第 49 卷 第 7 期
2022 年 7 月

湖南大学学报（自然科学版）
Journal of Hunan University (Natural Sciences)

Vol. 49 No. 7
July 2022

Open Access Article https://doi.org/10.55463/issn.1674-2974.49.7.14

Comparison of Fenton and Photo-Fenton Processes for Removal of Organic Pollutants from Tanneries, Department of Quindío, Colombia

Irma María García Giraldo[1], Henry Reyes Pineda[2], Eduardo Alexis Lobo[3]

[1] University of Quindío, Quindío, Armenia

[2] Research Group of Environmental Sciences INCIAM

[3] University of Santa Cruz do Sul (UNISC), Santa Cruz do Sul, RS, Brasil

Abstract: The wastewater produced by tanneries has many recalcitrant and toxic organic pollutants that do not meet the current environmental standard and are very dangerous for humans and biota. Therefore, there is an urgent challenge in developing robust oxidation processes guaranteeing their organic elimination to preserve water quality. Fenton and photo-Fenton techniques, which are part of advanced oxidation processes, are currently very innovative and effective for the decontamination of polluting organic agents and recalcitrant compounds in industrial wastewater. In this context, this research aimed to apply the reagents Fenton (Fe^{+2}/H_2O_2) and photo-Fenton (Fe^{+2}/H_2O_2 + uv) in contaminated waters from tanneries in the Department of Quindío, Colombia. For this, solutions of 1L of raw water extracted from the tanneries were prepared by adjusting the pH to 4.0. Then, Fenton's reagent was added and stirred for 2 hours at 150 rpm. Later these same solutions were exposed to ultraviolet light at 269 nm for 2 hours to perform the photo-Fenton process. The results indicated that better decontamination of these effluents was obtained with the photo-Fenton process, although the differences between the two reagents were not statistically significant ($p > 0.05$). However, we found a decrease in water turbidity, chemical oxygen demand (COD), total organic carbon (TOC), and color, in a higher percentage with photo-Fenton (92%), which makes these techniques sustainable to improve the environment and the quality of life of people who live around these industries. In addition, the advanced oxidation processes are very economical when implemented since, in the photo-Fenton case, solar energy, a type of renewable energy, is used. It should also be noted that they are very efficient techniques when removing organic contaminants for the tannery industries since these have been reported as one of the most polluting industries in the world. Therefore, these processes are recommended for the effective decontamination of organic residues in the effluents produced by the tanning processes.

Keywords: tanneries, Fenton, photo-Fenton, wastewater.

芬顿和照片-芬顿工艺去除制革厂有机污染物的比较,哥伦比亚金迪奥省

摘要：制革厂产生的废水含有许多不符合现行环境标准的顽固性和有毒有机污染物,对人类和生物群非常危险。因此,开发稳健的氧化工艺以保证其有机物的消除以保持水质是一项紧迫的挑战。芬顿和照片-芬顿技术是高级氧化工艺的一部分,目前对于工业废水中的污染性有机物和顽固性化合物的去污非常创新和有效。在此背景下,本研究旨在将试剂芬顿(铁+2/过氧化氢) 和照片-芬顿(铁+2/过氧化氢 +紫外线) 应用于哥伦比亚金迪奥省制革厂的污染水中。为此,从制革厂提取的 1 大号原水溶液通过将酸碱度调节至 4.0 来制备。然后,加入芬顿试剂并以 150 转数的速度搅拌 2 小时。随后将这些相同的溶液暴露在 269 纳米的紫外光下 2 小时以进行光芬顿工艺。结果表明,尽管两种试剂之间的差异没有统计学意义(p>0.05),但使用光芬顿工艺可以更好地去除这些流出物。然而,我们发现水浊度、化学需氧量(鳄鱼)、总有机碳(目录)和颜色的降低,使用照片-芬顿(92%) 的百分比更高,这使得这些技术可持续改善环境和生活在这些行业周围的人们的生活质量。此外,高级氧化工艺在实施时非常经济,因为在光芬顿案例中,

Received: April 18, 2022 / Revised: May 15, 2022 / Accepted: June 13, 2022 / Published: July 30, 2022

Fund Project: The University of Quindío

About the authors: Irma María García Giraldo, University of Quindío, Quindío, Armenia; Henry Reyes Pineda, Research Group of Environmental Sciences INCIAM; Eduardo Alexis Lobo, University of Santa Cruz do Sul (UNISC), Santa Cruz do Sul, RS, Brasil

使用了太阳能,一种可再生能源。还应该指出的是,它们在去除制革行业的有机污染物时是非常有效的技术,因为据报道这些是世界上污染最严重的行业之一。因此,推荐使用这些工艺来有效净化制革工艺产生的废水中的有机残留物。

关键词：制革厂, 芬顿, 照片-芬顿, 废水.

