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Use of statistical experimental design to optimize the degradation of textile effluents by the Fenton homogeneous process with organic complexes

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ABSTRACT

One of the main limitations of the conventional Fenton process applied to the treatment of textile effluents is the need to acidify the effluent at a pH close to 3. In order to allow the treatment of a textile effluent at a pH near neutral, the application of the Fenton homogeneous process with six organic complexants alone was evaluated in this research, these being: ascorbic acid (AA), citric acid (CA), ethylenediaminetetraacetic acid (EDTA), gluconic acid (GA), oxalic acid (OA) and tartaric acid (TA). The optimization of the reactor operating conditions pH, catalyst concentration (Fe^{2+}), oxidant (H_2O_2) and the complexing agent were obtained by the experimental design of the Rotational Central Compound Design (RCCD). (1:1.31:1.2:27.94) of the different total organic carbon (TOC) molar ratios of the textile effluent, Fe^{2+}, complexant and H_2O_2 (TOC:Fe^{2+}:AG:H_2O_2), followed by the TA when subjected to the molar ratio [1:0.74:0.94:32.13], both with no change in the pH value of the textile effluent (6.71) were used to obtain 82.30% TOC, 99.27% turbidity and 99.19% apparent color, with the use of GA for 15 h of reaction and 75.05% of TOC, 97.84% of turbidity and 96.75% apparent color in 12 h of reaction with TA application. Thus, the Fenton homogeneous process with organic complexes TA and GA allowed the average removal of 75% and 82%, respectively, under a wide operational pH range (4–11) for TOC. Finally, the use of an organic complexant allowed the treatment of textile effluent in a wide range of pH values, hence optimizing the Fenton process application in the treatment of these effluents.

Keywords: Fenton process; Tartaric acid; Gluconic acid

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1. Introduction

The high content of recalcitrant organic matter [1] and dyes used in the textile industry, if not properly treated, affect surface water sources and are responsible for reducing photosynthesis and cause different degrees of toxicity to biota. Nevertheless, they have mutagenic and carcinogenic characteristics of living beings [2].

These compounds are usually persistent to biological degradation making it necessary to adopt treatment technologies capable of promoting the degradation of organic pollutants and achieving high levels of mineralization [3].

In this sense, technologies based on advanced oxidation processes (AOPs) have proven to be highly effective in

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degrading organic compounds in aqueous solution. AOPs can generate species with high oxidizing power, such as hydroxyl radicals (OH), which interact with the pollutant, degrade it and reach complete mineralization [4].

In the treatment of textile effluents, studies demonstrated the efficiency of AOPs through heterogeneous photocatalysis – TiO_2/H_2O_2 [5], heterogeneous photoelectrocatalysis [6]; electro-Fenton [7]; photo-electro-Fenton [8]; Fenton [9], photo-Fenton [10]; UV/H_2O_2 [11] e; O_3 [12].

Among the AOPs, the Fenton process has been recommended in large-scale applications due to several benefits, such as ease of application, high chemical kinetics and low by-product generation during the treatment process [13]. The classic Fenton process requires pH control between 2.0 and 4.0 to allow the formation of OH and avoid the precipitation of ferric oxyhydroxides [14]. Several studies have demonstrated that Fenton reactions in the treatment of textile effluent are dependent on the initial pH, with recommended values close to 3.0 [15].

However, although the Fenton process is widely investigated, it is restricted to acidic pH values, with high costs for industrial scale applications. To overcome these disadvantages, the modified Fenton processes can be successfully performed at neutral pH by adding complexing agents [3].

The use of complexing agents in the Fenton process can prevent or delay the formation of ferric oxyhydroxides and allow the treatment of effluents at pH values near neutrality. Fukushima et al. [16] studied the use of the organic complexant ascorbic acid and found the possibility of degrading the contaminant pentachlorophenol at pH 6.0. Through studies of azo dye discoloration using ascorbic acid with an addition of H_2O_2, a color removal of 90% in 15 min of reaction at an initial pH ranging from 3.0 to 9.0 was identified [17]. Promising results have also been discovered with the use of organic complexing citric acid (CA), which allowed the removal of more than 90% of the ethylene contaminant when applied to the Fenton homogeneous process [18]. Jing et al. [19] studied the photodegradation kinetics of the orange methyl dye with the use of the organic complexing CA and found that the photodegradation was slow when iron or the complexing agent was added alone, however, the reaction speed increased considerably in the presence of the catalyst and complexing agent. Knepper [20] evaluated twenty main compounds used in industries and verified the efficiency of gluconic acid (GA) in metal complexes. In these studies, it was evidenced that Fenton reactions with organic complexants were governed by the molar relationship between the catalyst, the complexing agent and the oxidant.

Consequently, in order to optimize the concentrations of oxidant, catalyst, complexant and initial pH of the effluent, the experimental design of the rotational central compound design (RCCD) is a strategy that allows variables influencing the Fenton homogeneous process (catalyst, organic complexes and oxidant) to be analyzed simultaneously at different levels. In addition, it determines the most significant variables for the desired response, subsequently minimizing the number of experiments to obtain optimized results [23].

Therefore, the objective of this research was to evaluate the use of the organic complexes: ascorbic acid (AA), citric acid (CA), ethylenediaminetetraacetic acid (EDTA), gluconic acid (GA), oxalic acid (OA) and tartaric acid (TA), in the treatment of textile effluents through the Fenton homogeneous process and statistically optimize the operational conditions: concentration of oxidant, catalyst, organic complexer and initial pH, with the aid of RCCD.

2. Materials and methods

2.1. Textile effluent, organic complexes, oxidizer and catalyst

The textile effluent was collected in an industrial laundry located in the Western Region of the State of Paraná (Brazil) daily for 15 d and the samples mixed to obtain the composite sample. According to the industry, the effluent contained a mixture of various commercial reactive azo dyes, generally Synozol navy blue HB, Synozol red HB, Synozol yellow HB and Novacron Black W-NN.

The treated and untreated samples were preserved according to the Standard Methods [24]. All chemical reagents were of analytical grade and were used as received. Chemicals applied in this study include AA; CA; EDTA; GA; OA; TA (Sigma-Aldrich), hydrogen peroxide (30% v/v: Vetec), ferrous sulphate heptahydrate - $FeSO_4{}^-H_2O$ (Synth), sodium hydroxide (Synth) and hydrochloric acid (Synth). All solutions were prepared in ultrapure water (18 MΩ cm – Sistema Milli-Q).

2.2. Experimental setup and procedure

A laboratory scale reactor operated batch-wise system (500 mL of erlenmeyer) was used and all experiments were performed with 250 mL textile effluent. Each experiment was conducted in an open system, without stirring and at room temperature (25 ± 2ºC). The effluent was added to the oxidant (H_2O_2) and then a solution containing the catalyst (Fe^{2+}) and the complexing agent. The reaction time was 24 h.

The experiments were carried out in three stages: 1) Preliminary test for the determination of the best total organic carbon [(TOC): Fe^{2+}: complexant: H_2O_2] molar ratio and performance evaluation of AA, CA, EDTA, GA, AO, TA;2) Experimental planning and statistical analysis, carried out by means of RCCD, to obtain the optimized values of oxidant, catalyst, complexing and initial pH; 3) Evaluation of the efficiency of Fenton homogeneous process with organic complexes when operated under optimized conditions at different reaction times. In this step, a comparative analysis was also performed between the results obtained and the standards for the release of the treated effluent, according to the maximum values permitted (MVP) in Laws - Resolutions N° 375/2005 [21] and N° 430/2010 of the CONAMA [22].

