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Comparative study of various advanced oxidation processes for the treatment of tannery wastewater

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ABSTRACT

The leather tanning process generates a large amount of residue. The present work aims to apply an experimental design to assess several parameters of different advanced oxidation processes for tannery residue treatment, such as UV/H_2O_2, Fenton, photo-Fenton and sono-Fenton, using 70% hydrogen peroxide. As an optimization strategy, chemometric techniques were applied to evaluate the reaction factors: volume of H_2O_2, HNO_3, Fe(II) and reaction time. The evaluated response was the absorbance at 375 nm, which is the maximum absorbance wavelength for this wastewater. Thus, the optimum conditions obtained by response surface methodology for Fenton method were 10.30 mL of 70% H_2O_2 and 0.124 mL of 0.06 g mL^{-1} Fe(II). Under these conditions, 96% decrease in absorbent species and 95% of COD removal occur in 30 min using the sono-Fenton process at pH 3.0 and 298 K. This result for discoloration is approximately 5.4-fold higher than that obtained with the use of UV/H_2O_2 with 0.87 mL of HNO_3 at 298 K and 1.65 h of reaction with 60% of COD removal.

Keywords: Tannery wastewater; 70% hydrogen peroxide; UV radiation; Fenton's reaction; Photo-Fenton; Sono-Fenton

1. Introduction

The production process of tanned leather consumes a large amount of water and, consequently, also generates a large amount of liquid effluents and solid waste [1–4]. On average, 250 kg of tanned leather is produced from 1 t of salted skin, which requires 25 m^3 of water for the entire tanning process. Tanneries finish approximately 20%–30% of their raw material by using a similar approach, resulting in the production of 780 kg of solid waste and 25 m^3 of liquid effluent (with 250 kg of COD and 100 kg of BOD) [5,6].

Tanning effluents are already subjected to primary and secondary treatment processes. Chemical coagulation, reverse osmosis, activated carbon adsorption, ion exchange, electrocoagulation, flocculation, membrane filtration (MF), electrodialysis, biological and advanced oxidation processes (AOPs) are the main solutions proposed and used in the treatment of tannery wastewater [2,7–16]. However, in large-scale industries, these processes have not proven to be effective in producing desirable characteristics for disposal in the environment, especially in relation to organic material and sulfide. As an alternative treatment, in recent works [17,18], we have tested bifunctional photocatalytic systems to treat tannery wastewater to recover energy as molecular hydrogen with the simultaneous degradation of pollutants. In this process, tannery wastewater was treated photocatalytically with simulated solar power using CdS and RGO/CdS/ZnO (composites obtained from hybridization of reduced graphene oxide [RGO], cadmium sulfide [CdS] and zinc oxide [ZnO]) as photocatalysts under anaerobic conditions [17,18]. However, despite the production of 20 mmol g_{cat}^{-1} of hydrogen and 90% sulfide removal after 24 h of irradiation using $RGO/(CdS)_{1.0}/(ZnO)_{0.4}$ [18], the system proved to be ineffective in degrading all pollutants, and additional

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treatment is required to obtain desirable characteristics for reuse or final dispose.

AOPs have received attention in the research and development of wastewater treatment technologies in recent decades. These processes (e.g., cavitation, photocatalysis, Fenton reaction, ozonation) have been successfully applied for the removal or degradation of recalcitrant pollutants or used as pretreatments to convert pollutants into compounds that can be treated in a conventional manner or by biological methods. The efficiency of these processes depends on the generation of free radicals, with hydroxyl radical ($^{\bullet}OH$) being the most important [19]. Among the most commonly used methods, notable methods include the use of hydrogen peroxide with UV radiation (UV/H_2O_2) [20] and the Fenton method (Fe(II)/H_2O_2), which may be coupled or not with UV radiation (photo-Fenton) [21,22] and, more recently, with ultrasonic radiation (sono-Fenton) [23,24]. For both cases, UV and ultrasonic radiation (US), the aim is to improve the generation of hydroxyl radicals, according to Fenton's general reactions (Eqs. (1)–(4)).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \tag{1}$$

$$^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet} \tag{2}$$

$$R^{\bullet} + Fe^{3+} \rightarrow R^+ + Fe^{2+} \tag{3}$$

$$R^+ + H_2O \rightarrow ROH + H^+ \tag{4}$$

Recently, AOPs have been successfully employed in the treatment of tannery wastewater. Sivagami et al. [7] achieved 80%–90% reduction of COD using a three-step process (coagulation + aeration + O_3) in 30 min, Charumol and Keerthinarayana [15] took 4 h to achieve 91% COD removal using Fenton method and Abdel-Aal et al. [16] achieved 90% COD removal using photo-Fenton within 2 h of reaction.

The most commonly used reagent in AOPs is 30% hydrogen peroxide. However, 70% hydrogen peroxide, which has recently been produced, has limited application in chemistry. Ferreira et al. [25] used 70% hydrogen peroxide in a digestion system to determine lead in wine by employing electrothermal atomic absorption spectrometry (ETAAS). Likewise, Felix et al. [26] used 70% hydrogen peroxide and UV radiation for the degradation and subsequent determination of chromium in beer by employing ETAAS.

In this way, the present work aims to investigate the treatment of tannery wastewater after energy recovery for hydrogen production using AOPs, such as UV/H_2O_2, Fenton, photo-Fenton and sono-Fenton, using 70% hydrogen peroxide. The optimization of the digester procedure was performed using a Doehlert design for different processes to identify the optimal conditions of the reaction to reach total organic matter degradation.

