

Case Report

An activated steel scale waste catalyst to degrade Methylene Blue via the Heterogeneous Fenton Process

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ABSTRACT

Methylene Blue (MB) generates colored effluents that are difficult to treat. Solid Scale Waste (SSW) was studied as a catalyst in a Heterogeneous Fenton process for MB removal. The SSW was identified as a non-porous material with 97.5 % iron oxides. For the oxidative process, the exposure to light, amount of catalyst, and H_2O_2 dose were tested. The best conditions to enhance MB removal were 0.01g of catalyst, 0.035 mL of H_2O_2 , and light; under these conditions, a removal percentage of 97.41 % was achieved. The kinetics results showed a pseudo-first-order reaction and an Activation Energy of 81.92 kJ/mol.

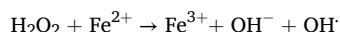
1. Introduction

Dyes are widely used in industrial processes that produce textiles, rubber, printing, cosmetics, medicine, plastic, concrete, and paper [1,2]. All these processes generate colored wastewater containing organic chemicals [3]. Dyes in water affect aquatic ecosystems by blocking sunlight and interfering with phytoplankton photosynthesis [4,5]. Because these synthetic dyes are very light and oxidation stable, they resist decomposition [6]. Synthetic dyes also leave poisonous and carcinogenic compounds, which can bioaccumulate in aquatic biota, where they enter the food chain and threaten human health [7,8]. This non-biodegradable pollutant has adverse effects on human health, including eyeburn, mental confusion [9], profuse sweating, vomiting, nausea, blindness, gastritis, death of premature cells, shock, tissue necrosis, jaundice [2] anaphylaxis [10]; and breathing problems. Doses over 5 mg/kg can induce serotonin toxicity [6,10]. One of the most used dyes is Methylene Blue (MB), a cationic heterocyclic dye with an azo group. MB is commonly used to dye silk, wool, cotton, paper, and leather [2] and as an oxidation-reduction indicator [11] as well as a disinfectant [3].

Dyes such as MB have traditionally been removed from textile bath effluents by processes such as adsorption, coagulation-flocculation, biological treatments, or their combinations [12–14]. However, Advanced Oxidation Processes (AOP), including ozonation, direct UV, $\text{UV}/\text{H}_2\text{O}_2/\text{O}_3$, Fenton, and photo-Fenton, more successfully break down

complex contaminants into simpler non-toxic molecules [3,15,16].

Throughout the Fenton process, organic colors are mineralized in wastewater [17,18]. This non-selective degradation process utilizes hydroxyl radicals generated during this chemical reaction:



The Fenton reaction can be homogeneous or heterogeneous. In the homogeneous process all the reactants are in the same phase, generally liquid. Industrial wastewater with an ideal pH of 2.5–3.0 reacts in a stoichiometric relationship between Fe^{2+} and H_2O_2 [19]. However, this process generates a sludge by-product with high iron content that is both difficult to remove and a source of secondary pollution [20].

The heterogeneous Fenton process is an alternative to avoiding sludge formation. This process uses a solid catalyst that is more stable during the process; thus, it is more cost-effective and environmentally beneficial. Moreover, it enables the recovery of the catalyst and has high activity. In the solid catalyst, chemical reactions develop on the catalyst's surface, and mass transfer could limit the adsorption of reactants. Therefore, the process design should be considered to avoid mass transfer being the determinant [21]. However, the use of heterogeneous catalysis presents more advantages than disadvantages; in Table 1, examples of dye removal by heterogeneous Fenton are presented with the reaction conditions. The results of these investigations show that a high dye removal percentage (in most cases more than 90 %) can be achieved with small amounts of catalyst and hydrogen peroxide, in short periods

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Table 1
Heterogeneous Fenton processes examples.