2.2.1. Preliminary test

In order to determine the ideal molar ratio between the TOC present in the effluent, Fe^{2+}, complexing alone (AA, CA, EDTA, GA, AO, TA) and H_2O_2, nine molar ratios were tested: 1) [1:1:1:1]; 2) [1:1:1:25]; 3) [1:1:1:100]; 4) [1:1:0.5:25]; 5) [1:1:2:25]; 6) [1:1:10:25]; 7) [1:0.5:1:25]; 8) [1:2:1:25] and 9) [1:10:1:25].

The concentrations of Fe^{2+} used in all experiments were equal to the sum of the iron from the ferrous sulphate heptahydrate and the total dissolved iron present in the untreated effluent. The tests were carried out, maintaining the pH of the raw effluent (unchanged). After 24 h of reaction, the efficiency in the TOC removal determined the choice of the ideal molar ratios and the best complexants.

2.2.2. Experimental design and statistical analysis

Based on the preliminary test results, a RCCD 2^4 + 8 axial points and 4 repetitions were performed at the central point, totaling 28 tests, according to the methodological procedures described by [25]. The RCCD considered four independent variables: $H_2O_2(x_1)$, $Fe^{2+}(x_2)$, complexant (x_3), initial effluent pH value (x_4).

The values of the independent variables presented by: factor scores (–1 and +1) that indicate the minimum and maximum level of each variable; central point (0) with quadruplicate and; the axial points (–1.41 and +1.41) which determine the quadratic terms [23], were determined after the preliminary tests were performed.

For the optimization of Fenton homogeneous process with organic complexes with addition of organic complexants, for the response variables X_1, X_2, X_3 and X_4, the removal efficiency of TOC was considered after 24 h of reaction.

Afterwards, the experimental results were submitted to statistical analysis by the Statistica® software in the experimental design mode, with analysis of the main interaction effects, analysis of variance (ANOVA), which considers the terms of the model statistically significant for a confidence level of 95% (p-value < 0.05) and three-dimensional surface graphs of responses for the determination of optimum operating conditions.

2.2.3. Reaction kinetics

Once the optimized values of the independent variables x_1, x_2, $x_3$and x_4 were obtained, the textile effluent treatment was executed using these optimized conditions. Thus, aliquots of the effluent were collected and analyzed after 3; 6; 9; 12; 15; 18; 21 and 24 h of reaction. The reactions of the Fenton homogeneous process with organic complexes were ceased immediately after their collection in the batch reactor, by means of the addition of bovine catalase enzyme according to procedures described by [26].

2.4. Analytical determinations

The physico-chemical characterization parameters of the raw and treated effluent were performed according to the methodology described in [24], these being: apparent color (uH); total dissolved iron (mg L^{-1}); nitrate (mg L^{-1}); ammoniacal nitrogen (mg L^{-1}); pH; sulfate (mg L^{-1}); turbidity (NTU) and; maximum absorption wavelength (λ_{max}).

The TOC (mg L^{-1}) was measured using a total organic carbon analyzer (Shimadzu Model TOC-L). The H_2O_2 (mg L^{-1}) were determined using the method of ammonium metavanate [27]. This method is based on the reaction between the H_2O_2 and the metavanadate in an acid medium, to form a compound of orange-red color, measured at a wavelength of 450 nm.

Prior to analysis, all samples were filtered through a nylon membrane (diameter 0.45 mm, diameter 25 mm).The determinations of TOC, residual H_2O_2, color and turbidity preceded the addition of bovine catalase. All analytical determinations were achieved in triplicate.

3. Results and discussion

The untreated effluent showed a deep blue color (2.95 ± 0.25 uH). The molecular absorption spectrum showed high absorbance at 600 nm and peak at 310 nm, wavelength characteristic of aromatic compounds. It is characterized by a near neutral pH (6.71) and high values of turbidity (687 ± 3.9 NTU).

Concentrations of TOC, dissolved total iron, ammonia, and sulphate are respectively 94.11 ± 3.19 mg C L^{-1}, 4.23 ± 0.05 mg Fe L^{-1}, 8.72 ± 0.11 mg NH_3 L^{-1} and 74.96 ± 0.40 mg SO_4^{2-} L^{-1} .

3.1. Ideal molar ratio between the variables and the performance of the complexers

The percentages of TOC removals showed that the complexants produced different efficiencies in the treatment of textile effluent (Table 1).

The AA complexant showed the highest efficiency in removal of TOC (61%) under molar ratio [1:1:1:100]. A similar result (60%) was obtained in the ratio [1:1:1:25]. It is observed that the increase or reduction of the molar concentrations of Fe^{2+} in relation to the AA complexant caused a reduction in the efficiency of the treatment, however, the greater the approximation of the molar ratio [1:1], the greater the TOC removal.

Although AA possesses the ability to reduce iron to the ferrous form, avoiding the formation of insoluble complex of ferric hydroxide [28], it has the capacity to form hydroxyl radicals [29], promote the degradation of contaminants at neutral pH [16], and contribute to the discoloration of dyes [17]. In this study, its use did not provide the best TOC reduction result for the treatment of the textile effluent.

Table 1
TOC removal (%) at different molar ratios between TOC, Fe^{2+}, complexing and H_2O_2, by using the complexing AA, CA, EDTA, GA, OA and TA

Molar ratio	TOC removal (%)					
[TOC: Fe^{2+}: complexing: H_2O_2]	AA	CA	EDTA	GA	OA	TA
1:1:1:1	37	11	21	27	23	31
1:1:1:25	60	49	33	79	52	75
1:1:1:100	61	45	35	76	50	75
1:1:0.5:25	53	37	32	72	38	66
1:1:2:25	52	38	26	60	36	54
1:1:10:25	36	23	39	36	41	49
1:0.5:1:25	43	39	23	75	43	70
1:2:1:25	49	23	20	62	31	61
1:10:1:25	32	5	18	32	30	41

Note: (TOC) total organic carbon; (AA) ascorbic acid; (CA) citric acid; (EDTA) ethylenediaminetetraacetic acid; (GA) gluconic acid; (OA) oxalic acid; (TA) tartaric acid.

The highest TOC removals observed with the use of CA were obtained with the molar ratios [1:1:1:25] and [1:1:1:100], being 49 and 45%, respectively. The low mineralization of organic carbon in this work may be related to the ability of CA to solubilize mineral components, such as metal species [30].

The organic complexant EDTA was the one that promoted the lowest TOC removal when compared to the other complexants. The best EDTA performance (39%) was obtained using the molar ratio [1:1:10:25].

The results obtained for the OA complexer showed that its performance was superior only to the EDTA and CA complexes. The highest TOC removal (52%) occurred when the effluent was treated using the molar ratio [1:1:1:25]. The complexing OA has contributed to the formation of Fe (III) complexes, though the degradation of organic compounds is limited by the absence of irradiation [3].

