

Performance of Liparite-supported Hematite as a Fenton-like Catalyst for Continuous Methylene Blue Degradation

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Abstract—The presence of synthetic dyes in industrial effluents, such as methylene blue, represents a significant environmental challenge due to their persistence and resistance to conventional treatment. This study evaluated a Fenton-like catalyst synthesized from iron recovered from acid mine drainage originating from the Quilacocha tailings in Peru, with the aim of degrading methylene blue in a fixed-bed reactor. Iron was selectively precipitated (pH 2.5–4.0), converted into ferric hydroxide, thermally transformed into hematite ($\alpha\text{-Fe}_2\text{O}_3$), and supported on liparite. The catalytic performance was evaluated using a Taguchi L8 experimental design considering pH (3.5–5.0), temperature (40–50 °C), hydrogen peroxide concentration (0.15–3.00 g/L), and flow rate (0.006–0.010 L/min). Results showed that the acid mine drainage, characterized by a high iron concentration, enabled the synthesis of a catalyst containing 46.84% to 52.83% iron, suitable for heterogeneous Fenton-like oxidation. Optimal degradation of methylene blue was achieved at pH 3.5, 50 °C, 3 g/L hydrogen peroxide, and a flow rate of 0.006 L/min, reaching removal efficiencies of up to 90.3%. Main-effect and interaction analyses confirmed that pH, temperature, and flow rate were the most influential factors. These findings demonstrate that materials derived from acid mine drainage constitute efficient, economical, and sustainable alternatives for the treatment of dye-contaminated industrial wastewater.

Keywords—acid mine drainage, hematite, heterogeneous Fenton-like, methylene blue, fixed-bed reactor, circular economy

I. INTRODUCTION

The release of synthetic dyes into water bodies remains a major environmental concern due to their toxicity, persistence, and resistance to conventional treatment processes. Methylene blue, widely used in the textile and chemical industries, is particularly problematic because even at low concentrations, it can disrupt aquatic ecosystems and is difficult to remove using conventional treatment methods. Growing evidence has highlighted the increasing environmental and health risks associated with dye-contaminated wastewater, highlighting the need for more efficient and sustainable treatment technologies [1]. Advanced oxidation processes provide an attractive alternative, and heterogeneous Fenton-like systems have attracted increasing attention because of their ability to generate highly reactive oxidizing species without the limitations associated with traditional homogeneous reactions.

These processes rely on the generation of hydroxyl radicals ($\bullet\text{OH}$), which are capable of mineralizing complex organic pollutants into simpler and less harmful compounds [2, 3]. Current efforts have focused on improving catalyst efficiency, stability, and reusability through the

design of supported and composite materials [4].

Iron oxides such as hematite are promising catalysts for these processes, and their performance largely depends on the availability and cost of suitable iron precursors. Recent advances have shown that waste-derived materials, such as activated sludge ash and industrial residues, can be effectively transformed into Fenton-like catalysts capable of achieving high degradation efficiencies of methylene blue [5]. Acid Mine Drainage (AMD), which contains high concentrations of dissolved iron, represents both an environmental challenge and a potential resource for catalyst production. Recovering iron from this waste stream and transforming it into functional materials aligns with sustainable strategies for wastewater treatment.

Previous investigations have explored the use of AMD-derived materials for pollutant removal, including adsorption and catalytic applications, confirming their potential as low-cost and environmentally sustainable resources [6, 7].

Mining residues have also been investigated as secondary resources for metal recovery through hydrometallurgical processes, demonstrating their potential for sustainable resource utilization and circular economy approaches [8].

Natural materials such as volcanic tuffs and zeolitic rocks have also been investigated as catalyst supports due to their high porosity, low cost, and environmental compatibility, showing effective performance in photo-Fenton-like degradation processes [9].

Despite these advances, most reported studies are still based on batch systems and synthetic or laboratory-prepared materials, limiting their scalability and practical application in continuous treatment systems. Furthermore, limited attention has been given to the integration of waste-derived catalysts with fixed-bed reactor configurations under controlled operating conditions.

This study synthesizes hematite from AMD and evaluates its performance as a heterogeneous Fenton-like catalyst for the degradation of methylene blue in a fixed-bed reactor. In this context, the present work addresses this gap by integrating (i) the valorization of acid mine drainage as a source of iron, (ii) the use of liparite as a natural support material, and (iii) the evaluation of catalytic performance under continuous-flow conditions using a Taguchi experimental design. The objective is to assess whether AMD-derived hematite can serve as an efficient, low-cost, and environmentally sustainable alternative for treating dye-contaminated effluents.

