OPERATING CONDITIONS OF THE FENTON PROCESS ON THE HERBICIDE ATRAZINE DEGRADATION IN WASTEWATERS

CONDIÇÕES OPERACIONAIS DO PROCESSO FENTON NA DEGRADAÇÃO DO HERBICIDA ATRAZINA EM ÁGUAS RESIDUÁRIAS

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Resumo

Este estudo investigou os efeitos das condições operacionais do processo Fenton na degradação do herbicida atrazina em águas residuárias. Propôs-se um delineamento composto central rotacional (DCCR) 2², cobrindo 11 ensaios, com os seguintes fatores: a concentração de Fe^{2+} (2,95; 5,00; 10,00; 15,00; 17,05 mgL^{-1}) e a concentração de H_2O_2 (29,50; 50,00; 100,00; 150,00 e 170,50 mgL^{-1}). Estes fatores foram otimizados com base nos valores da degradação da atrazina, com tempo de tratamento de 30 minutos e medidas realizadas através de Cromatografia Líquida de Alta Eficiência. Para determinar as condições ótimas de operação do processo, os resultados foram estudados pela análise de variância (ANOVA) através dos efeitos dos dois fatores e suas possíveis ações combinadas, seguindo-se a metodologia da superfície de resposta. Assim, as condições ótimas de operação do processo foram: concentração de Fe^{2+} = 17,05 mgL^{-1} e de H_2O_2 = 128 mgL^{-1}. Nestas condições, o processo mostrou-se promissor, alcançando valores de 91,00% de degradação da atrazina aos 30,0 min. de tratamento, apresentando-se como uma alternativa eficiente a ser usada como polimento final.

Palavras-chave: Cromatografia Líquida de Alta Eficiência. Delineamento Composto Central Rotacional. Processos Oxidativos. Tratamento de Água Residuária.

Abstract

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This study investigated the effects of the operating conditions of the Fenton process on the herbicide atrazine degradation in wastewaters. A 2^2 central composite rotational design (CCRD) was proposed covering 11 tests, with the following factors: Fe^{2+} concentration (2.95, 5.00, 10.00, 15.00, and 17.05 mgL^{-1}) and H_2O_2 concentration (29.50, 50.00, 100.00, 150.00 and 170.50 mgL^{-1}). These factors were optimized based on atrazine degradation values, with a treatment time of 30 minutes and measurements performed by High Performance Liquid Chromatography. To determine the optimal operating conditions of the process, the results were studied by analysis of variance (ANOVA) by the effect of the 2 factors and their possible combined actions, following the response surface methodology. Thus, the optimal operating conditions for the process were Fe^{2+} concentration = 17.05 mgL^{-1} and H_2O_2 concentration = 128.00 mgL^{-1}. Under these conditions, the process showed to be promising, reaching values of 91.00% of atrazine degradation at the 30.0 min of treatment time, presenting itself as an efficient alternative to be used as final polishing.
Keywords: Central Composite Rotational Design, High Performance Liquid Chromatography, Oxidative Processes, Wastewater Treatment.

1. **INTRODUÇÃO**

The selective herbicide atrazine, with the molecular formula $C_8H_{14}ClN_5$ (1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine), presents molar mass 215.68 g/mol, melting point 175 °C and boiling point 200 °C.

Widely used in the control of broad-leaved weeds and grasses in sugarcane, corn, sorghum, pineapple crops, it presents varying biodegradation rates, with potential accumulation and persistence in soils, surface and groundwater. Its application has been restricted in the United States and banned in several European countries since 1990 (ZHAO *et al.*, 2017), but it continues to be applied in many countries, totalizing an annual expenditure of 70,000–90,000 tons (ALBUQUERQUE *et al.*, 2020). In Brazil, it is the third most marketed agrochemical, with 33,321.11 tons employed, only in 2020 (IBAMA, 2022), with a maximum allowable limit in fresh waters of 2.0 μgL^{-1} (CONAMA, 2005).

Whereas in Brazil this herbicide is classified as III (Moderately Toxic), in the European Union it is listed on the Pesticide Action Network (PAN), labeled as Highly Hazardous. Atrazine is classified by the European Union as a substance with evidence of causing endocrine disruption, affecting the hormonal system and acting as a type C carcinogen (SINGH *et al.*, 2018).

The toxic effects of atrazine are due to the its persistency in the environment, caused by its chemical stability, water solubility and high lipophilicity (CIMINO-REALE *et al.*, 2008; ROSTAMI *et al.*, 2021).