2. Experimental

2.1. Reagents, solutions and effluent

All experiments were performed utilizing deionized water obtained from a Milli-Q system (Millipore, Bedford, USA) with a specific resistivity of 18 MΩ-cm. Concentrated nitric and sulfuric acids, ferrous sulfate and 70% (w/w) hydrogen peroxide (Peroxy, Bahia, Brazil) were used in the experiments as purchased. The effluent was obtained from a tannery located in Petrolina, Pernambuco, Brazil. When received in the laboratory, the material was immediately packed in plastic bottles and refrigerated until testing. Before performing the AOP tests, the tannery residue was photocatalytically treated using the composite RGO/$(CdS)_{1.0}$/$(ZnO)_{0.4}$ as a photocatalyst under visible-light irradiation for energy recovering [18]. For 24 h of irradiation ($\lambda \geq 420$ nm) in an oxygen-free atmosphere, using 60 mg of the photocatalyst and 60 mL of the wastewater, the hydrogen production reached 1.2 mmol [18]. Some of the effluent parameters before and after photocatalytic treatment for hydrogen production are shown in Table 1.

Sulfide content in the tannery wastewater decreased 90% after photocatalytic treatment for hydrogen production [18]. However, COD and absorbance are still high after photocatalytic reaction, which requires an additional treatment for effective degradation of all pollutants. Thus, a comparative study of various AOPs was performed for total removal of recalcitrant organic matter.

2.2. Equipment

For the UV/H_2O_2 and photo-Fenton tests, a high-pressure 500 W Hg–Xe arc lamp (Newport) was used as the light source (Fig. 1). The light beam passes through an IR filter (Newport) with cooling by means of a thermostatic bath (Quimis, Brazil) and a 370-nm cutoff filter was used. For the sono-Fenton tests, an ultrasonic probe (R2D091109, Unique) was used with a power of 80 W, and the titanium probe was directly immersed to a depth of approximately 80% in the mixture in the beaker for 15–30 min. The absorbance of the samples was determined by UV-VIS UV-1800 spectrophotometer (Shimadzu, Japan) with 1-cm cell optical path length. pH measurements were performed using a digital pH meter (Omega PHH 37, UK).

2.3. Optimization strategy

The digester procedures optimization was performed using a Doehlert design for the different AOPs processes. This design was chosen based on the guidelines presented by Leardi [27], considering that the quality of the results

Table 1
Effluent parameters before and after photocatalytic treatment for hydrogen production

Parameter	Before	After
Abs at 375 nm	3.814	2.626
pH	11.0	13.0
COD (mg L^{-1})	4,992	3,525
Sulfide (mg L^{-1})	55,000	5,400
Sulfate (mg L^{-1})	3,800	7,000
Density (g mL^{-1})	1.03	1.03

COD: Chemical oxygen demand.

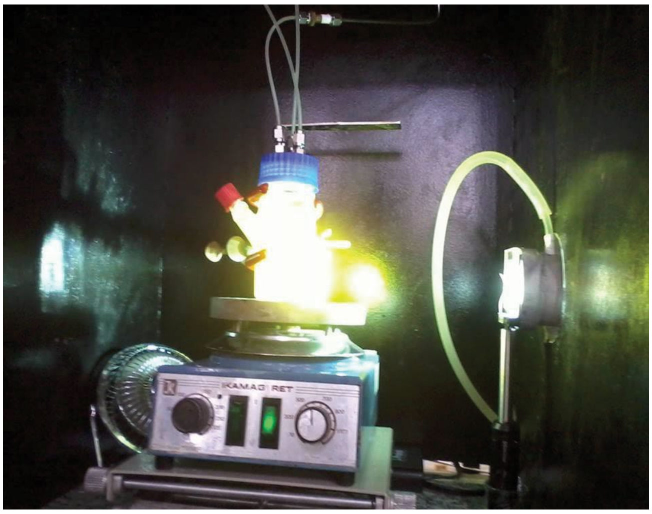

Fig. 1. Photo-reactor used in the UV/H_2O_2 and photo-Fenton processes.

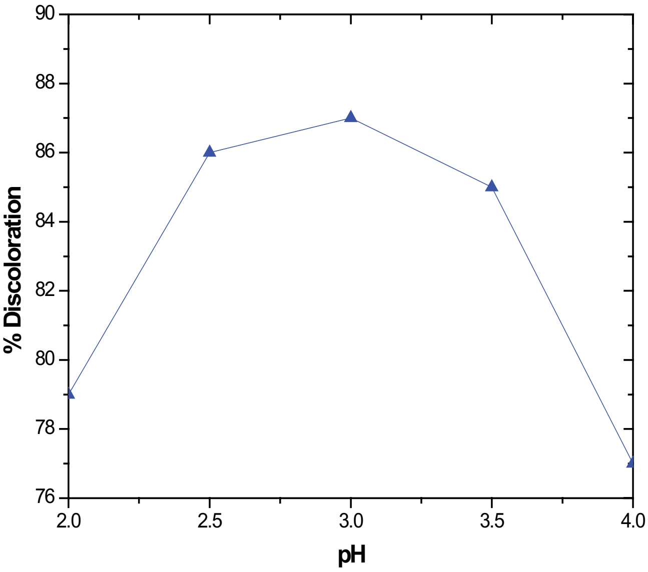

Fig. 2. Effect of initial pH on the discoloration (absorbance measured at 375 nm) by Fenton process using 60 mL of tannery wastewater, 10 mL of 70% H_2O_2, 1 mL of 0.06 g mL^{-1} Fe(II); time and temperature set at 30 min and 298 K, respectively.

depends on the distribution of the experiments in the experimental domain and a more efficient design that offers a minimum number of experiments while studying a greater number of experimental levels. The evaluated response was the absorbance at 375 nm, which is the maximum absorption wavelength for the wastewater. For the UV/H_2O_2 process, the variables involved were 70% hydrogen peroxide volume, nitric acid volume and reaction time. For the Fenton process, the following variables were investigated: 70% hydrogen peroxide volume and 0.06 g mL^{-1} Fe(II) solution volume; the time was set at 30 min and the pH as 3.0. The reaction time for the complete oxidation of Fe(II) to Fe(III) has been reported to be between 10 and 30 min, according to Gulkaya et al. [28].

