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Textile effluent treatment by reductive process using commercial steel wool followed by oxidative process

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Abstract: Textile industries stand out as one of the main polluters of water resources, generating large amounts of liquid effluents with variable composition and intense coloration. The objective of this work is the integration of the reductive process using commercial steel wool, combined with oxidative processes, in the treatment of textile effluent. The effect of the variables of the reductive process were studied using a 3^2 factorial design. After 30 minutes, the reductive process allowed a reduction of 68% COD, 46% TOC, 62% true color and 72% of total phenols, but showed an increase in color apparent and turbidity, due to the iron species formed by the oxidation of steel wool during the process. With the combined process using sunlight, the reduction was 73% COD, 50% TOC, 97% phenols, 93% true color and 48% apparent color. With artificial light, the reduction was 94% COD, 63% TOC, 95% phenols, 98% true color and 65% apparent color. The evaluation of the acute toxicity against *Daphnia magna* indicated that after the proposed treatments, the effluent did not present toxicity or the toxicity was reduced. It is concluded that the combined process can be considered an efficient alternative for the treatment of textile effluent.

Key words: combined process, degradation, industrial effluent, photo-Fenton.

INTRODUCTION

The textile industry has a prominent role, according to Global Industry Analysts (2020), the forecast is to reach more than US$ 3 billion in the global market by the year of 2025, however, it represents one of the industries with the greatest water resources polluting potential. In the different stages of production, large volumes of water are used (approximately 0.2 m^3kg^{-1} of tissue produced) (Raj et al. 2021, Dasgupta et al. 2015, Vajnhandl & Valvh 2014), and on average 0.2 to 0.35 m^3 of textile effluents per kg of finished product are generated (Raj et al. 2021). This effluent is characterized by its complex and variable composition and intense coloring, as it contains several synthetic chemical products, such as humectants, dispersants and, mainly, dyes (Khan et al. 2019). It is estimated that approximately 30% of the dyes used by the textile industry are lost in the final effluent due to non-fixation to the fibers during the dyeing process (Dissanayake et al. 2021).

There are several classes of dyes used by textile industries, however, reactive azo dyes are the most used, representing approximately 60-70% of all dyes used (He et al. 2012) and are currently one of the biggest pollutants worldwide (Almaguer et al. 2018). They are characterized by containing, as a chromophore group, one or more azo groups (-N=N-) linked to aromatic rings in their structure (Chen et al. 2021, Fu et al. 2010). These compounds are responsible for causing a change in the color of the water, which inhibits the penetration of sunlight, and consequently, reduces the photosynthetic action, harming the oxygenation of the water body. Additionally, when subjected to natural degradation, they produce aromatic amines as by-products, formed from the cleavage of the azo bond (Jayapal et al. 2018). These substances are toxic, and have a proven carcinogenic and mutagenic effect (Kurade et al. 2015, Mathur & Bhatnagar 2007).

Textile industries generally adopt physicochemical systems followed by biological processes for the treatment of effluents, but these have only helped in the partial treatment of the effluent (Raj et al. 2021, Turgay et al. 2011). Therefore, several technologies have been developed and studied in order to promote the total degradation of these compounds, among which chemical treatment processes stand out, which are capable of completely degrading several contaminating species due to chemical reactions, such as the Reductive Process and the Advanced Oxidation Processes (AOPs).

The reductive process is a chemical process, based on the use of metallic iron (Fe^0), a relatively strong reducing agent against several substances (E^0 Fe^0/Fe^{2+} 0.44 V) (Stefaniuk et al. 2016, Chatterjee et al. 2010). One of the advantages presented by the process is the possibility of using simple and low-cost materials as a source of Fe^0, for example, steel wool, which has shown high efficiency in dye degradation (Ren et al. 2018). In the degradation process, Fe^0 is oxidized to ferrous ions (Fe^{2+}), releasing two electrons (Equation 1), which can quickly combine with the organic compounds present in the medium, resulting in its reduction. Thus, when receiving electrons, contaminating species are transformed into non-toxic or less toxic species (Fu et al. 2014).

$$Fe^0_{(s)} \rightarrow Fe^{2+} + 2e^- \qquad (1)$$

In the presence of water, in addition to reduction reactions due to oxidation of Fe^0 to Fe^{2+}, two other reductive pathways can be processed. One is a function of the oxidation of ferrous ions to ferric ions (Fe^{3+}), and the other is mediated by H2 that arises from corrosion of iron by water in an anoxide environment (Santos-Juanez et al. 2019).

The use of the reductive process in the degradation of dyes is able to promote high discoloration of these molecules, through the rapid reduction of the azo bond. However, it cannot reach the total mineralization of these compounds, and aromatic amines can be formed as final products (Dutta et al. 2016). Despite this inconvenience, the Fe^{2+} and Fe^{3+} ions, generated during this process, can catalyze Fenton and photo-Fenton type oxidative processes. These processes are capable of oxidizing the reduced substrates, via hydroxyl radical (·OH), an agent with high oxidizing power (E^o=2.8 V) and low selectivity.

The Fenton-type oxidative process is characterized by the reaction between Fe^{2+} and H_2O_2 to generate ·OH (Equation 2) (García-Leiva et al. 2019, Weng et al. 2013). The performance of this process can be superior when assisted by an ultraviolet (UV) or visible (Vis) radiation source, thus characterizing the photo-Fenton process (Equation 3). With the presence of radiation, the photoreduction of Fe^{3+} to Fe^{2+} ions occur, which react with H_2O_2 from the medium and consequently increase the number of hydroxyl radicals formed (Equations 2 and 3) (García-Leiva et al. 2019).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\cdot}OH \qquad (2)$$

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + {}^{\cdot}OH + H^+ \qquad (3)$$

Therefore, by combining these processes, a viable treatment alternative is obtained that allows for considerable levels of mineralization to be achieved.

In this context, this study aims to evaluate the potential of the reductive process using commercial steel wool as a source of Fe0, combined with the photo-Fenton oxidative process, in the treatment of textile effluent.

MATERIALS AND METHODS

The research was carried out at the Environmental Chemistry Laboratory and at the Environmental Sanitation and Water Quality Laboratory, of the Department of Environmental Engineering of the Universidade Estadual do Centro Oeste, Campus de Irati, Parana state, Southern of Brazil. In Figure 1, there is a flowchart with the activities developed.

Reagents

The main chemical reagents used were: hydrochloric acid; sulfuric acid; ammonium metavanadate; sodium hydroxide; 25% v/v aqueous hydrogen peroxide solution (all analytical grade) and bovine catalase (Sigma-Aldrich). As a source of metallic iron, carbon steel fibers were used, commercially distributed as steel wool.