The half-life of atrazine in soil is 60 days but can be up to 2 years. In Germany, atrazine and its residues were found in soil more than two decades after the last herbicide application (KRUTZ *et al.*, 2010). In water, the half-life of atrazine ranges from 20 to 100 days (VONBERG *et al.*, 2014).

The ecotoxicity of atrazine can lead to serious neurological and immunological damage, biochemical changes in humans, various effects on the reproductive system and contamination of water bodies, affecting their quality and purification capacity. The atrazine produces several adverse impacts in human beings: tumors, carcinomas, lymphomas, and leukemia. It causes congenital defects and loss of weight in humans (ALBUQUERQUE *et al.*, 2020). Therefore, research on the atrazine degradation, present in wastewaters, is extremely important (MIKLOS *et al.*, 2018; SINGH *et al.*, 2018; LIU *et al.*, 2021; Matias *et al.*, 2021)

Among the processes investigated in the treatment of wastewater are advanced oxidation processes (AOPs), which have stood out as wastewater treatment technology (GARRIDO-CARDENAS *et al.*, 2019). They are effective methods and can decrease environmental impacts with success at the removal and degradation of recalcitrant pollutants (CHEN *et al*., 2016).

Recent studies have shown that AOPs are viable alternatives on herbicides degradation, as well as a promising alternative in the degradation and/or removal of excess contaminants, not removed by biological or chemical treatment systems (QIN *et al.*, 2020).

The Fenton process stands out among AOPs as a promising method in the treatment of wastewater. Fenton reaction consists in the formation of the hydroxyl radical (•OH), with a high oxidation potential, being used as oxidant hydrogen peroxide and as catalyst ferrous cations iron, in an acid reactive medium.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \bullet OH \quad \text{(Equation 1)}$$

The process presents as advantage the operating simplicity due to its homogeneity, as well as high degradation efficiency (DOMINGUES *et al.*, 2021), and can be used as a complementary process for pre or post treatment.

It should be noted that the metabolites resulting from the degradation of atrazine can also contaminate soil and water, although the degradation pathways of atrazine are not well known. Three degradation products (desethylatrazine, desisopropylatrazine, and 2-hydroxyatrazine) were identified (FAREED *et al.*, 2021; ROSTANI *et al.,* 2021). A study has shown that Fenton reaction can degrade atrazine to toxicologically inactive molecules such as oxalic acid, urea, formic acid, acetic acid, and acetone, or mineralize atrazine to CO_2 and H_2O (MACHUL'AK *et al.*, 2011).

The Fenton process was investigated on the herbicide paraquat degradation (50 mg L^{-1}, in water) by Trovó *et al.*, 2013, being observed both in scale and pilot reactors similar results in removal efficiency and mineralization.

The process is used to treat wastewaters contaminated with mixtures de herbicides: Abdessalem *et al.* (2010) conducted a study with an effluent containing chlorotoluron, carbofuran, and bentazone and discovered that high concentrations of H_2O_2 decelerated the decontamination, with an increase in the competitive reactions.

The Fenton process was also used on the herbicide simazine degradation: with 15 minutes of treatment, the contaminant was no longer detected in the wastewater, with the use of 50.00 mgL^{-1} of H_2O_2 and 15.00 mg L^{-1} of Fe^{2+} (CATALKAYA; KARGY, 2009).

In this context, the aim of this study was to investigate the effects of operating parameters of the Fenton process on the atrazine herbicide degradation.

2. MATERIALS AND METHODS

2.1 Location of study

The studies of atrazine degradation were carried out at the Laboratory of Environmental Sanitation of the Western Paraná State University, at the Campus of Cascavel, PR, Brazil.

2.2 Preparation of the synthetic effluent of the herbicide atrazine

The synthetic effluent was prepared with the addition of 20 ppm of the atrazine, according to LOURENÇO, 2014, to distilled water, totalizing 1000 mL of the synthetic effluent. The atrazine Primóleo® (Syngenta) was composed of 400 gL^{-1} of atrazine and 660 g L^{-1} of inert compounds. The solution was prepared inside a borosilicate beaker with a volume of 2000 mL and stirred on a magnetic stirrer for 24 hours, at 160 RPM and ambient temperature in order to ensure solubility, in a dark place so that its degradation did not occur.

2.3 Preparation of the reactor

The treatment of the synthetic effluent was carried out in a laboratory-scale photochemical reactor, consisting of a 2000 mL borosilicate beaker with a final volume material of 1000 mL, with a magnetic stirrer (Corning, PC-420), responsible for the effluent homogenization.

