Application of the advanced oxidative process on the degradation of the green leaf and purple açaí food dyes with kinetic monitoring and artificial neural network modelling

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ABSTRACT

The study evaluated the advanced oxidative processes concerning the degradation of green leaf and purple açaí dyes, as well as the prediction of data through artificial neural networks (ANNs). It was verified that percentage of degradation on the wavelengths (λ) of 215, 248, 523 and 627 nm was 5.95, 49.99, 98.17 and 95.99%, respectively, when UV/H_2O_2 action and UV-C radiation was applied. A non-linear kinetic model proposed by Chan and Chu presented a good fit to the experimental data, reaching an R^2 value between 0.978 and 0.999, for the studied λ. Within the ANN simulations through Statistica 6.0, the multilayer perceptron (MLP) (3-9-4) presented a better fit to the experimental data. However, higher values of R^2 were obtained when utilizing the sklearn package with Python language and an MLP (4-5-4) model. Assays with *Staphylococcus aureus* and *Staphylococcus pyogenes* bacteria isolates were performed and it was verified that after employing the UV/H_2O_2 process, there was a decrease in the toxicity of the solution of dyes. In evaluating *S. aureus* toxicity, normal growth was observed. However, for *S. pyogenes* bacteria, it was found that when using the UV/H_2O_2 process, toxicity was evidenced at post-treatment solution concentrations of 100, 70 and 50%.

Key words | artificial neural networks, food dyes, kinetic modelling, toxicity, UV/H_2O_2

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INTRODUCTION

Progress has been made regarding the technology employed in the food industries, which allowed the introduction of chemical additives in the food production process. These additives have the function of assigning sensory characteristics to the products, like consistency, coloring and flavor, as well as acting to guarantee a greater longevity, that is, shelf life (Honorato *et al.* 2013). Among the most used additives by the food industry are dyes, which have the function of conferring the desired coloration to the final product, making it more attractive to consumers (Anastácio *et al.* 2016).

The chromophore groups present in the dye composition are responsible for conferring color to the product. However, it is known that the coloration does not fully occur, because there is a certain resistance in the dyes to fixing it in the product, which is due to the presence of another group, the auxochromes, also responsible for the color intensity (Christie 2001; Zhang *et al.* 2018). Therefore, the effluents generated by these industries are strongly stained and require adequate treatment (Akceylan *et al.* 2009; Barros *et al.* 2014).

Among the most used food dyes are the purple açaí and green leaf. Each of these dyes is composed of a mixture of

other dyes; açaí purple is composed of Bordeaux red and blue bright (Marchi *et al.* 2005; Silva *et al.* 2008), containing azo and triphenylmethane chromophore groups, respectively; the green leaf is composed of tartrazine yellow and indigotine blue (Marchi *et al.* 2005; Santos *et al.* 2010), of azo and indigoid chromophore groups (Itoh *et al.* 1989).

Having such a rich mixture of various types of dyes, the effluents of the food industry are harmful to the environment since they have the power to modify the biological properties of water resources, due to the pigmentation. This coloration prevents the passage of light, inhibiting the photosynthesis and therefore affecting organisms dependent on the photosynthetic activity. Moreover, such matrices have a high organic load and the presence of suspended solids, making it difficult to maintain the life of some microorganisms in that environment. Thus, the occurrence of these dyes in the watercourses have been verified, even at low concentrations (Pavan *et al.* 2007), and the treatment of this residual water becomes necessary before its disposal in the watercourses.

Although the conventional treatments can reduce the organic load of the effluent, these have not been sufficient to promote the reduction of pigmentation, even when it is in low concentrations. Thus, more effective methods should be used, such as the advanced oxidation processes (AOPs). An AOP acts by mineralizing contaminants, including organic matter, through the formation of oxidizing species such as the hydroxyl radical ($\cdot OH$) (Chakma *et al.* 2015). These processes occur in the presence or absence of light (ultraviolet (UV) or solar radiation). There are various types of AOP, Fenton, photo-Fenton, UV/H_2O_2 and ozonation being the most used (Salazar & Izário Filho 2009; Deng & Zhao 2015; Nair *et al.* 2016).

The AOP that deserves special attention, as it has shown good efficiency discoloring dyes (Machado & Stülp 2010) and does not make necessary the use of a catalytic agent, is the UV/H_2O_2 process. This process happens combined with UV radiation that is capable of promoting the homolytic breakdown of hydrogen peroxide (standard redox potential $= +1.78$ V), which is a strong oxidizing agent, capable of forming the hydroxyl radical ($E_0 = +2.80$ V) to promote oxidation of the pollutants (Vilar *et al.* 2017). According to studies developed by Jamal *et al.* (2015), Silva *et al.* (2014), and Zuorro *et al.* (2013), it is possible to prove the efficacy of the UV/H_2O_2 AOP for the degradation of effluents containing artificial dyes. All the results obtained, in terms of percentage of discoloration, were above 95% for the different types of dyes used

in this study. The kinetics of dye degradation processes usually follow pseudo-first-order models, and sometimes depend on the H_2O_2 concentration used. However, despite the fact that AOPs have been showing good results, the presence of by-products, also known as intermediary reactions, can be found to be equally or more toxic than the initial impurities (Araújo *et al.* 2016). Therefore, toxicity tests have been carried out to evaluate the viability of AOPs according to Lima *et al.* (2016) and Zaidan *et al.* (2017a).

The artificial neural network (ANN) has been increasingly applied in AOPs (Moraes *et al.* 2016; Lira *et al.* 2017; Nascimento *et al.* 2018). In recent studies, Zarei *et al.* (2010), Dil *et al.* (2016), Çelekli *et al.* (2016) and Lenzi *et al.* (2016) show that the ANN has been used as an alternative to predict results of the degradation of artificial dyes, achieving linear regression coefficients (R^2) between 0.98 and 0.99.