The complexes TA and GA were the ones that presented the best performance in TOC removal. For TA, there was a 75% removal for both molar ratios [1:1:1:25] and [1:1:1:100]. Using GA, it was possible to observe a 79% reduction in TOC using the molar ratio of [1:1:1:25]. Increasing the H_2O_2 concentration [1:1:1:100] resulted in the reduction of efficiency to 76%. Parra et al. [31] have suggested that the loss of efficiency in the Fenton process with the use of H_2O_2can occur due to the auto-decomposition of H_2O_2, or the excess H_2O_2reacts with the hydroxyl radicals (•OH), competing with the organic pollutant and, consequently, decreasing treatment efficiency.

The results presented in Table 1 indicate that an increase in the concentration of chelates results in the binding of more ferrous ions in the solution. It can also be observed that 100% of ferrous ion chelation in the solution is obtained for the GA/Fe ratio of 5:1 around pH 8, where complexant/Fe is the molar ratio of GA chelate and Fe species (II) [32].

Although the complexes had different performances in TOC removal, they all achieved higher percentages when the molar ratio [1:1] between the catalyst and the complexing agent was used. The results corroborate with that described by [33], which state that many metal chelates form in a molar ratio [1:1] between the metal ion and the complexing agent.

The complexes that presented the highest TOC removal (GA and TA) were chosen for the treatment of the textile effluent and the processes were denominated Fe(II)-GA and Fe(II)-TA, respectively. The optimization of the variables involved in the processes was performed using RCCD experiments 2^4 + 8 axial points and 4 repetitions at the central point. The molar ratio [1:1:1:25] relative to [TOC: Fe^{2+}: complexant: H_2O_2] was used at the central point of the design.

Table 2 shows the levels of the independent variables x_1, x_2, x_3 and x_4.

3.2. Experimental design and statistical analysis: optimization of variables

The results obtained using the RCCD 2^4 + 8 axial points and 4 repetitions at the central point showed that the TOC removal varied between 59 and 81% for Fe(II)-GA and between 50 and 77% for Fe(II)-TA (Table 3).

The results obtained were statistically analyzed by combining the actions among the independent variables, using the mathematical model described in Eq. (1).

$$R = a_0 + (a_{1*} x_1) + (a_{2*} x_2) + (a_{3*} x_3) + (a_{4*} x_4) + (b_{11*} x_1^2) + (b_{22*} x_2^2) + (b_{33*} x_3^2) + (b_{44*} x_4^2) + (b_{12*} x_{1*} x_2) + (b_{13*} x_{1*} x_3) + (b_{14*} x_{1*} x_4) + (b_{23*} x_{2*} x_3) + (b_{24*} x_{2*} x_4) \quad (1)$$

R being the experimental response; a_o is the intercept; a_1, a_2, a_3, a_4, b_{11}, b_{22}, b_{33}, b_{44}, b_{12}, b_{13}, b_{14}, b_{23}, and b_{24} are the coefficients of the terms of the equation; x_1, x_2, x_3 and x_4 are the variables or factors as linear terms of the equation; x_1^2, x_2^2, x_3^2 ε x_4^2 are the variables or factors as quadratic terms of the equation and $(x_{1*}x_2)$, $(x_{1*}x_3)$, $(x_{1*}x_4)$, $(x_{2*}x_3)$ ε $(x_{2*}x_4)$ are the interactions between variables.

The values of TOC removal predicted by the model showed a high correlation with the values observed experimentally (Fig. 1), resulting in an r^2 of 0.958 and 0.979 for the Fe(II)-GA and Fe(II)-TA processes, respectively. The values btained through the mathematical models and those observed in the experiments showed little dispersion, which confirms a good fit of the models for the experimental data.

To validate the fit of the proposed model, the analysis of variance (ANOVA) was performed (Table 4).

Table 2
Levels of the variables used in the RCCD experiments in Fe(II)-GA and Fe(II)-TA processes

Process	Variables	Codification of the variables	Levels of variables (g L^{-1})				
			–2	–1	0*	1	+2
Fe(II)-GA	H_2O_2	x_1	0.2	0.3	0.4	0.5	0.6
	Fe^{2+}	x_2	0.02	0.05	0.08	0.11	0.14
	GA	x_3	0.01	0.20	0.30	0.40	0.50
	pH initial	x_4	1	4	7	10	13
Fe(II)-TA	H_2O_2	x_1	0.2	0.3	0.4	0.5	0.6
	Fe^{2+}	x_2	0.02	0.05	0.08	0.11	0.14
	TA	x_3	0.04	0.14	0.24	0.34	0.44
	pH initial	x_4	1	4	7	10	13

Note: (GA) gluconic acid; (TA) tartaric acid; *[TOC: Fe^{2+}: complexing: H_2O_2] = 1:1:1:25.

Table 3
Experimental conditions adopted and TOC removal (%) of the textile effluent using the complexing GA and TA in RCCD 2^4 + 8 axial points experiments with quadruplicate at the midpoint

Exp.	H_2O_2 (x_1)	Fe^{2+} (x_2)	GA (x_3)	TA (x_3)	Initial pH (x_4)	TOC removal (%)	
	Levels of variables/concentration (g L^{-1})					GA	TA
1	–1/(0.3)	–1/(0.05)	–1/(0.2)	–1/(0.14)	–1/(4)	81	63
2	1/(0.5)	–1/(0.05)	–1/(0.2)	–1/(0.14)	–1/(4)	64	72
3	–1/(0.3)	1/(0.11)	–1/(0.2)	–1/(0.14)	–1/(4)	60	53
4	1/(0.5)	1/(0.11)	–1/(0.2)	–1/(0.14)	–1/(4)	68	59
5	–1/(0.3)	–1/(0.05)	1/(0.4)	1/(0.34)	–1/(4)	70	50
6	1/(0.5)	–1/(0.05)	1/(0.4)	1/(0.34)	–1/(4)	59	61
7	–1/(0.3)	1/(0.11)	1/(0.4)	1/(0.34)	–1/(4)	66	62
8	1/(0.5)	1/(0.11)	1/(0.4)	1/(0.34)	–1/(4)	71	61
9	–1/(0.3)	–1/(0.05)	–1/(0.2)	–1/(0.14)	1/(10)	81	59
10	1/(0.5)	–1/(0.05)	–1/(0.2)	–1/(0.14)	1/(10)	65	68
11	–1/(0.3)	1/(0.11)	–1/(0.2)	–1/(0.14)	1/(10)	65	54
12	1/(0.5)	1/(0.11)	–1/(0.2)	–1/(0.14)	1/(10)	61	63
13	–1/(0.3)	–1/(0.05)	1/(0.4)	1/(0.34)	1/(10)	70	50
14	1/(0.5)	–1/(0.05)	1/(0.4)	1/(0.34)	1/(10)	61	64
15	–1/(0.3)	1/(0.11)	1/(0.4)	1/(0.34)	1/(10)	65	56
16	1/(0.5)	1/(0.11)	1/(0.4)	1/(0.34)	1/(10)	69	68
17	–2/(0.1)	0/(0.08)	0/(0.3)	0/(0.24)	0/(7)	74	52
18	2/(0.6)	0/(0.08)	0/(0.3)	0/(0.24)	0/(7)	64	77
19	0/(0.4)	–2/(0.02)	0/(0.3)	0/(0.24)	0/(7)	72	68
20	0/(0.4)	2/(0.14)	0/(0.3)	0/(0.24)	0/(7)	71	61
21	0/(0.4)	0/(0.08)	–2/(0.1)	–2/(0.04)	0/(7)	67	56
22	0/(0.4)	0/(0.08)	2/(0.5)	2/(0.44)	0 (7)	63	51
23	0/(0.4)	0/(0.08)	0/(0.3)	0/(0.24)	–2/(1)	65	60
24	0/(0.4)	0/(0.08)	0/(0.3)	0/(0.24)	2/(13)	64	66
25	0/(0.4)	0/(0.08)	0/(0.3)	0/(0.24)	0/(7)	76	73
26	0/(0.4)	0/(0.08)	0/(0.3)	0/(0.24)	0/(7)	76	74
27	0/(0.4)	0/(0.08)	0/(0.3)	0/(0.24)	0/(7)	75	74
28	0/(0.4)	0/(0.08)	0/(0.3)	0/(0.24)	0/(7)	76	75

(Exp.) experiment; (TOC) total organic carbon; (GA) gluconic acid; (TA) tartaric acid.