Effluent

The textile effluent used in this work was provided by a textile industry located in the region of Curitiba – Parana - PR The company provides dyeing and finishing services, in addition to having its own laboratory for the development of new dye colors. Currently, according to company data, it has an average production of 200 – 300 tons of finished fabric per month. The industry treats the effluents generated in the dyeing and finishing processes in its own wastewater treatment plant (WTP). The system consists of the stages of sieving, homogenization tank, chemical coagulation and flocculation, decanter, aerobic lagoon and Parshall chute. In Figure 2, there is a representative flowchart of the station, as well as the collection point.

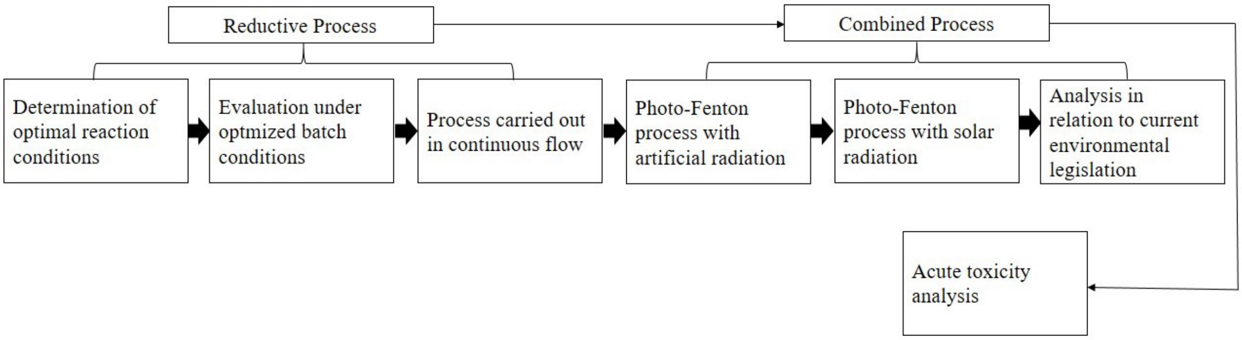

Figure 1. Flowchart of activities developed in the research.

Experimental apparatus

Reductive process carried out in continuous flow

The reductive process in continuous flow was applied in a system consisting of a reservoir for conditioning the effluent to be treated and a column filled with steel wool, built with PVC tubes. The samples were conducted from the reservoir to the column from a pipeline controlled by a register, used to keep the inlet flow constant, and an outlet register located below the column. The photo of the system and its representative schematic is shown in Figure 3.

Photo-Fenton process with artificial light

The photo-Fenton oxidative process assisted by artificial radiation was carried out in a benchtop photochemical reactor with a capacity of 300 mL, magnetic stirring and a cooling system.

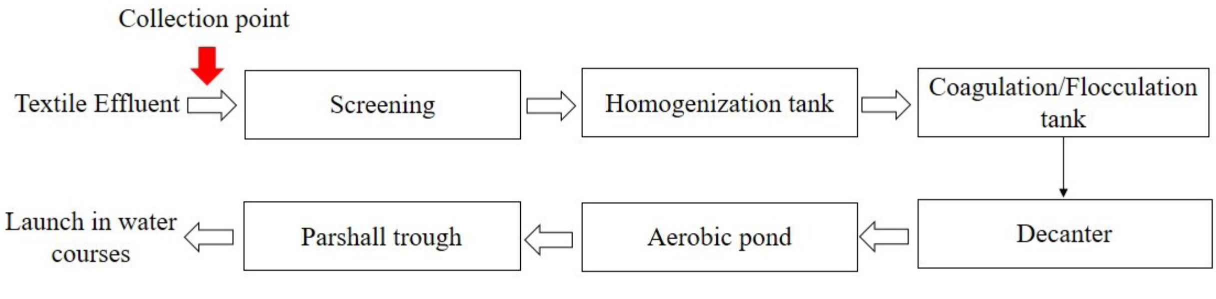

Figure 2. Representative flowchart of the textile industry WTP.

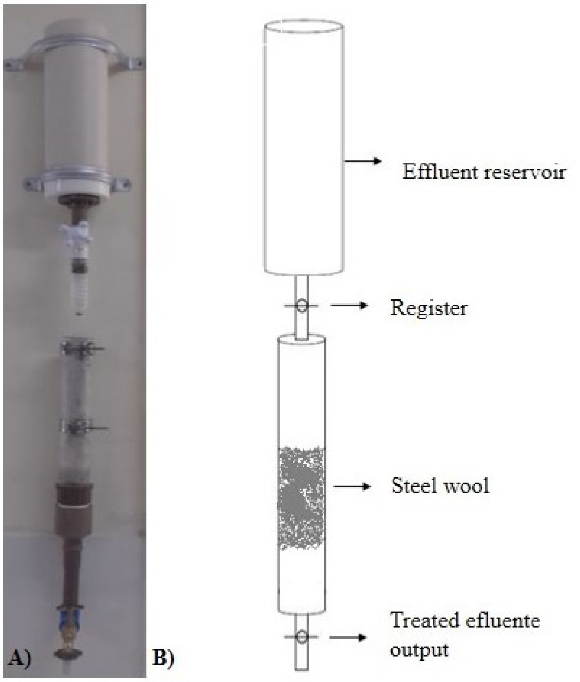

Figure 3. (a) Photo of the system used to apply the column reductive process and (b) Representative diagram.

The ultraviolet radiation was provided by a 125 W mercury vapor lamp, which was inserted into the samples surrounded by a quartz bulb, in order to allow the full use of ultraviolet radiation, that is, UV-wavelengths A (315 - 400 nm), UV-B (280 - 315 nm) and UV-C (200 - 800 nm). Under these conditions, the mean radiation intensity was determined with a Vilber Lourmat®-VLX 3W radiometer, with a 254 nm sensor. The representative schematic of the reactor is shown in Figure 4.

Photo-Fenton process assisted with sunlight

The photo-Fenton process assisted by solar radiation was carried out in a 250 mL beaker, equipped with a magnetic stirring system and aluminum-coated parabolic solar collector (Figure 5). The experiments were carried out in the municipality of Irati (Latitude: 25° 28’ 02” S and Longitude: 50º 39’ 04” W), on clear days and with minimal presence of clouds, between 11:00 am and 4:00 pm.

