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Catalysis, kinetics and reactors

Fenton process by volcanic ash to eliminate aniline of aqueous solution from the dyeing of toquilla straw crafts

Remoción de colorantes de aguas coloreadas con anilinas provenientes del teñido de artesanías de paja toquilla a través del proceso Fenton con ceniza volcánica

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Abstract

The toquilla straw hat is a cultural tourist attraction in the province of Azuay-Ecuador. Its production is carried out artisanally, with the dyeing process being one of the major problems due to the production of difficult-to-treat water that has an eco-toxicological impact on water-receiving bodies. A highly effective alternative for decoloring dyes is Advanced Oxidation Processes (AOP), the Fenton-like process that uses waste as catalysts as a source of iron that can be removed by filtration. In this work, the removal of dyes (red and black) in an aqueous solution used in the dyeing of handicrafts was carried out using ashes from the Cotopaxi volcano as a catalyst. The variable evaluated was the dye concentration reached when different amounts of ash and H_2O_2 were tested. Also, acute ecotoxicity tests were carried out with Daphnia Magna (D.M.) to determine its immobilization after 48 hours of exposure. For the black dye, a discoloration of 98.2 % was achieved after 48 hours of treatment using a Fe^{3+}: H_2O_2 ratio of 2:2 (gml^{-1}), while for the red dye in the same timeframe, a discoloration of 75.62 % was achieved with a Fe^{3+}: H_2O_2 ratio of 2:4 (gml^{-1}). Regarding the tests with D.M., they showed complete immobilization before the treatment and 0 % immobilization after the treatment, demonstrating water quality recovery.

Keywords: Fenton-like; volcanic ash, dyes.

Resumen

El sombrero de paja toquilla es una atracción turística cultural en la provincia de Azuay, Ecuador. Su producción se lleva a cabo de manera artesanal, siendo el proceso de teñido uno de los principales problemas debido a la generación de agua difícil de tratar que tiene un impacto eco-toxicológico en los cuerpos receptores de agua. Una alternativa altamente efectiva para la eliminación de tintes son los Procesos de Oxidación Avanzada (AOP), entre ellos el proceso similar al de Fenton que utiliza residuos como catalizadores como fuente de hierro y que puede ser eliminado mediante filtración. En este trabajo, la eliminación de tintes (rojo y negro) en una solución acuosa utilizada en el teñido de artesanías se llevó a cabo utilizando cenizas del volcán Cotopaxi como catalizador. La variable evaluada fue la concentración del tinte durante la reacción a diferentes concentraciones de ceniza y H_2O_2. Además, se realizaron pruebas de ecotoxicidad aguda con Daphnia Magna (D.M.) para determinar su inmovilización después de 48 horas de exposición. Para el tinte negro, se logró una remoción del 98.2 % después de 48 horas de tratamiento utilizando una relación Fe^{3+}: H_2O_2 de 2:2 (gml^{-1}), mientras que, para el tinte rojo en el mismo periodo, se logró una remoción del 75.62 % con una relación Fe^{3+}: H_2O_2 de 2:4 (gml^{-1}). En cuanto a las pruebas con D.M., mostraron una inmovilización del 100 % antes del tratamiento y del 0 % después del mismo demostrando que el agua ha recuperado la calidad.

Palabras clave: Fenton-like; ceniza-volcánica, colorantes.

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1 Introduction

The "Panama hats" were adopted due to the productive tradition of the indigenous people of the provinces of Azuay and Cañar, although their production in Ecuador dates back centuries (Farfán 2023; Malla 2020). Toquilla straw hats were declared Intangible Cultural Heritage of Humanity by UNESCO in 2012 (Galán 2022). The manufacturing process begins with the cultivation of palm trees called toquillales on the Ecuadorian coast. The stems are collected to separate the fiber from the green bark and boiled to eliminate the chlorophyll. Then, the fibers are dried and bleached with sulfur. With the raw materials ready, spinning, weaving, and punching hats and crafts begin. In the finishing phase, dyeing is done before ironing and baking. Although it is traditional to maintain the natural color of the straw in the finished products, the demand for hats and specially colored crafts is very high, making the dyeing process important, where producers prefer to use synthetic anilines due to the cost and duration of finished products (Macías, Ruiz, & Pedraza 2023).