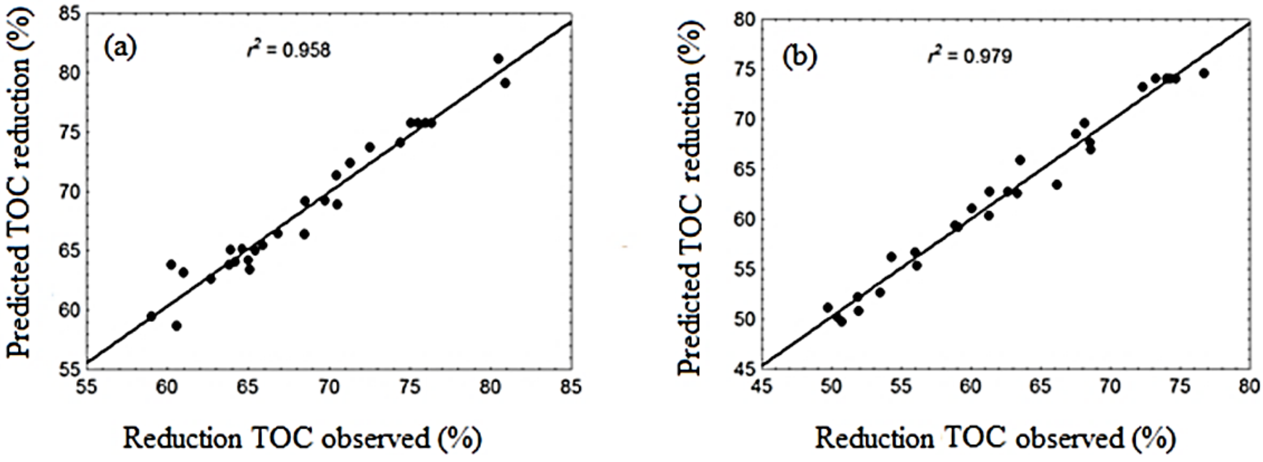

Fig. 1. Correlation between the values observed for the TOC reduction and the values predicted by the proposed statistical model for the treatment of textile effluent by the Fenton homogeneous process with organic complexes using the complexant GA (a); TA (b).

Table 4
Two-way ANOVA test of the predicted model for TOC removal (%) of textile effluent by Fe(II)-GA and Fe(II)-TA processes at a confidence level of 95% ($p < 0.05$)

Process	Source	Sum of squares	Degree of freedom	Mean square	*F*		Significance level (%)
					Calculated	Statistical	
Fe(II)-GA	Regression	965.51	14	68.96	21.22	2.53	<0.05
	Residues	42.07	13	3.23			
	Total	1007.58	27				
Fe(II)-TA	Regression	1877.57	14	134.11	43.54	2.53	<0.05
	Residues	40.05	13	3.08			
	Total	1917.62	27				

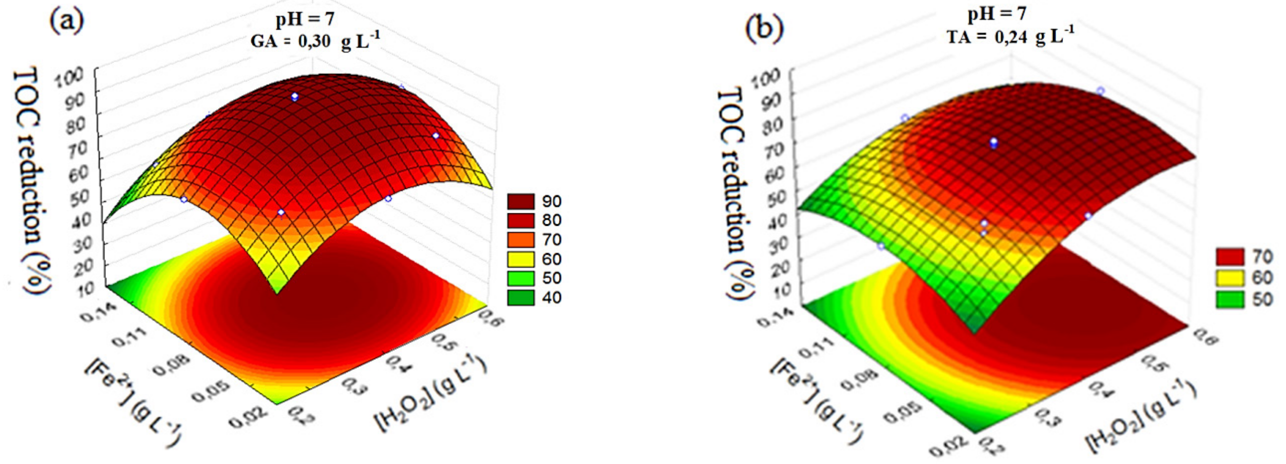

Fig. 2. Response surface in relation to the reduction of TOC by the process Fe(II)-GA (a) and Fe(II)-TA (b).

The ANOVA showed that the predicted model [Eq.(1)] is valid in the 95% confidence interval ($p < 0.05$), as presented in Table 4. The values of $F_{\text{calculated}}$ (21.22; 43.54) > $F_{\text{statistical}}$ (2.53) state that the models tested to represent the TOC removal in Fe(II)-GA and Fe(II)-TA treatment processes resulted in a good reproduction of the experimental results.

The results can be visualized in Fig. 2, when, based on the responses (R%) obtained in the experimental design, the three-dimensional graphs were constructed using the proposed statistical model.

The effects of the interactions between the parameters, Fe^{2+}, H_2O_2, complexing and initial pH, on the coefficients predicted by the models (Table 5), showed that the initial pH ($a_4 > 0.05$) was not significant in the TOC removal when the GA and TA were used for the treatment of textile effluent. This demonstrates that the Fe(II)-GA and Fe(II)-TA processes were effective under different initial pH values.

