°$ (002) were observed in the XRD standard of the PET-TiO_2 film. These data were indicative of the successful immobilization of TiO_2 in the PET polymer matrix. According to Xing *et al.* (2018) when TiO_2 catalyst does not undergo heat treatment processes it is not possible to notice changes in the structure of TiO_2 in a significant way, consequently, remaining in higher concentration of anatase in the mobilized material.

Comparing Figure 1(c) and 1(d), it is possible to observe intense changes in the surface of the material after the immobilization process. In Figure 1(c), the smooth surface of the PET material can be observed. After the immobilization process with 100 mg of TiO_2 (Figure 1(d)), the plate presented irregularities that differ from the uniform structure of the PET plate previously observed. The irregularities refer to the agglomeration of TiO_2 particles in the material, showing that it was well adhered to the surface. In the work of De Barros *et al.* (2014), the formation of irregularities in PET plates after different cycles of immobilization with TiO_2 were observed.

Preliminary tests

The experiments performed in the absence of radiation did not reach significant degradation after 360 min in any of the studied systems. In absence of radiation, the formation of hydroxyl radical, which is responsible for the degradation of organic molecules with high strength and stability such as dyes, has probably not occurred. The same result was observed by Santos *et al.* (2018) and Nascimento Júnior *et al.* (2018) when studying the degradation of dye mixtures using titanium dioxide.

The degradation curves of the dyes in the preliminary tests for UVC and solar radiation are presented in Figure 2.
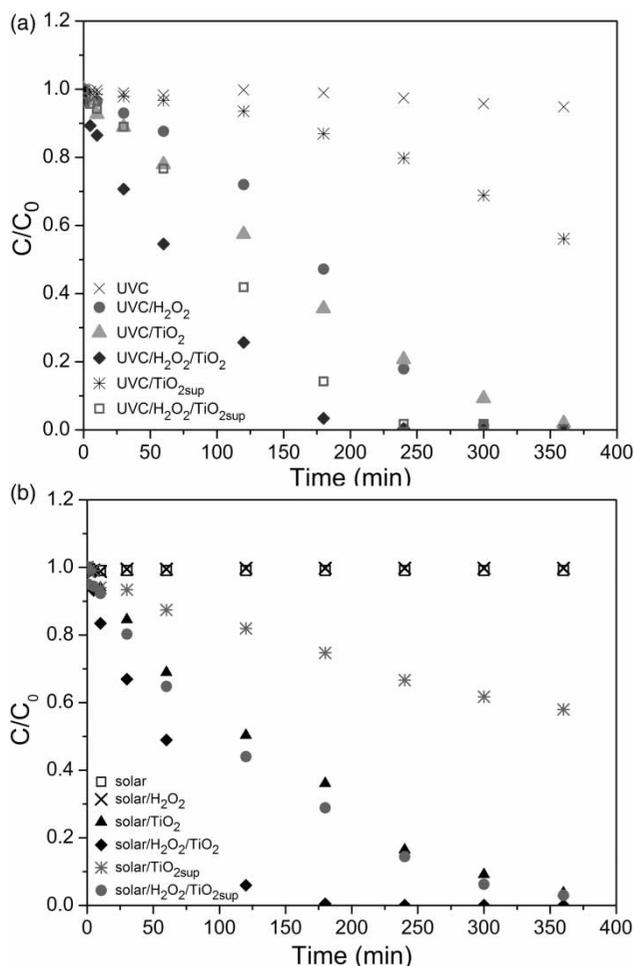
Figure 2 │ Degradation curves of the dye mixture red Bordeaux and yellow tartrazine in aqueous solution by AOP during 360 min: (a) UVc radiation and (b) solar radiation. $[C_0] = 35 \text{ mg.L}^{-1}$ of each dye; $[H_2O_2] = 5.79 \text{ mmol.L}^{-1}$; $m_{TiO_2} = 100 \text{ mg}$.

In the treatments using photolysis, only a decrease less than 5% was observed in both radiations.