For each test, 1000 mL of the synthetic effluent was added to the beaker with the pH kept at 3.0 by standard solutions of H_2SO_4 (3.0 mol L^{-1}) and NaOH (3.0 mol L^{-1}) (BARBUSIŃSKI; FILIPEK, 2001). Subsequently, the value of the concentration FeSO4.7H_2O was added and the solution was stirred for 1 minute and then the concentration of H_2O_2 was added. The values of the Fe^{+2} and H_2O_2 concentrations were established according to the experimental design. The beaker was then placed under a magnetic stirrer and taken to the inside of a wooden camera for the process to take place without light influence, during a reaction time of 30 minutes.

2.4 Experimental planning

A Central Composite Rotational Design (CCRD) containing four factorial points, four axial points, and three replications at the central point was used to determine the optimal conditions in the atrazine degradation by the Fenton process, assessing the effects of Fe^{+2} and H_2O_2 concentrations in the efficiency of the system.

The levels of factors were adopted based on information from the literature about herbicide contaminated effluents (ARELLANO *et al.*, 2013; DBIRA *et al.*, 2014; LOURENÇO, 2014; COLADES *et al.*, 2018) and the concentration ratio of 1:10 (Fe^{+2}/H_2O_2) for the Fenton process (KLAMERTH *et al.*, 2013). Thus, the levels of the factors adopted in the experimental design were the concentrations of H_2O_2 from 29.50 to 170.50 mgL^{-1} and Fe^{+2} from 2.95 to 17.05 mgL^{-1}.

The representative mathematical models were analyzed and the model with the highest determination index was proposed. To obtain the mathematical models representative of the process, the software Statistica® 12.0 was used (STATSOFT, 2017).

Based on the efficiency of the Fenton process related to atrazine degradation, influenced by the actions of factors, it was proposed a quadratic mathematical model adjusted from the experimental data, according to Equation 2, where b_0, b_i, b_{ii}, b_{ij} are the coefficients of the regression model and X_i and X_j are the independent variables in coded values.

$$\hat{y} = b_0 + \sum_{i=1}^{2} b_i X_i + \sum_{i=1}^{2} b_{ii} X_i^2 + \sum_{i,j=1}^{2} b_{ij} X_i X_j \quad \text{(Equation 2)}$$

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The significance of the mathematical model was assessed by the analysis of variance (ANOVA) at 95% confidence level. The graphical representation of the model forms a response surface graph, which presents the optimal operating region.

2.5 Analytical determinations

The pH of samples was determined by a digital pH meter and atrazine degradation analysis was carried out by a Shimadzu® Prominence high-performance liquid chromatography (HPLC). From an atrazine analytical standard (Sigma-Aldrich, 99.9%), a calibration curve was obtained by interpolating the data obtained from the stock solution of 50.00 mgL^{-1} of the herbicide in methanol in the range of atrazine concentration of 0.02 to 30.00 $mgL^{-1.}$ Nine concentration values were used to construct the calibration curve, with the measurements conducted in triplicate.

The operational conditions, employed at the HPLC for the atrazine analysis were: column C-18 (4.6 mm × 150 mm × 5 µm), acetonitrile/water mobile phase (50:50, v/v), UV chromatographic detection at 230 nm, mobile phase flux of 1 $mLmin^{-1}$, oven temperature of 35 °C, sample injection volume of 20 µL and analysis time of 6 minutes.

The concentrations of residual H_2O_2 were determined by the spectrophotometric method in absorbance based on the formation of the peroxovanadium cation after reaction with ammonium metavanadate in an acid medium. The concentration of residual H_2O_2 in the aliquot of each process was determined from a calibration curve. An aliquot of 2.00 mL of sample was added to 2.00 mL of ammonium metavanadate and absorbance readings were performed at 450 nm in a spectrophotometer (HACH, DR/2010), immediately after the aliquot removal from the reactor.

The total ferrous cations were determined with air/acetylene flame by atomic absorption spectrometry (Shimadzu AA 3600), with flame atomization. The total concentration was determined from an equation obtained in the calibration curve with a ferrous cation standard of 1000 mg L^{-1}. The following conditions were used: 248.3 nm wavelength, 0.2 nm spectral crack, 12 mA hollow cathode lamp current, 2.2 L min^{-1} acetylene and 15.0 L min^{-1} air.

3. RESULTS AND DISCUSSION

The results obtained after the application of the CCRD as a function of atrazine degradation in the treatment time of 30 minutes are shown in Table 1.