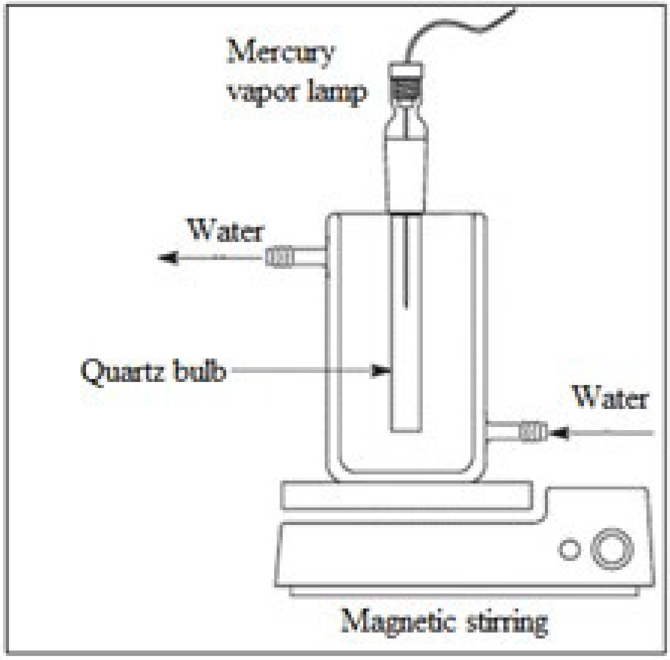

Figure 4. Representative scheme of the photochemical reactor used in the photo-Fenton process with artificial light.

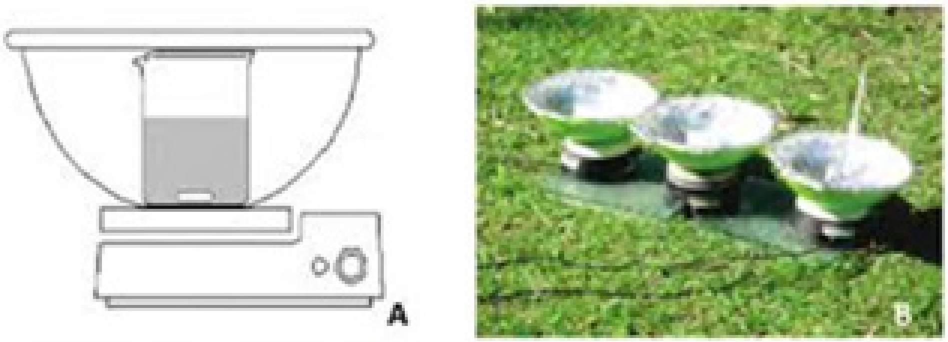

Figure 5. Representative scheme (a) and Photo (b) of the photochemical reactor with sunlight.

Experimental procedure

Preliminary treatment of steel wool

In order to remove oxides and hydroxides that may be deposited on the surface of the steel wool used in the reductive degradation and make it more homogeneous, this was previously immersed in 250 mL of an aqueous solution of sulfuric acid (H_2SO_4) 1% (v/ v) for 15 minutes, and then washed with approximately 500 mL of distilled water.

Optimization of the reductive process

To ensure greater efficiency of the reductive process in the treatment of textile effluent, the optimization of operational variables of relevance to the process (pH and steel wool weight) was carried out. For this, a complete factorial design of experiments was used, in which the variables are evaluated simultaneously.

Each variable was studied at three levels, resulting in 9 experiments, which were performed in triplicate and in random order. The levels of the variables were chosen based on previous work using commercial steel wool in the reductive treatment of textile effluents and dye degradation (Souza & Peralta-Zamora 2006), and the decolorization efficiency in 30 minutes was chosen as the answer. The completely randomized design is shown in Table I.

Initially, a spectral scan of the effluent between 200-800 nm was performed, before and after 30 minutes of reductive process in each condition tested. Then, to calculate the discoloration, the highest absorbance value identified in this same region was used, which was 600 nm. The equation used to calculate discoloration is shown in Equation 4.

Table I. **Completely randomized design used in factorial planning.**

Variables	**Level (-)**	**Level (0)**	**Level (+)**
pH	3	5	7
Mass (g)	6	8	10

Experiment	**Variables**	
	pH	**Mass (g)**
1	3	6
2	3	10
3	3	8
4	7	6
5	7	10
6	7	8
7	5	6
8	5	10
9	5	8

SOURCE: The author (2022).

$$\text{Discoloration (\%)} = \left[1 - \left(\frac{Abs_f}{Abs_0}\right)\right] \times 100\% \quad (4)$$

Where:
Abs_f: absorbance value after 30 minutes of reductive process;
Abs_0: absorbance value before the reductive process.

It is noteworthy that all experiments were carried out in batches, using 250 mL of sample.

Reductive process carried out in continuous flow

In this test, a hydraulic detention time (HDT) of 30 minutes was used and a volume of 500 mL of textile effluent was used to carry out these tests. Thus, the determined inlet flow was calculated according to Equation 5:

$$Qe = \frac{V}{HDT} \quad (5)$$

Where Qe is Inlet flow rate adopted in the experiments (mL min-1), V represents the volume of sample used (mL) and HDT corresponds to the best reaction time determined in batch tests (min.).

To establish the inlet flow in the record above the column, successive previous tests were carried out, with the aid of a 1L graduated cylinder and a stopwatch (volume by time), using water. An outflow was not established, therefore, the register below the column was kept open during all tests carried out in continuous flow. The treated textile effluent was collected for analysis of physical-chemical parameters apparent color, true color, turbidity, COD, TOC, total phenols, after passing the entire volume of effluent through the column.

Combined Process

The photo-Fenton oxidative process was carried out using 250 of the effluent initially treated by a reductive process carried out in continuous flow. Furthermore, at the end of the oxidative processes and analysis of the parameters COD, TOC, concentration of total phenols, apparent and true color, turbidity, the pH of the samples was adjusted to neutrality (between 6 to 9), using NaOH.

Subsequently, the oxidative processes were carried out with 100 mgL^{-1} of H_2O_2, and thus, aliquots were removed at intervals of 15, 30, 45, 60, 90 and 120 minutes for UV-Vis spectral monitoring and residual H_2O_2 concentration. Area data in the 200 to 350 nm wavelength region of the spectrum were used for the kinetic study of the combined processes.

Analytical control

The physicochemical characterization of the effluent, as well as the analyzes to assess the efficiency of the proposed treatment systems, were carried out according to the methods specified in the Standard Methods for the Examination of Water and Wastewater (APHA 2017), listed in Table II.

In addition to the analyzes presented in Table II, the spectrophotometric profile of the samples was performed in a HACH model 6000 UV-Vis spectrophotometer, monitoring the region between 200 and 800 nm.

To quantify the residual H_2O_2 concentration after the photo-Fenton process, a methodology adapted from procedures described in the literature was used (Oliveira et al. 2001). The Total Organic Carbon (TOC) was also determined in a TOC analyzer, brand SHIMADZDU model TOC-L CSH, at the

Table II. Physical-chemical characterization parameters, analytical methods.