When analyzing the degradation curves shown in Figure 2, it was observed that the UVC/H_2O_2 and solar/H_2O_2 photochemical processes degraded after 240 min of reaction 82.1% and 0.18% of the aqueous dye solution, respectively. According to Zuorro & Lavecchia (2014), the degradation of contaminants in the UV/H_2O_2 process with UVC radiation is usually higher than with solar radiation, since the homolytic breakdown of the H_2O_2 molecule to form free radicals is higher in $\lambda > 290 \text{ nm}$.

The UVC/TiO_2 and solar/TiO_2 systems degraded 3.9 and 2.5 times more after 240 min than the UVC/TiO_{2SUP} and solar/TiO_{2SUP}, respectively. When TiO_{2SUP} was used, the contact between the catalyst and the solution is reduced. This happens because the surface area is smaller, which reduces the efficiency in the photocatalytic activity due to the reduction of the radiation capture; this behavior was

also observed by Shen et al. (2016). Although the degradation process is lower in experiments with immobilized TiO$_2$, its use favors the recovery of the supported TiO$_2$ after treatment (Hir et al. 2017).

The percentages of degradation obtained for the dyes were 99.6% and 98.2% for the UVC/H$_2$O$_2$/TiO$_2$ and UVC/H$_2$O$_2$/TiO$_{2SUP}$ processes, and 99.9% and 85.5% for the solar/H$_2$O$_2$/TiO$_2$ and solar/H$_2$O$_2$/TiO$_{2SUP}$, respectively, after 240 min. These systems showed the highest efficiency in the degradation of the aqueous solution of dyes. The combination of TiO$_2$ and H$_2$O$_2$ may facilitate the increase of photocatalytic activity. Literature reports that suppression of the recombination of e/h$^+$ occurs, resulting in an increase in the overall generation rate of HO• radicals in the system (Abeledo-Lameiro et al. 2017).

Although the degradation is lower in studies carried out with immobilized TiO$_2$, it is considered advantageous because it avoids the operational cost in the process of catalyst separation from the suspension. In addition, the use of PET-media has a low cost because it is a recyclable material, being an advantage over other supports studied by Santos et al. (2018), Hir et al. (2017) and Xing et al. (2018).

Experimental planning

Based on the experimental results obtained from the experimental design, the main effects and their 2-factor and 3-factor interactions and their respective standard errors (s) were calculated at a 95% confidence level with $p = 0.05$ using the Statistical program 6.0. Figure 3 shows the Paretos charts (significant effects $p > 0.05$).

Figure 3 shows that all the main effects were statistically significant during the process of degrading the aqueous solution of dyes at a 95% confidence level, as well as the interactions of the factors H$_2$O$_2$*Potency and TiO$_2$*H$_2$O$_2$ for the system UVC/H$_2$O$_2$/TiO$_{2SUP}$ and TiO$_2$*H$_2$O$_2$ for the solar/H$_2$O$_2$/TiO$_{2SUP}$ system.