No.	Dye, mg/L	Catalyst, mg/L	Operation Conditions	Time, min	H ₂ O ₂ , mM/L	Removal, %	Ref
1	50, Methylene blue	600, Zeolite-supported Fe ₃ O ₄	NS pH = 3 photo-Phenton (UV-6W)	5	0.00194	~100	[8]
2	10, Rhodamine B (RhB)	20, MnFe ₂ O ₄ -Graphene Oxide	NA pH = 3 Electro-Phenton (3V)	60	NA	97.51	[22]
3	50, Toluidine blue O (TBO)	1200, Fe/active carbon	20 °C pH = 3.5	3	4	99	[23]
4	10, Reactive Orange (RO29)	3000, Natural Pyrite	NS pH = 2	120	3	94.4	[24]
5	50, Methylene blue	1000, Yolk-shell Fe ₃ O ₄ @MOF-5	30 °C pH = 4	60	30	100	[25]
6	50, Crystal violet	50, Fibrous catalyst (25 mg/5 mL, PET-NH ₂ -Fe, PET-Si-NH ₂ -Fe, and PET-SH-Fe)	22 °C pH = 5	Equilibrium time	100	99	[26]
7	10, Methylene blue	15,000, Calamine (zinc mineral) type II	Room temperature pH = 3	180	0.00294	99	[27]
8	10, Methylene blue	2000, MnO ₂ -Fe ₃ O ₄ /CuO	T = 23 °C pH = 2	45	32	>90	[28]
9	30.69, 4.63, 11.34 Residual water from flower dyeing	558, Fe	Room temperature pH = 2.3	300	1.129	97	[29]
10	50, Direct Red 80, Direct Blue 80, and Direct Brown 103	960, Magnetic activated carbon catalyst produced from date palm waste	Room temperature pH = 7	84	0.0097	92.69; 97.07; 73.85	[30]
11	100, Methylene blue	500, Fe-impregnated biochar	NS pH = 4	3	0.0021	99.9	[31], p. 202
12	10, Acid yellow 36 (AY36)	1000, Pyrite	NS pH = 3 Fluidized bed reactor	60	2	95	[32]
13	10, Methylene blue	200, Black Nikel mud	NS	30	0.882	87.15	[27]
14	25, Methylene blue	20 Fe ₃ O ₄ , 20 α-Fe ₂ O ₃ , and 20 α-FeOOH	NS pH = 6.5	120	0.882	56, 60, and 82	[33]
15	25, Methylene blue (MB) and Acid blue 29 (AB29)	40 (AB29) and 20 (MB), Electric arc furnace steel slag	30 °C Dark Fenton	NS	6 (AB29) and 8 (MB)	95 (AB29) and 82 (MB)	[34]

of time, therefore exploring the use of materials with high Fe content as catalyst for a Fenton process can be proved to be successful.

Although very effective for removal, one of the drawbacks is the cost of the process. A material with high iron content, such as waste from the steel industry, is a viable option for preparing heterogeneous Fenton catalysts at a low cost. The literature on using steel production wastes as catalysts is limited and focuses mainly on steel slag and no other types of residues [35]. Steel scale waste (SSW), also known as calamine, is a layer of iron oxide that detaches from the surface of steel plates during hot rolling treatments [34,36,37]. Some of this residue is reused within the cement industry, but a non-recyclable amount usually ends up in landfills. Since this material has a high Fe content, it is suitable as a catalyst for a heterogeneous Fenton process. Using waste material as a catalyst, the Fenton process would be carried out from a circular economy model, where recycling and reusing existing materials and products many times create added value. In this way, the life cycle of the products is extended.

This research investigates the effects of the amount of an SSW catalyst (recycled material), hydrogen peroxide dose, and the presence of light to determine the best treatment conditions in a Fenton-like process to remove MB from an aqueous solution. A kinetic study complements the understanding of the process.

2. Material and methods

2.1. Steel scale waste activation

The SSW, obtained from an Ecuadorian carbon steel producer, was activated according to methodology described by Nasua et al. (2021).

Briefly, the SSW sample was immersed in a 20 wt% sulfuric acid solution from Fisher Chemical (Center Valley, PA, USA) for 4 h, then filtered and washed until a pH = 7 was obtained. The sample was dried in an oven at 100 °C for 24 hours and then heated at 400 °C for 2 h. The sample obtained was used as a heterogeneous catalyst in the Fenton process to degrade methylene blue.

2.2. Catalyst characterization

The Brunauer–Emmet–Teller (BET) technique was used on Quantachrome NOVA 2200e equipment (Anton Paar, Austria) to determine the surface area and pore size of the catalyst. The surface area was calculated with Multipoint BET with the isotherms obtained. The pore size was calculated with DFT.