The optimum pH is well known in the Fenton reaction as 3.0. At high pH values (pH > 4), the generation of hydroxyl radicals becomes slow because of the formation of ferrous hydroxyl complexes. On the other hand, at low pH values (pH < 2), peroxide is solvated in the presence of a high concentration of H^+ ions to form the stable oxonium ion $[H_3O_2]^+$, which reduces its reactivity with Fe(II) [19,22–24]. However, different samples could exhibit optimal performance at different pH values. Thus, we tried Fenton experiments in a pH range between 2.0 and 4.0 and room temperature (298 K), in order to decide the best operating pH for our tannery wastewater. The volume of H_2O_2 and Fe(II) was defined according to previous works in the literature [28–30], which have used a ratio of 10:1 to H_2O_2:Fe(II) for optimum degradation.

For pH analysis, the reaction time was 30 min, using 10 mL of 70% H_2O_2 and 1 mL of 0.06 g mL^{-1} Fe(II). Fig. 2 shows that the highest discoloration (absorbance measured at 375 nm) was achieved in the range of pH between 2.5 and 3.0. Consequently, the pH was fixed at 3.0 for the subsequent investigations.

For UV/H_2O_2 and Fenton processes, the temperature was set at 298 K to make the process economically viable for the industrial sector. In addition, at elevated temperatures, H_2O_2 undergoes significant decomposition into oxygen and water and does not effectively contribute to degradation [29]. For UV/H_2O_2 process, 10 mL of 70% H_2O_2 and 1 mL of HNO_3 were used to perform the Doehlert design likewise Fenton design.

For all processes, 60 mL of tannery wastewater after the photocatalytic treatment for hydrogen production were filtered to remove the photocatalyst. For the Fenton, photo-Fenton and sono-Fenton processes, pH adjustment was performed with diluted sulfuric acid and sodium hydroxide. Thirty minutes were allowed for complete reaction, followed by 30 min of precipitation and after that, the supernatant was filtered. The pH of the resulting solution was adjusted to 7, and after 4 h of precipitation, the supernatant was again filtered for absorbance determination.

Chemical demand of oxygen (CDO) before and after treatment by AOPs was determined by Standard Method for the Examination of Water and Wastewater 5220 A/C.

3. Results and discussion

3.1. Optimization of the UV/H_2O_2 process

The experimental conditions for the discoloration of the tannery residue using the UV/H_2O_2 process were optimized using a Doehlert design. The following factors were assessed: 70% hydrogen peroxide solution volume, nitric acid volume and reaction time; Temperature was set at 298 K. The wastewater discoloration was evaluated by measuring the absorbance of the solution at 375 nm (response). The Doehlert matrix contains $k^2 + k + 1$ points for k variables and replicates are only required at the central level in order to validate the mathematical model by means of pure error associated with repetition and lack of fit estimation [31,32]. In this way, a set of 13 experiments are required for three variables with

Table 2
Experimental Doehlert matrix and responses (absorbance at 375 nm) for the optimization of the UV/H_2O_2 process (initial absorbance at 375 nm = 2.626)

Exp.	H_2O_2 volume (mL)	HNO_3 volume (mL)	Time (h)	Absorbance (λ_{max} = 375 nm)
1	14	0.50	1.5	0.781
2	12	0.25	1.0	1.125
3	12	0.25	2.0	0.913
4	12	0.75	1.0	0.802
5	12	0.75	2.0	0.712
6	10	0.00	1.5	1.312
7(C)	10	0.50	1.5	0.759
8(C)	10	0.50	1.5	0.755
9(C)	10	0.50	1.5	0.759
10	10	1.00	1.5	0.606
11	8	0.25	1.0	1.258
12	8	0.25	2.0	1.132
13	8	0.75	1.0	0.985
14	8	0.75	2.0	0.825
15	6	0.50	1.5	1.233

(C): central level

a triplicate on the central point, which results in 15 experiments that are shown in Table 2. After volume and time optimization, different pH values were investigated.

From the results, optimization was proceeded using response surface methodology (RSM). Linear and quadratic models were fitted to the obtained experimental data. Although both fitted model have presented lack of fit, the quadratic model can better describe the data behavior. As can be seen in the supplementary material (Table S1, Figs. S1 and S2), the quadratic model presented a correlation of R^2 = 0.9818 between observed and predicted values. Still according to Fig. S2b, less dispersed residues are also verified when the quadratic model is applied.

Fig. 3 presents the surfaces for the quadratic model obtained by multivariate regression. This surface is characterized by presenting a minimal point.

The maximum discoloration is found using the following values: 11.40 mL 70% H_2O_2, 0.87 mL HNO_3 and 1.65 h of time reaction. In these values, the predicted value for absorbance is 0.596. The observed value when these parameters were employed was 0.584.