The dyeing process consumes high volumes of water, generating effluents with different concentrations of dyes and chemicals (Khan *et al*. 2023). Water contaminated with dyes contains different auxiliary components that are included from the preparation stage to the finishing stage; these effluents, in large part or their entirety, are discharged into the nearest body of water or directly into the sewage network where they cause multiple damages to the ecosystem and environment since their main characteristics are a high Chemical Oxygen Demand (COD), and Biochemical Oxygen Demand (BBO), high Total Organic Carbon (TOC), high Color intensity and relatively high Hydrogen potential (pH, basic) (Lin *et al*. 2023; Uddin *et al*. 2023). Although some of the most biodegradable auxiliary dyes can be completely removed from dry cleaning effluent, conventional treatment systems cannot achieve "destructive" decolorization since textile dyes are intentionally designed to resist biological, photolytic, and chemical degradation (Tavares *et al*. 2020; Yue *et al*. 2021). During the last decade and a half, various technologies have been developed in the world to treat wastewater from various origins given that regulations are increasingly strict and due to a commitment to the environment, which is why industrialized countries have resorted to these technologies called Advanced Oxidation Processes (AOP) (Babuponnusami *et al*. 2023; Ángel-Hernández *et al*. 2021), However, in countries with emerging economies such as Latin American countries, although studied, these technologies have been little disseminated and not applied on a real scale. AOPs are generally applied on a small or medium scale where conventional methods lose efficiency; for example, in the case of waters with a very high concentration of non-biodegradable toxic contaminants (> 1 gl^{-1}), or very low (< 5 mgl^{-1}). AOPs can generally be used alone or in combination with each other and can also be applied to air and soil contaminants. Two processes develop within the AOP treatment: one is the formation of free radicals or oxidants such as hydroxyl radicals (OH·) and other species, and the second is the chemical reaction of radicals produced as organic compounds (Giwa *et al*. 2021).

One of the most used Advanced Oxidation Processes is the Fenton process; this classic method is one of the most economical and fastest methodologies within the AOP. The Fenton method initially uses a Ferrous Iron (Fe^{2+}) salt as a catalyst; the iron is oxidized to Ferric Iron (Fe^{3+}); the reaction occurs in an aqueous medium at acidic pH, the oxidizing agent hydrogen peroxide (H_2O_2) that in the presence of the catalyst yields the Hydroxide Ion [OH-] and the Hydroxyl radical [OH·] which is the leading actor to oxidize the organic matter (Contreras-Bustos *et al*. 2020), see Eq. 1.

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

Fenton is effective for treating colored water as it completely removes the color and partially removes the COD from a textile effluent (Rojas-Valencia *et al*. 2020; Nour, Tony, y Nabwey 2023). Several investigations have been carried out using Fenton to remove dyes in textile wastewater; generally, Iron Sulfate ($FeSO_4$) is used, and pH is between 2 and 4 (Thomas, Dionysiou, and Pillai 2021). However, one of the significant disadvantages of classic Fenton is that since it is a homogeneous process, the recovery of the catalyst is complicated, needing neutralization and filtration at the end of the process to recover the catalyst. Currently, research seeks to reduce costs, which is possible by using heterogeneous catalysts in Fenton-like processes where the catalysts are easily recovered at the end (Hussain, Aneggi, y Goi 2021). If waste containing transition metals such as iron or copper is also used, the process will have a circular economy approach to waste recovery. In Table 1, you can see examples of heterogeneous Fenton investigations using waste for dye removal.

Table 1 shows that the Fenton-like process achieved discolorations of over 80 %, except for Rhodamine 6G, which achieved a discoloration of 78 %. Sources of Fe^{+2} was mainly used as catalysts; the pH values range between 3-4 and, or, between 6-7.

With this background, the removal of dyes in artisanal dyeing effluents was carried out through the Fenton process using volcanic ash as a catalyst in this work.

Table 1. Studies using Fenton-like to decolorize dyes in water.