The present work had the objective of evaluating the degradation of an aqueous solution containing a mixture of green leaf and açaí purple food dyes, and evaluating the toxicity before and after the treatment. The experimental data were adjusted to the kinetic model and an ANN was applied to predict the percentage of degradation of the dyes.

METHODOLOGY

Identification and quantification of the dyes

Firstly, the wavelengths (λ) of maximum absorbance for the mixture of green leaf and açaí purple dyes (F. Trajano) were determined through a UV-Visible spectrophotometer (Thermo Scientific, model Genesys 10S). For this, a scanning in the range of λ of 190 to 1,100 nm was made. Then, analytical curves with a working range of 2 to 50 mg·L^{-1} were constructed for each of the λ previously selected and the limits of detection (LOD) and quantification (LOQ) of the method were determined, as well as the coefficient of variation (CV), according to the Instituto Nacional de Metrologia Qualidade e Tecnologia (INMETRO 2011).

Working solution and reagents

A solution of the commercial dyes green leaf and purple açaí (F. Trajano) was prepared with deionized water, at a concentration of 50 mg·L^{-1} of each dye. This work solution was

used throughout the process of evaluation of the dye degradation through AOPs. In the degradation step, the following reagents were used: hydrogen peroxide (30% w/v, Química Moderna) as oxidizing agent; H_2SO_4 1 mol·L^{-1} (Merck) for pH adjustment and $FeSO_4·7H_2O$ (Vetec) as the source of iron.

Preliminary study

In order to identify the advanced oxidation process (AOP) that presents greater efficiency for the degradation of the dyes under study, a preliminary study was carried out using Fenton, photo-Fenton, photolysis and UV/H_2O_2 processes. The work solution was submitted to the different AOPs using a concentration of hydrogen peroxide ($[H_2O_2]$) equal to 50 mg·L^{-1} and pH between 5 and 6 (pH of natural solution), iron concentration ([Iron]) equal to 5 mg L^{-1} in a period of 60 minutes. The aliquots were irradiated in the UV-A, UV-C and sunlight reactors. A schematic drawing of the reactor with UV-A radiation is shown in Figure 1, while the UV-C and sunlight reactors were the same as used by Zaidan *et al.* (2017a, 2017b) and Santana *et al.* (2017), respectively. For each reactor the photon emissions were measured with the aid of a radiometer (Emporionet).

Hydrogen peroxide evaluation and pH study

In possession of the results from the preliminary study, the best $[H_2O_2]$ was evaluated for the AOP that presented a higher degradation percentage. The working solution was irradiated for 60 min, varying $[H_2O_2]$: 30, 35, 40, 45, 50, 55, 60, 65 and 70 mg·L^{-1}. After, the influence of pH on the AOP study was evaluated by varying the pH of the working solution in three ranges 3–4, 4–5 and 5–6, using the same period of time.

Modelling

Kinetic modelling

Along with the best experimental conditions (reactor, $[H_2O_2]$ and pH), a kinetic study was performed, irradiating 1 L of the working solution. For this, aliquots were quantified and the percentages of degradation were quantified at the times of: 0, 30, 60, 75, 90, 95, 100, 110, 120 and 150
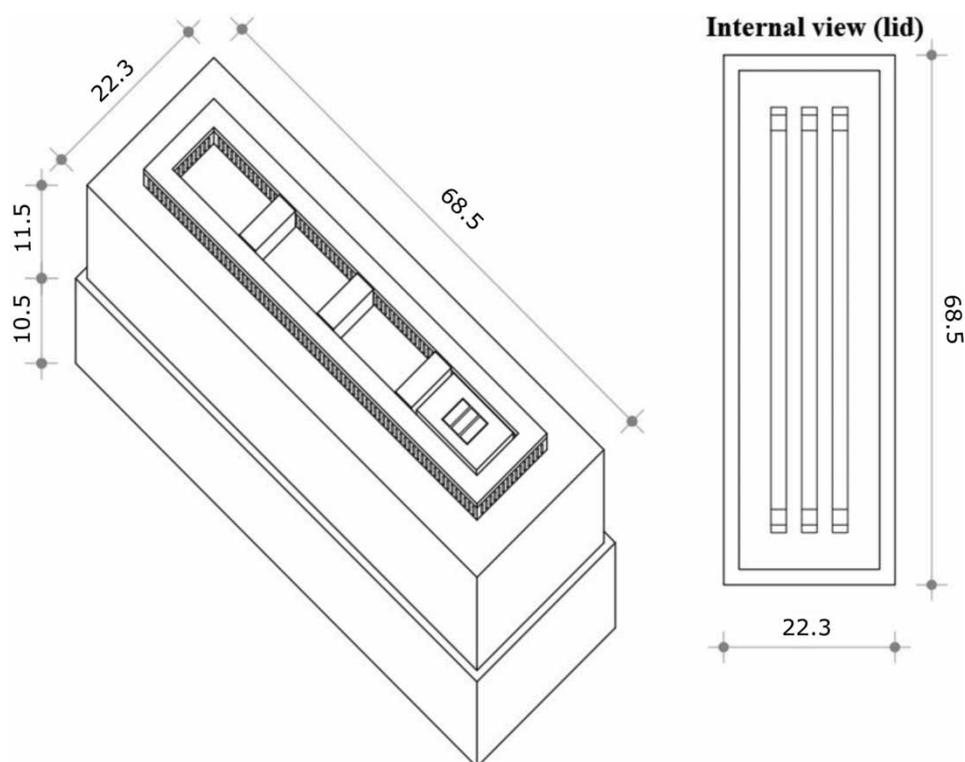

Figure 1 | Illustration of bench reactor UV-A (dimensions in cm).

minutes. Then, the fit of the data to the kinetic model proposed by Chan & Chu (2003), shown in Equation (1), was verified.

$$C = C_0 \left(1 - \frac{t}{\rho - \sigma t} \right) \tag{1}$$

In this equation, C is the remaining concentration of the product after the reaction time t (mg·L^{-1}), C_0 is the initial concentration of the dye (mg·L^{-1}), t is the reaction time (min) and ρ and σ indicate the reaction kinetics (min) and the oxidative capacity of the system (dimensionless), respectively.