Based on the effects of interactions between the variables (x_1, x_2, x_3 and x_4) on the predicted coefficients (Table 5), the polynomial models for the TOC removal by Fe(II)-GA and Fe(II)-TA shown in Eqns. (2) and (3).

$$\text{TOC}_{\text{removal(Fe(II)-GA)}} = 75.74 - 5.01x_1 - 3.33(x_1)^2 - 2.41x_2 - 2.22(x_2)^2 - 1.93x_3 - 5.60(x_3)^2 - 5.67(x_4)^2 + 8.31{*}x_1{*}x_2 + 2.13{*}x_1{*}x_3 + 5.75{*}x_2{*}x_3 + 0.01{*}x_{3*}x_4 \quad (2)$$

$$\text{TOC}_{\text{removal(Fe(II)-TA)}} = 74.06 + 11.20x_1 - 5.33(x_1)^2 - 3.63x_2 - 5.02(x_2)^2 - 2.81x_3 - 10.76(x_3)^2 - 5.91(x_4)^2 - 1.92{*}x_1{*}x_2 + 2.63{*}x_1{*}x_3 + 4.77{*}x_2{*}x_3 + 3.45{*}x_2{*}x_4 \quad (3)$$

The models presented allowed the calculation of the optimal conditions for the operational variables (x_1, x_2, x_3 and x_4) using the Statistica software to obtain the maximum efficiency of the proposed processes for the treatment of the textile effluent. The results showed that the highest efficiency of the Fe(II)-GA process in the TOC removal was achieved under the following operating conditions: pH_{initial} of 6.39, 0.447 g L^{-1} of H_2O_2, 0.335 g L^{-1} of GA and 0.105 g L^{-1} of Fe^{2+}, whereas the higher efficiency of the Fe(II)-TA process was achieved using pH_{initial} equal to 6.62, 0.514 g L^{-1} of H_2O_2, 0.225 g L^{-1} of TA and 0.059 g $L^{-1}$of Fe^{2+}. The ideal molar ratios of Fe(II)-GA and Fe(II)-TA were [1:1.31:1.12:27.94] and [1:0.74:0.93:32.13] at pH values close to neutral for the treatment of the textile effluent.

3.3. Efficiency of the Fe(II)-GA and Fe(II)-TA processes when operated under optimized conditions at different reaction times

The efficiency of each Fe(II)-GA and Fe(II)-TA process was tested under optimized conditions obtained in the RCCD at different reaction times. TOC removal followed

Table 5
Effects of interactions between reactor operating parameters in the coefficients for the efficiency of processes Fe(II)-GA and Fe(II)-TA in TOC removal from textile effluent with a 95% confidence level

Process	Actions of parameters	Coefficients	Values	Standard error	T_{Stat}	p-value
Fe(II)-GA	x_0	a_0	75.74	0.89	84.20	<0.05
	x_1	a_1	–5.01	0.73	–6.82	<0.05
	$(x_1)^2$	b_{11}	–3.33	0.73	–4.54	<0.05
	x_2	a_2	–2.41	0.73	–3.28	<0.05
	$(x_2)^2$	b_{22}	–2.22	0.73	–3.03	<0.05
	x_3	a_3	–1.93	0.73	–2.63	<0.05
	$(x_3)^2$	b_{33}	–5.60	0.73	–7.62	<0.05
	x_4	a_4	–0.58	0.73	–0.80	0.43
	$(x_4)^2$	b_{44}	–5.67	0.73	–7.72	<0.05
	$x_{1*}x_2$	b_{12}	8.31	0.89	9.24	<0.05
	$x_{1*}x_3$	b_{13}	2.13	0.89	2.37	<0.05
	$x_{1*}x_4$	b_{14}	–1.44	0.89	–1.60	0.13
	$x_{2*}x_3$	b_{23}	5.75	0.89	6.40	<0.05
	$x_{2*}x_4$	b_{24}	–1.20	0.89	–1.33	0.20
	$x_{3*}x_4$	b_{34}	0.01	0.89	0.01	0.98
Fe(II)-TA	x_0	a_0	74.06	0.87	84.38	<0.05
	x_1	a_1	11.20	0.71	15.63	<0.05
	$(x_1)^2$	b_{11}	–5.33	0.71	–7.44	<0.05
	x_2	a_2	–3.63	0.71	–5.06	<0.05
	$(x_2)^2$	b_{22}	–5.02	0.71	–7.01	<0.05
	x_3	a_3	–2.81	0.71	–3.92	<0.05
	$(x_3)^2$	b_{33}	–10.76	0.71	–15.02	<0.05
	x_4	a_4	1.18	0.71	1.65	0.12
	$(x_4)^2$	b_{44}	–5.91	0.71	–8.25	<0.05
	$x_{1*}x_2$	b_{12}	–1.92	0.87	–2.19	<0.05
	$x_{1*}x_3$	b_{13}	2.63	0.87	3.00	<0.05
	$x_{1*}x_4$	b_{14}	–0.06	0.87	–0.07	0.93
	$x_{2*}x_3$	b_{23}	4.77	0.87	5.44	<0.05
	$x_{2*}x_4$	b_{24}	3.45	0.87	3.93	<0.05
	$x_{3*}x_4$	b_{34}	1.20	0.87	1.37	0.19

Note: (T_{Sta}) t-statistical

the pseudo-first order kinetics for the two processes. The calculated rate constants *k* (h^{-1}), were 0.049 with r^2 of 0.938 in the Fe(II)-GA process and 0.061 with r^2 of 0.966 in the Fe(II)-TA process.

The maximum TOC removal (Fig. 3a) occurred in 12 h of treatment (75%) for Fe(II)-TA and in 15 h (80%) for Fe(II)-GA. There was no change in TOC removal after this period.

The Fe(II)-GA process allowed the removal of 99% of color and turbidity in a time of 12 h and 9 h, respectively. While the Fe(II)-TA process removed 97% of color in 12 h and 97% of turbidity in 6 h of treatment of the textile effluent.

Considering the mineralization of TOC, its removal stopped before the Fe(II)-TA process reached 12 h. It can be seen in Fig. 3a that, after 9 h, stabilization of total dissolved iron (TDI) concentration occurred in approximately 9 mg L^{-1}. After 9 h of reactionin the Fe(II)-GA process, there was still a TDI concentration of 51.6 mg L^{-1}, which continued to decrease for 18 h. After that period, the concentration remained constant at approximately 4.5 mg L^{-1}. The fact that TDI remains in solution at a higher concentration for a longer time may justify the continuation of TOC removal in the Fe(II)-GA process and therefore, its higher efficiency.

The reduction of TDI concentration in both processes may be directly related to the formation of other oxidizing species, such as high valence iron intermediates such as FeO^{3+} and iron ion FeO^{2+} [34].

The residual H_2O_2 concentrations (Fig. 3b) were identical for the two processes in 12 h (90 mg L^{-1}). After this period, the consumption of $H_2O_2$was faster in the Fe(II)-TA process, that is, 10 mg L^{-1} in 15 h and after 18 h, the $H_2O_2$was no longer detected. The reduction of H_2O_2in the Fe(II)-TA and Fe(II)-GA processes is directly related to the consumption of this oxidant in the mineralization of the organic matter, consequently in the reduction of TOC of the textile effluent