Table 1. Results of the atrazine degradation efficiency.

	Real /coded values		
Test	Fe^{2+}(mgL^{-1})	H_2O_2 (mg L^{-1})	Atrazine degradation (%)
1	5.00 (−1)	50.00 (-1)	81.35 ± 0.28
2	15.00 (1)	50.00 (-1)	88.89 ± 0.01
3	5.00 (-1)	150.00 (1)	49.90 ± 0.46
4	15.00 (1)	150.00 (1)	81.37 ± 0.05
5	2.95 (-1.41)	100.00 (0)	57.92 ± 2.80

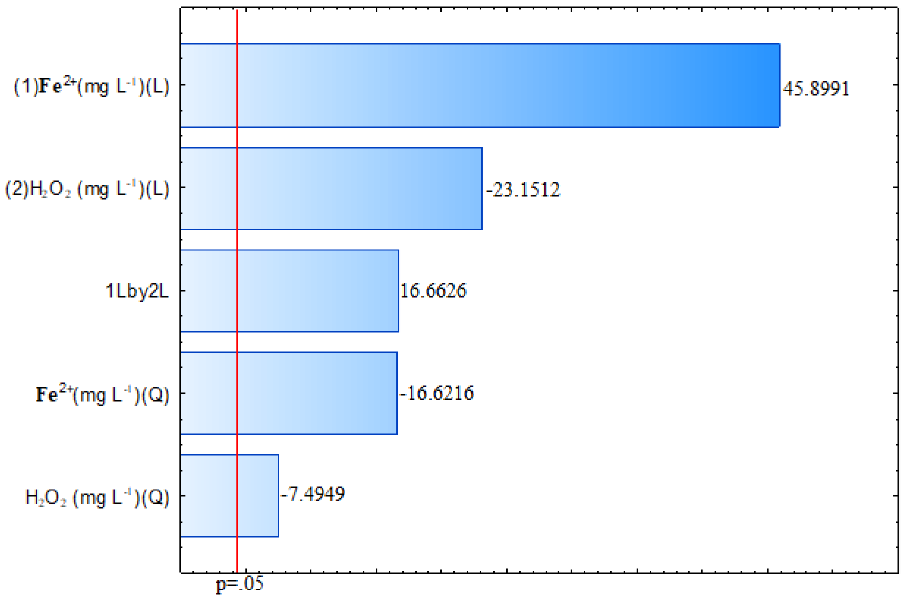
6	17.05 (1.41)	100.00 (0)	96.27 ± 3.58
7	10.00 (0)	29.50 (−1.41)	85.43 ± 0.17
8	10.00 (0)	170.50 (1.41)	79.77 ± 1.27
9	10.00 (0)	100.00 (0)	85.21 ± 0.14
10	10.00 (0)	100.00 (0)	85.38 ± 0.69
11	10.00 (0)	100.00 (0)	84.06 ± 0.78

The tests provided between 49.90 and 96.27% of atrazine degradation. The results suggest that the best efficiency in the process is achieved with values at higher concentrations of Fe^{2+}, whose test (6) using 17.05 mgL^{-1} of Fe^{2+} and 100.00 mgL^{-1} of H_2O_2 presented 96.27% atrazine degradation. The lowest degradations occurred in tests 3 and 5, when the lowest concentrations of Fe^{2+} were added. These results are in accordance with those found by Khandarkhaeva *et al.* (2017), who observed that after 30 minutes of treatment atrazine was no longer detected.

The central points (tests 9, 10, and 11) presented similar values, evidencing a low experimental error. From the results, it can be predicted that the iron cation concentration is the limiting factor in the Fenton process since it becomes responsible for catalyzing H_2O_2 decomposition, necessary for the generation of •OH. The ferrous cation concentration in the reaction is related to the process acceleration.

The Figure 1 shows the Pareto diagram with the significance level of factors by the t-test. The quadratic effect demonstrates a maximum or minimum point and, when negative, it indicates optimal conditions.

Figure 1. Pareto diagram of the experimental design in the atrazine degradation.



Source: the authors (2021)

All the factors in linear and quadratic terms showed a significant effect ($p<0.05$), indicating

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that factors have a significant influence on atrazine degradation ($R^2 = 0.90$).