	Dye	Concentration, mgl^{-1}	Catalysts	Catalysts concentration, gl^{-1}	H_2O_2 mM	pH	Θ, min	% Removal	Ref.
1	Methylene Blue	-	Fly ash	0.004	1ml	3	240	93	(Saechan *et al*. 2023)
2	Methylene Blue	10	Food waste-biochar	1	80	5	300	98	(Chu *et al*. 2020)
3	Crystal violet	200	Food waste-biochar	2.5	1.8	3	50	88	
4	Rhodamine 6G	25	Volcanic ash	5	1.14ml	3	120	78	(DJOWE *et al*. 2018)
5	Methylene blue	10	Calamine type 2 (high carbon)	15	2.94	3	360	99.8	(Acero, Avendaño-Sánchez, & Bermúdez-Castañeda 2023)
6	Methylene blue	10	Biomass-hydrocarbon	0.4	99.70	6.4	60	97.77	(Wang, Huang, & Sun 2020)
7	Waste water from dry cleaners	250 ml	Pyrite (FeS_2)	24	10.00	6	120	99	(Chen *et al*. 2021)

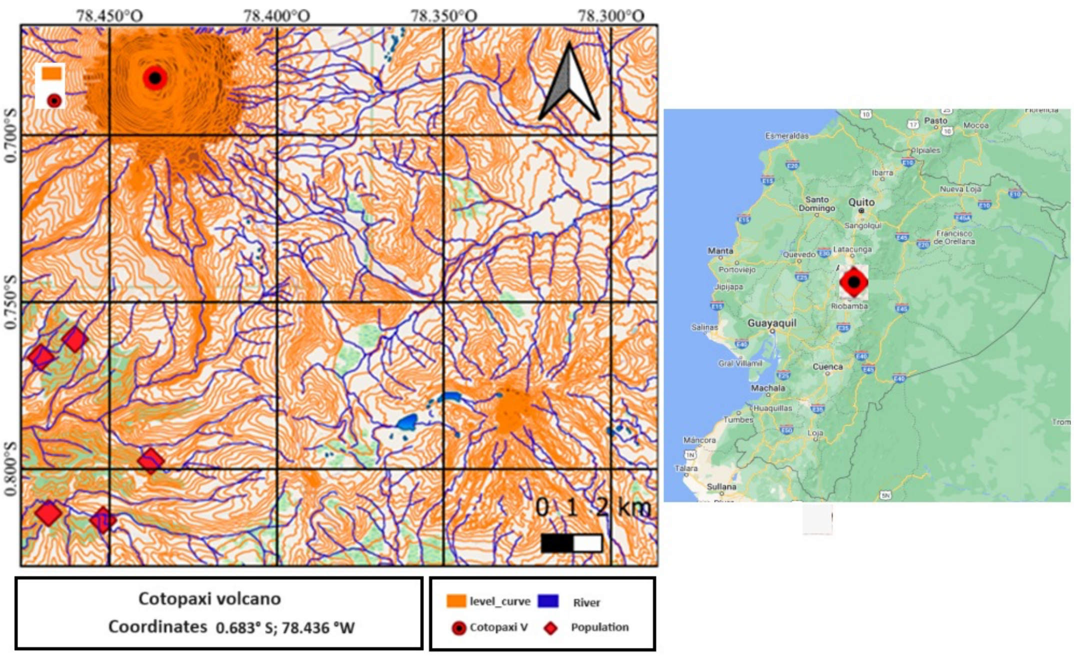

Fig. 1. Georeferenced map of the volcano Cotopaxi - Ecuador (QGIS Desktop 3.24.0).

2 Materials and methods

2.1 Model contaminants

Two black and red aniline powders were selected, which are widely used in the dyeing process of toquilla straw hats. Aqueous solutions of 1 gl^{-1} concentration of each color were prepared at room temperature ~ 17 °C to 19 °C.

Color concentrations in the aqueous solution were determined using an ultraviolet-visible (UV-Vis) spectrophotometer, Thermo Scientific Genesys TM 10S. The wavelength for black was 450 nm, and for red, it was 650 nm. For each solution, a calibration curve was made with concentrations varying from 12.5 to 100 ppm.

2.2 Volcanic ash

In this study, volcanic ash from the active Cotopaxi volcano (located 33 km northeast of the city of Latacunga-Ecuador; see Fig.1) was used as a catalyst for the Fenton method due to its ease of obtaining and operation. The ash sample was sieved to guarantee a uniform particle size distribution, which presented magnetic properties.