ANN modelling

For the modelling using the ANN, two different methodologies were used. The first methodology applied the sklearn package allied with the Python programming language. The strategy used a multilayer perceptron (MLP) network consisting of a layer with four neurons for the input: time (min), pH range (two inputs) and [H$_2$O$_2$]; a layer with four output neurons; and two hidden layers, with five neurons each (MLP (4-5-4)). Therefore, a learning curve of 0.001 was used, with a constant learning rate and a logistic activation function. The maximum number of interactions was 100,000.

The Statistica 6.0 software was also used to model the data obtained experimentally. The correlation was accomplished from the input data: time (min), pH, [H$_2$O$_2$]; and output: percentage of degradation at wavelengths of 215, 248, 523 and 627 nm. Sampling was performed randomly with percentages of train, test and validation of 70%, 15% and 15%, respectively. The networks tested were the MLP and the radial basis function (RBF) and the activation functions used were identity, logistic, hyperbolic and exponential. The number of neurons in the hidden layer was limited to between 3 and 10, and 1,000 interactions were performed for each training. The program tested 50 networks but retained only the top 10. In the end, the ANN model was chosen with the highest linear regression coefficient (R²) among them.

Toxicity

Toxicity tests were carried out using strains of human pathogenic bacteria *Staphylococcus aureus* UFPEDA-02 and *Streptococcus pyogenes* ATCC-16642 obtained from the culture collection (WDCM114) of the Departamento de Antibióticos from the Universidade Federal de Pernambuco. The microbiological toxicity was performed with the initial solution (IS) and post-treatment dye solutions previously filtered on a syringe filter (0.22 μm). The bacteria were cultured in Muller Hinton agar plates overnight at 36 °C and were subsequently fitted to a cell suspension at 10^6 colony-forming units per mL (CFU·mL^{-1}). The samples, as well as the sterile ultrapure water, which was the negative control (4.5 mL), were added to a solution of the bacterial inoculum (0.5 mL) and Muller Hinton broth (1 mL) for 24 h at 36 °C. After this time the post-treatment solution (PTS) was successively diluted 1:10, 1:100, 1:1,000 and 1:10,000 in sterile ultrapure water and then inoculated with a platinum loop (1 μL) into Petri dishes and incubated again (24 h at 36 °C). The classification of bacterial growth was obtained in comparison with the growth observed in the negative control.

RESULTS AND DISCUSSION

Identification and quantification of the dyes

For the identification of the dye mixture under study, green leaf and purple açaí, four wavelengths (λ) were detected: 215 and 248 nm (aromatic groups), 523 and 627 nm concerning the chromophore groups.

After identifying the characteristic λ, the analytical curves were constructed, obtaining correlation coefficients (r) higher than 0.99, indicating a good linearity of the method (ANVISA 2003; INMETRO 2011). The LOD and LOQ values varied between 1.85 and 2.78 mg·L^{-1} and 2.22 and 3.82 mg·L^{-1}, respectively. The CV values were less than 5%, indicating that the methodology used is accurate, as CV values were less than 5% (ANVISA 2003).

Preliminary study

A preliminary study was carried out according to the proposed methodology. The efficiency of the AOP was measured in terms of degradation percentage of the aqueous solution of the dyes, and the emission of photons of each reactor was obtained through a radiometer: UV-A (1.82 × 10^{-4} W·cm^{-2}), UV-C (1.44 × 10^{-3} W·cm^{-2}) and sunlight (5.35 × 10^6 W·cm^{-2}).

The best result was verified while using UV/H$_2$O$_2$ action with the UV-C reactor, reaching a color removal of 91.05% (λ = 523 nm) and 92.06% (λ = 627 nm). Regarding the

degradation of the aromatic groups, 17.94% ($\lambda = 215$ nm) and 43.24% ($\lambda = 248$ nm) were obtained. This same process using UV-A radiation achieved a color removal percentages lower than 13.68% and 57.57% ($\lambda = 215$ nm) and 49.89% ($\lambda = 248$ nm). When using the sunlight reactor, no degradation of the studied groups was observed, so it was decided to continue the study using UV-C radiation, since this one was able to remove the color of the solution under study more efficiently.

The photo-Fenton process achieved its optimum result when using sunlight radiation, obtaining 82.99% ($\lambda = 523$ nm) and 78.21% ($\lambda = 627$ nm) of degradation, while the photolysis and Fenton processes promoted an inefficient degradation of the chromophore groups, being less than 34%.

Concentration of hydrogen peroxide evaluation and pH study

The UV/H_2O_2 process was used to define the concentration of H_2O_2 that best fits the degradation process. It was noticed that the best condition was with H_2O_2 equal to 40 and 45 mg·L^{-1}, since the concentrations of hydrogen peroxide diverged around 2% for all λ, which was confirmed by the analysis of spectral scan performed for the two [H_2O_2], as can be seen in Figure 2.