Based on the efficiency of the Fenton process related to atrazine degradation and influenced by the actions of factors (H_2O_2 and Fe^{2+} concentrations), a mathematical model was proposed from the experimental data, being obtained Equation 3. The coefficients were estimated by multiple linear regression analysis using the least square method. This method is a mathematical optimization technique used to search for the best fit of the dataset by minimizing the sum of the squares of the differences between estimated and observed values.

$$\text{Atrazine degradation (\%)} = 84.90 + 11.67q_1 - 5.04q_1^2 - 5.88q_2 - 2.27q_2^2 + 5.98q_1q_2 \quad \text{(Equation 3).}$$

where, q_1= encoded value of the Fe^{2+} concentration (mgL^{-1}), $q_{2=}$ encoded value of the H_2O_2 concentration (mgL^{-1}).

The analysis of variance of the model predicted in the Fenton process was performed for validating the proposed model for atrazine degradation with 95% confidence level ($p < 5\%$), as shown in Table 2.

Table 2. Summary of ANOVA at 95% confidence level ($p < 5\%$).

Parameter	Source of variation	Sum of squares	Degree of freedom	Mean square	F Cal.	F Tab.
Atrazine degradation	Regression	1652.24	5	330.45	8.74	1.00
	Residual	189.04	5	37.81		
	Total	1841.28	10			

The results obtained by the analysis of variance for atrazine degradation at a 95% confidence interval, with the ratio between F_{cal}/F_{tab} 8.74, demonstrate that the model is significant. Thus, the adopted CCRD statistical model was validated and confirmed by the determination coefficient ($R^2 = 0.90$). In this context, we may infer that the mathematical model provided a good fit to the experimental data.

The response surface graph shown in Figure 2 was found from Equation 3. The best efficiencies of atrazine degradation occurred when higher concentrations of Fe^{2+} (between 10.00 and 17.05 mgL^{-1}) were added, considered as a catalyst in the Fenton process. The efficiency of degradation is lost with the increase in H_2O_2 concentration.

Figure 2. Response surface for atrazine degradation.

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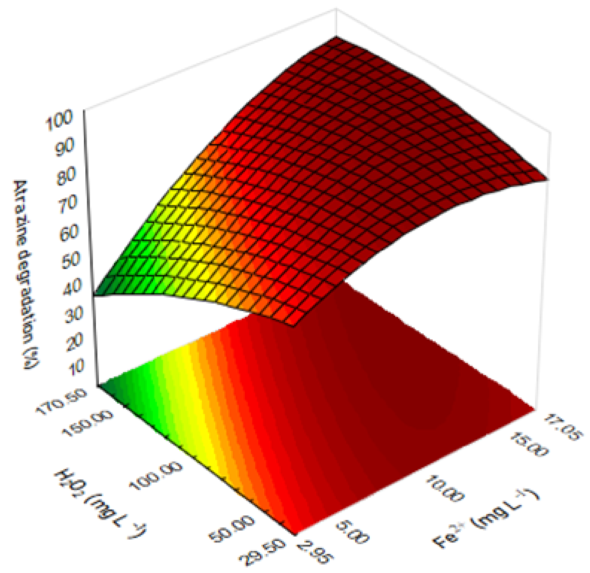
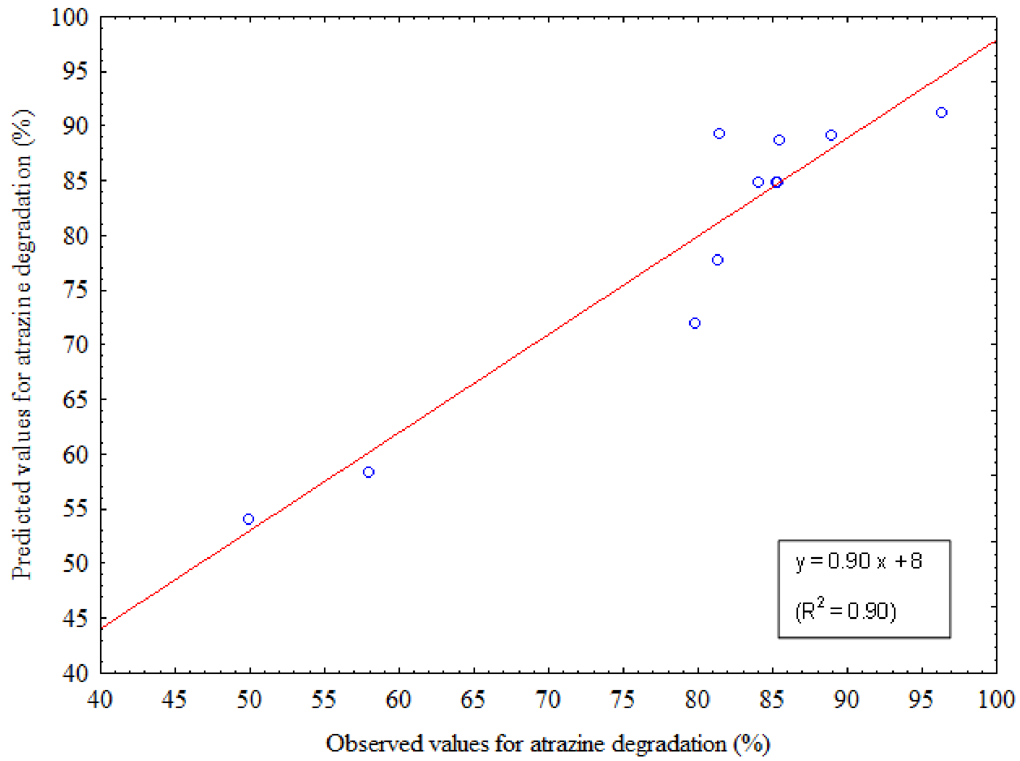