Among the variables studied in the UVC/H$_2$O$_2$/TiO$_{2SUP}$ system, the most influential in the efficiency of the degradation process was hydrogen peroxide concentration (H$_2$O$_2$). This result indicates that a higher concentration of H$_2$O$_2$ increases the efficiency in the process of dye degradation at the levels studied. Similar results were obtained by Shen et al. (2016), when a greater amount of H$_2$O$_2$ increased the efficiency of the dye degradation process. In the case of the solar/H$_2$O$_2$/TiO$_{2SUP}$ system, the TiO$_2$ variable was the most significant, probably because the semiconductor presents a better efficiency under solar radiation because it requires less energy to excite the electron in the valence layer (Borges et al. 2016).
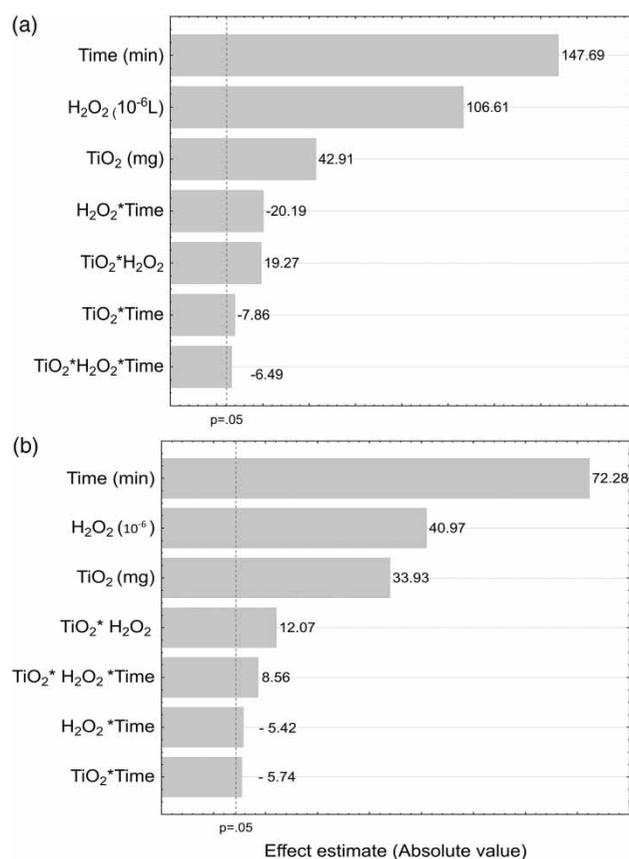
Figure 3 │ Pareto chart for the results of the factorial planning (a) UVC/H$_2$O$_2$/TiO$_{2SUP}$ pure error = 0.093 and (b) solar/H$_2$O$_2$/TiO$_{2SUP}$ pure error = 0.5149.
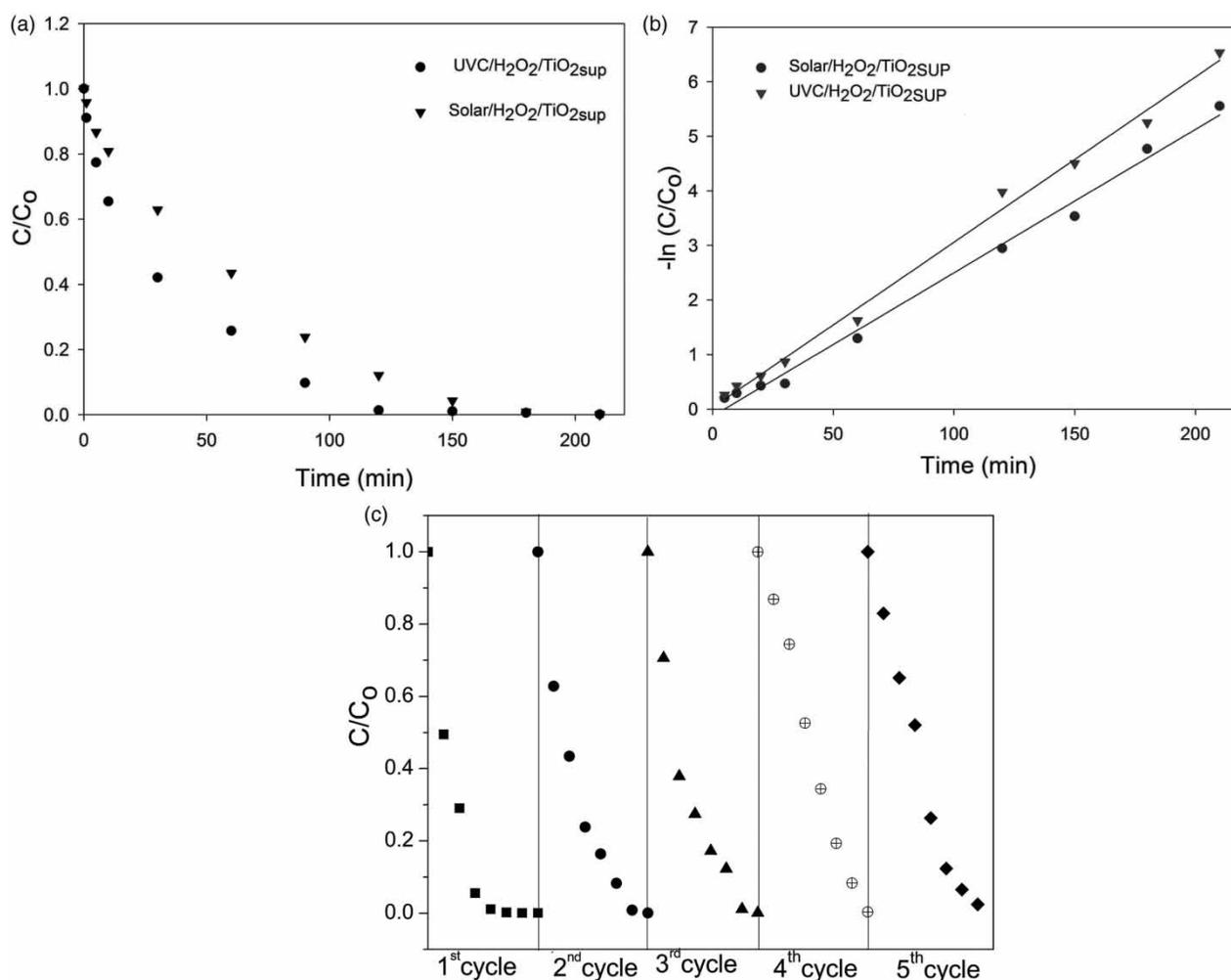
Kinetics