It can be verified through the analysis of Figure 2 that an overlap of the spectra of the two [H_2O_2] under discussion occurred, indicating that there are no significant differences between the percentages of degradation obtained. Therefore, the [H_2O_2] of 40 mg·L^{-1} was chosen, considering the cost associated with this reagent. Then, the influence of the pH of the solution in the degradation process was evaluated, being analyzed for three different pH ranges: 3–4, 4–5 and 5–6.
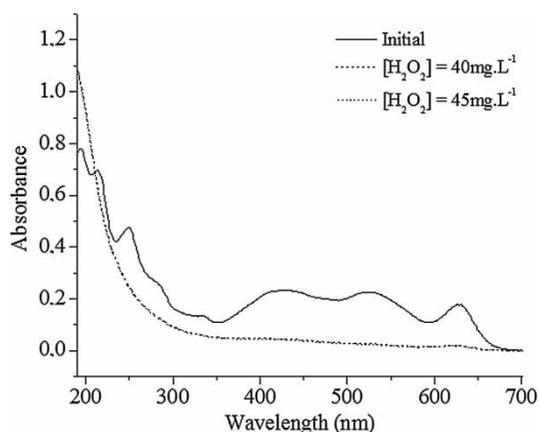

Figure 2 | Scan for the study of hydrogen peroxide concentration of 40 and 45 mg·L^{-1}.

It was found that a higher degradation was obtained in a pH range of 5–6, achieving 5.95% ($\lambda = 215$ nm), 49.99% ($\lambda = 248$ nm), 98.17% ($\lambda = 523$ nm) and 95.66 ($\lambda = 523$ nm).

Modelling

Kinetic modelling

After the best operating condition for discoloration (UV-C radiation, [H_2O_2] of 40 mg·L^{-1} and natural solution pH (5–6)) was determined, the kinetic study was performed. The kinetic monitoring was achieved by withdrawing aliquots of the working solution at the times of: 30, 60, 75, 90, 95, 100, 110, 120 and 150 min. Figure 3(a) shows the kinetic monitoring of the degradation of the chromophore groups and the aromatic groups over time, based on the adjustment to the model proposed by Chan & Chu (2003), and Figure 3(b) shows the residual values of the percentage of degradation over time.

The analysis of Figure 3(a) shows that the experimental data fitted well with the kinetic model proposed by Chan & Chu (2003). There is also a rapid degradation of the chromophore groups with λ equal to 523 and 627 nm, since the decay rate of the concentration of these groups is much higher in the first minutes.

It can be stated from the analysis of Figure 3(b) that the degradation of green leaf and purple açaí dyes employing the UV/H_2O_2 process presented a good kinetic adjustment for the proposed model, since for all λ analyzed, the R^2 values were greater than 0.90 (Figure 3(c)). Paulino *et al.* (2015) also obtained values of R^2 between 0.989 and 0.999, strengthening the usage of this model for kinetic monitoring of dyes. Finally, the results of each of the parameters of the kinetic model, whose values obtained are presented in Figure 3(c), were evaluated.

It is known that the maximum discoloration capacity is represented by the value of the constant $1/\sigma$, which is obtained when the time goes to infinity. Therefore, according to the data in Figure 3(c), it can be inferred that the oxidation capacity of the process for the characteristic λ of the color is much higher than the values obtained for the λ characteristic of aromatic groups, since there is a difficulty to degrade them. Thus, it is necessary to study the toxicity of the solution after treatment (Paulino *et al.* 2015).

Artificial neural network

Among all the simulations from the Statistica 6.0 software, it was verified that the RBF model was not accurate since the
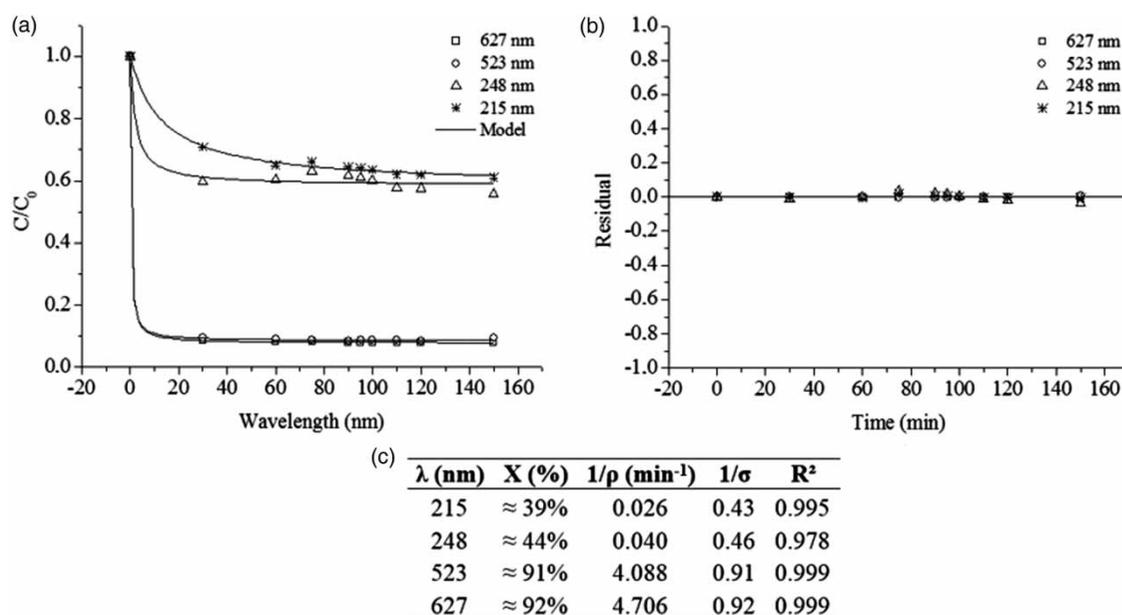
Figure 3 │ (a) Kinetic monitoring of the degradation of green leaf and purple açaí dyes, (b) residual graph of the percentage of degradation over time and (c) conversion data and kinetic parameters for the oxidation reaction (X: percentage degradation).