X-ray fluorescence (ISO29581-2 standard method) was used to determine the chemical composition of the SSW. For qualification and semi-quantification, the crystalline structure of the activated SSW was analyzed by X-ray diffraction analysis in a diffractometer D8 Advance with the software Diffract Plus (EVA and TOPAS). The detection limit was 1 %.

2.3. Fenton-like process

A Fenton-like degradation of MB was analyzed under dark and light conditions. The reaction was performed in glass containers with 100 mL of a solution of 100 mg/L of MB. The bubbles formed from aeration were used as a mixing agent. The experimentation time was 24 hours, at room temperature (~18°C). Twenty-one combinations of catalysts formed

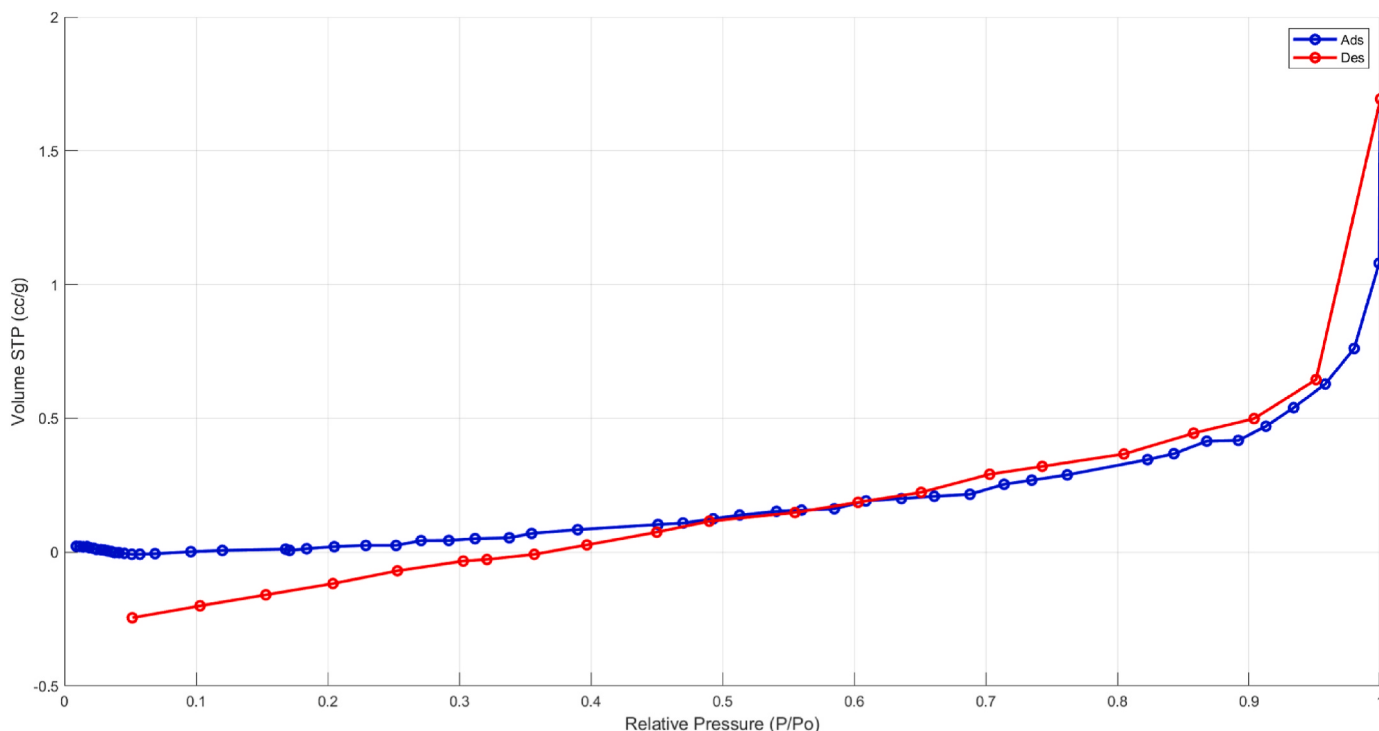


Fig. 1. Isotherm of steel scale waste.

from SSW and hydrogen peroxide (Merck, Germany) were tested.