Based on the results of the factorial design kinetic studies of degradation of aqueous mixture of dyes YT and VB for photocatalytic processes UVC/H$_2$O$_2$/TiO$_{2SUP}$ and solar/H$_2$O$_2$/TiO$_{2SUP}$ were conducted, as shown in Figure 4.

Figure 4(a) shows that the systems UVC/H$_2$O$_2$/TiO$_{2SUP}$ and solar/H$_2$O$_2$/TiO$_{2SUP}$ degraded 99.5% and 99.1% after 180 min, respectively; both systems obtained a shorter degradation time compared to the preliminary test of the studied systems. The systems did not have a significant difference in their degradation results, so it is preferable to use the solar radiation source because it is renewable.

The regression analysis for the pseudo-first-order model for the degradation of the dyes was done, obtaining the parameters of the model according to Figure 4(b). The velocity constants (K$_{app}$ min^{-1}) were estimated at 0.03 min^{-1} for the UVC/H$_2$O$_2$/TiO$_{2SUP}$ system and 0.0213 min^{-1} for the solar/H$_2$O$_2$/TiO$_{2SUP}$ system.

The half-life time was 23.10 min and the correlation coefficient was 0.9926 for the UVC/H$_2$O$_2$/TiO$_{2SUP}$ system

Figure 4 │ (a) Degradation kinetics and (b) adjustment to zero order kinetic model for RB and YT dye mixture treated by UVC/H$_2$O$_2$/TiO$_{2SUP}$ and solar/H$_2$O$_2$/TiO$_{2 SUP}$. [C$_0$] = 35 mg.L^{-1} of each dye; [H$_2$O$_2$] = 5.79 mmol.L^{-1}; m$_{TiO2}$ = 150 mg. (c) Study of the efficiency of the reuse of the support in five cycles in the degradation of the dye solution to the UVc/H$_2$O$_2$/TiO$_{2SUP}$ system.

and the solar/H$_2$O$_2$/TiO$_{2SUP}$ system obtained a half-life of 32.54 min and the correlation coefficient of 0.9911. The pseudo-first-order model describes the degradation behavior of the dyes by the UVC/H$_2$O$_2$/TiO$_{2SUP}$ and solar/H$_2$O$_2$/TiO$_{2SUP}$ processes since R^2 values higher than 0.90 meet the standards for linearity required by the INMETRO (2016).

According to Aoudjit *et al.* (2018) and Santos *et al.* (2018), the degradation of the dye mixture RB and YT for the photocatalytic processes UVC/H$_2$O$_2$/TiO$_{2SUP}$ and solar/H$_2$O$_2$/TiO$_{2SUP}$ were efficient. Comparing the results obtained by Santos *et al.* (2018) in relation to the dye removal rate in 180 min and the value of the degradation constant (K$_{app}$) is equivalent to the values found in this work for UVC/H$_2$O$_2$/TiO$_{2SUP}$ radiation. The immobilization process of TiO$_2$ in PET Support presented the advantage of being a recycled material, making the process cost-effective. In addition, the technique used to immobilize the catalyst is simple and showed a good adhesion efficiency of TiO$_2$ on the surface of the support (De Barros *et al.* 2014).