R^2 values were lower than 0.9 (INMETRO 2011). The best result was found when applying the MLP model with nine neurons in the hidden layer (MLP 3-9-4). The hidden activation layer and output activation layer were Tahn and Logistic, respectively, with SOS (sum of squares) as an error function. The R^2 obtained for the training, test and validation were, respectively, 0.957, 0.976 and 0.897. The error obtained for training was 0.016 and for the test was 0.017. The values for the input, concealment and exit layer weights are shown in Table 1.

From the experimental data, the adjustment for the ANN models was verified: MLP (4-5-4) and MLP (3-9-4). Figure 4 shows the linear regression for the models used.

The analysis of Figure 4 revealed that R^2 values between 0.979 and 0.997 were obtained for MLP (4-5-4) model and between 0.901 and 0.922 for MLP (3-9-4) model. These results indicate a good fit of the experimental data when using MLP (4-5-4) model.

It can also be stated that the MLP (3-9-4) model fitted well to the experimental data, but with a greater dispersion, especially for the characteristic wavelengths of the aromatic groups. The results obtained for the ANN MLP (4-5-4) are in agreement with the literature, as the values of R^2 ranged

Table 1 │ Weight for the inputs, concealment and exit layer

| Neuron	Weight							
	Time (min)	pH	[H$_2$O$_2$]	Bias input layer	215 nm	248 nm	523 nm	627 nm
1	2.665	0.954	−0.809	0.202	1.156	−0.209	0.227	0.800
2	−0.767	−0.199	0.476	0.068	1.325	1.198	−0.153	−0.259
3	1.084	0.447	−0.474	−0.252	0.629	1.540	−0.233	0.126
4	−1.127	0.241	0.102	−1.310	1.330	0.678	0.827	−0.402
5	0.462	−0.291	0.120	−0.838	−0.659	−0.251	1.528	−0.204
6	−0.342	−0.899	−0.020	−0.036	0.365	0.972	0.578	0.450
7	0.798	2.304	0.748	0.378	−0.478	−0.475	−0.666	1.535
8	−0.549	−0.437	−0.034	0.877	−0.254	0.323	1.012	0.462
9	0.262	0.107	−0.829	0.377	0.423	−0.528	−0.393	−0.601
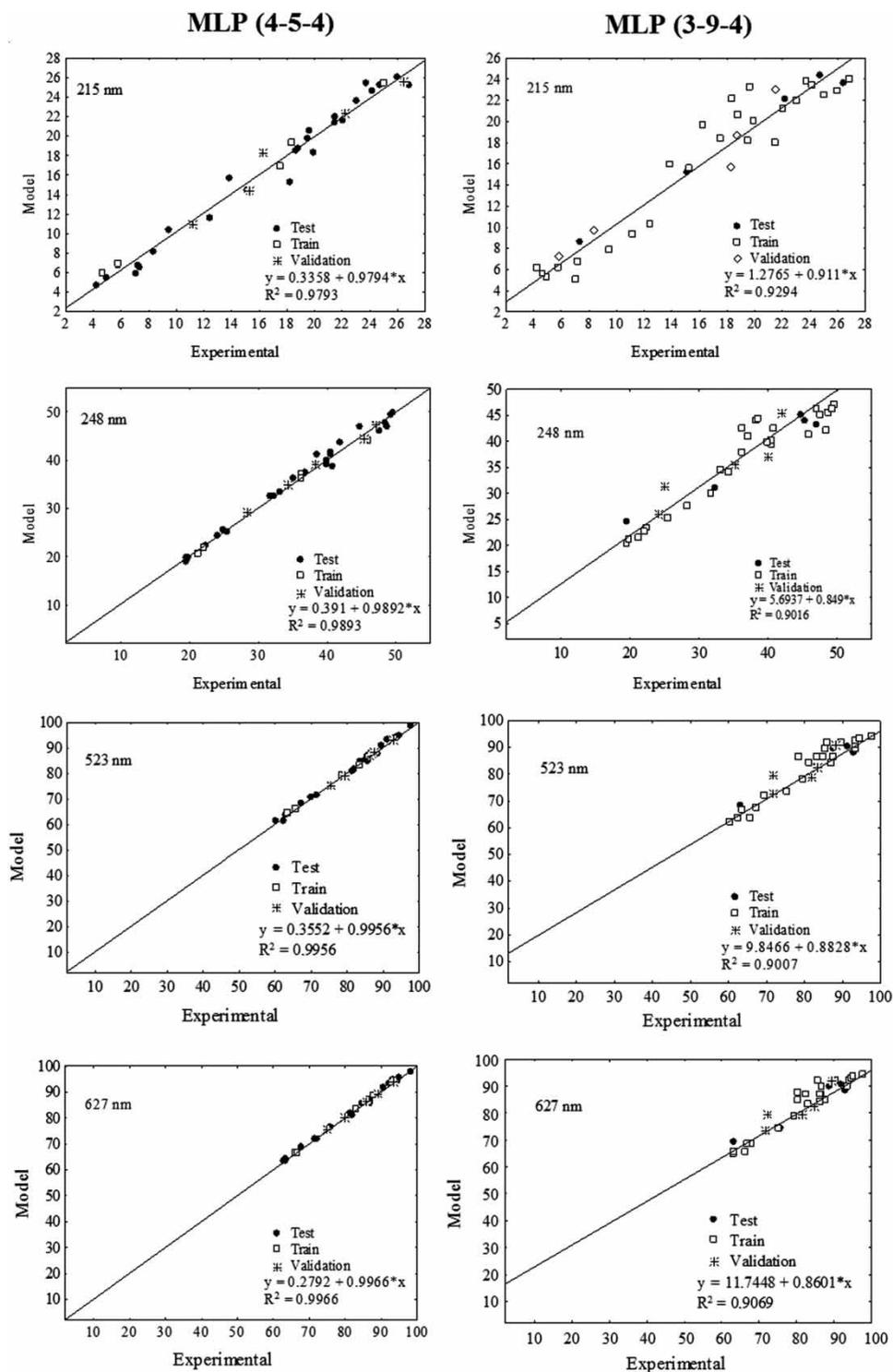
Figure 4 │ Parity plots of the models used.