Parameter	Analytical method	APHA reference (2017)
pH	Potentiometric	4500-H^+ B
Apparent and True Color (uC)	Spectrophotometric	2120 C
Total and soluble COD (mgL^{-1})	Closed/colorimetric reflux	5220 D ou B
Chloride (mgL^{-1})	Titrimetric	4500 – Cl^- B
Conductivity ($mscm^{-1}$)	Potentiometric	2510 B
Total solids (mgL^{-1})	Gravimetric	2540
Total Suspended Solids (mgL^{-1})	Gravimetric	2540 D
Total Dissolved Solids (mgL^{-1})	Gravimetric	2540 C
Turbidity (uT)	Nephelometric	2130 B
Phenols (mgL^{-1})	Spectrophotometric	5550 B
Iron (mgL^{-1})	Colorimetric	3500 D

Laboratory of Applied Chemistry at the Universidade Estadual de Ponta Grossa (UEPG), Ponta Grossa, Parana state, Southern of Brazil.

Acute toxicity assessment

The acute toxicity tests were carried out at the Environmental Toxicology Laboratory located in the Department of Environmental Engineering of the Universidade Estadual do Centro Oeste, Campus de Irati, Parana state, Southern of Brazil, using the microcrutaceous Daphnia magna as test organisms.

The cultivation of Daphnia magna and toxicity tests were carried out in accordance with technical standard NBR 12.713 (ABNT 2009). The method consisted of exposing neonates aged between 2 h and 26 h in sample dilutions, for a period of 48 h.

The acute toxicity of samples of raw effluent, effluent treated by a reductive process and effluent treated by combined processes (photo-Fenton with artificial light and sunlight) was evaluated. For samples obtained after photo-Fenton treatment to decompose the residual H_2O_2 concentration, bovine catalase was added. For every 250 mL of sample containing 10 mg L^{-1} of residual H_2O_2, 1 drop of catalase (1% v/v) was added, leaving it to act for 10 minutes.

Prior to the tests, six dilutions were prepared (concentrations 3.1; 6.2; 12.5; 25; 50 and 100% (v/v)) of each sample, called test-solutions, and a control. In the control and as a diluent for preparing the test solutions, dilution water, also known as ISO medium, was used. In the tests, each test solution plus the control were divided into three containers (three replicates), containing approximately 30 mL each. In each container 10 test organisms were placed, totaling 30 organisms for each tested dilution plus the control. Then, the containers were covered with PVC film and taken to an incubator, where they were kept at a temperature of 20 to 22°C, without food. After 48 hours of exposure, immobile organisms were counted and recorded in each container.

From these results, the calculation of the median effective concentration of the sample that causes an effect on 50% of the organisms exposed to EC_{50} was performed. The test was considered valid if the percentage of immobile or dead organisms in the control was less than 10% (ABNT 2009). Values were also expressed in acute toxic units (Uta), which is directly related to the presented toxicity, and was calculated according to Equation (6).

$$Uta = 100/EC_{50} \tag{6}$$

Where Uta is Acute Toxic Unit and EC_{50} corresponds to median effective concentration of the sample that affects 50% of the population studied.

Statistical data analysis

In order to help interpret the data and increase the reliability of the results, different convenient statistical methodologies were used with the objective of some stages of the work. For this, the data were previously checked for normality, using the Shapiro-Wilk test. In addition, the significance level adopted for all statistical tests was 5% (p-value < 0.05), and all analyzes were performed using the free and open-source software R version 3.3.3.

In order to optimize the reductive process, to identify the main and interaction effects of the variables under study on the response, an Analysis of Variance (ANOVA) of the results was used, followed by the Tukey test, using the 'ExpDes.pt' package ' (Ferreira et al. 2014). In addition, the response surface graph was also generated, which indicates the optimal reaction condition, with the 'rsm' package (Lenth 2009).

To evaluate the performance of the reductive process, Student's t test was used for dependent samples for the parameters COD, phenols, true and apparent color, turbidity and TOC.

Comparison of the effluent quality before and after the application of the two options of combined processes (photo-Fenton process with artificial light or sunlight), using ANOVA followed by the Tukey test.

To calculate the EC_{50} (%) in acute toxicity tests, the 'drc' package was used (Ritz et al. 2016)

RESULTS AND DISCUSSION

Physical-chemical characterization of textile effluent

The results of the physical-chemical characterization of the textile effluent used in this study are presented in Table III.

According to the results of the physicochemical parameters selected for characterization, they manifest themselves in a high way: the color presented by the effluent, the amount of organic matter expressed in the form of COD and TOC and the concentration of total phenols, which are found above of the values established in the CONAMA legislation nº 430/2011 and 357/2005, and in Annex 7 of the CEMA resolution 070/2009 (Brasil 2005, 2011, Paraná 2009), and for that reason they were selected to evaluate the efficiency of the processes of treatment proposed in the present work.

According to the other parameters evaluated, the effluent also presents the basic pH as a characteristic, which is in agreement with most studies found in the literature. This is mainly due to the large number of alkaline solutions used in the fabric preparation step, and also in the dyeing phase, for fixing the dyes to the fabric. There is also a high concentration of chloride, also very common in textile effluents, since in the preparation step chlorinated compounds are also added

Table III. Physical-chemical characterization of textile effluent.

Parameter	Textile Effluent
Chemical Oxygen Demand (mg L^{-1})	335,83 ± 23,63
Total Organic Carbon (mg L^{-1})	297,60 ± 14,90
pH	7,1 ± 0,08
Turbidity (uT)	31,17 ± 3,50
Apparent Color (uC)	1825 ± 91,91
True color (uC)	1490 ± 14,14
Total Phenols (mg L^{-1})	12,05 ± 1,09
Chloride (mg L^{-1})	635,98 ± 138,00
Total Iron (mg L^{-1})	N.D
Total solids (mg L^{-1})	1146 ± 216,03
Total Dissolved Solids (TDS)	892 ± 110,12
Total Suspended Solids (TSS)	130 ± 114,08

Caption: N.D – Not detected.

for the whitening of the fabric, and in the dyeing step, a high amount of sodium chloride is generally used for assist in fixing dyes to tissues (Pizato 2017).

In relation to solids, there is a low concentration of total suspended solids, and a high concentration of total dissolved solids, which represent approximately 80% of total solids. The large presence of total dissolved solids is usually due to the large presence of dyes that were not fixed to the fibers and also to the presence of salts.

The concentration of solids found can be correlated with the results of the apparent and true color parameters, which showed little difference between the values, demonstrating that most of the effluent color is attributed to the presence of dissolved solids and not suspended solids that also are responsible for the turbidity of the effluent.