Kinetics by neural networks

The results of the ANN training data for the studied compound degradation are shown in Figure 5.

In Figure 5(a) and 5(b) it is possible to observe the input layer represented by the time in normalized minutes (from 0 to 210 for −1 to 1); as a result the concentration, also renormalized (from 0 to 1 for −1 to 1). During the computation, the network multiplies the weights (values above the lines connecting the neurons) by the input, and sums the bias, value above the neurons, and is then computed by the sigmoid function, to obtain a result that is again multiplied
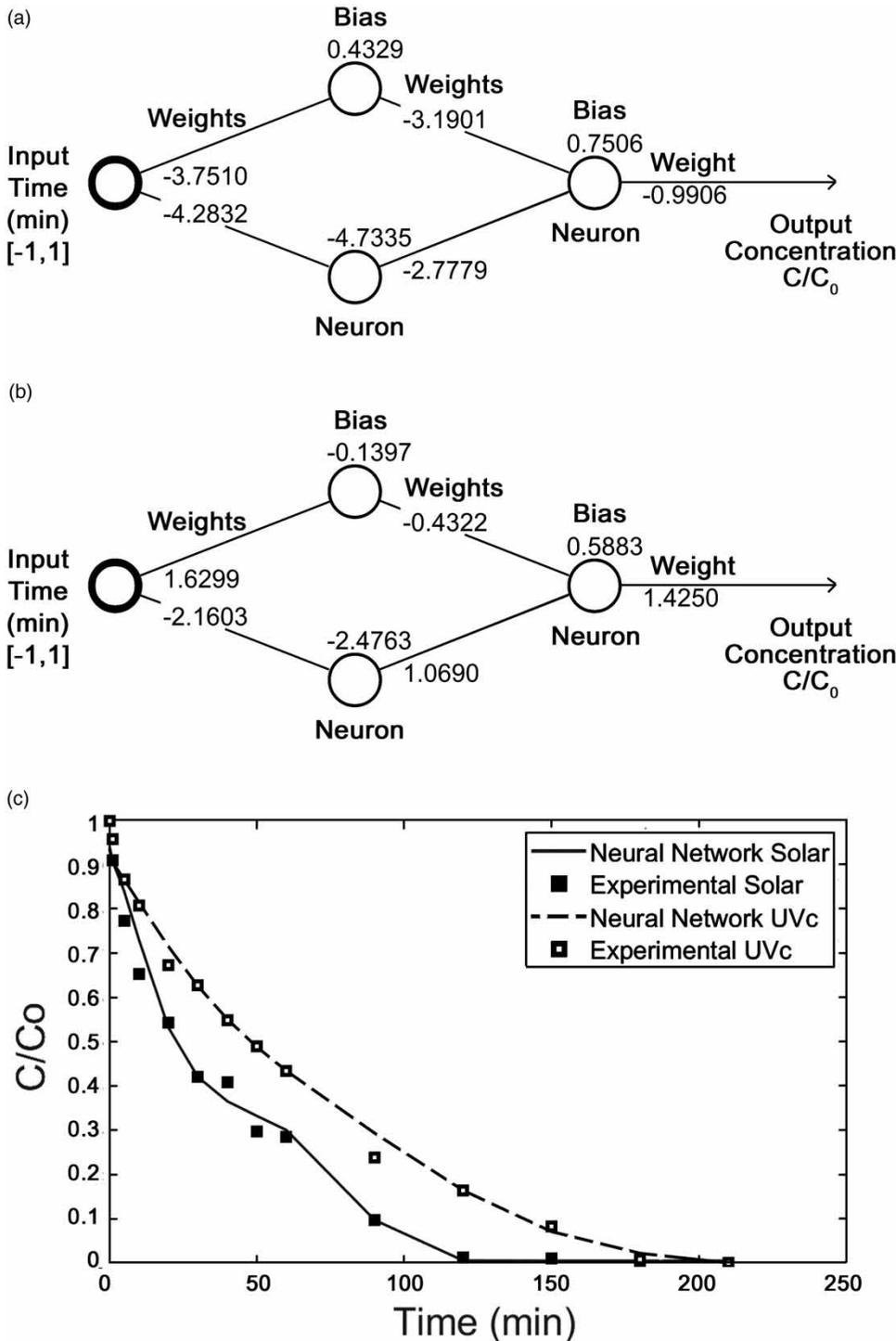
Figure 5 | ANN resulting from the training of degradation data by: (a) solar radiation and (b) UVC radiation. (c) Results of the neural network model confronted with the experimental data for both solar and UVC systems.