The ash sample was analyzed for its metal content with inductively coupled plasma mass spectrometry (ICP-MS), model NexION 350, Perkin Elmer brand. The analysis used the EPA method 200.8 (US EPA, 1994). To check reliability, two of the standards used in the calibration curve were read after having read every 20 samples. In total, 43 metals were analyzed.

An X-ray diffraction (XRD) analysis was also carried out in which the mineralogical components of a 1 g ash sample were identified. An X-ray Diffractometer was used brand: Bruker, model: D2

PHASER; the measurements were carried out with the help of the Difrac plus software, and the EVA software and the TOPAS 4 software were used for identification.

2.3 *Fenton process*

To the colored solution whose pH was adjusted to 3 with 98 % sulfuric acid from Fisher Chemical (Center Valley, PA, USA), volcanic ash (source of Fe_2O_3) and hydrogen peroxide (H_2O_2, 3%, 10 Vol., PARACELSO), the added quantities correspond to an experimental design of two factors (amount of ash and dose of hydrogen peroxide or molar doses of ash/oxidant (Fe^{3+}/H_2O_2) at three levels each factor, ash as a source of Fe^{3+} (6 g, 4 g, 2 g) and H_2O_2 (3 ml, 2 ml, 1 ml), keeping constant the concentration of the dye (1000 ppm) and the pH of the medium. The response will be the percentage of removal in 24 and 48 hours. Three replicates were carried out for each experiment. Once the reaction was completed, the resulting solution was neutralized using sodium hydroxide (NaOH, extra pure, ACROS ORGANICS) to precipitate the iron in the solution, and the iron sludge was separated by filtration.

2.4 *Analysis of data*

The data were analyzed using R software with an R Studio interface. The two-way ANOVA statistical test was applied at a significance level of 5% to determine whether the individual or combined effects were significant. For the statistically significant models, a post hoc was applied to determine which pairs the differences occurred between.

2.5 *Kinetics*

Once the optimal design was determined, the reaction kinetics study was carried out. For this, the concentrations of the dye were measured over a certain period. The kinetic data were tested using the different mathematical models of the integral method to determine the order and kinetic constant of the reaction. The design equation for the batch reactor with a constant volume is $-r_A = dC_A/dt$. The partial reaction orders (n) took values of 0, 1, and 2 to integrate the equation, resulting in eq 2, 3 and 4. The dye was considered the limiting reagent, and hydrogen peroxide was considered an excess reagent (Levenspiel 2010).

$$n = 0, -r_A = k, C_A = C_A0 - kt \tag{2}$$

$$n = 1, -r_A = kC_A, \ln C_A = \ln C_{A0} - kt \tag{3}$$

$$n = 2, -r_A = kC_A^2, C_A^{-1} = C_{A0}^{-1} - kt \tag{4}$$

2.6 *Ecotoxicity tests with Daphnia magna*

Acute biotoxicity tests were performed with Daphnia magna at 48 h. Daphnias from the third clone, which was less than 24 hours old, were used for this. Each test was done in quintuplicate using 10 ml of the sample of each color of the specimens before and after treatment with 5 neonates per test. After 48 hours of exposure, the immobility count of the organisms was carried out (Li *et al*. 2023; Pinos 2021).

3 Results and discussion

3.1 *Catalyst characterization*

Table 2 presents the results of the composition of volcanic ash through plasma mass spectrometry (ICP-MS) analysis. One of the highest percentages is Iron (Fe 57), with 13.50 mgg^{-1}.

Table 2. Composition of volcanic ash (Cotopaxi Volcano) by ICP MS.

Minerals/Metals	mgg^{-1}	Minerals/Metals	mgg^{-1}	Minerals/Metals	mgg^{-1}
Ag < LD	Eu	< LD	Pr	0.001	
Al	7.067	Fe	13.50	Rb	0.001
As	0.001	Ga	0.002	S	8.128
B	0.0004	Gd	0.001	Se	0.001
Ba	0.023	K	0.363	Sm	0.001
Be	< LD	Li	0.001	Sr	0.0610
Ca	7.979	La	0.004	Ti	0.807
Cd	< LD	Lu	< LD	Th	< LD
Ce	0.008	Mg	0.113	Tl	< LD
Co	0.005	Mn	0.066	Tm	< LD
Cr	0.006	Na	0.001	U	0.0002
Cs	< LD	Nd	0.004	V	0.068
Cu	0.014	Ni	0.003	Yb	< LD
Dy	0.001	P	0.360	Zn	0.0156
Er	< LD	Pb	0.001		

< LD: less than detection limits.