An experimental design was applied to determine the best conditions to enhance the oxidative process. This design accounts for three factors: two levels of exposure to light (light, darkness); three levels of amount of the catalyst (0.01, 0.02, 0.04 g of SSW); and six levels of hydrogen peroxide dosage (0.005, 0.01, 0.035, 0.05, 0.07, 0.1 mL of H₂O₂ 30 % v/v). The catalyst was added to 100 mL of a 100 mg/L of MB solution. The peroxide was continuously mixed with bubbling air from a hose. Each experiment was performed in duplicate and with a blank sample (without peroxide) for comparison.

The response variable was the percentage of MB removed within 24 hours. The dye concentration from each reaction was determined by ultraviolet–visible (UV–Vis) spectrophotometry (Thermo Scientific Genesys TM 10S). The wavelength was 644 nm. Concentrations from the calibration curve ranged from 6.25 to 100 ppm. The percentage of dye removal was calculated with Equation (1).

$$\% \text{ Removal} = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100 \quad (\text{Equation 1})$$

Where % removal = dye removal percentage; C_{initial} = dye initial concentration; and C_{final} = dye final concentration.

R version 4.3.1 with the RStudio interface was used to analyze the results, the Phia package to generate the graphs, and the Pid package to create Pareto graphs.

2.4. Kinetics degradation study

The kinetics of the discoloration process with the best combinations of catalyst and peroxide were studied. The experiment was repeated in triplicate, and a sample was taken every half hour. The dye concentration data were analyzed using the integral method to determine the reaction order. This method fits data to linear models with pseudo kinetics. Because an excess of peroxide is used, the results are presented as pseudo kinetics (Equation (2)). Furthermore, the kinetic constant was calculated with Arrhenius, at room temperature, 25, and 30 °C, with Equation (3).

Table 2

X-ray fluorescence results for the SSW.

Formula	Content (%)
Fe ₂ O _x	97.5
SiO ₂	0.67
Al ₂ O ₃	0.23
CaO	0.22
MgO	0.10
SO ₃	0.07

$$-\frac{dC}{dt} = k C^n \quad (\text{Equation 2})$$

Where n = the order of reaction (0, 1, or 2) evaluated; C = the concentration of the dye; and k = the kinetic constant.

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (\text{Equation 3})$$

Where k = kinetic constant at different temperatures; A = frequency factor; E_a = activation energy; T = temperature; and R = gas constant.

3. Results and discussion

3.1. Catalyst characterization

Results of the BET showed a surface area of 0.224 m²/g; a pore volume of 0.001 cc/g; a half pore width 27.193 °Å; and an isotherm

Table 3

X-ray diffraction results for the SSW.

Mineral	Formula	Content (%)
Magnetite	Fe ₃ O ₄	81
Kamacite	Fe, Ni	8
Hematite	Fe ₂ O ₃	6
Wustite	FeO	4
Maghemite	Fe ₂ O ₃	1

Table 4
MB dye removal percentage in the tested conditions.

Catalyst amount (g)	Hydrogen peroxide (mL)	Light	Darkness
		Removal percentage (%)	Removal percentage (%)
0.01	0.005	76.09 ± 0.13	84.25 ± 0.30
	0.01	86.60 ± 0.39	87.60 ± 0.46
	0.035	97.41 ± 0.19	95.38 ± 0.22
	0.07	97.46 ± 0.20	97.34 ± 0.11
	blank	31.25 ± 0.14	30.72 ± 0.36
0.02	0.005	72.22 ± 0.50	81.36 ± 0.50
	0.01	85.07 ± 0.08	89.88 ± 0.66
	0.035	96.60 ± 0.12	96.77 ± 0.34
	0.07	97.32 ± 0.30	97.18 ± 0.25
	blank	55.59 ± 0.70	33.50 ± 0.22
0.04	0.005	80.89 ± 0.65	74.08 ± 0.18
	0.01	88.64 ± 0.08	86.87 ± 0.54
	0.035	97.59 ± 0.16	97.55 ± 0.33
	0.07	98.18 ± 0.44	97.92 ± 0.22
	blank	31.82 ± 0.20	42.32 ± 0.44

(Fig. 1) that corresponds to type III and hysteresis type H3, a macro-porous or non-porous material [38].

The X-ray fluorescence showed the sample was 97.5 % iron oxides (Table 2), congruent with the 97.88 % reported for SSW [35]. The iron oxide concentration varied across several types of steel, depending on the steel production process as well as the raw material used.

Further X-ray diffraction (Table 3) determined magnetite was the predominant iron phase, a finding congruent with the literature [38–41]. However, the percentages were at variance with reports of 36.1 % by Ref. [42] and 8 % [35] for SSW.