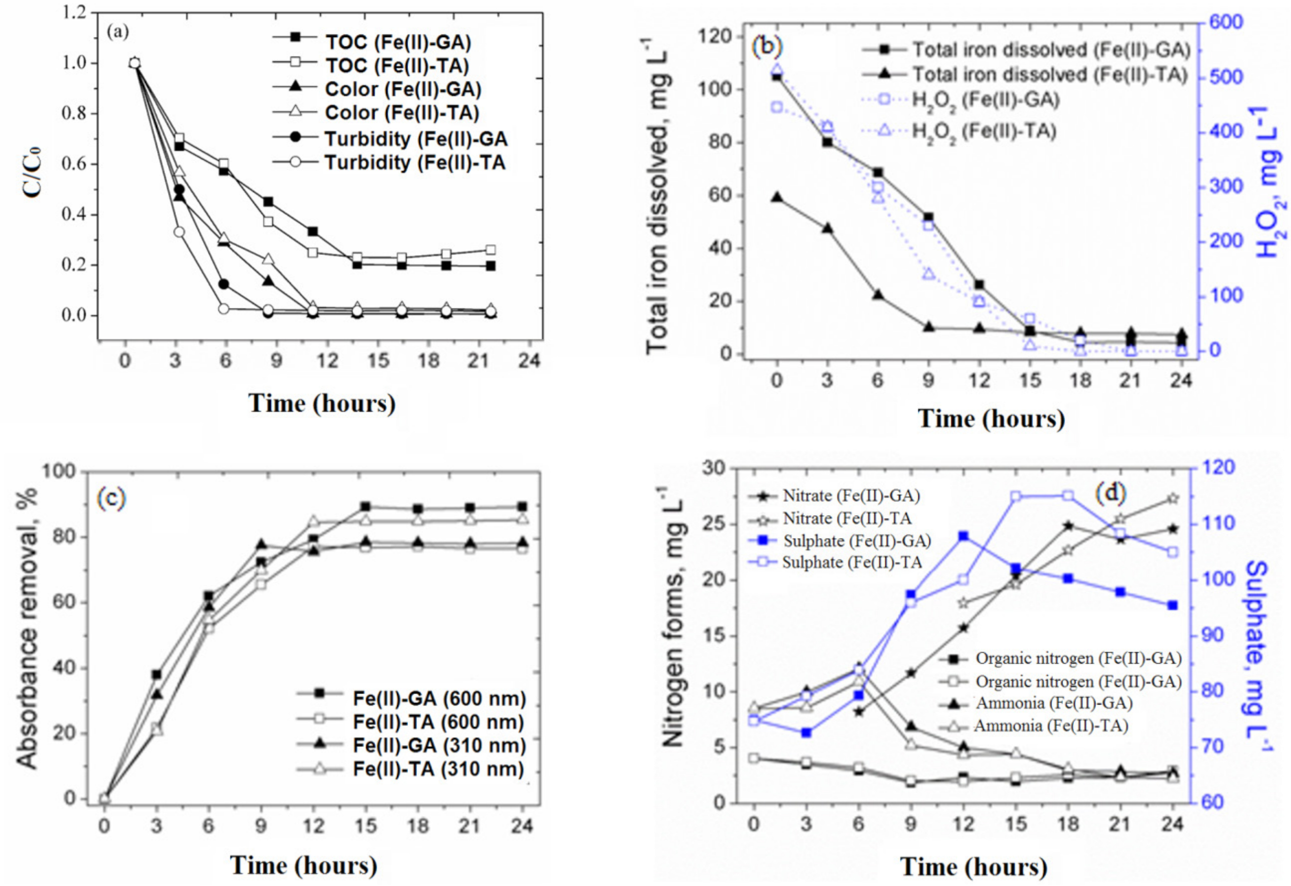

Fig. 3. Removal of color, TOC and turbidity (a); total dissolved iron and residual H_2O_2 as a function of the effluent treatment time using the complexing GA and TA (b). Absorbance removal (c); evolution of the nitrogen and sulfate forms, as a function of the treatment time of the effluent using the complexing GA and TA (d). Experimental conditions: Fe(II)-GA ($pH_{initial}$ = 6.39, Fe^{2+} = 0.105 g L^{-1}, GA = 0.335 g L^{-1}, H_2O_2 = 0.447 g L^{-1}) e Fe(II)-TA ($pH_{initial}$ = 6.62, Fe^{2+} = 0.059 g L^{-1}, TA = 0.225 g L^{-1}, H_2O_2 = 0.514 g L^{-1}).

through the treatment by the Fenton homogeneous process with organic complexes. Other factors that may be related to H_2O_2 reduction are the undesirable reactions of oxidant decomposition in water and oxygen [31].

The absorbance removal (Fig. 3c) at the maximum wavelength of absorption (λ_{max}) of the textile effluent (600 nm) in the Fe(II)-GA process was maximal at 15 h of treatment (89%) and for the process Fe(II)–TA, the stabilization in absorbance removal occurred in 12 h (77%). At 310 nm, a characteristic wavelength of aromatic compounds, removal of 78 and 85% was observed for GA and TA, respectively, at a reaction time of 12 h.

The high absorbance removal can be explained by the oxidizing ability to break down the double bonds of the organic compounds, causing the molecules to lose the ability to absorb light in the Visible region [35]. These results demonstrate an efficient degradation of the chromophore group and virtually complete reduction of the spectral signal recorded between 300 and 600 nm.

In Fig. 3d, the behavior of the nitrogen forms along the treatment of the textile effluent by the Fenton homogeneous process with organic complexes is presented. The breakdown of dye molecules containing N = N bonds results in different intermediates and simpler forms such as ammonia, nitrite and nitrate can be formed by the direct or indirect oxidation of the organic nitrogenous matter. The organic nitrogen remained practically stable, consequently, the increase of the nitrate occurred, whereas the ammoniacal nitrogen was reduced to nearly total elimination.

The initial sulfate concentration in the effluent was 74.96 g L^{-1}. The addition of this ion by $FeSO_4·7H_2O$ was small, 0.18 and 0.10 mg L^{-1}considering the two processes used, Fe(II)-GA and Fe(II)-TA, representing increases of 0, 24 and 0.13%, respectively, which was considered negligible. However, it is expected that there will be an increase in sulfate concentrations by the oxidation of sulfur-containing dye molecules in its composition, such as Synozol navy blue HB ($C_37H_23ClN_{10}O_22S_7·6Na$), present in the textile effluent. In the Fe(II)-GA process, the sulphate concentration reached the maximum value of 107.95 mg SO_4^{2-} L^{-1} in 12 h. In the Fe(II)-TA process, the highest sulfate concentration 115.41 mg SO_4^{2} L^{-1} occurred between 15 and 18 h of reactions (Fig. 3d). After this period, the sulfate concentration was reduced in both processes, which may be related to the formation of salts of iron sulphate, which are highly soluble in water and probably removed by adsorption in iron oxides and/or hydroxides [36].

Table 6
Physico-chemical parameters of the textile effluent treated by Fenton homogeneous process with the organic complexants gluconic acid and tartaric acid, compared to the maximum values permitted by CONAMA Resolutions 357/2005 and 430/2011 for industrial effluent discharges in water bodies

Parameters	Raw effluent	Fe(II)-TA	Fe(II)-GA	MVP
Apparent color (uH)	2,950	23.9	95.75	75.0(1)
TOC (mg L^{-1})	74.11	13.12	18.49	SS(1)
Total iron (mg L^{-1})	4.23	7.19	14.86	–
Dissolved iron (mg L^{-1})	3.38	4.60	10.00	15.0(2)
Residual H_2O_2 (mg L^{-1})	nd	0.02	0.01	
Nitrate (mg L^{-1})	nd	20.22	14.33	10.0(1)
Ammoniacal nitrogen (mg L^{-1})	8.72	4.43	5.14	20.0(2)
pH	6.71	6.10	6.37	6.0 a 9.0(2)
Sulphate (mg L^{-1})	71.44	102.08	100.75	250(1)
Turbidity (NTU)	686.9	5.01	14.87	100.0(1)

Notes: (nd) not detected; (1) Resolution 357/2005 of CONAMA; (2) Resolution 430/2011 of CONAMA; (–) parameter not provided for in Resolutions 357/2005 and 430 of CONAMA; (MVP) maximum values permitted; (SS) maximum value 10 mg L^{-1} intended only for waters classified as Salinas or Salobras.