from 0.97 to 0.99 (Yonar & Kilic 2014; Eskandarloo et al. 2016; Thivaharan et al. 2016).

It is worth emphasizing that the present study considered only an aqueous solution of the mixture of leaf green and açaí purple dyes, and it is necessary to carry out future studies to test the validity of the ANN model proposed in real matrices, since these are more complex due to the presence of other contaminants.

Toxicity

For the same treatment conditions described in the kinetic study, toxicity tests were performed. After the incubation time (24 h at 36 °C) of the aliquots containing 1 μL of the samples, the viable cell counts (CFU·mL^{-1}) were obtained in comparison to the initial inoculum. Then, the percentage of bacterial growth was determined for each of the bacteria under study (Table 2).

According to Table 2, it was observed that *S. aureus* presented a behavior similar to the negative control for the solutions before and after treatment, except for 100% PTS. This result indicates that there was normal bacterial growth and the treatment employed did not influence the growth of the bacterium in question after the dilution process was carried out.

However, for *S. pyogenes*, it was verified that the solution from the treatment using UV/H$_2$O$_2$ showed toxicity in the PTS concentrations of 100, 70 and 50%. Nevertheless, normal growth was observed when the PTS concentration was 10% and higher growth was noticed for PTS 5% and PTS 1%. The presence of toxicity may have been evidenced, since, as observed in the kinetic study, even after the treatment there are intermediate compounds that may present a higher toxicity than the initial compound.

CONCLUSION

The obtained results indicate that UV/H$_2$O$_2$ action is a viable method to degrade an aqueous solution containing

purple açaí and green leaf dyes when applying UV-C radiation for 60 minutes, achieving a degradation percentage of 5.95, 49.99, 98.17 and 95.99% for λ equal to 215, 248, 523 and 627 nm, respectively. It was noticed that the [H$_2$O$_2$] interferes in the process, concluding that 40 mg·L^{-1} showed the best results. However, as pH did not present a significant influence on the removal of the color, it was chosen to work with the natural solution pH. A good fit of the Chan and Chu model was verified as obtained values of R^2 for the chromophore and aromatic groups were above 0.99. Also, the ANN modelling managed to predict and describe the degradation process since the obtained R^2 values, especially for MLP (4-5-4), were above 0.97. The toxicity results pointed out that for both bacteria (*S. aureus* and *S. pyogenes*), the pre-treatment solution presented higher toxicity than the post-treatment.

Table 2 | Viability of *Staphylococcus aureus* and *Streptococcus pyogenes* after the treatment

	Bacteria	
Samples	*Staphylococcus aureus*	*Streptococcus pyogenes*
Control (not treated)	+	+
IS	+	+
PTS 1%	+	++
PTS 5%	+	++
PTS 10%	+	+
PTS 50%	+	–
PTS 70%	+	–
PTS 100%	–	–

+ normal growth; ++ significant growth; – no growth.
IS, initial solution; PTS, post-treatment solution.

REFERENCES

Akceylan, E., Bahadir, M. & Yilmaz, M. 2009 Removal efficiency of a calix[4]arene-based polymer for water-soluble carcinogenic direct azo dyes and aromatic amines. *Journal of Hazardous Materials* **162** (2–3), 960–966. https://doi.org/10.1016/j.jhazmat.2008.05.127.

Anastácio, L. B., Oliveira, D. A., Delmaschio, C. R., Antunes, L. M. G. & Chequer, F. M. D. 2016 Corantes Alimentícios Amaranto, Eritrosina B e Tartranzina, e seus possíveis Efeitos Maléficos à Saúde Humana. *Journal of Applied Pharmaceutical Science* **2** (3), 16–30.

ANVISA (Agência Nacional De Vigilância Sanitária) 2003 Resolução nº 899, de 29 de maio de 2003. Guia para validação de métodos analíticos e bioanalíticos. *Diário Oficial da União, Brasília,* 2 June 2003.

Araújo, K. S., Antonelli, R., Gaydeczka, B., Granato, A. C. & Malpass, G. R. P. 2016 Processos oxidativos avançados: uma revisão de fundamentos e aplicações no tratamento de águas residuais urbanas e efluentes industriais. *Revista Ambiente & Água* **11**, 387–401. http://dx.doi.org/10.4136/ambi-agua.1862.

Barros, W. R. P., Franco, P., Steter, J. R., Rocha, R. S. & Lanza, M. R. V. 2014 Electro-Fenton degradation of the food dye amaranth using a gas diffusion electrode modified with cobalt (II) phthalocyanine. *Journal of Electroanalytical Chemistry* **722–723** (1), 46–56. https://doi.org/10.1016/j.jelechem.2014.03.027.