3.2. Fenton-like process

The Heterogenous Fenton Process with activated SSW as the catalyst is a viable option for the treatment of colored effluents; the removal percentage ranged from 30.72 to 98.18 % (Table 4). The results of this study are similar to those presented in the literature where other residues or waste materials are used as catalysts (Table 1). With electric arc furnace steel slag used as the catalyst in a Fenton-like process, removal percentages of 82 % and 95 % for MB and Acid blue 29 effluents,

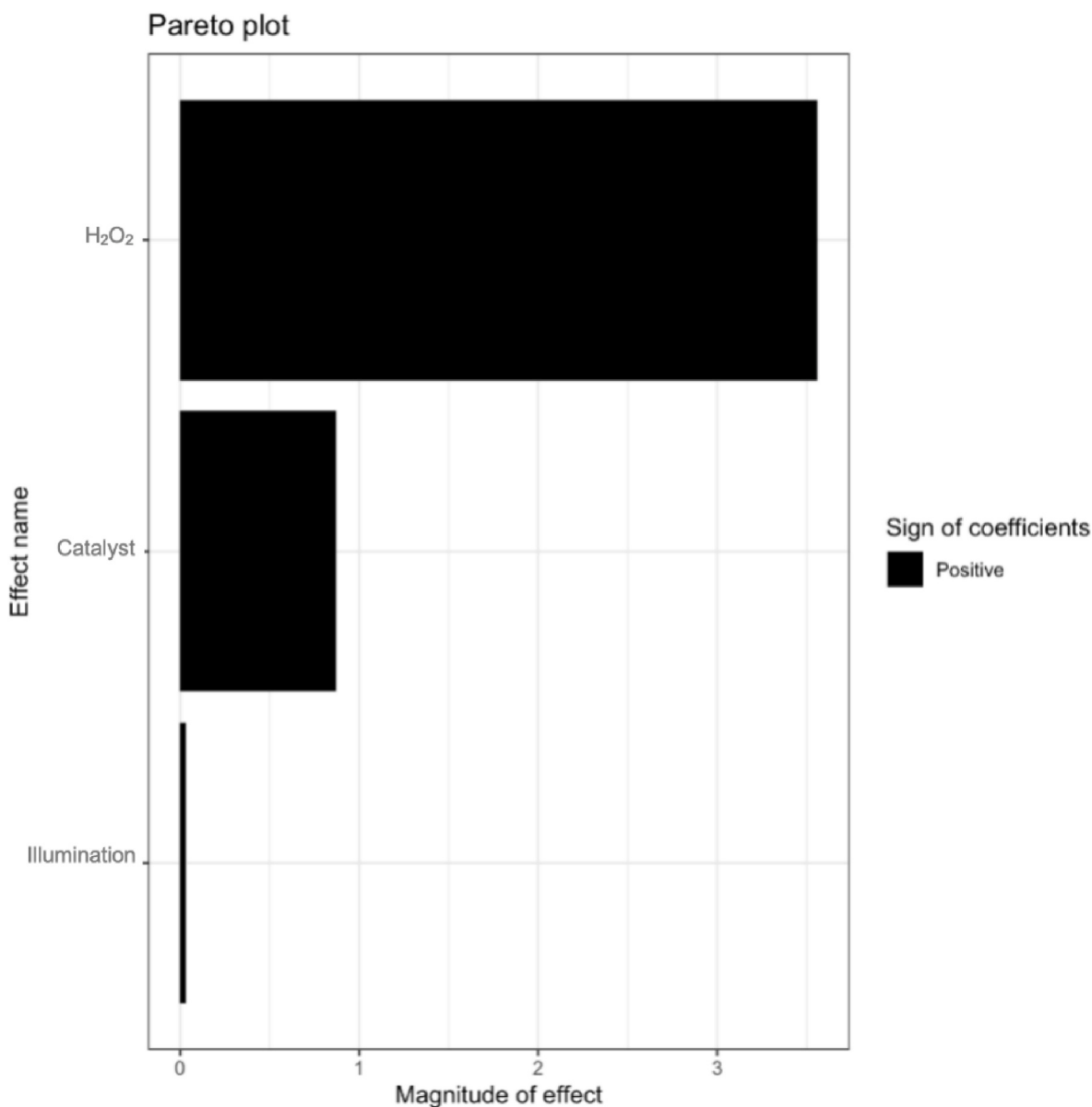


Fig. 2. Pareto plot of the magnitude of the effect for the factorial design model of the discoloration of the Methylene blue.