The results of the physic-chemical values of the raw effluent and treated by the Fe(II)-GA and Fe(II) -TA processes in comparison to the MVPby law are presented in Table 6.

After 15 h of treatment of the textile effluent with Fe(II) -GA and 12 h Fe(II)-TA, it was identified that all parameters analyzed, except nitrate for Fe(II)-TA and the apparent color and nitrate for Fe(II)-TA were in accordance with the MVP by Resolutions 357/2005 and 430/2010. Nitrate is considered the most oxidized and least damaging form in which nitrogen can be found in water bodies. Nevertheless, high concentrations of nitrate limit the increased efficiency of the Fenton process as the anions sequester the hydroxyl radicals and form complexes with iron ions [37].

3.4. Effect of pH

The influence of pH in relation to TOC reduction (Fig. 4) was verified in the optimal time of removal for this parameter, Fe(II)-GA (15 h) and Fe(II)-TA (12 h).

The Fe(II)-GA and Fe(II)-TA processes allowed for the average removal of 75% and 82%, respectively, at a pH between 4 and 11 for TOC. Thus, it was verified that the initial pH adjustment of the effluent textile is not essential for its treatment by the Fenton homogeneous process with organic complexes (GA and TA). Unlike the conventional Fenton reactions, which consequently undergo a strong influence of the pH of the reaction medium [38]. The low efficiency of conventional Fenton processes at neutral pH is mainly related to iron precipitation. This precipitation can be avoided by suitably adding iron complexing agents as in the Fenton homogeneous process with complexes [3].

Failure to perform acidification stages of the raw effluent and neutralization of the treated effluent together with the cost reduction involved in these steps of the conventional Fenton process make the Fenton process modified with the addition of complexing agents advantageous, especially when considering its real-scale application [39;3].

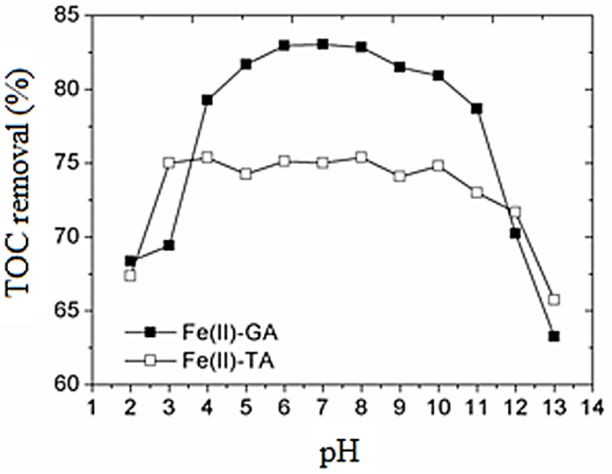

Fig. 4. TOC removal relative to the initial pH of the effluent. Experimental conditions: Fe(II)-GA (Fe^{2+} = 0.105 g L^{-1}, GA = 0.335 g L^{-1}, H_2O_2 = 0.447 g L^{-1}) and Fe(II)-TA (Fe^{2+} = 0.059 g L^{-1}, TA = 0.225 g L^{-1}, H_2O_2 = 0.514 g L^{-1}). Reaction time: 12 h for Fe(II)-TA and 15 h for Fe(II)-GA.

4. Conclusion

It was possible to establish optimized operating conditions with the use of RCCD as a tool to evaluate the effects of the independent variables x_1, x_2, x_3 and x_4, as well as their interactions in the TOC removal of the textile effluent by the Fenton homogeneous process with organic complexes, along with addition of complexing agents (TA and GA).

The Fe(II)-TA process showed the highest TOC reduction (81%) when submitted to the molar ratio of [1:1,31:1,2:27,94] to [COT:Fe^{2+}:AG:H_2O_2]. The Fe(II)-GA process allowed the maximum TOC removal (77%) when submitted to the molar ratio [1:0.74:0.94:32.13].

The x_4 (pH) dependent variable was efficient in a wide operational range (pH 3–11) in the Fe(II)-TA and Fe(II)-GA processes, making possible the application of the Fenton process in the textile effluent with the initial pH being neutral and basic.

It was identified that the reaction time to obtain the maximum efficiency of the Fenton homogeneous process with organic complexes was 12 h and 15 h with the use of TA and GA, respectively. Thus, it is suggested to conduct studies of the Fenton process with the mass relations [TA = 1: 1,31: 1,2: 27,94] and [GA = 1: 0,74: 0,94: 32,13], in a system under continuous agitation, in order to identify the greater efficiency and a possible reduction in the treatment time of the textile effluent. This is because the Fenton process in a batch reactor under continuous agitation usually promotes the maximum removal of organic compounds or the breakdown of aromatic compounds within a few minutes of reaction. It is also recommended to consider studies of biodegradability and ecotoxicity of the treated effluent, since the addition of chemical species to the modified Fenton process, despite allowing global optimization of TOC removal, may contribute to the increase of effluent toxicity.

Finally, the use of RCCD and the statistical analysis of the results allowed a better understanding of the Fenton process with the use of organic complexants. These results encourage the applicability of these complexants to the Fenton process as a promising alternative for the treatment of textile effluent, especially those with alkaline pH.

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References

[1] M. Kim, D. Han, F. Cui, W. Bae, Recalcitrant organic matter removal from textile wastewater by an aerobic cell-immobilized pellet column, Water Sci. Technol., 67 (2013) 2124–2131.

[2] H.M. Pinheiro, E. Touraud, O. Thomas, Aromatic amines from azo dye reduction: status review with emphasis on direct UV spectrophotometric detection in textile industry wastewater, Dyes Pigm., 61 (2004) 121–139.

[3] L. Clarizia, D. Russo, Di. Somma, R. Marotta, R. Andreozzi, Homogeneous photo-Fenton processes at near neutral pH: A review, Appl. Catal., B, 209 (2017) 358–371.

[4] M. Sánchez-Polo, M.M. Abdel-Daiem, R. Ocampo-Pérez, J. Rivera-Utrilla, A.J. Mota, Comparative study of the photodegradation of bisphenol A by HO, SO_4^- and CO_3^-/HCO_3 radicals in aqueous phase, Sci. Total Environ., 463–464 (2013) 423–431.

[5] J.C. Garcia, J.I. Simionato, A.E.C. Silva, J. Nozaki, N.E. Souza, Solar photocatalytic degradation of real textile effluents by associated titanium dioxide and hydrogen peroxide, Sol. Energy Mater. Sol. Cells, 83 (2009) 316–322.

[6] Y.B. Xie, X.Z. Li, Interactive oxidation of photoelectrocatalysis and electro-Fenton for azo dye degradation using TiO_2–Ti mesh and reticulated vitreous carbon electrodes, Mater. Chem. Phys., 95 (2006) 39–50.

[7] M. Panizza, G. Cerisola, Electro-Fenton degradation of synthetic dyes, Water Res., 43 (2009) 339–344.