However, as an AOP, this method presents low efficiency in the discoloration of tannery residue if only hydroxyl radical generation is considered since the lowest absorbance is found in the presence of HNO_3. This result can be attributed to the high turbidity of the material, which makes difficult the penetration of radiation, in turn decreasing the number of UV photons that reach the solution [17].

Nitric acid is the most widely used oxidizing mineral acid because solutions thereof (commercial reagents) with high purity can be easily found and its reaction products are generally metal nitrates, which are mostly soluble in aqueous media [20]. The oxidizing power of nitric acid is moderate, and this acid can be used at high temperatures (when under reflux or in a closed system). The general reaction between this acid and organic matter is given by Eq. (5).

$$(CH_2)n + HNO_3 + heat \rightarrow CO_2(g) + 2NO(g) + 2H_2O \quad (5)$$

A mixture of HNO_3 and H_2O_2 is widely employed due to the oxidizing characteristics of hydrogen peroxide [25,26]. In addition to increased degradation efficiency, the great advantage of this blend is that water is a decomposition product, which facilitates waste disposal.

For better UV/H_2O_2 process comprehension, different pH values were investigated (Table 3).

As can be seen in Table 3, there is no significant difference in absorbance in pH range of 13.0–7.0, indicating that the UV/H_2O_2 process can be performed immediately after photocatalytic treatment, without pH adjustment. However, the UV irradiation in the presence of HNO_3 (pH 3.0) reached the maximum discoloration of the residue.

3.2. Optimization of the Fenton process

For the Fenton process, Doehlert design for two variables was applied. The variables studied for the optimization of tannery wastewater discoloration were the volume of 70% hydrogen peroxide and volume of 0.06 g mL^{-1} Fe(II) solution; the reaction time was fixed at 30 min, pH 3.0 and room temperature (298 K). The reaction time for the complete oxidation of Fe(II) to Fe(III) has been reported to be in the range of 10–30 min, according to Gulkaya et al. [28]. The evaluated response was also the absorbance at 375 nm. A set of seven experiments are required for two variables with a triplicate on the central point, which results in nine experiments [31,32]. The results obtained for all experiments from the Doehlert design are shown in Table 4.

From the results, optimization was proceeded using RSM. Linear and quadratic models were fitted to experimental data using least square regression. Again, both fitting model have presenting lack of data fit, but the quadratic model provide a better description of the data behavior. As can be seen in the supplementary material (Table S2, Figs. S3 and S4), the quadratic model presented a correlation of R^2 = 0.9908 between observed and predicted values. Less dispersed residues are also verified when the quadratic model is applied according to Fig. S4b. The response surfaces for the quadratic model applying the response surface methodology are shown in Fig. 4.

The critic values for the maximum discoloration are 10.30 mL of 70% H_2O_2 and 0.124 mL of 0.06 g mL^{-1} Fe(II). The predicted value is 0.132 while the observed value when these parameters were employed was 0.131.

The results presented in the response surface methodology indicate that all factors are significant. However, as Fe(II) concentration increases, the absorbance also increases, which means that the discoloration process becomes less efficient. In addition, an increase in H_2O_2 volume promotes discoloration until a certain limit. This can be explained by the reaction in Eq. (6), in which an excess of H_2O_2 can lead to the formation of $HOO^\bullet$ radicals, which are less reactive than hydroxyl radicals [20].