by a weight and goes forward to the next layer; consequently the result is generated. This model is able to predict the degradation response for the degradation of the dye under the given conditions.

Figure 5(c) shows the agreement between the experimental data and the data predicted by the ANN models; the absolute mean error was 0.0246 for the solar radiation system and 0.0231 for the UVC system, which leads to an

R^2 of 0.987 and 0.991, respectively. It is important to remark that ANN modelling was done with dye water solutions. Thus, it presents some limitation to describe the dyes removal in a real wastewater. In this case, additional experiments should be done.

Reuse of PET Support

The advantage of using a system with the supported catalyst is due to prolonged reuse of the photocatalytic plate, enabling the treated wastewater to be directly discharged, as there is no need for a costly filtration unit. The TiO$_{2SUP}$ reuse for degradation of the YT and RB dyes was tested in the UVC/H$_2$O$_2$/TiO$_{2SUP}$ system using a solution in the 35 mg.L^{-1} concentration of each dye for 210 min irradiation for each cycle (Figure 4(c)).

The impregnation of TiO$_2$ in the PET matrix was efficient with the possibility of reuse in the degradation of the dye mixture over the five replicates of the treatment process. This efficiency was observed due to the reduction of only 0.9% in the percent degradation of the dye mixture from the first (99.2%) to the fifth (98.1%) cycle. Already with Shen *et al.* (2016), the degradation rates decreased from 99.2% to 87.4% after five consecutive cycles using a TiO$_2$@CF catalyst in the removal of dyes.

Physical-chemical analysis and toxicity

A decrease in TOC can be observed after the treatment of UVC/H$_2$O$_2$/TiO$_{2SUP}$ and solar/H$_2$O$_2$/TiO$_{2SUP}$ systems studied. The reduction of 97.9% of TOC indicates an effective oxidation of the organic species to CO$_2$ and other by-products, indicating the reduction of the oxidizable organic matter, improving as a consequence the quality of the sample. Garcia *et al.* (2009) evaluated the photocatalytic degradation of acid red G under nanoporous TiO$_2$ photo-anodes, with and without doping, and attained maximum total organic carbon removal rates (TOC) of 75% after 2 h of treatment. Oliveira *et al.* (2012), studying the degradation of the dye Ponceau 4R with TiO$_2$/ZnPc, observed a 50% decrease in TOC in 120 min.

By means of acute ecotoxicity tests performed with lettuce seed (*Lactuca sativa*), it was verified that in the negative control all the seeds germinated, but in the positive control there was no germination of the same. IC50 values that there was a considerable reduction in seed phytotoxicity after UVC/H$_2$O$_2$/TiO$_{2SUP}$ and solar/H$_2$O$_2$/TiO$_{2SUP}$ systems, since the IC50 for the samples after treatment was higher than for the dye mixture. It was also observed that

solar treatment was more efficient in reducing phytotoxicity in relation to UVC treatment. In the work of Nascimento Júnior *et al.* (2018), the removal of bright blue and yellow dyes tartrazine also showed a 39.3% (v v) increase to 87.7% (v/v) at the IC50 value after treatment in the UVC/H$_2$O$_2$/TiO$_2$ compared to the initial solution.

CONCLUSION

The TiO$_2$ immobilization process on PET surface was efficient as demonstrated in the XRD and FT-IR characterization. In addition, the used support comes from reuse of the material after consumption, thus representing a matter of interest from both economic and environmental perspectives.