[8] A.R. Khataee, M. Safarpour, A. Naseri, M. Zarei, Photoelectro-Fenton/nanophotocatalysis decolorization of three textile dyes mixture: response surface modeling and multivariate calibration procedure for simultaneous determination, J. Electroanal. Chem., 672 (2012) 53–62.

[9] Y. Du, M. Quiu, Comparative study of advanced oxidation for textile wastewater, Desal. Water Treat., 51(31–33) (2013) 5954–5958.

[10] G.F. Torres, J.A. Méndez, D.L. Tinoco, E.D. Marin, J. Arãna, J.A. Herrera-Melián, Application of advanced oxidation technologies and sand filter for the detoxification of effluents from small textile industries in Ecuador, Desal. Water Treat., 57(51) (2016) 24288–24298.

[11] M.E. Nagel-Hassemer, C.R.S. Carvalho-Pinto, W.G. Matias, F.R. Lapolli, Removal of coloured compounds from textile industry effluents by UV/H_2O_2 advanced oxidation and toxicity evaluation, Environ. Technol., 16 (2011) 1867–1874.

[12] F.Y. Qian, X.B. Sun, Y.D. Liu, Removal characteristics of organics in bio-treated textile wastewater reclamation by a stepwise coagulation and intermediate GAC/O_3 oxidation process, Chem. Eng. J, 214 (2013) 112–118.

[13] R.C.C. Costa, F.C.C. Moura, J.D. Ardisson, J.D. Fabris, R.M. Lago, Highly active heterogeneous Fenton-like systems based on Fe_0/Fe_3O_4 composites prepared by controlled reduction of iron oxides, Appl. Catal., B, 83 (2008) 131–139.

[14] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol., 36 (2006) 1–84.

[15] M. Pérez, F. Torrades, X. Domènech, J. Peral, Fenton and photo-Fenton oxidation of textile effluents, Water Res., 36 (2002) 2703–2710.

[16] M. Fukushima, M. Kawasaki, A. Sawada, H. Ichikawa, K. Morimoto, K. Tatsumi, S. Tanaka, Facilitation of pentachlorophenol degradation by the addition of ascorbic acid to aqueous mixtures of tetrakis (sulfonatophenyl) porphyrin and iron (II), J. Mol. Catal. A: Chem., 18 (2002) 201–213.

[17] P. Verma, P. Baldrian, F. Nerud, Decolorization of structurally different synthetic dyes using cobalt (II)/ascorbic acid/hydrogen peroxide system, Chemosphere, 50 (2003) 975–979.

[18] Y. Seol, I. Javandel, Citric acid-modified Fenton's reaction for the oxidation of chlorinated ethylenes in soil solution systems, J. Hazard. Mater., 72 (2008) 537–542.

[19] G. Jing, D. Yanvan, L. Yeqing, M. Jingdong, Photodegradation mechanism and kinetics of methyl orange catalyzed by Fe (III), J. Hazard. Mater., 186 (2011) 2083–2088.

[20] T.P. Knepper, Synthetic chelating agents and compounds exhibiting complexing properties in the aquatic environment, TrAC, Trends Anal. Chem., 22 (2003) 10.

[21]CONAMA., ConselhoNacional de Meio Ambiente, Resolução 357, de 17 de março de 2005 [National Council for the Environment, Resolution 357 of march 17, 2005]. Available from: http://www2.mma.gov.br/port/conama/legiabre.cfm?codlegi=459.

[22] CONAMA., ConselhoNacional de Meio Ambiente, Resolução430, de 17 de março de 2005 [National Council for the Environment, Resolution 430, of march 17, 2005]. Available from: http://www2.mma.gov.br/port/conama/legiabre.cfm?codlegi=646.

[23] D. Núñez-Gómez, A.A. Alves, F.R. Lapolli, M.A. Lobo-Recio, Application of the statistical experimental design to optimize mineimpacted water (MIW) remediation using shrimp-shell, Chemosphere, 167 (2017) 322–329.

[24] APHA., AWWA., WPCF., Standard Methods for the Examination of Water and Wastewater, 21st ed., Am. J. Public Health, Washington, DC, 2012.

[25] B. Barros Neto, I.S. Spacino, R.E. Bruns, Como fazer experimentos: pesquisa e desenvolvimento na ciência e na indústria, 3° ed. Campinas, SP: Editora da UNICAMP, 2007.

[26] S. Malato, J. Blanco, A. Vidal, C. Richter, Photocatalysis with solar energy at a pilot-plant scale: An overview, Appl. Catal., B, 37 (2002) 1–15.

[27] R.F.P. Nogueira, M.C. Oliveira, W.C. Paterlini, Simple and fast spectrophotometric determination of H_2O_2 in photo-Fenton reactions using metavanadate, Talanta, 66 (2005) 86–91.

[28] P. Benito, D.M. Miller, Iron absorption and 5, bioavailability: an update review, Nutr. Rev., 54 (1996) 295–317.

[29] O.I. Aruoma, Assessment of potential prooxidant and oxidant actions, J. Am. Oil Chem. Soc., 73 (1996) 1617–1625.

[30] S.A. Wasay, S. Barrington, S. Tokunaga, Retention form of heavy metals in three polluted soils, J. Soil. Contam., 7 (1998) 103–119.

[31] S. Parra, V. Sarria, S. Malato, P. Péringer, C. Pulgarina, Photochemical versus coupled photochemical–biological flow system for the treatment of two bio recalcitrant therbicides: metobromuron and isoproturon, Appl. Catal., B, 27 (2000) 153–168.

[32] D.K.1. Ahuja, L.G. Bachas, D. Bhattacharyya, Modified Fenton reaction for trichlorophenol dechlorination by enzymatically generated H_2O_2 and gluconic acid chelate, Chemosphere, 66 (2007) 193–200.

[33] G.T. Blair, M.F. Zienty, Citric Acid: Properties and Reactions, Citro-tech Division, Miles Laboratories, Inc. Elkhart, Indiana, 1979.

[34] D.T. Sawyer, A. Sobkowiak, T. Matsushita, Metal [MLx; M = Fe, Cu, Co, Mn]/hydroperoxide-induced activation of dioxygen for the oxygenation of hydrocarbons: oxygenated Fenton chemistry, Chem. Res., 9 (1996) 409–416.

[35] E. Almeida, M.R. Assalin, M.A. Rosa, Tratamento de efluentes industriais por processos oxidativos na presença de ozônio, Quim. Nova, 27 (2004) 818–824.

[36] M. Murugananthan, R.G. Bhaskar, S. Prabhakar, Removal of sulfide, sulfate and sulfite ions by electro coagulation, J. Hazard. Mater., 109 (2004) 37–44.

[37] L.G. Devi, K.A. Raju, S.G. Kumar, K.E. Rajashekhar, Photo-degradation of di azo dye Bismarck Brown by advanced photo-Fenton process: Influence of inorganic anions and evaluation of recycling efficiency of iron powder, J. Taiwan Inst. Chem. Eng., 42 (2011) 341–349.

[38] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater., 98 (2003) 33–50.

[39] N. De la Cruz, J. Giménez, S. Esplugas, D. Grandjean, L.F. de Alencastro, C. Pulgarín, Degradation of 32 emergent contaminants by UV and neutral photo-Fenton in domestic wastewater effluent previously treated by activated sludge, Water Res., 46 (2012) 1947–1957.