1. Introduction

The pollutants from effluents produced by tanneries affect not only man but the entire ecosystem, causing damage to biota and therefore affecting the quality of life on our planet. Considering that water is a vital resource for our livelihood, it is necessary to generate processes that reduce the environmental impact produced by these pollutants, and provide the necessary mechanisms which can be replicated in other places with similar problems.

Fenton's process originates from the discovery reported in 1894 that ferrous ion strongly promotes the oxidation of tartaric acid by hydrogen peroxide [1]. However, only much later, the oxidation activity has been ascribed to the hydroxyl radical [2]. The mechanism of Fenton's process is quite complex, and some papers can be found in the literature where tens of equations are used for its description (e.g., [3]-[4]).

However, it can be summarized by the following steps: first, a mixture of H2O2 and ferrous iron in an acidic solution generates the hydroxyl radicals (Eq. 1) [5]-[6] which will subsequently attack the organic compounds present in the solution.

$$Fe^{+2} + H_2O_2 \quad Fe^{+3} + OH^- + OH^{\cdot} \qquad (1)$$

As iron (II) acts as a catalyst, it needs to be regenerated, which seems to occur through the following scheme:

$$Fe^{+3} + H_2O_2 \quad Fe\text{-}OOH^{+2} + H^+ \qquad (2)$$

$$Fe\text{-}OOH^{+2} \quad Fe^{+2} + HO_2 \qquad (3)$$

Oxidation with the Fenton's reagent has already shown to be effective and promising for the destruction of several compounds and, consequently, for the treatment of a wide range of wastewaters (e.g., [4], [7]-[9]). As its name suggests, the Photo-Fenton process is quite similar to that of Fenton, but it also uses radiation [4]. Its efficiency is attributed to the photolysis of Fe (III) cations in acidic media producing Fe (II) cations Eq. (4), with the reaction between Fe (II) and H2O2 to produce hydroxyl radicals (Fenton's reaction, step (5):

$$Fe(OH)^{+2} + HV \quad Fe^{+2} + OH \qquad (4)$$

$$Fe^{+2} + H_2O_2 \quad Fe\,(OH)^{+2} + OH \qquad (5)$$

In this process, the regeneration of Fe^{2+} by photo-reduction of Fe^{3+} (Eq. 4) is accelerated, this photo-reduction being an additional source of highly oxidative hydroxyl radicals, compared to the "simple" Fenton process. Nevertheless, the overall regeneration of the latter and process efficiency rate are considerably low [9]. However, the importance of Fe^{2+} regeneration through another step, namely the photo-reduction of the photochemical organic substrate or its degradation intermediates, was pointed out by some authors [10]:

$$Fe^{+3}\,L + HV \rightarrow Fe^{+2} + L^{\cdot}\ (L=RCOO^-, RO^-OH^-) \qquad (6)$$

In addition to Fe, other transition metals can catalyze the reactions mentioned (e.g., copper). For example, the reaction system using Cu as the photo-Fenton catalyst follows a similar network to Fe and is referred to as a photo-Fenton type reaction [11]. Recently, much attention has been paid to the Photo-Fenton and Photo-Fenton processes, mainly focusing on the heterogeneous process [10]. However, this process is closely related to the disadvantages associated with the homogeneous process, that is, the formation at the end of the process of large amounts of sludge containing metal, with high environmental impact and associated costs. Furthermore, a large amount of the catalytic metals is lost in these sludges. According to [11] and [12], the costs associated with processing these sludges may limit the application of the homogeneous Photo-Fenton process, highlighting how numerous attempts have been made to find heterogeneous systems/supports for Fe species.

Fenton and photo-Fenton techniques, which are part of the advanced oxidation processes, are currently proving to be very innovative and effective for the decontamination of polluting organic agents and recalcitrant compounds in industrial wastewater. In this context, this research aimed to apply the reagents Fenton (Fe^{+2}/H_2O_2) and photo-Fenton (Fe^{+2}/H_2O_2 + uv) in contaminated waters from tanneries in the Department of Quindío, Colombia.

2. Materials and Methods

2.1. Reagents and Preparation of Solutions

All reagents used in this work were analytical reagent grade and were used without further purification. Ferric sulfate hexahydrate ($FeSO_4.6H_2O$) 98%, hydrogen peroxide (30% w/w), unstabilized) Moreover, H_2SO_4 98% was purchased from Aldrich Chemical Company. All solutions were prepared in ultrapure water (Milli-Q water, Millipore).