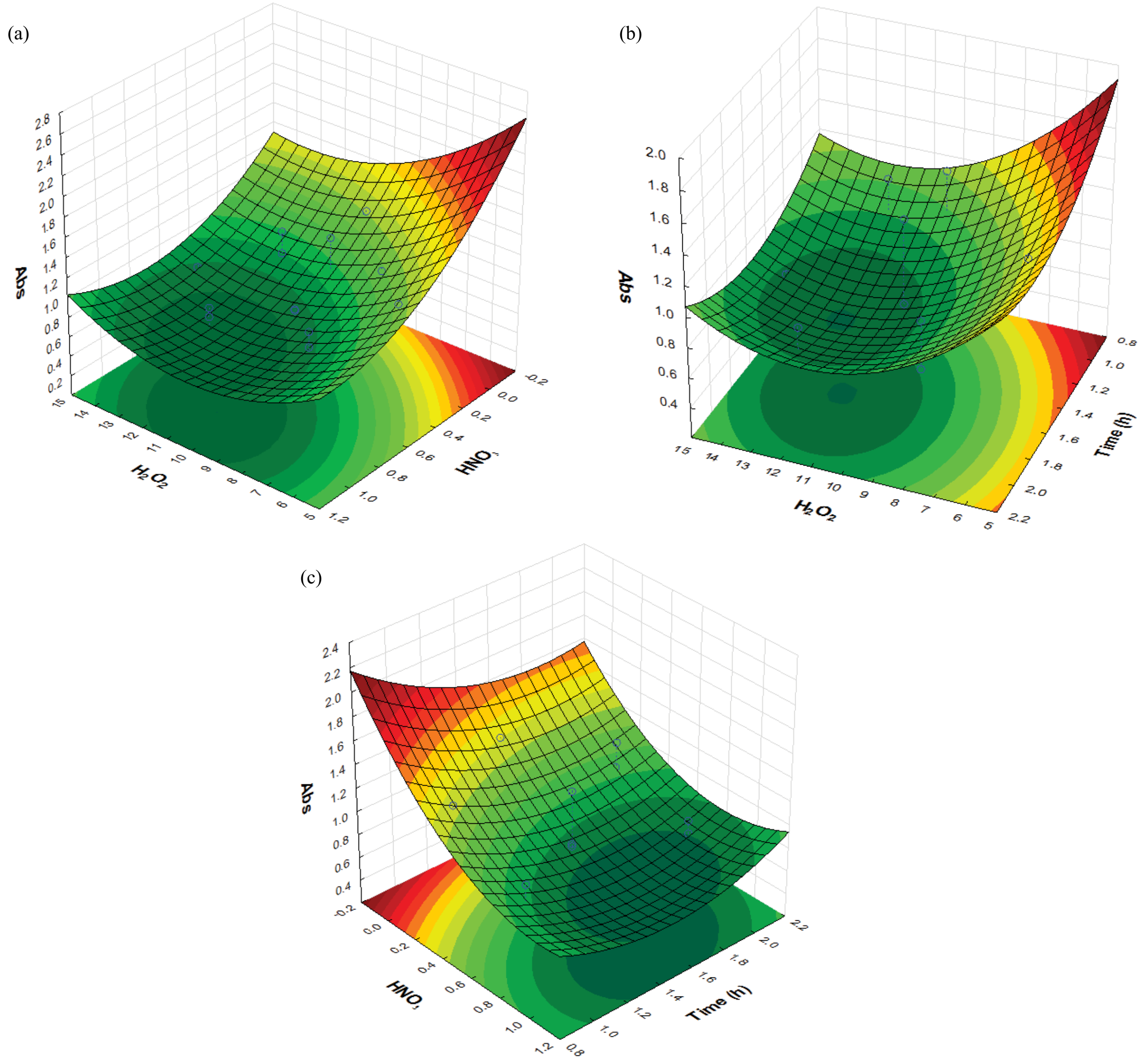

Fig. 3. Response surface methodology for the quadratic model for UV/H_2O_2/HNO_3 process.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (6)$$

An increase in Fe(II) concentration results in a decrease in residue discoloration. The excess iron ions can lead to the consumption of hydroxyl radicals by the following reaction [27]:

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \quad (7)$$

The small content of Fe(II) in the reaction can be explained by Eqs. (1)–(3). Fe(II) acts as a catalyst in the reaction and is regenerated constantly after Fe(III) formation, promoting the reaction with concomitant H_2O_2 consumption. The excess of Fe(II) ions that do not act on the discoloration can lead to the formation of absorbing species in the UV region, increasing the absorbance [28–30].

Table 3
pH assessment for UV/H_2O_2 process using 11.40 mL of 70% H_2O_2 and 1.65 h of time reaction (initial absorbance at 375 nm = 2.626)

Process	pH	Absorbance (λ_{max} = 375 nm)
UV/H_2O_2	13.0	1.200
UV/H_2O_2	11.0	1.185
UV/H_2O_2	9.0	1.162
UV/H_2O_2	7.0	1.154
UV/H_2O_2/HNO_3	3.0	0.584

3.3. Optimization by the photo-Fenton and sono-Fenton processes

From the results obtained by the optimization of the Fenton process, tests involving the use of UV irradiation and ultrasound irradiation (US) were carried out to promote

Table 4
Optimization of the Fenton process using a Doehlert design (initial absorbance at 375 nm = 2.626)

Exp.	H_2O_2 volume (mL)	Fe(II) (0.06 g mL^{-1}) volume (mL)	Absorbance (λ_{max} = 375 nm)
1	8	3	1.356
2	12	3	0.981
3	6	2	1.121
4(C)	10	2	0.551
5(C)	10	2	0.551
6(C)	10	2	0.551
7	14	2	0.416
8	8	1	0.323
9	12	1	0.245

(C): central level.

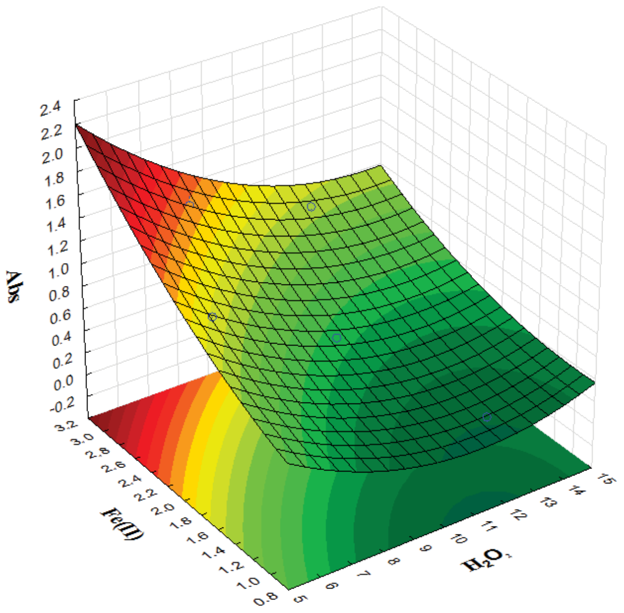

Fig. 4. Response surfaces for the quadratic model for Fenton process.

the maximum discoloration of the residue. To evaluate the efficiency of UV and US irradiation in the discoloration process, the following experiments were performed (Fig. 5): (i) only UV, (ii) UV + H_2O_2, (iii) UV + Fe(II) + H_2O_2 (photo-Fenton), (iv) only US, (v) US + H_2O_2, (vi) US + Fe(II) + H_2O_2 (sono-Fenton) and (vii) Fenton.