Çelekli, A., Bozkurt, H. & Geyik, F. 2016 Artificial neural network and genetic algorithms for modeling of removal of an azo dye on walnut husk. *Desalination and Water Treatment* **57**, 15580–15591. https://doi.org/10.1080/19443994.2015. 1070759.

Chakma, S., Das, L. & Moholkar, V. S. 2015 Dye decolorization with hybrid advanced oxidation processes comprising sonolysis/Fenton-like/photo-ferrioxalate systems: a mechanistic investigation. *Separation and Purification Technology* **156** (1), 596–607. https://doi.org/10.1016/j. seppur.2015.10.055.

Chan, K. H. & Chu, W. 2003 Modeling the reaction kinetics of Fenton's process on the removal of atrazine. *Chemosphere* **51** (4), 305–311. https://doi.org/10.1016/S0045-6535(02) 00812-3.

Christie, R. 2001 *Colour Chemistry.* Royal Society of Chemistry, Cambridge, UK.

Deng, Y. & Zhao, R. 2015 Advanced oxidation processes (AOP) in wastewater treatment. *Current Pollution Reports* **1** (3), 167–176. https://doi.org/10.1007/s40726-015-0015-z.

Dil, E. A., Ghaedi, M., Ghaedi, A. M., Asfaram, A., Goudarzi, A., Hajati, S., Soylak, M., Agarwal, S. & Gupta, V. K. 2016 Modeling of quaternary dyes adsorption onto ZnO–NR–AC artificial neural network: analysis by derivative spectrophotometry. *Journal of Industrial and Engineering Chemistry* **34** (25), 186–197. https://doi.org/10.1016/j.jiec.2015.11.010.

Eskandarloo, H., Badiei, A., Bennajady, M. A. & Ziarani, G. M. 2016 Hybrid homogeneous and heterogeneous photocatalytic processes for removal of triphenylmethane dyes: artificial neural network modeling. *Clean Soil Air Water.* **44** (7), 739–908. https://doi.org/10.1002/clen.201400449.

Honorato, T. C., Batista, E., Nascimento, K. O. & Pires, T. 2013 Aditivos alimentares: aplicações e toxicologia. *Verde e Agroecologia e Desenvolvimento Sustentável* **8** (5), 1–11.

INMETRO (Instituto Nacional de Metrologia, Normalização e Qualidade Industrial) 2011 *DOQ-CGCRE-008: Orientações sobre Validação de Métodos Analíticos.* Rev. 04. INMETRO, Rio de Janeiro, Brazil.

Itoh, S., Ohno, S., Hasegawa, N. & Takahashi, H. 1989 Resonance Raman study of the structures of trans and cis isomers and the C=C stretching frequencies of N,N′-derivatives of indigo. *Journal of Raman Spectroscopy* **20** (7), 423–430. https://doi. org/10.1063/1.456917.

Jamal, M. A., Muneer, M. & Iqbal, M. 2015 Photo-degradation of monoazo dye blue 13 using advanced oxidation process. *Chemistry International* **1** (1), 12–16.

Lenzi, G. G., Evangelista, R. F., Duarte, E. R., Colpini, L. M. S., Fornari, A. C. & Menechini Neto, R. 2016 Photocatalytic degradation of textile reactive dye using artificial neural network modeling approach. *Desalination and Water Treatment* **57** (30), 14132–14144. https://doi.org/10.1080/ 19443994.2015.1064035.

Lima, D. R. S., Almeida, I. L. A. & Paula, V. I. 2016 Degradação do corante azul reativo 5G pelo processo oxidativo avançado UV/H_2O_2. *E-xacta* **9** (2), 101–109. http://dx.doi.org/10. 18674/exacta.v9i2.1915.

Lira, D. A. H., Zaidan, L. E. M., Silva, A. M. R. B., Brandão, Y. B., Napoleão, D. C., Benachour, M. & Silva, V. L. 2017 Degradation of 4-chlorophenol using advanced oxidative processes and artificial neural network modelling. *Journal of Environmental Science, Toxicology and Food Technology* **11** (3), 74–86. https://doi.org/10.5419/bjpg2016-0003.

Machado, V. R. & Stülp, S. 2010 Avaliação do processo de oxidação em fluxo de efluente sintético proveniente do tingimento de gemas contendo corante rodamina B. *Revista Destaques Acadêmicos* **2** (4), 39–47. http://dx.doi.org/10. 22410/issn.2176-3070.v2i4a2010.88.

Marchi, S. R., Martins, D., Costas, N. V., Terra, M. A. & Negrisoli, E. 2005 Degradação luminosa e retenção foliar dos corantes azul brilhante FDC-1 e amarelo tartrazina FDC-5 utilizados como traçadores em pulverizações. *Planta Daninha* **23** (2), 287–294. http://dx.doi.org/10.1590/S0100-83582005000200016.

Moraes, S. C. G., Zaidan, L. E. M. C., Napoleão, D. C., Carvalho, F. O., Montenegro, M. C. B. & Silva, V. L. 2016 Implementing artificial neural networks modelling after the treatment of oil refinery effluents using advanced oxidation processes. *Brazilian Journal of Petroleum and Gas* **10** (1), 23–32. https://doi.org/10.9790/2402-1103027486.

Nair, R. G., Bharadwaj, P. J. & Samdarshi, S. K. 2016 Design improvement and performance evaluation of solar photocatalytic reactor for industrial effluent treatment. *Ecotoxicology and Environmental Safety* **134** (2), 301–307. https://doi.org/10.1016/j.ecoenv.2015.07.036.