2.2. Equipment

A METTLER TOLEDO UV-visible

spectrophotometer was used to determine the color and turbidity, as well as a set of Fenton pots with UV lamp couplings (wavelength of 269nm) for photo-Fenton. A TOC - V CSH SHIMADZU equipment was used to determine the total organic carbon.

2.3. Reactions Conditions

All experiments were carried out using six continuous stirring reactors (jar test) for the reaction process with the Fenton reagent. First, the raw water solutions belonging to the tanneries of La María in the Department of Quindío were homogenized, adjusting the pH to 4. Then, different concentrations of Fe^{+2} and hydrogen peroxide were initially used to find which concentration obtained the best removal of organic pollutants and improved color and turbidity.

Subsequently, the photo-Fenton analyses were carried out according to the same protocol for the Fenton process. The samples were irradiated with ultraviolet light at 269 nm for two hours. The turbidity results were compared, including color, chemical oxygen demand (COD), and total organic carbon (TOC).

2.4. Data Analysis

Descriptive statistics (mean ± standard deviation, coefficient of variation) was used for data analysis. Significant differences were established by the non-parametric statistical test of Mann-Whitney, with significance levels of 5% ($\alpha = 0.05$). Analyses were processed using the software PAST version 2.17c [13].

3. Results and Discussion

3.1. Fenton Process Results

Table 1 lists the preliminary data of the removal percentage from the Fenton process, taking into account data found in the literature for this type of effluent, following equation 7.

$$\% \text{ Rem} = \frac{(Wo - WF)}{Wo} * 10 \quad (7)$$

where % Rem is the removal percentage, Wo is the original water obtained from untreated tanneries, and WF represents the water treated with Fenton. In the case of photo-Fenton, the variable was changed by WpF.

The highest removal percentages, above 76%, were selected from Table 1, following the recommendations of [9]. This way, it was possible to choose the following combinations for treating tanneries.

Table 1 Preliminary data from the Fenton process

Fe+2 (g/L)	H_2O_2 (ml)	pH	Time (min)	Agitation rpm	Remain (%)
0.823	42	3	75	21.1761	32.26
0.333	67	4	30	150	86.59
0.823	42	4.5	75	100	65.15
0.823	81	3	75	100	71.92
1.595	42	3	75	100	90.45
0.333	17	2	30	50	91.61
Continuation of Table 1					
1.313	67	4	30	50	57.71
0.823	42	1.4	75	100	16.85
1.313	67	2	30	50	3.74
1.313	67	2	120	150	87.10
0.823	42	3	75	100	81.81
0.333	17	2	120	50	55.20
0.823	42	3	75	100	39.27
1.313	17	2	30	150	86.30
0.333	67	4	120	50	76.71
1.313	17	4	120	150	89.11
1.313	17	4	120	50	56.73
0.823	42	3	146	100	58.12
0.823	42	3	4.1	100	7.59
0.823	2.2	3	75	100	66.35
0.333	17	4	30	150	75.09
0.823	42	3	75	178	26.32
0.051	42	3	75	100	82.02
0.333	67	2	120	150	84.15

The results found in Figures 1-5, and 6 for the Fenton process, were carried out, leaving the pH and agitation constant with values of (4) and (150rpm), respectively.

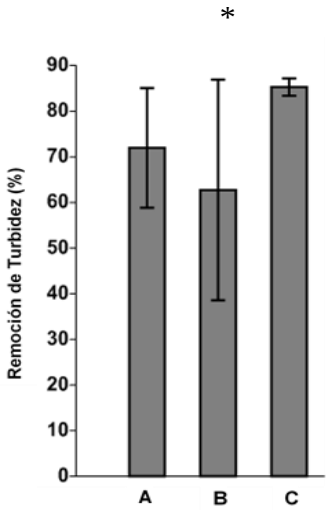

Fig. 1 Effect of the concentration of ferrous ion (Fe + 2) on the removal of turbidity (%). A: 0.9 g L-1. B: 1.2 g L-1. C: 1.5 g L-1. (*): non-significant difference ($p > 0.05$)

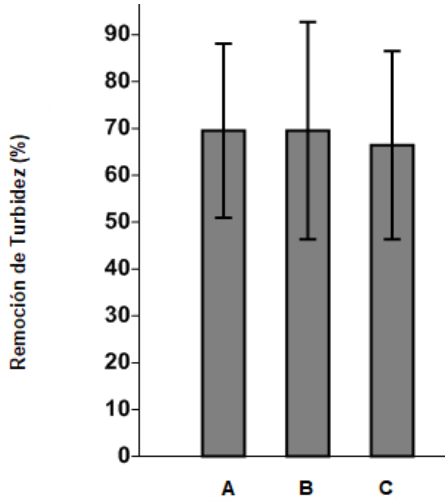

Fig. 2 Effect of peroxide concentration (H_2O_2) on turbidity removal (%). A: 3 ml. B:4 ml. C:5 ml. (*): non-significant difference ($p > 0.05$)