This approach provides new insights into the development of scalable and sustainable Fenton-like systems based on

mining residues for real wastewater treatment applications.

II. LITERATURE REVIEW

The presence of synthetic dyes in industrial effluents is an increasing environmental concern due to their persistence, toxicity, and difficulty in removal. Among them, Methylene Blue (MB) is one of the most widely used dyes in the textile industry and in clinical laboratories, and its discharge into natural water bodies generates adverse impacts, including reduced light transmission, disruption of aquatic photosynthesis, and direct toxicity to living organisms [10–13]. Its polycyclic aromatic structure confers high stability against biodegradation, contributing to its persistence in the environment [11, 12].

Conventional treatment technologies such as physical adsorption, coagulation, filtration, and biological processes show limitations in completely removing MB, especially at low concentrations or in complex matrices [14–16]. In response, low-cost adsorbents derived from biomass and agricultural wastes have been tested, achieving substantial initial removal but generally without significant mineralization [15, 16].

Advanced Oxidation Processes (AOPs) have emerged as highly effective technologies for degrading recalcitrant organic contaminants. Among them, Fenton and Fenton-like processes are widely studied due to their ability to generate reactive oxygen species, such as hydroxyl radicals ($\bullet\text{OH}$), capable of attacking complex aromatic structures [3, 17, 18]. In their heterogeneous variant, solid iron-based catalysts overcome limitations of homogeneous Fenton systems, including narrow pH operating ranges, production of ferric sludge, and limited catalyst recovery [3, 18–20].

In heterogeneous Fenton-like systems, hydrogen peroxide is activated at the surface of iron-based catalysts through redox cycling between Fe(III) and Fe(II) species, leading to the in-situ generation of hydroxyl radicals ($\bullet\text{OH}$). The catalytic mechanism involves surface-mediated electron transfer, where Fe(II) reacts with H_2O_2 to produce $\bullet\text{OH}$ and Fe(III), while Fe(III) can be reduced back to Fe(II) through reaction with H_2O_2 or intermediate radical species, thereby sustaining the catalytic cycle. Unlike homogeneous systems, radical formation and pollutant oxidation occur predominantly at or near the catalyst surface, where adsorption of both H_2O_2 and organic molecules facilitates oxidation via surface-bound reactive oxygen species. This interfacial mechanism reduces iron sludge formation and enables catalyst recovery while maintaining strong oxidative capacity for the degradation and eventual mineralization of recalcitrant organic compounds [2, 21].

Recent studies have further demonstrated that iron-based catalysts supported by oxide matrices exhibit complex Fe(II)/Fe(III) redox behavior governed by surface-mediated electron transfer processes. These interactions influence catalytic activity by modifying the electronic structure and facilitating continuous redox cycling. Although such mechanisms have been extensively investigated in thermal and catalytic conversion systems, they provide valuable insight into the behavior of iron species in heterogeneous catalytic environments [22, 23]. This understanding strengthens the interpretation of surface redox processes in heterogeneous Fenton-like systems. Hematite ($\alpha\text{-Fe}_2\text{O}_3$)

stands out among heterogeneous Fenton-like catalysts due to its low cost, abundance, chemical stability, and ability to facilitate Fe(III)/Fe(II) redox cycling at its surface. Recent studies have reported controlled transformations of ferrihydrite and goethite into nanocrystalline hematite with improved catalytic activity [19, 20, 24, 25]. Synthetic routes such as sol–gel, coprecipitation, or calcination of hydrated precursors allow control of crystallinity, surface area, particle size, and functional group density, all of which influence catalytic performance [24, 25].

Interest has also grown in the use of natural minerals and industrial residues to produce efficient iron-based catalysts. Laterites, clays, incinerated sludge ash, and ferrous industrial wastes have been shown to degrade dyes and emerging contaminants through combined adsorption and oxidative activation mechanisms [17, 26, 27]. In particular, incinerated sludge ash has been reported as a viable precursor for highly active Fenton-like catalysts for methylene blue degradation [5].

A particularly relevant research area is the valorization of AMD, a mining waste rich in iron present as sulfates and hydrated oxides. Neutralization of AMD produces ferric precipitates that can be converted into hematite through controlled calcination, yielding materials with suitable catalytic properties [26, 27]. Recent studies have shown that iron nanoparticles obtained directly from AMD are highly effective for methylene blue removal, combining adsorption and advanced oxidation pathways [28]. Other analyses have highlighted the environmental potential of AMD-derived iron precipitates even without extensive modifications [29].