Source: the authors (2021)

The Figure 3 shows the relationship between predicted and observed values for atrazine degradation.

Figure 3. Predicted values (y) as a function of observed values (x) for atrazine degradation.



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Source: the authors (2021)

The analysis of expected and observed values for atrazine degradation shown in Figure 3 allows observing that the experimental points are well adjusted and close to normality.

The good fit of the proposed model for the experimental data was confirmed by the points of atrazine degradation approximation (simulated atrazine degradation versus observed atrazine degradation) along the straight line. This behavior represents one perfect fit and indicates the date normality, considering that the differences between the observed and predicted values were small.

The profiles for the predicted and performed values and desirability were investigated for the optimization of the Fenton process, corroborating with the information shown in Figure 3. In this sense, the predicted desirability was 92.04%, being optimized by the axial point 1.41 of the Fe^{2+} concentration and the value between the central point and the axial point 1.41 for the H_2O_2 concentration. Thus, the optimal conditions for atrazine degradation by the Fenton process corresponded to 17.05 mgL^{-1} for Fe^{2+} and 128.00 mgL^{-1} for H_2O_2.

In addition, when concentrations higher than 128.00 mgL^{-1} of H_2O_2 are used, degradation efficiency is lost, similarly to the results met by Abdessalem *et al.* (2010).

To assess the optimal condition found by the proposed model, triplicate tests for atrazine degradation were performed by the Fenton process under the following operating conditions: 17.05 mgL^{-1} of Fe^{2+}, 128.00 mg L^{-1} of H_2O_2, pH of 3.0 and treatment time of 30 minutes.

The predicted value of the model optimization was expected to be 92.04% efficiency of atrazine degradation and the result found experimentally, according to the optimal condition, was 91.00%, with a reaction time of 30 minutes by the Fenton process. This provides a 1.13% error between the predicted and the experimental value, confirming the good reproducibility of degradation in the process and proving the presented validation.

3.1. Determination of the consumption of H_2O_2 and total ferrous cations

The consumptions of H_2O_2 and total iron were analyzed at the end of the degradation in the treatment time of 30 minutes. We added 128.00 mgL^{-1} of H_2O_2 to the treatment of atrazine degradation by the Fenton process, which presented consumption at the end of the process of 15.77% in relation to the initial concentration. Incomplete consumption was observed at the end of the reaction, being necessary a longer treatment time and/or a higher initial pollutant concentration.

An amount of 17.05 mgL^{-1} of ferrous cations was added to the treatment, which presented consumption at the end of the process of 12.16% relatively to the initial concentration. This result was close to that found by Lourenço (2014), investigating the treatment of wastewater contaminated by atrazine (with 10% ferrous cations consumption) in order to clarify that the residual concentration can be attributed to the insolubilization of ferrous ions.

4. FINAL CONSIDERATIONS

It was possible to analyze the interaction between the studied factors and determine the optimal operating conditions of the process to achieve the best efficiency of the Fenton treatment for atrazine degradation. Therefore, the treatment was performed with 128 mg L^{-1} of H_2O_2 and 17.05 mgL^{-1} of Fe^{2+} in an acidic medium with a pH of 3.0, resulting in 91.00% atrazine

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degradation. This response expresses the high efficiency of the process with 30 minutes of treatment. In this way, Fenton process showed to be effective in atrazine degradation and can be considered a technically feasible alternative and used as a polishing treatment.

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