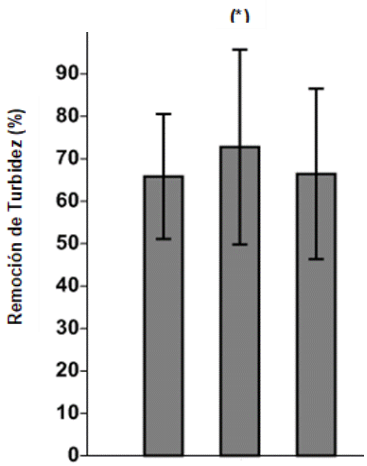

Fig. 3 Effect of time (t) on turbidity removal (%). A: 90 min. B: 12 0 min. C: 150 min. (*): Non-significant difference ($p > 0.05$)

Figures 1, 2, and 3 show the percentage of turbidity removal for concentrations A, B, and C, corresponding to 70 ± 20%, 60 ± 40%, and 85 ± 6% for ferrous ion concentration, hydrogen peroxide concentration, and reaction times, respectively. Despite the numerical differences in the mean values, there were no significant differences when $p > 0.005$ were statistically compared. Therefore, we recommend using the lowest concentrations and the lowest reaction time as this will save reagents, avoid waste and be more environmentally friendly.

In the case of color, three colors, yellow, red, and blue, at wavelengths of 436, 525, and 620nm, were evaluated in the ultraviolet spectrophotometer.

Table 2 Color results after using Fenton

Samples in triplicate	Original Water	Fenton 1	Fenton 2	Fenton 3	Fenton 4
Wavelengths	436	436	436	436	436
Absorbance	0.546	0.086	0.07	0.08	0.065
Removal (%)		84.249	87.179	85.347	88.095
Wavelengths	525	525	525	525	525
Absorbance	0.311	0.017	0.011	0.014	0.009
Removal (%)		94.533	96.463	95.498	97.106
Wavelengths	620	620	620	620	620
Absorbance	0.191	0.008	0.003	0.005	0.003
Removal (%)		95.811	98.429	97.382	98.429

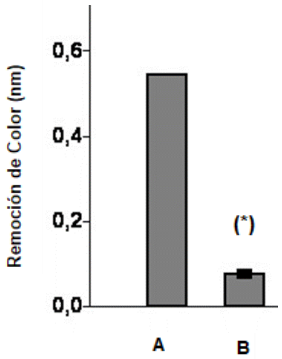

Fig. 4 Average (± standard deviation) of the color removal. A: absorbance of the color at 436 nm of the original water, B: absorbance of the color at 436 nm of the water after being treated with Fenton. (*): significant difference ($p < 0.05$)

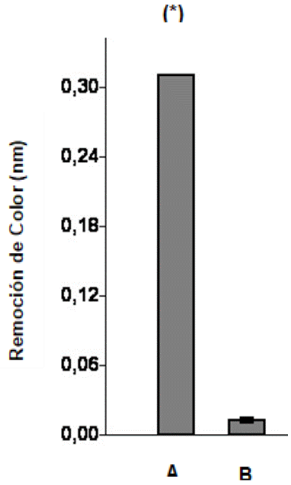

Fig. 5 Average (± standard deviation) of the color removal. A: absorbance of the color at 525 nm of the original water, B: absorbance of the color at 525 nm of the water after being treated with Fenton. (*): significant difference ($p < 0.05$)

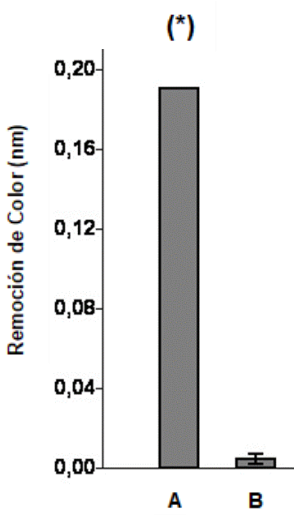

Fig. 6 Average (± standard deviation) of the color removal. A: absorbance of the color at 620 nm of the original water, B: absorbance of the color at 620 nm of the water after being treated with Fenton. (*): significant difference ($p < 0.05$)

Figures 4-6 represent color elimination at the three wavelengths, where A represents the color of the original water and B represents the color of the water after being treated with the Fenton process. The significant differences that exist between both effluents can be seen clearly (significant difference ($p < 0.05$)). Therefore, it is a treatment we recommend for this type of wastewater containing organic contaminants, achieving a color removal of over 90%.