Nascimento, G. E., Napoleão, D. C., Santana, R. M. R., Charamba, L. V. C., de Oliveira, J. G. C., Moura, M. C., Coelho, L. C. B. B. & Duarte, M. M. M. B. 2018 Degradation of textile dyes Remazol Yellow Gold and reactive Turquoise: optimization, toxicity and modeling by artificial neural networks. *Water Science and Technology* **2017** (3), 812–823. https://doi.org/10. 2166/wst.2018.251.

Paulino, T. R. S., Araújo, R. S. & Salgado, B. C. B. 2015 Estudo de oxidação avançada de corantes básicos via reação Fenton (Fe^{2+}/H_2O_2). *Revista de Engenharia Sanitária e Ambiental* **20** (3), 347–352. doi:10.1590/S1413-41522015020000111627.

Pavan, F. A., Gushikem, Y., Mazzocato, A. C., Dias, S. L. P. & Lima, E. C. 2007 Statistical design of experiments as a tool for optimizing the batch conditions to methylene blue biosorption on yellow passion fruit and mandarin peels. *Dyes and Pigments* **72** (2), 256–266. https://doi.org/10.1016/j. dyepig.2005.09.001.

Salazar, R. F. S. & Izário Filho, H. J. 2009 Aplicação de processo oxidativo avançado baseado em fotocatálise heterogênea (TiO_2/UV_{SOLAR}) para pré-tratamento de afluente lácteo. *AUGM_DOMUS* **1**, 27–44.

Santana, R. M. R., Nascimento, G. E., Napoleão, D. C. & Duarte, M. M. M. B. 2017 Degradation and kinetic study of Reactive blue BF-5G and Remazol red RB 133% dyes using Fenton and photo-Fenton process. *Revista Eletrônica em Gestão, Educação e Tecnologia Ambiental – REGET* **21** (2), 104–118. http://dx.doi.org/10.5902/2236117027358.

Santos, M. E., Demiate, I. M. M. & Nagata, N. 2010 Determinação simultânea de amarelo tartrazina e amarelo crepúsculo em alimentos via espectrofotometria UV-VIS e métodos de calibração multivariada. *Ciência e Tecnologia de Alimentos* **30** (4), 903–909. http://dx.doi.org/10.1590/S0101-20612010000400011.

Silva, C. P., Marmitt, S., Haetinger, C. & Stülp, S. 2008 Avaliação da degradação do corante vermelho bordeaux através de processo fotoquímico. *Engenharia Sanitária e Ambiental* **13** (1), 73–77. http://dx.doi.org/10.1590/S1413-41522008000100010.

Silva, F. A. R., Salgado, B. C. B., Pessoa, K. A. R., Silva, G. M. M. & Araújo, R. S. 2014 Estudos de descoloração oxidativa do azo corante acid red 27 em meio aquoso usando processo UV/H$_2$O$_2$. *Conexões Ciência e Tecnologia* **8** (3), 13–18. https://doi.org/10.21439/conexoes.v8i3.652.

Thivaharan, V., Ramesh, V., Raja, S. & Speck, F. 2016 Modelling and optimization of homogenous photo-Fenton degradation of rhodamine B by response surface methodology and artificial neural network. *International Journal of Environmental Research* **10** (4), 543–554. https://doi.org/10.22059/IJER.2016.59683.

Vilar, V. J. P., Moreira, F. C., Boaventura, R. A. R. & Brillas, E. 2017 Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters. *Applied Catalysis B: Environmental* **202**, 217–261. https://doi.org/10.1016/j.apcatb.2016.08.037.

Yonar, T. & Kilic, M. Y. 2014 Chemical oxygen demand and color removal from textile wastewater by UV/H$_2$O$_2$ using artificial neural networks. *Water Environment Research* **86** (11), 2159–2165. https://doi.org/10.2175/106143014X14062131178277.

Zaidan, L. E. M. C., Sales, R. V. L., Salgado, J. B. A. S., Silva, A. M. R. B., Napoleão, D. C., Rodríguez-Díaz, J. M., Marques, O. M., Benachour, M. & Silva, V. L. 2017a Photodegradation applied to the treatment of phenol and derived substances catalyzed by TiO$_2$/BiPO$_4$ and biological toxicity analysis. *Environmental Science Pollution Research* **24** (7), 6002–6012. https://doi.org/10.1007/s11356-015-5952-y.

Zaidan, L. E. M. C., Pinheiro, R. B., Santana, R. M. R., Charamba, L. V. C., Napoleão, D. C. & Silva, V. L. 2017b Evaluation of efficiency of advanced oxidative process in degradation of 2-4 dichlorophenol employing UV-C radiation reactor. *Revista Eletrônica em Gestão, Educação e Tecnologia Ambiental – REGET* **21** (2), 147–157. http://dx.doi.org/10.5902/2236117027766.

Zarei, M., Niaei, A., Salari, D. & Khataee, A. R. 2010 Removal of four dyes from aqueous medium by the peroxi-coagulation method using carbon nanotube–PTFE cathode and neural network modeling. *Journal of Electroanalytical Chemistry* **639** (1–2), 167–174. https://doi.org/10.1016/j.jelechem.2009.12.005.

Zhang, G., Bailey, A. D., Bucks, M. E. & Murphy, B. P. 2018 A new class of oxazolidinone- and phthalimide-based oxidation dye couplers and their effect on azomethine dye color. *Dyes and Pigments* **149**, 167–176. https://doi.org/10.1016/j.dyepig.2017.09.054.

Zuorro, A., Fidaleo, M. & Lavecchia, R. 2013 Response surface methodology (RSM) analysis of photodegradation of sulfonated diazo dye Reactive Green 19 by UV/H$_2$O$_2$ process. *Journal of Environmental Management* **127** (30), 28–35. https://doi.org/10.1016/j.jenvman.2013.04.023.