Furthermore, no concentration of total dissolved iron was found in the effluent, and visually, the collected effluent showed a dark blue color, which is in line with the peak of maximum absorption in the spectrum in the visible region (350-700 nm), the which corresponds to 600 nm. The effluent scanning UV-Vis spectrum is shown in Figure 6.

In the UV-Vis spectrum of the effluent, there is an intense signal in the UV region (200-350 nm), indicating high organic charge and a signal in the visible region (350-800 nm), indicating the color of the effluent, the which presents as the most intense signal at approximately 600 nm, wavelength characteristic of the blue color.

Optimization of the reductive process applied to the effluent

The optimization of the variables pH and steel wool mass was performed, using as a response the reduction of the spectral peak at 600 nm after 30 minutes. The factorial design matrix 3^2, containing the mean values of discoloration percentage and their respective standard deviations obtained, are presented in Table IV.

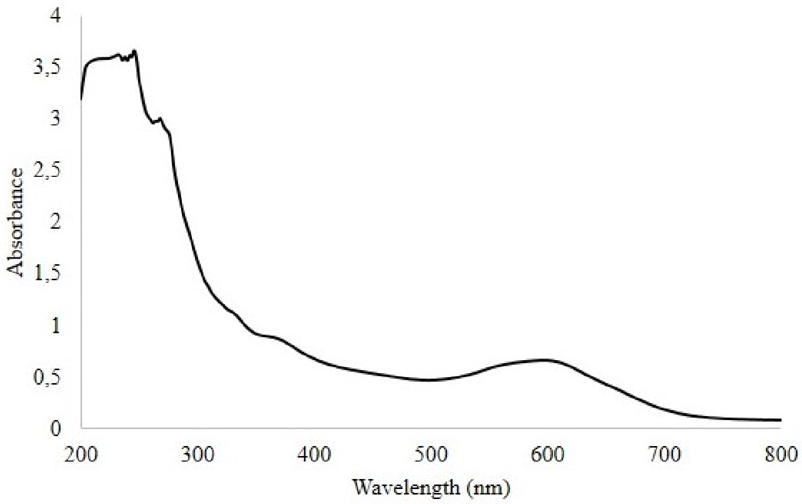

Figure 6. UV-Vis spectrum of textile effluent.

Table IV. Factorial design 3^2 used to verify the effect of pH and steel wool mass on effluent discoloration by the reductive process after 30 minutes.

Variables	Level (-)	Level (0)	Level (+)
pH	3	5	7
Mass (g)	6	8	10
Experiment	**Variables**		**Discoloration (%)**
	pH	**Mass (g)**	
1	-	-	36,17 ± 6,21
2	-	+	49,53 ± 7,13
3	-	0	39,24 ± 5,94
4	+	-	37,83 ± 6,88
5	+	+	40,07 ± 6,47
6	+	0	47,16 ± 11,50
7	0	-	22,64 ± 6,53
8	0	+	33,98 ± 12,88
9	0	0	33,33 ± 2,56

The data presented in Table IV, show that the conditions used in experiment 2 (pH 3 and 10 g of steel wool) presented the highest percentage of effluent discoloration by the reductive process (49%). Satisfactory and very similar results, with 47% of average discoloration, were also achieved with the conditions employed in experiment 6 (pH 7 and 8 g of steel wool).

The ANOVA result of the results obtained is shown in Table V

The results revealed that only the pH variable significantly interfered in the percentage of discoloration ($p < 0.05$). The interaction between the pH and mass variables was also not significant, confirming that they act independently in the discoloration of the effluent by the reductive process. The non-significant interference of the mass on the response suggests that steel wool is a good source of metallic iron to be applied in the reductive process for the treatment of textile effluent used in full scale, because regardless of the amount used, it is continuously oxidized to Fe^{2+} and Fe^{3+}, reducing dyes present in its composition and promoting its discoloration.

Tukey's Test, used only to analyze the variable pH that showed significance on the response, showed that at pH 3 the highest average decolorization efficiency was obtained, although it did not differ statistically from the process applied with the natural pH of the effluent (pH 7). The effluents generated in the textile industry are generally basic, with a pH around 7, so the possibility of using the effluent at its natural pH makes it possible to spend less on reagents such as acidifying and neutralizing to adjust the pH, confirming the wide range of pH that can be applied in this process.

The response surface graph shown in Figure 7 confirms the results presented by the Tukey Test, as it presented linear variation along the representation of the discoloration results obtained.

Therefore, it is concluded that, taking into account the results of the factorial design, the conditions used in experiment 6 (pH 7 and 8 g of steel wool) were the best to obtain the effluent discoloration, and thus, were used in subsequent experiments to evaluate the effluent treatment by the reductive process.

Application of the reductive process carried out in continuous flow

The tests were carried out with 500 mL of the effluent at its natural pH and with the column filled with 8 g of steel wool. The inlet flow was 16.67 $mLmin^{-1}$, as the hydraulic detention time previously established was 30 minutes.

Table VI shows the values of the parameters evaluated for the effluent before and after reductive treatment, of the sample collected after passing the entire volume of effluent to be treated through the column.

Taking into account the results, it is possible to note that the reductive process performed allowed significant removal of COD, TOC, true color and phenols ($p < 0.05$), and an increase in turbidity values (significant $p < 0.05$) and apparent color (not significant $p > 0.05$) of the effluent.

Table V. Anova results applied to the 3^2 factorial planning of the reductive process.

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Squares	Calculated F	P-values
pH	2	793,6	396,80	4,4139	0,02755*
Mass	2	421,3	210,65	2,3432	0,12461
pH x Mass	4	242,7	60,68	0,6749	0,61801
Residual	18	1618,2	89,90	-	-
Total	26	3075,8	-	-	-

CAPTION - * significant at 5% probability by F test.

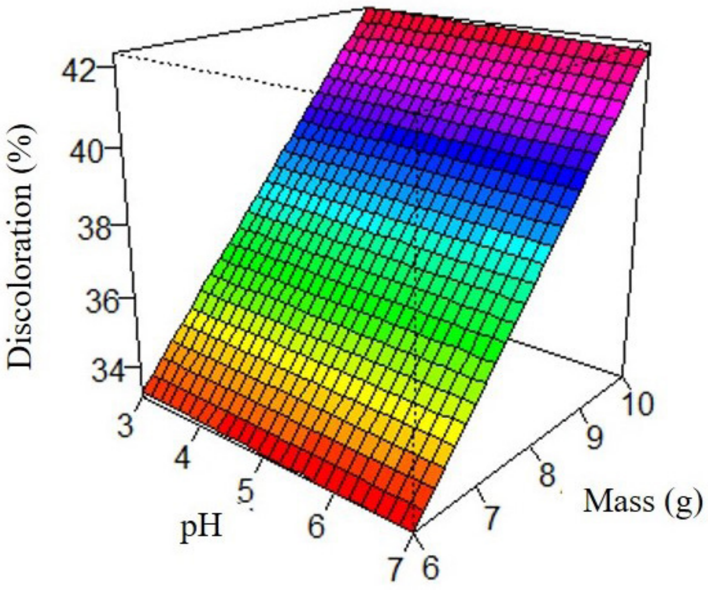

Figure 7. Response surface generated from the result of factorial planning for the reductive process applied in the discoloration of textile effluent.