3.2. Photo-Fenton Process Results

Those concentrations of Fe^{+2} and hydrogen peroxide that had worked more efficiently in the Fenton process were chosen for the photo-Fenton analyzes. Therefore, the jar equipment assembly was used. A box with ultraviolet light lamps with a 269nm wavelength was attached to irradiate the solutions for 2 hours and in this way to be able to compare the removal processes for

both experiments.

For this method, we also use the Mann-Whitney statistical analysis to establish if there are significant differences between the ferrous ion concentration, peroxide concentration, and the reaction time concerning turbidity removal.

Figures 7, 8, and 9 show the percentage of turbidity removal for concentrations AB and C, corresponding to 70 ± 20%, 60 ± 40%, and 85 ± 6%, for ferrous ion concentration, hydrogen peroxide concentration, and reaction times, respectively. Despite the numerical differences in the mean values, there were no statistically significant differences when compared p> 0.005 for the photo-Fenton process. Therefore, we recommend using the lowest concentrations and the lowest reaction time as this will save reagents, avoid waste and be more environmentally friendly.

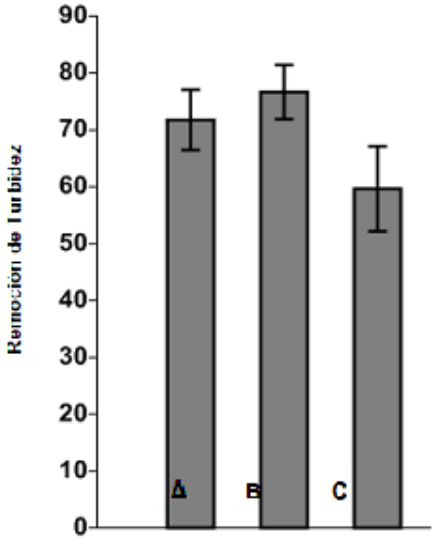

Fig. 7 Effect of ferrous ion concentration (Fe^{+2}) on turbidity removal (%). A: 0.9 g L-1. B: 1.2 g L-1. C: 1.5 g L-1. (*): non-significant difference (p > 0.05)

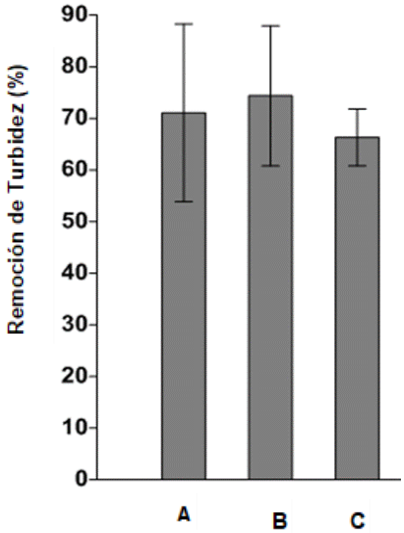

Fig. 8 Effect of peroxide concentration (ml) on turbidity removal (%). A: 3 ml. B: 4 ml. C: 5 ml. (*): non-significant difference (p > 0.05)

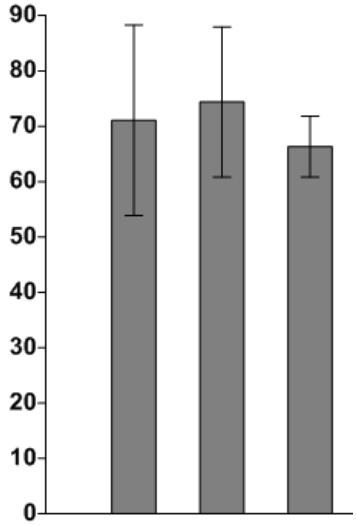

Fig. 9 Effect of time (t) on turbidity removal (%). A: 90 min. B: 120 min. C: 150 min. (*): non-significant difference (p > 0.05)

Also, we analyzed the effects of the color reduction in the samples irradiated with photo-Fenton, and the results shown in Table 3 were obtained.

Table 3 Color results after using photo-Fenton

Samples in triplicate	Original Water	Photo F1	Photo F2	Photo F3	Photo F4
Wavelengths	436	436	436	436	436
Absorbance	1.388	0.02	0.113	0.033	0.02
Removal (%)		99.998	99.991	99.997	99.998
Wavelengths	525	525	525	525	525
Absorbance	1.034	-0.03	0.045	-0.025	-0.032
Removal (%)		100.002	99.995	100.002	100.003
Wavelengths	620	620	620	620	620
Absorbance	0.868	-0.037	0.028	-0.033	-0.039
Removal (%)		104.262	96.774	103.803	104.493