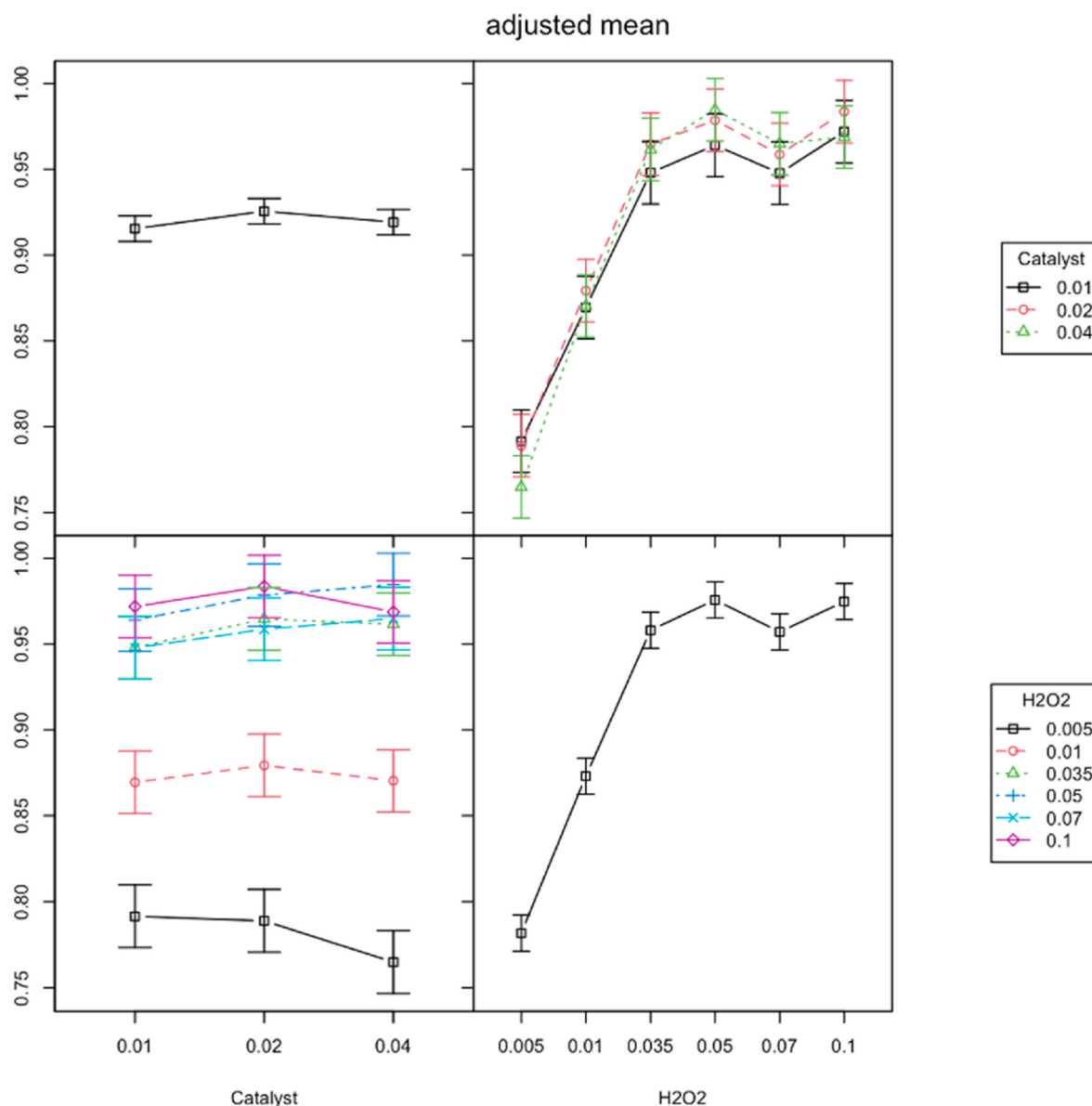


Fig. 3. Effects of the catalyst and hydrogen peroxide on MB discoloration in experiments performed in light.

respectively, were obtained [34]. Under similar conditions, with pyrite as a catalyst for the removal of acid yellow, a removal percentage of 95 % was obtained in 60 minutes [32]. A range of removal percentages between 73 and 99.9 % was obtained with Fe impregnated on biochar and activated carbon, both produced from palm residues [30].