Among the studied AOP, the ones that presented the best degradation performance in the preliminary tests were UVC/H$_2$O$_2$/TiO$_{2SUP}$ and solar/H$_2$O$_2$/TiO$_{2SUP}$, being able to observe the synergistic effect of the association of TiO$_2$ and H$_2$O$_2$. However, the process using UVC radiation provided better results than solar. However, the solar process still represents a good energy strategy in the degradation of the dye solution due to its lower cost when compared to UVC.

The pseudo-first-order model presented a good fit to the experimental data of the degradation kinetics of the UVC/H$_2$O$_2$/TiO$_{2SUP}$ and solar/H$_2$O$_2$/TiO$_{2SUP}$ processes. The TiO$_{2Sup}$ can be used up to five cycles with loss of less than 1% in the percent degradation. The use of artificial neural network was efficient to predict the degradation of the dye in question, resulting in mean absolute errors lower than 0.02266 and determination coefficient superior to 0.987, with the intensification of the use of machine learning technologies, the use of the neural network in this work is promising.

Phytotoxicity tests ensured the treatment efficiency in reducing the toxic potential of the sample, increasing the IC50 for the treated samples compared to the initial solution, and also obtained reduction in TOC analyses. Based on these results, the UVC/H$_2$O$_2$/TiO$_{2SUP}$ and solar/H$_2$O$_2$/TiO$_{2SUP}$ systems using TiO$_2$ immobilized on the PET Support were efficient in the removal of aqueous solutions from YT and RB dyes.

REFERENCES

Abeledo-Lameiro, M. J., Reboredo-Fernández, A., Polo-López, M. I., Fernández-Ibáñez, P., Ares-Mazás, E. & Gómez-Couso, H. 2017 Photocatalytic inactivation of the waterborne protozoan parasite *Cryptosporidium parvum* using

TiO₂/H₂O₂ under simulated and natural solar conditions. *Catalysis Today* **280**, 132–138.

Alijani, S., Vaez, M. & Moghaddam, A. Z. 2014 Photocatalytic degradation of acid red 73 using TiO₂ nanoparticles immobilized on alumina foam. *International Journal of Environmental Science and Development* **5**, 2–5.

Aoudjit, L., Martins, P. M., Madjene, F., Petrovykh, D. Y. & Lanceros-Mendez, S. 2018 Photocatalytic reusable membranes for the effective degradation of tartrazine with a solar photoreactor. *Journal of Hazardous Materials* **344**, 408–416.

APHA 2012 *Standard Methods for the Examination of Water and Wastewater*, 22nd edn. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC, USA.

Barros Neto, B. & Scarminio, I. S. 2010 *Como fazer experimentos: pesquisa e desenvolvimento na ciência e na indústria (How to do Experiments: Research and Development in Science and Industry)*, 4th edn. Bookman, Campinas, Brazil.

Borges, S. S., Xavier, L. P. S., Silva, A. C. d., Aquino, S. F. d., Borges, S. S., Xavier, L. P. S., Silva, A. C. d. & Aquino, S. F. d. 2016 Immobilized titanium dioxide (TiO₂) in different support materials to use in heterogeneous photocatalysis. *Química Nova* **39**, 836–844.

De Barros, A. L., Domingos, A. A. Q., Fechine, P. B. A., De Keukeleire, D. & Do Nascimento, R. F. 2014 PET as a support material for TiO₂ in advanced oxidation processes. *Journal of Applied Polymer Science* **131**, 1–9.

Garcia, J. C., Simionato, J. I., Almeida, V. d. C., Palácio, S. M., Rossi, F. L., Schneider, M. V. & de Souza, N. E. 2009 Evolutive follow-up of the photocatalytic degradation of real textile effluents in TiO₂ and TiO₂/H₂O₂ systems and their toxic effects on Lactuca sativa seedlings. *Journal of Brazilian Chemical Society* **20**, 1589–1597.

Giroto, J. A., Guardani, R., Teixeira, A. C. S. C. & Nascimento, C. A. O. 2006 Study on the photo-Fenton degradation of polyvinyl alcohol in aqueous solution. *Chemical Engineering and Processing: Process Intensification* **45**, 523–532.

Hir, Z. A. M., Moradihamedani, P., Abdullah, A. H. & Mohamed, M. A. 2017 Immobilization of TiO₂ into polyethersulfone matrix as hybrid film photocatalyst for effective degradation of methyl orange dye. *Materials Science and Semiconductor Processing* **57**, 157–165.