Table VI. Percentage of reduction of the parameters evaluated for the textile eluent before and after the reductive treatment.

Parameter	Textile Effluent	Reductive Process	Removal (%)	T	p-value
COD (mgL^{-1})	335,83	113,75	68,62	9,65	0,0053*
TOC (mgL^{-1})	297,60	162,2	45,50	7,14	0,0095*
Phenols (mgL^{-1})	12,05	4,54	62,25	6,86	0,010*
True Color (uC)	1490	423,33	71,60	6,44	0,0127*
Apparent Color (uC)	1825	1935,33	-	0,74	0,2677
Turbidity (uT)	31,17	96,2	-	-3,84	0,0308*

CAPTION: * significant at 5% probability by Student's t test.

Regarding the concentration of phenols, the process did not allow for compliance with the release standards required by current legislation (0.05 mgL^{-1}), although it showed a significant removal (62.25%).

Relevant reduction was also observed for the true color parameter, obtaining a reduction of 71% from its initial value, which attests to the high potential of the reductive process carried out in a continuous system to remove the effluent color, also observed by other authors (Zanella et al. 2010, Souza & Peralta-Zamora 2006).

It is noteworthy that, after the reductive process, a total iron concentration of 15 mgL^{-1} (1.5 mgL^{-1} of Fe^{2+} and 12.5 mgL^{-1} of Fe^{3+}) was determined, a concentration compatible with the legislation and sufficient to catalyze photo-Fenton processes.

Souza (2006) studied the treatment of effluent generated in the dyeing and washing processes of a textile effluent by the reductive process with commercial steel wool in a continuous treatment system. The process took place under the following conditions: effluent pH equal to 3, reductive column filled with 10 g of steel wool (pretreated with a sulfuric acid solution) and column inlet flow of 6 $mLmin^{-1}$. As the main result, Souza (2006) obtained: 60% color removal, 20% reduction in COD, practically unchanged chloride concentration and 43.8 mgL^{-1} of dissolved iron at the end of the reductive treatment.

It is thus concluded that the reductive process using commercial steel wool as metallic iron source is a simple and viable alternative to be used as a pre-treatment of oxidative processes of the photo-Fenton type, or of biological processes, present in most textile industry effluent treatment plants. This is because, although it has provided significant removals of the parameters evaluated in the effluent, it is not yet compatible with current environmental legislation for discharge into water bodies, with the exception of the COD.

Reductive/Oxidative Combined Processes

Considering that at the end of the reductive process, soluble iron species are generated in a concentration compatible with that used in oxidative processes of the photo Fenton type, the combined process was explored. Thus, after 30 minutes of pre-treatment by a reductive process, the effluent was conducted to photo-Fenton type oxidative processes assisted by artificial light and sunlight. Before being submitted to these processes, the effluent pH, which after the reductive process was around 7.4, was adjusted to 3 (ideal pH condition of the photo-Fenton process) and H_2O_2 was added.

Photo-Fenton process with artificial radiation

Initially, the application of the photo-Fenton process with artificial radiation was evaluated, in reaction times of 30, 60, 90 and 120 minutes. The behavior of the spectral profile in the UV-Vis region of the effluent before, after the reductive process and after the photo-Fenton process with artificial radiation in the different reaction times is shown in Figure 8.

Analyzing the spectral profiles, it is possible to notice that after 30 minutes of the reductive process, the effluent color signal decreased considerably, represented by the absorbance values in the visible region (350 to 800 nm), which corroborates the results of reduction of true color shown

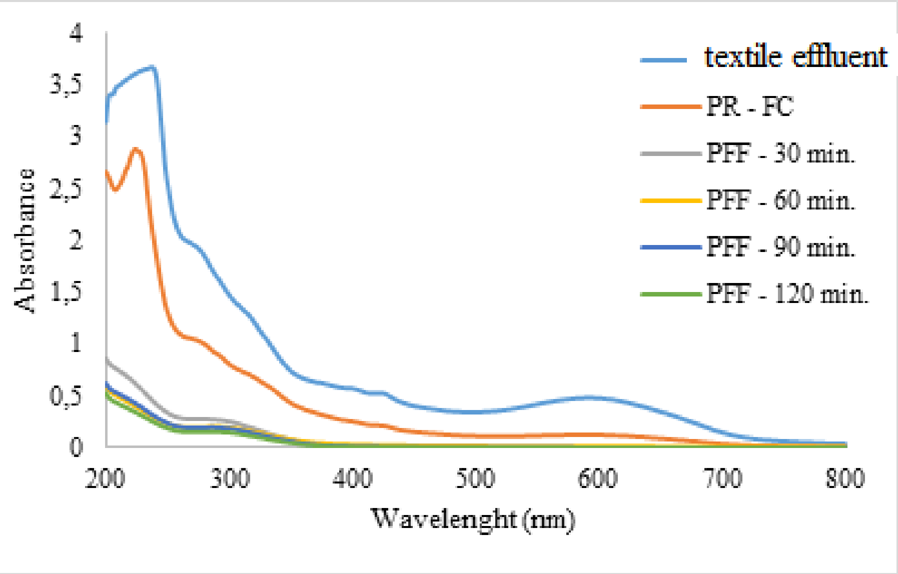

Figure 8. Monitoring of the spectral profile in the effluent treatment by the reductive process (30 min.) followed by the photo-Fenton process with artificial light.

above (71%). Furthermore, the process allows a significant change in the spectral signal of the characteristic region of the organic charge (200-350 nm), agreeing with the results of removal of TOC (43%), COD (68.62%) and total phenols (62.25%).

As for the photo-Fenton process with artificial radiation, it can be seen that up to 60 minutes of photo-Fenton treatment there was a continuous and significant reduction in the organic load and in the remaining color after the reductive process, however, from 60 to 120 the spectral signal remained virtually unchanged. Considering that the process can be applied in a treatment plant of a textile industry, this small reduction observed would not justify an increase in the treatment time, as the photo-Fenton process with artificial radiation requires energy, which would result in an expense larger for the application of this process on an industrial scale.

The consumption of H_2O_2 in this process was stabilized at 57% of the initial concentration in 60 minutes of reaction, which assumes that the stabilization of the process occurred in this reaction time, as observed by the spectrum. In this way, the time of 60 minutes was fixed for the analysis of the physical-chemical parameters, presented in Table VI.