Fig. 2 presents a Pareto Plot for the three factors: exposure to light; amount of catalyst; and hydrogen peroxide dose. The latter was the only significant factor. The same results were obtained from the ANOVA analysis; only the effect of hydrogen peroxide was significant ($F = 109.412$, $p = 9.79 \times 10^{-15} < 0.005$). No other main effects or any two- or three-way interactions were significant. The post hoc analysis showed significant differences in the removal rate in the first doses of hydrogen peroxide, those between 0.005 mL and 0.01 mL. Above doses of 0.035 mL, no statistically significant differences were found. The optimum was set at the minimum amount of 0.01 g of catalyst, with light, and a dose of 0.035 mL of hydrogen peroxide. The MB removal percentage achieved under the best conditions (0.01 g of catalyst, 0.035 mL of hydrogen peroxide and light for 24 hours) was 97.41 %.

The three factors investigated in our study – the catalyst, hydrogen peroxide, and degree of light – produced different outcomes. The

response variable showed no significant change in response to the catalyst contrary to another study that demonstrated that a higher amount of catalyst increased the rate of decolorization [43]. Contrary to the reported elsewhere [34] our study also showed that neither light nor darkness affected the experiment. Therefore, natural light should not affect the results.

However, our study did show that the amount of hydrogen peroxide does influence the oxidative process, although from 0.035 mg/L onwards, there is no significant increase in decolorization. A 1:1 stoichiometric relationship between the dye and hydrogen peroxide has been shown to increase the mineralization of organic matter, but above that threshold, hydrogen peroxide eliminates reactive species [19]. Doses of hydrogen peroxide beyond that threshold have also been shown to increase the chemical oxygen demand of the effluent and to elevate the costs of the treatment [44]. Fig. 3 shows the interactions of two of the three factors, the catalyst and hydrogen peroxide.

3.3. Kinetic analysis

The MB degradation mechanism, in this Fenton process, suggest that

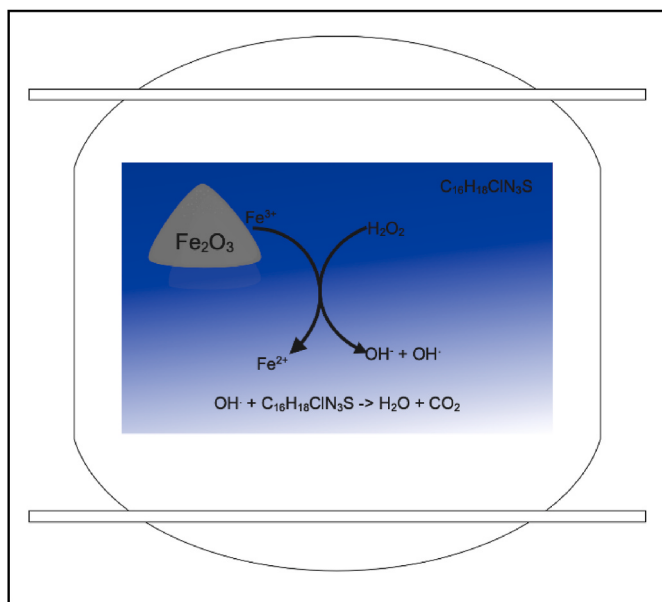


Fig. 4. Fenton process mechanism for MB degradation.

the iron oxide present in the activated SSW catalyzes the decomposition of H_2O_2 , generating hydroxyl radicals. These radicals then oxidize the organic matter, promoting the MB mineralization (See Fig. 4).

The rate of dye removal ($\text{OH}^\cdot$ radical oxidation) followed a pseudo-first-order reaction (Fig. 5a). This means that the reaction rate depends on the concentration of the limiting reagent, in this case, the dye (methylene blue). The resultant equation was $-r_{\text{MB}} = 0.0157C_{\text{MB}}$ (Equation 4): the rate decreased as the dye concentration decreased. In

the Arrhenius study (Fig. 5b), the activation energy for this reaction was 81.92 kJ/mol. In this case, activation energy suggests that the reaction may be sensitive to changes in temperature and may require specific conditions to occur efficiently. The results can be observed in figura b).