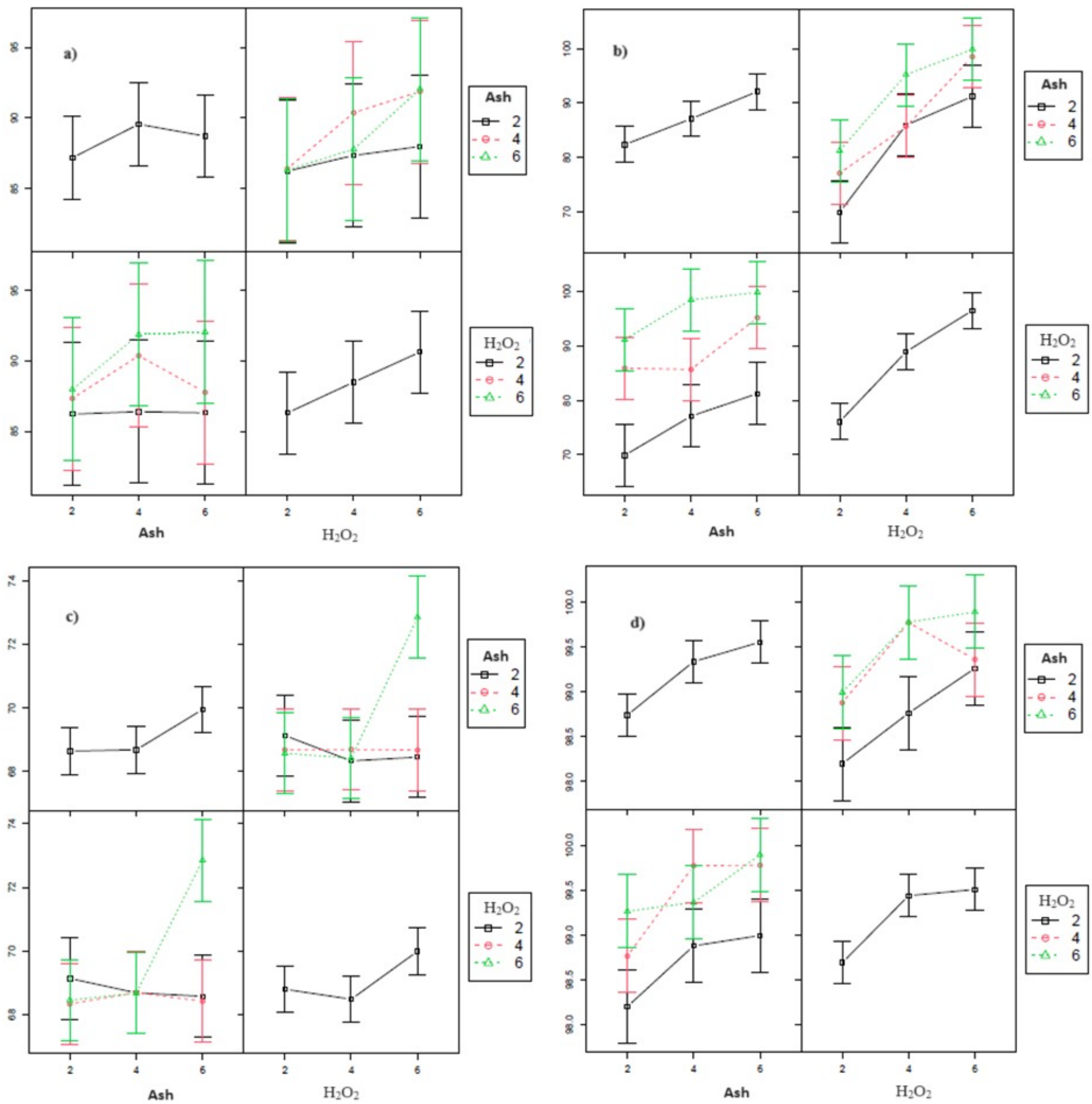

Fig. 2. Figure of effects a) black dye at 24 hours, b) black dye at 48 hours, c) red dye at 24 hours, d) red dye at 48 hours.