Photo-Fenton process with solar radiation

Similar to tests conducted with artificial light, the effluent was treated with sunlight, after going through the reductive process. Studies with solar radiation were carried out between 11 am and 4 pm, on clear days with the minimum presence of clouds in the month of September. Under these conditions, mean UVA radiation intensities (300 to 400 nm) of 3.19 mWcm-2 were recorded.

The monitoring of the spectral profile in the UV-Vis region of the effluent, after the reductive process and after the photo-Fenton process with sunlight, at treatment times of 30, 60, 45 and 90 minutes, is shown in Figure 9.

Observing the results presented in Figure 9, it is possible to see that the photo-Fenton process with solar radiation after the reductive process presented a spectrophotometric behavior very similar to the process applied with artificial radiation. In just 30 minutes of treatment, the process promoted

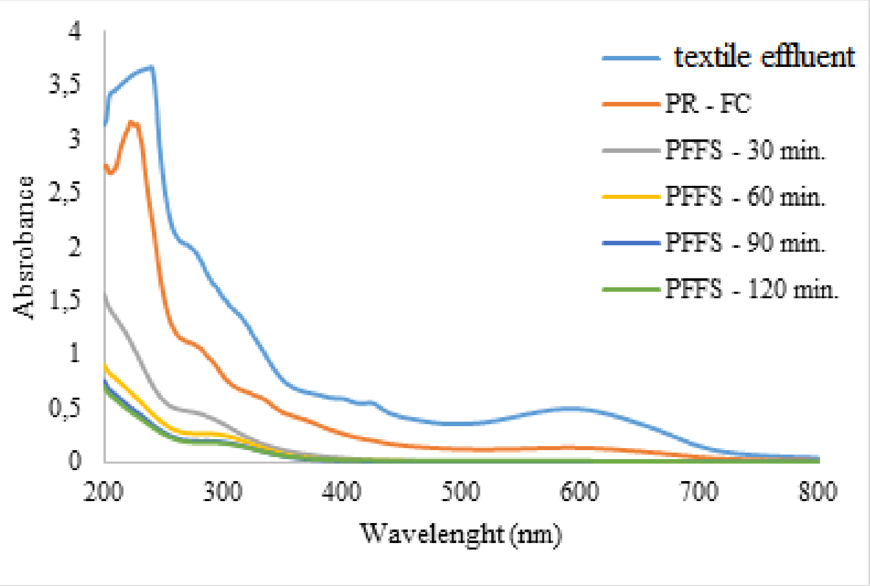

Figure 9. **Monitoring of the spectral profile in the effluent treatment by the reductive process (30 min.) followed by the photo-fenton process with sunlight.**

the complete reduction of the signal in the region of the residual color of the reductive process, as well as a reduction in the region of organic load.

The H_2O_2 in this process was also stabilized at 60% of the initial concentration used, in 60 minutes of reaction, as well as in the photo-Fenton process with artificial light.

In both spectrophotometric monitoring, the residual signal in the UV region, centered at 200 nm, may be due to the formation of Oxalic Acid in the process. Starling (2016), when analyzing by high performance liquid chromatography (HPLC), the formation of intermediate compounds during the photo-Fenton Solar process in the treatment of effluent from the washing step, carried out after dyeing in the textile industry, the chromatographic results showed than Oxalic Acid, was the only final degradation product after the process.

Thus, as well as for the process using artificial light, the time was set at 60 minutes for the analysis of physical-chemical parameters (Table VII).

According to the results of the ANOVA test of the results obtained, with 95% confidence, it can be confirmed that there was a significant difference in the quality of the effluent before and after the two systems combined.

With regard to COD, it was considerably reduced after the two combined systems evaluated (94.60% for RP/PFFA, and 72.07% PR/PFFS). However, the combination where the photo-Fenton Solar process was used, the COD presented a value statically higher than the process where artificial light was used, demonstrated by the Tukey Test. Despite this, regardless of the radiation source used, it can be seen that the combined systems are capable of producing a treated effluent that meets Annex 7 of CEMA resolution 0070/2009 (PARANÁ, 2009), which limits the COD value in 200 mgL^{-1} for release of effluents from textile industries into the receiving body.

In relation to the TOC of the textile effluent, reductions of 63.31% and 49.55% were obtained for the combinations PR/PFFA and PR/PFFS, respectively, and again for the combination where the photo-Fenton Solar process was used, TOC presented a value statically higher than the process with artificial light. These results confirm that it is possible to obtain the removal of organic matter present in the effluent by combined processes.

The two systems combined, achieved mean removals greater than 90% of total phenols. The highest mean value of phenols was obtained after the system where the RP/PFFA system was used,

Table VII. Results of the parameters evaluated in the combined reductive/photo-Fenton Artificial (RP/PFFA) and reductive/photo Fenton solar (RP/PFFS) processes.

Parameter	Textile Effluent	RP/PFFA	RP/PFFS	Removal (%)	
				RP/PFFA	RP/PFFS
COD (mg L^{-1})	335,83	19,58	101,25	94	73
TOC (mg L^{-1})	297,6	109,19	150,13	63,31	49,55
Phenols (mg L^{-1})	12,05	0,52	0,28	95,17	97,65
True Color (uC)	1490	27,00	96	98,19	93,56
Apparent Color (uC)	1825	633,33	940	65,30	48,49
Turbidity (uT)	31,17	52,57	52,67	-	-

not differing statistically from the value obtained after RP/PFFS. However, in the combined system where the solar photo-Fenton process was used, the average residual value of 0.28 mgL^{-1} was well below the limit of 0.5 mgL^{-1} that is established in Resolution 430/2011 from Conama (BRASIL, 2011) for the conditions of release of effluents into receiving bodies, and the average value obtained of 0.52 mgL^{-1} after the RP/PFFA system was also included for release, as it was within the experimental error of the analysis.

Regarding the true color, after the PR/PFFA system a removal of 98.19% can be obtained, while for the PR/PFFS system a reduction of 93.56% was achieved, proving the high capacity of the process in degradation of dyes present in the final effluent of the textile industry. Although the mean of this parameter was higher than the PR/PFFS system, the two did not show statistical differences between the means. Considering the limit value of true color of 75 uC established by Resolution 357/2005 of Conama (Brasil 2005) for water bodies of Class 2 and 3, only the process involving artificial radiation was efficient for framing this parameter with an average residual value of 27 uC.

On the other hand, there was an average apparent color removal of 65.06% for the RP/PFFA system and 48.49% for the RP/PFFS system. Although the mean residual value after RP/PFFS has shown mean values of higher apparent color, this did not show any statistical difference from the mean value of the effluent treated in the PR/PFFA system.