When only UV radiation is employed, the discoloration of tannery wastewater based on the absorbance at 375 nm is only approximately 5% after 30 min. This is because the residue has high turbidity, which makes difficult the penetration of radiation [17]. When UV/H_2O_2 is used, higher discoloration is observed than with UV alone since UV radiation helps in H_2O_2 decomposition to give rise to $^{\bullet}OH$ radicals; 21% discoloration is reached after the same period. When the photo-Fenton process is applied, the discoloration reaches 41% in 15 min and reaches a maximum of 95% in 30 min.

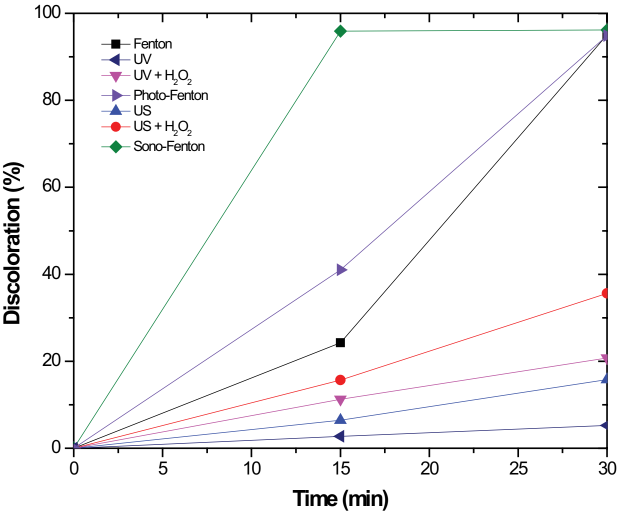

Fig. 5. Discoloration by different processes using 10.30 mL of 70% H_2O_2, 0.124 mL of 0.06 g mL^{-1} Fe(II), pH 3.0, 298 K and 60 mL of effluent.

Similarly, when only ultrasonic irradiation is used, discoloration is approximately 16% after 30 min. At high frequencies, this type of irradiation leads to the generation of free radicals by the homolytic breakdown of water or oxygen molecules [23,24]. In the presence of US/H_2O_2, the discoloration was 35% in 30 min. The increase in discoloration compared with that with only ultrasound can be attributed to the formation of more hydroxyl radicals originating from the ultrasonic irradiation of H_2O_2 [23,24]. Hydrogen peroxide decomposes and produces hydroxyl radicals in the presence of ultrasonic irradiation, as represented in Eq. (8). Furthermore, the generation of hydroxyl radicals by H_2O_2 is possible by the reaction described in Eq. (9).

$$H_2O_2 + US \rightarrow 2HO^{\bullet} \tag{8}$$

$$H_2O_2 + H^{\bullet} \rightarrow 2HO^{\bullet} + H_2O \tag{9}$$

When the sono-Fenton method is used, 96% discoloration is achieved in only 15 min of reaction, approximately equal to the value after 30 min of reaction; thus, sono-Fenton is the most efficient method of discoloration evaluated in this work.

Chemical oxygen demands (CODs) were assessed to investigate the real degradation of the recalcitrant organic matter in the wastewater after submitted to different AOPs in the optimized conditions, as follows: UV/H_2O_2 (11.40 mL of 70% H_2O_2, 0.87 mL of HNO_3 and 1.65 h of time reaction); Fenton, photo-Fenton and sono-Fenton (10.30 mL of 70% H_2O_2, 0.124 mL of 0.06 g mL^{-1} Fe(II), pH 3.0 and 30 min of reaction). COD results shown in Table 5 confirm the organic matter degradation during AOP treatment.

Our results are very promising for tannery wastewater treatment compared with those of the literature. We achieved

Table 5
COD results for residues after treatment by different AOPs

AOP	COD (mg L^{-1})
UV/H_2O_2	1,410
Fenton	458
Photo-Fenton	388
Sono-Fenton	176
Before treatment by AOPs	3,525

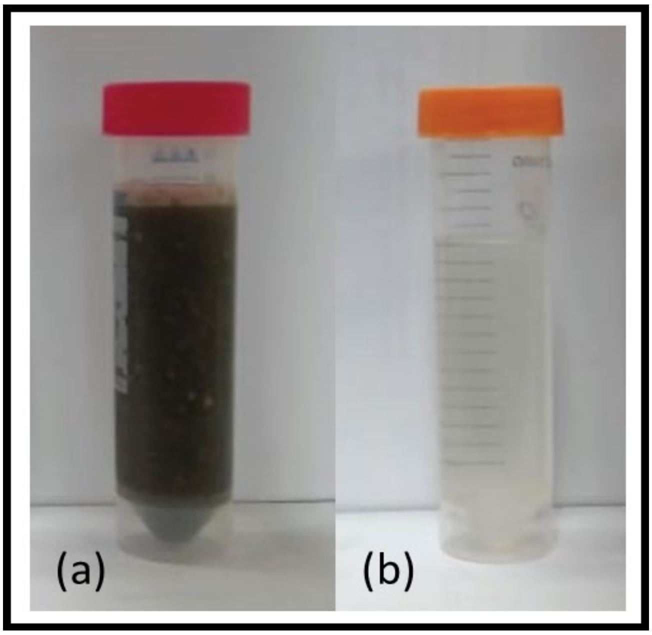

Fig. 6. Tannery wastewater (a) after photocatalytic treatment for hydrogen production and (b) after sono-Fenton treatment.

95% degradation of the organic matter in 30 min with sono-Fenton treatment in only one step (Fig. 6), while the maximum COD removal reported was 91% in 4 h [16] or achieving 90% reduction of COD in the same time but in a three-step process (coagulation + aeration + O_3) [7].