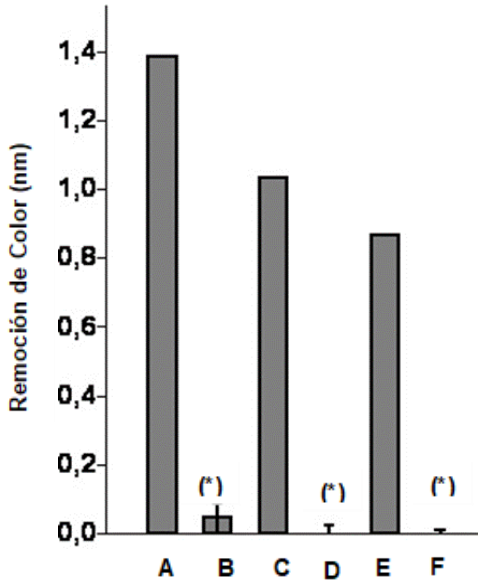

Fig. 10 Average (± standard deviation) of the color removal, A: absorbance of the color at 436 nm of the original water, B: absorbance of the color at 436 nm of the water after being treated with photo-Fenton, C: absorbance of the color at 525 nm of the original water, D: absorbance of the color at 525 nm of the water after being treated with photo- Fenton, E: absorbance of the color at 620 nm of the original water, F: absorbance of the color at 620 nm of the water after being treated with photo- Fenton. (*): significant difference between different wavelengths (p < 0.05)

The different wavelengths examined for color in the photo-Fenton process also showed significant differences compared to untreated water, obtaining a 100% color removal. This indicates that this technique is favorable for decontaminating colorants from industrial wastewater.

Finally, we compared the total organic carbon removals (TOC) and the chemical oxygen demand (COD) with the Fenton and photo-Fenton processes, as shown in Tables 4 and 5.

Table 4 Comparison of the TOC for the Fenton and photo-Fenton processes

Water AOF	TOC (mg/L)	Removal (%)
AOFF	645.50	54.30
F1	270.32	57.98
F2	253.50	60.58
F3	260.36	59.53
F4	258.75	59.78
F5	249.56	61.21
F6	238.96	62.86
FOF1	244.90	62.06
FOF2	226.33	64.93
FOF3	222.20	65.57
FOF4	233.55	63.81
FOF5	224.80	65.17
FOF6	218.50	66.15

Table 5 Comparison of the COD for the Fenton and photo-Fenton processes

Absorbance	COD	Water process	Removal (%)
0.156	681.75	FF1	31.43
0.157	681.75	FF2	31.43
0.158	731.75	FF3	26.40
0.159	636.75	FF4	35.95
0.16	669.25	FF5	32.58
0.161	795.75	FF6	19.96
0.162	994.25	DQO AOFF	
0.163	764.25	F1	11.31
0.164	656.75	F2	23.78
0.165	671.75	F3	22.04
0.166	734.25	F4	14.79
0.167	714.25	F5	17.11
0.168	796.75	F6	7.54
0.169	861.75	DQO AOF	

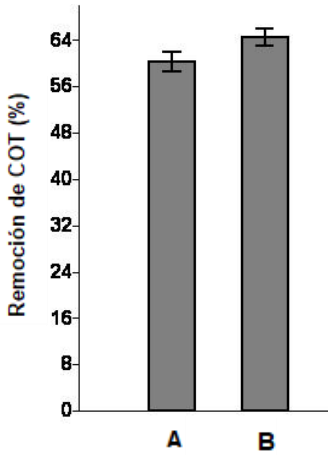

Fig. 11 Comparison of TOC removal, using the Fenton and photo-Fenton process, A: water with the Fenton, B: Water with the photo-Fenton process. (*): significant difference ($p < 0.05$)

When comparing the removal of total organic carbon (TOC) using the Fenton and photo-Fenton processes, as shown in Figure 11, significant differences were obtained in the statistical analyses. Therefore, it is recommended to use the photo- Fenton process to remove organic contaminants as it is much more efficient than Fenton alone.

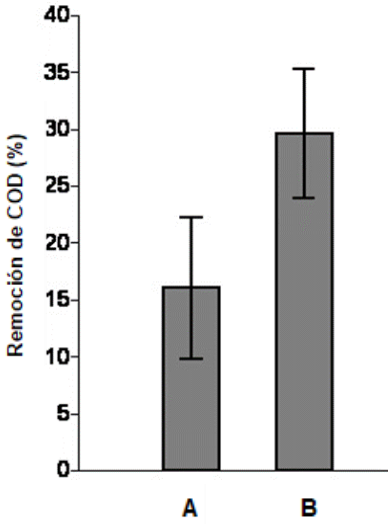

Fig. 12 Comparison of COD removal, using the Fenton and photo-Fenton process. A: water with the Fenton, B: Water with the photo-Fenton process. (*): significant difference ($p < 0.05$)

Figure 12 shows the demand for chemical oxygen removals for the waters treated with Fenton and photo-Fenton. We also performed a statistical analysis comparing these removals. A significant difference was obtained, which infers that the waters treated with the process of photo-Fenton obtain a better removal than the waters treated only with Fenton. Therefore, we also recommend using this process for polluted industrial waters. However, we also observed that the COD removal as a percentage function was not very high in most cases due to interferences of biological or inorganic origin, such as photosynthetic algae and heavy metals. For this reason, we will use electrochemistry or electro photo-Fenton to optimize this parameter.