The X-ray diffraction analysis shows that the volcanic ashes have the following composition: 64.57 % of albite high K.0.16, 9.85 % of andesine, 7.79 % of muscovite, 6.88 % of diopside, 4.93 % of gypsum, 2.84 % of phengite, 2.18 % of walstromite, between others.

3.2 *Fenton-like process with ash*

Figure 2 shows the individual and double effects of the black and red dye at 24 and 48 hours. According to ANOVA, there are no statistically significant differences either at 24 or 48 h with the black dye because, in all cases, the p-value was greater than the level of significance, 5% (0.05). In the case of the red dye, no statistically significant differences were found at 24 h between the removals of the different red treatments. However, differences were found after 48 hours of removal in the case of peroxide, p (0.00548) < 0.05. In the post hoc, it was determined that there were no differences between the results obtained using 4 or 6 ml of peroxide, p (0.06) <0.5; differences were found between the use of 2 ml of peroxide and 4 ml, p (0.012) <0.05 and between the use of 2 ml of peroxide and 6 ml, p (0.00006) <0.05. In both cases, less removal was found with 2 ml.

The four figures have in common that using the relationship with the highest doses of catalyst and peroxide (Fe^{3+}:H_2O_2 → 6:6 gml^{-1}), the highest percentages of decolorization dye was obtained,

Table 3. Design matrix and results obtained for the Fenton treatments at their respective molar doses of each experimental sample of the black solution in 24 and 48 hours, pH of 3.

Fe^{3+}/ H_2O_2 gml^{-1}	% Black dye discoloration Mean ± SD		% Red dye discoloration Mean ± SD	
	24 h	48 h	24 h	48 h
2:02	86.22±0.086	98.20±0.015	69.14±0.009	68.97±0.009
2:04	86.39±0.078	98.88±0.002	68.68±0.002	75.62±0.093
2:06	86.30±0.057	99.00±0.005	68.57±0.001	78.03±0.065
4:02	87.33±0.059	98.77±0.006	68.33±0.002	84.87±0.214
4:04	90.36±0.042	99.78±0.001	68.69±0.002	82.60±0.114
4:06	87.76±0.101	99.78±0.001	68.42±0.001	94.31±0.069
6:02	87.96±0.070	99.27±0.001	68.45±0.001	88.94±0.101
6:04	91.87±0.053	99.37±0.004	68.68±0.004	96.82±0.037
6:06	92.04±0.080	99.90±0.000	72.85±0.053	99.23±0.008

however, as indicated above, these differences are not significant compared to the use of lower doses, so this treatment could be carried out using the lowest doses without affecting efficiency. Red obtained noticeably less removal than black within this same time because each dye has a different chemical structure, with red being more recalcitrant. From the results obtained, the molar ratio 2:2 is set for black and 2:4 for red (See table 3).

Comparing the results obtained in this study with the bibliography (Table 1), the majority of treatments achieve a removal greater than 80 %, with time being the factor that makes the difference between investigations, due to the different treatment conditions. operation and factors such as pH, iron concentration, H_2O_2, and even the type of dye to be treated. Each investigation seeks the ideal operation with these variables; for example, a certain change in pH decreases the efficiency of the treatment, or a poor concentration of H_2O_2 would generate problems with the generation of hydroxyl radicals that are responsible for destroying organic compounds if the catalyst to be used is a good source of iron.

In entries 2 and 3 of table 1, it is observed that for the removal of methylene blue and crystal violet, they experimented with biochar as a catalyst and varied all the reaction parameters, obtaining the best results for the removal of methylene blue (98 %) in which a greater amount of catalyst, H_2O_2 and a longer time (300 min) were used. With a similar strategy in entry 6 using biomass-hydrocarbon to remove methylene blue, they obtained removal of approximately 98 % in 60 min. The difference between these two studies lies in the amount of H_2O_2 used. In the present work, the removal time is longer. This may be due to the catalyst's characteristics and the dyes' recalcitrance.