4. Conclusions

Our results have demonstrated that Doehlert design coupled with RSM is a powerful tool to evaluate the influence of each reaction parameter and their interactions in the degradation of pollutants, such as in the treatment of organic matter remaining in tannery residue after energy recovery for hydrogen production. Additionally, our findings demonstrate that 70% hydrogen peroxide is a highly efficient substance to aid in the oxidation of pollutants. This work is one of the pioneer efforts in the use of this reagent, which still has limited application in chemistry. Among all systems assessed here, the sono-Fenton method was the most efficient in organic matter degradation. It requires only 15 min to discolor the tannery wastewater, with absorbance decrease by 96%, and promotes a COD removal of 95% in 30 min of reaction. In this way, this work shows that a highly polluting agent such as tannery wastewater, after energy recovery, can be treated quickly to obtain clean water able to be reused instead of disposing into the environment, in accordance with the green chemistry.

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Supplementary information:

Table S1
Model analysis for UV/H_2O_2 process: (a) linear and (b) quadratic

(a)

Source	SS	dF	MS	F(calc)	F(tab)
Regression	0.5895	3	0.1965	16.71	3.587
Residual	0.1293	11	0.01176		
Lack-of-fit	0.1293	9	0.01436	2693	16.38
Pure error	0.000011	2	0.000005		
Total	0.7188	14			

(b)

Source	SS	dF	MS	F(calc)	F(tab)
Regression	0.7056	9	0.07840	29.97	4.772
Residual	0.01308	5	0.002616		
Lack-of-fit	0.01307	3	0.004356	816.7	19.16
Pure error	0.000011	2	0.000005		
Total	0.7187	14			

Table S2
Model analysis for Fenton process: (a) linear and (b) quadratic

(a)

Source	SS	dF	MS	F(calc)	F(tab)
Regression	1.071	2	0.5355	31.82	5.143
Residual	0.1010	6	0.01683		
Lack-of-fit	0.1008	4	0.02520	345	19.247
Pure error	0.000146	2	0.000073		
Total	1.172	8			

(b)

Source	SS	dF	MS	F(calc)	F(tab)
Regression	1.065	5	0.2129	59.56	9.013
Residual	0.1073	3	0.003575		
Lack-of-fit	0.01058	1	0.01058	145	18.513
Pure error	0.000146	2	0.000073		
Total	1.172	8			

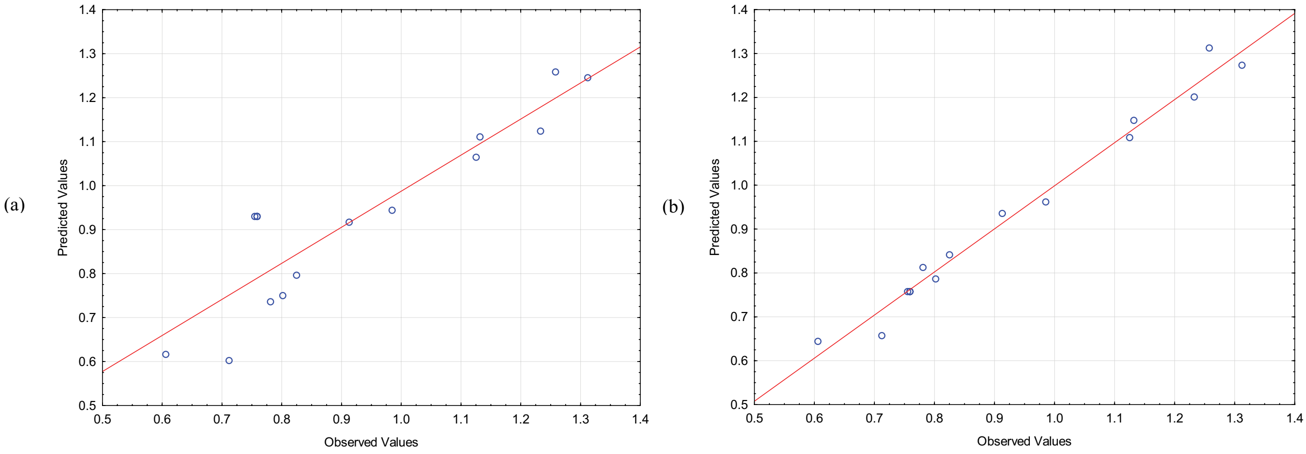

Fig. S1. Observed vs. predicted values for (a) linear ($R^2 = 0.8201$) and (b) quadratic ($R^2 = 0.9818$) models for UV/H_2O_2 process.