Giving the high costs associated with traditional catalysts and the challenges of recovering them, in this research an effective alternative was proposed within the framework of a circular economy, successfully utilizing industrial waste. The findings on the optimal catalyst and hydrogen peroxide doses, when combined with a comprehensive kinetic analysis, provide a solid foundation for understanding the decolorization mechanism and serve as the basis for a future larger-scale process application. Additionally, the catalyst's magnetic properties offer a significant advantage for recovery (See Fig. 6 for a qualitative reference), although these properties were not measured in this study. Future research should address this gap by thoroughly evaluating the magnetic properties and assessing the reusability cycles of the prepared catalyst. Moreover, it would be beneficial to apply this Heterogeneous Fenton Process to other dyes. This will ensure the feasibility and sustainability of using this waste-derived catalyst on a larger scale.

4. Conclusions

A catalyst prepared from SSW was successfully used in a Heterogeneous Fenton Process to remove MB. Three characteristics – the high iron content (97.5 % of Fe_2O_3); the surface area ($0.224 \text{ m}^2/\text{g}$); and the magnetic properties (81 % magnetite) of the activated SS – combined to make the catalyst efficient in the oxidative process. The best conditions for the removal of MB were determined by three factors: exposure to light, the amount of catalyst, and the dose of hydrogen peroxide. The latter was the most significant contributing factor to the process. The optimal dose of H_2O_2 was 0.035 mL; above this value no significant statistical difference was observed. The discoloration kinetics followed a

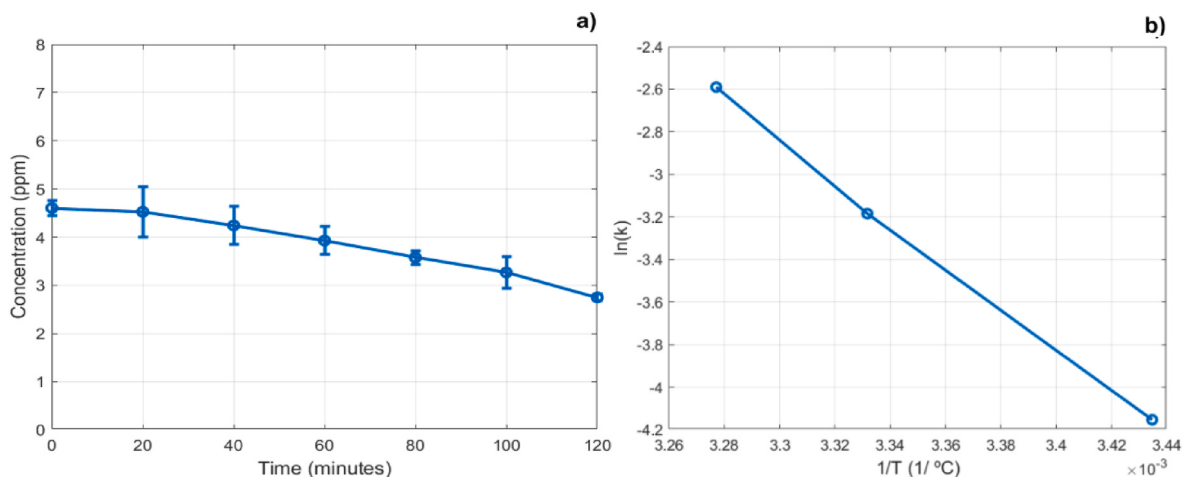


Fig. 5. a) Concentration vs time to determine k. b) Results of Arrhenius.



Fig. 6. a, b) Activated catalyst, and c) Residual sludge after Fenton Process magnetic characteristic.

pseudo-first-order with a kinetic constant of 0.0157 mg/mL. The presented process could be scaled up as an alternative effluent treatment in a circular economy model.

CRedit authorship contribution statement

Mónica Abril-González: Methodology, Investigation. **Doménica Seminario:** Methodology, Investigation, Formal analysis. **Verónica Pinos-Vélez:** Writing – review & editing, Formal analysis, Conceptualization. **Angélica Vele:** Resources, Methodology, Formal analysis. **Paulina Echeverría-Paredes:** Writing – review & editing, Supervision, Project administration, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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