4. Conclusion

In this research, where we compare the efficiency of two advanced oxidation processes, Fenton and photo-Fenton, applied to wastewater produced by the tanning industry in the Department of Quindío, it can be concluded that:

i. The sample quantities used in this study to evaluate parameters such as ferrous ion concentration, peroxide concentration, and reaction time showed no significant differences. Therefore, in this study, we chose the least sample quantities to save costs and energy and be more environmentally friendly.

ii. The Fenton process used to improve turbidity,

color, COD, and TOC indices was very efficient for real wastewater from the tanneries of La María in the Department of Quindío, obtaining turbidity removal higher than 84%. As with color, TOC removals greater than 62% and COD removals of 32% were also achieved.

iii. When comparing the Fenton process with the photo-Fenton process, it can be observed that turbidity removal, COD color, and TOC were more efficient for wastewater treated with ultraviolet light, that is, with the photo-Fenton treatment, since significant differences were obtained. Therefore, it is advisable to use this process for industrial product wastewater.

iv. Optimal results for wastewater decontamination and energy savings were obtained for the photo-Fenton analysis since sunlight was used as renewable energy. In addition, there was very little reagent expenditure, making it a friendly technique with the environment compared to others. Therefore, the authors recommend this technique for decontaminating wastewater in tanning industries.

5. Limitations and Further Study

The limitations in this study were mainly that the laboratories still did not have full access because the alarm about the pandemic continued. This situation caused the process to be delayed a bit. Regarding future studies, we will combine these Fenton and photo-Fenton techniques with electrochemical analysis to optimize the decontamination processes of wastewater produced by the tanning industry.

Acknowledgment

The authors thank the University of Quindío for financial support in obtaining and publishing the research results and the University's water laboratory for allowing us to carry out these tests. We also want to thank the spaces provided for research processes at the University of Santa Cruz del Sur (UNISC), Santa Cruz del Sur, Brazil.

References

[1] FENTON H J H. LXXIII - Oxidation of Tartaric Acid in Presence of Iron. *Journal of the Chemical Society, Transactions*, 1894, 65: 899–910.

[2] HABER F, & WEISS J. The catalytic decomposition of hydrogen peroxide by iron salts. *Proceedings of the Royal Society of London. Series A - Mathematical and Physical Sciences*, 1934, 147(861): 332–351. https://doi.org/10.1098/rspa.1934.0221

[3] GALLARD H, & DE LAAT J. Kinetic modelling of Fe(III)/H2O2 oxidation reactions in dilute aqueous solution using atrazine as a model organic compound. *Water Research*, 2000, 34(12): 3107–3116. https://doi.org/10.1016/S0043-1354(00)00074-9

[4] PERA-TITUS M, GARCÍA-MOLINA V, BAÑOS M. A, et al. Degradation of chlorophenols by means of advanced oxidation processes: A general review. *Applied Catalysis B: Environmental*, 2004, 47(4): 219–256. https://doi.org/10.1016/j.apcatb.2003.09.010

[5] COMAN V, ROBOTIN B, & ILEA P. Nickel recovery/removal from industrial wastes: A review. *Resources, Conservation and Recycling*, 2013, 73: 229–238. https://doi.org/10.1016/j.resconrec.2013.01.019

[6] WALLING C, CAMAIONI D M, & KIM S S. Aromatic Hydroxylation by Peroxydisulfate. *Journal of the American Chemical Society*, 1978, 100(15): 4814–4818. https://doi.org/10.1021/ja00483a030

[7] ANDREOZZI R, CAPRIO V, INSOLA A, & MAROTTA R. Advanced oxidation processes (AOP) for water purification and recovery. *Catalysis Today*, 1999, 53(1): 51–59. https://doi.org/10.1016/S0920-5861(99)00102-9

[8] GARRIDO-RAMÍREZ E G, THENG B K G, & MORA M L. Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions - A review. *Applied Clay Science*, 2010, 47(3–4): 182–192. https://doi.org/10.1016/j.clay.2009.11.044

[9] HERNEY-RAMIREZ J, VICENTE M A, & MADEIRA L M. Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review. *Applied Catalysis B: Environmental*, 2010, 98(1–2): 10–26. https://doi.org/10.1016/j.apcatb.2010.05.004