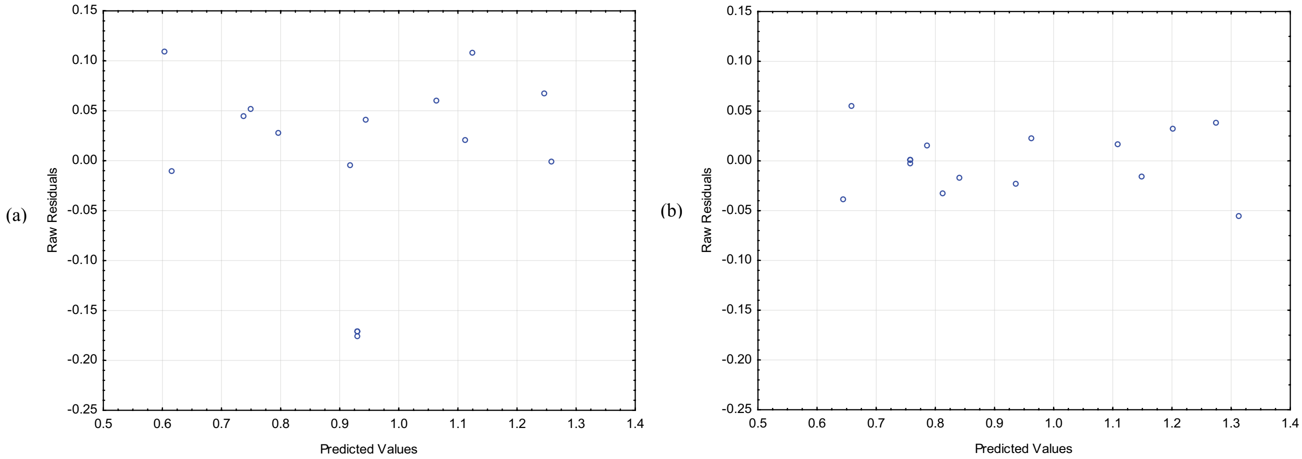

Fig. S2. Predicted vs. residual values for (a) linear and (b) quadratic models for UV/H_2O_2 process.

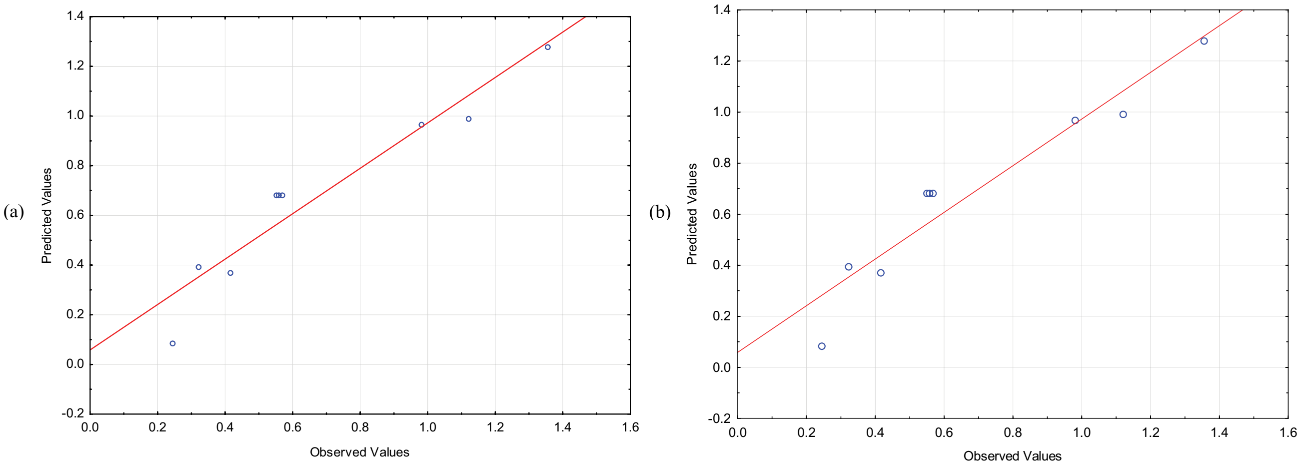

Fig. S3. Observed vs. predicted values for (a) linear ($R^2 = 0.9139$) and (b) quadratic ($R^2 = 0.9908$) models for Fenton process.

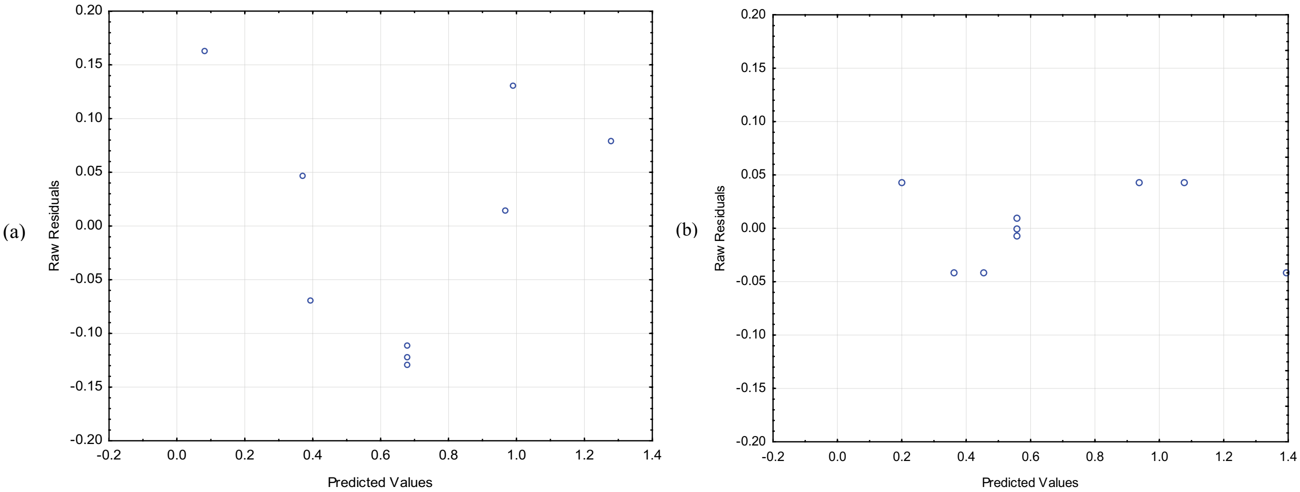

Fig. S4. Predicted vs. residual values for (a) linear and (b) quadratic models for Fenton process.