The turbidity of the effluent treated by the combinations was higher than the initial turbidity value of the raw textile effluent, and therefore, regardless of the radiation source used, this parameter was not removed. As already mentioned, the iron species formed during the reductive process were responsible for the increase in turbidity in the effluent, interfering not only in the increase in the effluent turbidity, but also in the increase in the apparent color.

At the end of the oxidative processes, the pH of the treated effluent was still acidic (around 3). As CONAMA Resolution 430/2011 stipulates that to release the treated effluent into the receiving body, the pH must be between 5-9, the pH of the effluent treated by these processes was adjusted to 7. In addition to adjusting the effluent pH to the range acceptable by legislation, neutralization allows precipitation of soluble iron, which can guarantee the classification of the treated effluent in relation to this parameter (15 mgL^{-1} of soluble iron) in accordance with the legislation. Also, pH adjustment can remove suspended solids from the effluent, responsible for the increase in the apparent color and turbidity of the treated effluent in relation to the raw effluent.

Souza (2006) studied the treatment of effluent generated in the dyeing and washing processes of a textile industry effluent by the reductive process, also in continuous flow with photo-Fenton processes with sunlight and artificial light. Both processes were used at pH 3 and with an initial concentration of H_2O_2 of 100 mgL^{-1}, as in the present work. With regard to the combination with artificial light, it showed almost complete color removal and a 71% reduction in the effluent COD at the end of 60 minutes of treatment. In the process involving sunlight, evaluated in a treatment time of 90 minutes and with two additional additions of hydrogen peroxide, a complete removal of color and 70% of COD from the effluent was also obtained.

In the work developed by Zanella et al. (2010), when analyzing the association of the reductive process with steel wool, applied continuously, with a photo-Fenton process with artificial radiation in the treatment of dye baths (brown, marine and burgundy), complete color removal from all evaluated baths, and also significant reduction of organic load (COD removal between 40 to 70%) were obtained.

Considering all the parameters evaluated, it is concluded that the application of artificial light in systems combined with the photo-Fenton process is not justified, since using the process with solar radiation, it was possible to obtain significant removals of the evaluated parameters, and still obtain the framing of the treated effluent with regard to most parameters. Thus, the use of solar radiation can minimize the costs associated with the photo-Fenton process, which are generally not used on larger scales, due to the high cost due to the need for artificial sources of radiation (Malato et al. 2009).

Acute Toxicity Assessment

The evaluation of Acute toxicity against Daphnia magna was carried out with the textile effluent samples, after a reductive process carried out in batch (30 minutes), after combining the reductive process with the photo-Fenton process with ultraviolet radiation and the photo-Fenton process with solar radiation.

Toxicological tests represent the potential of all substances present in textile effluent to cause a deleterious effect on a living organism. Thus, these tests were carried out in order to assess whether there was a difference in the effects caused by the proposed treatment processes in relation to the raw textile effluent.

The results were expressed as EC_{50}, which, in the case of the microcrustacean Daphnia magna, indicates the effluent concentration that causes mortality or immobility in 50% of the individuals observed after 48 hours of testing. The EC_{50} expresses an inverse relationship to toxicity, that is, the higher the EC_{50}, the lower the effluent toxicity (Justino et al. 2019). Values were also expressed in acute toxic units (Uta), which is directly related to the presented toxicity.

Table VIII shows the mean EC_{50} results and the Uta values of the evaluated samples.

Justino et al. (2019), found EC_{50} and Uta values of 25.67% and 3.89, respectively, for the textile effluent studied by the author, and Verma (2008) found EC_{50} values between 14.12 and 29.67%. Thus, the EC_{50}(%) and UTa values calculated for the effluent studied in the present work were lower, however, very close to the EC_{50} and Uta values of the textile effluents studied by the authors against Daphnia magna.

Generally, textile effluents contain a high concentration of salts, such as chloride ions, therefore, it is important to take into account that part of the toxicity verified, both for the raw effluent and for the treated effluent, may be related to the presence of salts in the effluent.

The reductive process allowed for the reduction of all the toxicity of the raw effluent, since the EC_{50} value cannot be calculated. This result suggests that, in addition to removing the acute toxicity of

Table VIII. EC50 (%) and UTA of the evaluated samples.

Samples	EC_{50} (%)	TUa
Textile Effluent	35,26	2,83
RP (30 min)	Non toxic	Non toxic
RP/PFFA (60 min)	Non toxic	Non toxic
RP/PFFS (120 min)	77,03	1,29

CAPTION: EC50 - Effective concentration that causes effect to 50% of tested organisms; TUa - Acute Toxic Unit.

the textile effluent, transformation products such as phenolic compounds or aromatic amines were not formed or were not present in sufficient concentration to confer toxicity after this process.

The combination of the reductive and photo-Fenton process with artificial radiation also allowed for the complete removal of the acute toxicity of the raw textile effluent. As for the combination of the reductive process with photo-Fenton with solar radiation, the removal of acute toxicity was not complete, with 54.22% of the raw effluent Uta remaining.

CONCLUSIONS

Based on the results achieved in the factorial design, the variables pH and steel wool mass, only the pH had a significant effect on the discoloration of the effluent. The reductive process using commercial steel wool is a simple and viable alternative because it provided significant reductions in COD, TOC, total phenols, true color of the textile effluent, but it presents the inconvenience of increasing apparent color and turbidity.

Combining the reductive process with an oxidative process of the photo-Fenton type independent of the radiation source used, it proved to be an efficient alternative to obtain suitable effluent in relation to the parameters COD, total phenols and true color for release into the receiving body according to current environmental legislation, with emphasis on the photo-Fenton process assisted by solar radiation.

The evaluation of acute toxicity indicated high toxicity of the effluent used in this work against the biological indicator Daphnia magna, and after treatment by a reductive and combined process, the treated effluent did not show reduced toxicity or toxicity.

In general, it is concluded that although all studies were carried out on a laboratory scale, the results suggest that the reductive process using commercial steel wool, combined with the oxidative process, can be considered a highly efficient alternative, which can be used in the treatment of effluents from the dyeing stage, mainly composed of dyes, and also in the treatment of the final effluent from the textile industry.

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Author contributions

The work was developed by the Master's student Ana Carolina Figueiredo as part of her master's project. The research was supervised by Professor Dr. Kely Viviane de Souza, who, together with the student, developed the prototype of the system used in the reductive process as well as in the process assisted by sunlight. The laboratory analysis part was carried out by Ana Carolina Figueiredo, while the factorial planning for the optimization of the experiments was developed by Kely Viviane de Souza. The data analysis and discussion were conducted by both authors.