INMETRO 2016 *Orientações Sobre Validação de Métodos Analíticos (Guidelines on Validation of Analytical Methods)*. DOQ-CGCRE-008, Rio de Janeiro, Brazil.

Kennedy, J. & Eberhart, R. 1995 Particle swarm optimization. *IEEE International Conference on Neural Networks* **4**, 1942–1948.

Kumar, M. S., Sonawane, S. H., Bhanvase, B. A. & Bethi, B. 2018 Treatment of ternary dye wastewater by hydrodynamic cavitation combined with other advanced oxidation processes (AOP's). *Journal of Water Process Engineering* **23**, 250–256.

Li, H., Gao, S., Cao, M. & Cao, R. 2013 Self-assembly of polyoxometalate-thionine multilayer films on magnetic microspheres as photocatalyst for methyl orange degradation under visible light irradiation. *Journal of Colloid and Interface Science* **394**, 434–440.

Nascimento Júnior, W. J. D., da Rocha, O. R. S., Dantas, R. F., da Silva, J. P. & Barbosa, A. A. 2018 Kinetic study of food dyes removal from aqueous solutions by solar heterogeneous photocatalysis with artificial neural networks and phytotoxicity assessment. *Desalination and Water Treatment* **104**, 304–314.

Nidheesh, P. V., Zhou, M. & Oturan, M. A. 2018 An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes. *Chemosphere* **197**, 210–227.

Oliveira, D. F. M., Batista, P. S., Muller, P. S., Velani, V., Frana, M. D., De Souza, D. R. & Machado, A. E. H. 2012 Evaluating the effectiveness of photocatalysts based on titanium dioxide in the degradation of the dye Ponceau 4R. *Dyes and Pigments* **92**, 563–572.

Santos, M. M. d. M., Duarte, M. M. M. B., Nascimento, G. E., Souza, N. B. G. & Rocha, O. R. S. 2018 Use of TiO₂ photocatalyst supported on residues of polystyrene packaging and its applicability on the removal of food dyes. *Environmental Technology* **40** (12), 1494–1507.

Shen, Y., Wang, W. & Xiao, K. 2016 Synthesis of three-dimensional carbon felt supported TiO₂ monoliths for photocatalytic degradation of methyl orange. *Journal of Environmental Chemical Engineering* **4**, 1259–1266.

Sobrero, M. C. & Ronco, A. 2004 *Ensayo de toxicidad aguda con semillas de lechuga Lactuca sativa L. (Acute Toxicity Test with Lettuce Seeds Lactuca Sativa L.)* (G. Castillo, ed.). Ensayos Toxicológicos y Métodos de Evaluación de Calidad de Aguas, Ottawa, Canada, pp. 65–71.

Solomons, T. W. G. & Fryhle, C. B. 2012 *Química Orgânica (Organic Chemistry)*, 10th edn. J. Wiley & Sons, Rio de Janeiro, Brazil.

Sridewi, N., Tan, L. T. & Sudesh, K. 2011 Solar photocatalytic decolorization and detoxification of industrial batik dye wastewater using P(3HB)-TiO₂ nanocomposite films. *Clean – Soil, Air, Water* **39**, 265–273.

Xing, X., Du, Z., Zhuang, J. & Wang, D. 2018 Removal of ciprofloxacin from water by nitrogen doped TiO₂ immobilized on glass spheres: rapid screening of degradation products. *Journal of Photochemistry and Photobiology A: Chemistry* **359**, 23–32.

Zangeneh, H., Zinatizadeh, A. A. L., Habibi, M., Akia, M. & Hasnain Isa, M. 2015 Photocatalytic oxidation of organic dyes and pollutants in wastewater using different modified titanium dioxides: a comparative review. *Journal of Industrial Engineering Chemistry* **26**, 1–36.

Zuorro, A. & Lavecchia, R. 2014 Evaluation of UV/H₂O₂ advanced oxidation process (AOP) for the degradation of diazo dye reactive green 19 in aqueous solution. *Desalination and Water Treatment* **52**, 1571–1577.