To identify which part of the process had a contribution from homogeneous Fenton, additional tests were conducted under conditions that yielded the best results. These tests focused on evaluating iron leaching. To do so, the process was repeated using ash soaked for 48 hours in an environment with a pH of 3.

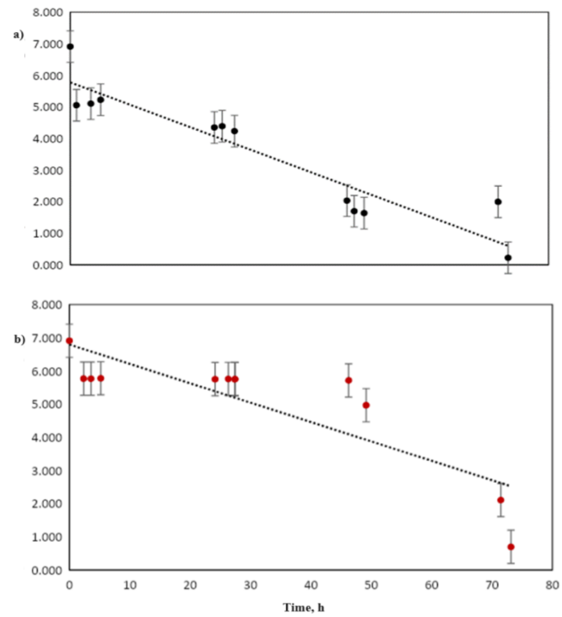

Fig. 3. a) Kinetic data from the 2:2 black test adjusted to the first-order model; b) Kinetic data of the red color from the 2:4 test adjusted to the pseudo first-order model.

After this soaking period, the mixture was filtered, and hydrogen peroxide was added to the resulting effluent lending, acting for an additional 48 hours. The results indicated a discoloration percentage of 27 % for the red dye and 14.6 % for the black test. Proving that the most outstanding contribution of discoloration with ashes is through heterogeneous catalysis.

3.3 *Oxidation kinetics in the Fenton-like process*

The rate of consumption of the contaminants by the oxidation of the hydroxyl radical (OH.) adjusts to a pseudo first order reaction, see Fig.3. The kinetic equation for the black dye is $-r_{black} = -0.93C_{black}$, while for red we have $-r_{red} = -0.0607C_{red}$. As equations that correspond to the pseudo first order, their speed decreases as the concentration decreases, that is, the increase in degradation at the beginning is high, but as time passes the degradation speed decreases.

3.4 Ecotoxicity tests and wastes management

In the ecotoxicological tests with Daphnia magna, it was found that in the four replicates of the untreated samples, all D.M. were immobilized. In comparison, in the 4 replicates of the test with the treated solution, all D.M. survived, this for each color. This proves that the water quality has been recovered and that it can be returned to the environment. It is important to note that this process utilized volcanic ash, highlighting its sustainable and eco-friendly nature. In the end, the ash can be reused in multiple cycles of the Fenton process, maximizing its efficiency, and minimizing environmental impact, thereby promoting more responsible and environmentally friendly wastewater treatment practices. Once its use in the Fenton process is complete, volcanic ash can find various beneficial applications. For example, after a thorough analysis to detect the presence of heavy metals or other contaminants, it could be used in manufacturing ceramics or cement production, thus contributing to circular economy principles and sustainable resource utilization.

Conclusions

In this study, a Fenton-like process with volcanic ash was effectively used to decolorize aniline-colored waters from the dyeing of toquilla straw handicrafts with color removals of 69 % and up to 86.2 % at 48 h. For the black color, was setting the most optimal molar dose concerning removal performance in Fe^{3+}: $H_2O_2 \rightarrow 2{:}2$ (gml^{-1}), while for red dye, it was set at Fe^{3+}: $H_2O_2 \rightarrow 2{:}4$ (gml^{-1}). The ash recovered at the end of the Fenton-like process is reusable for other decolorization processes since it does not lose its chemical and magnetic properties so that it could be used at least a second or third time. Fenton-like process effluents guarantee a permissible level of toxicity. Finally, despite some considerable disadvantages, such as pH control operations that incur costs for additional reagents and the generation of sludge due to the neutralization of solutions in the final stage, this treatment technology turns out to be very efficient, relatively economical, and environmentally friendly.

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