[10] SUM O S N, FENG J, HU X, & YUE P L. Pillared laponite clay-based Fe nanocomposites as heterogeneous catalysts for photo-Fenton degradation of acid black. *Chemical Engineering Science*, 2004, 59(22–23): 5269–5275. https://doi.org/10.1016/j.ces.2004.09.032

[11] LI B, DONG Y, ZOU C, & XU Y. Iron(III)-alginate fiber complex as a highly effective and stable heterogeneous Fenton photocatalyst for mineralization of organic dye. *Industrial and Engineering Chemistry Research*, 2014, 53(11): 4199–4206. https://doi.org/10.1021/ie404241r

[12] PLAKAS K V, KARABELAS A J, SKLARI S D, & ZASPALIS V T. Toward the development of a novel electro-Fenton system for eliminating toxic organic substances from water. Part 1. in situ generation of hydrogen peroxide. *Industrial and Engineering Chemistry Research*, 2013, 52(39): 13948–13956. https://doi.org/10.1021/ie400613k

[13] HAMMER Ø, HARPER D A T, & RYAN P D. PAST: Paleontological Statistics Software Package for Education and Data Analysis. *Palaeontologia Electronica*, 2001, 4(1): 9p.

参考文:

[1] FENTON H J H. LXXIII -存在铁时酒石酸的氧化。化学学会杂志,交易，1894，65：899-910。

[2] HABER F, 和 WEISS J. 铁盐催化分解过氧化氢。伦敦皇家会刊。一系列一个- 数学和物理科学，1934，147（861）：332–351。https://doi.org/10.1098/rspa.1934.0221

[3] GALLARD H, 和 DE LAAT J. 使用阿特拉津作为模型有机化合物的稀水溶液中铁(III)/过氧化氢 氧化反应的动力学模型。水研究，2000，34(12)：3107–3116。https://doi.org/10.1016/S0043-1354(00)00074-9

[4] PERA-TITUS M、GARCÍA-MOLINA V、BAÑOS M. A 等人。通过高级氧化工艺降解氯 综述。应用催化乙:环

境，2004，47（4）：219–256。https://doi.org/10.1016/j.apcatb.2003.09.010

[5] COMAN V、ROBOTIN B 和 ILEA P. 工业废物中回收/去除 综述。资源、保护和回收，2013，73：229–238。https://doi.org/10.1016/j.resconrec.2013.01.019

[6] WALLING C、CAMAIONI D M 和 KIM S S. 过二硫酸盐的芳族病分。美国化学学会杂志，1978，100（15）：4814-4818。https://doi.org/10.1021/ja00483a030

[7] ANDREOZZI R、CAPRIO V、INSOLA A 和 MAROTTA R. 用于水净化和回收的高级氧化工艺(AOP)。今日催化，1999，53(1)：51-59。https://doi.org/10.1016/S0920-5861(99)00102-9

[8] GARRIDO-RAMÍREZ E G、THENG B K G 和 MORA M L. 粘土和氧化物矿物作为芬顿反应中的催化剂和纳米催化剂 - 综述。粘土科学，2010，47（3-4）：182-192。https://doi.org/10.1016/j.clay.2009.11.044

[9] HERNEY-RAMIREZ J、VICENTE M A 和 MADEIRA L M. 用于废水处理的柱状粘土基催化剂的多相光芬顿氧化:综述。应用催化 B:环境，2010，98（1-2）：10-26。https://doi.org/10.1016/j.apcatb.2010.05.004

[10] SUM O S N, FENG J, HU X, 和 YUE P L. 柱状 皂石粘土基铁纳米复合材料作为多相催化剂用于酸性黑的光芬顿降解。化学工程科学，2004, 59(22–23): 5269–5275. https://doi.org/10.1016/j.ces.2004.09.032

[11] LI B, DONG Y, ZOU C, 和 XU Y. 铁(III)-藻酸盐纤维复合物作为一种高效稳定的非均相芬顿光催化剂用于有机染料的矿化。工业与工程化学研究，2014, 53(11): 4199-4206. https://doi.org/10.1021/ie404241r

[12] PLAKAS K V、KARABELAS A J、SKLARI S D 和 ZASPALIS V T. 开发一种用于消除水中有毒有机物质的新型电芬顿系统。第 1 部分。过氧化氢的原位生成。工业与工程化学研究，2013, 52(39): 13948-13956. https://doi.org/10.1021/ie400613k

[13] HAMMER Ø、HARPER D A T 和 RYAN P D. 过去的:用于教育和数据分析的古生物学统计软件包。电子古生物学, 2001, 4(1): 9。