Globally, various natural and modified materials are being explored for pollutant removal via Fenton-like processes, consolidating them as promising alternatives for industrial wastewater treatment [30]. Additionally, iron-based materials, modified geopolymers, and hybrid catalysts have demonstrated highly satisfactory performance in methylene blue degradation in recent studies [5, 31–33].

In this context, recovering iron from AMD and converting it into hematite ($\alpha\text{-Fe}_2\text{O}_3$) represents an environmentally and technologically valuable opportunity to obtain an efficient, low-cost, and sustainable catalyst. This work analyzes the synthesis of hematite derived from AMD and its performance in methylene blue degradation in a packed-bed reactor, demonstrating the potential of AMD-derived materials as heterogeneous Fenton-like catalysts for industrial wastewater treatment.

III. MATERIALS AND METHODS

A. Study Area and AMD Characteristics

Acid Mine Drainage (AMD) samples were collected from the Quiulacocha mining area in the Pasco region, located in the central Peruvian Andes. The site is situated at 4,266 m above sea level within a historically exploited polymetallic mining area characterized by intensive sulfide ore extraction. Prolonged mining activities in the area have led to the formation of acidic effluents enriched in dissolved metals, mainly because of sulfide mineral oxidation. The Quiulacocha mining area forms part of the Cerro de Pasco polymetallic district in central Peru, characterized by Zn–Pb–Ag–Cu mineralization hosted in sulfide-rich deposits.

The tailings and waste-rock materials contain high proportions of pyrite (FeS_2) and other sulfide minerals, which generate acid mine drainage through oxidative weathering processes. The oxidation of pyrite in the presence of oxygen and water produces sulfuric acid and releases significant concentrations of dissolved iron into the surrounding drainage systems. Previous mineralogical and geochemical investigations in the area have documented low pH values and elevated concentrations of Fe, Zn, and Pb in the AMD [34, 35].

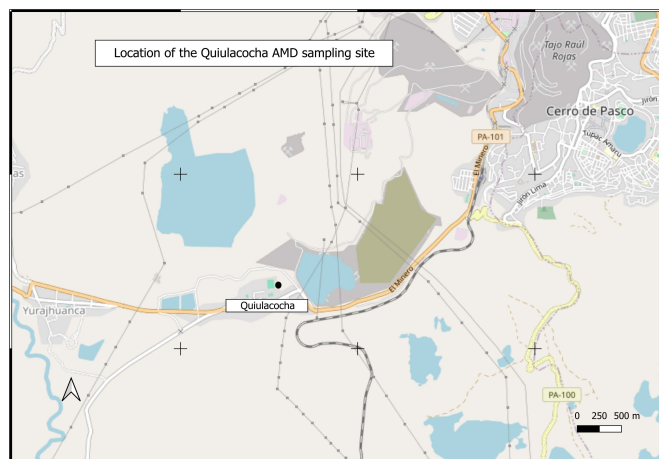


Fig. 1. Location of the Quiulacocha mining site in central Peru.

Iron used as the precursor for synthesizing the catalyst was obtained from AMD from the Quiulacocha mining site in Cerro de Pasco, Peru. The location of the study area is shown in Fig. 1. Table 1 presents the characteristics of the sample provided by the environmental management company. As shown, iron is the dominant dissolved metal in the AMD sample, supporting its use as a precursor for iron recovery and hematite synthesis.

Table 1. Initial metal concentrations in Acid Mine Drainage (AMD) from the Quiulacocha mining site

Cu (mg/L)	Pb (mg/L)	Zn (mg/L)	Fe (mg/L)	Ag (mg/L)
1.37	1.01	464.00	2427.50	0.001

B. Synthesis of Hematite from AMD

Hematite was obtained from the AMD iron present as sulfate complexes via selective precipitation [21, 36]. Fe(II) was first oxidized to Fe(III) using hydrogen peroxide at an acidic pH of 2.5–4.0, followed by the formation of ferric hydroxide using sodium hydroxide. The Fe(OH)_3 precipitate was filtered, washed, and dissolved in a minimal amount of sulfuric acid. The solution was adjusted to a final volume of 1 L with distilled water and re-precipitated using ammonium hydroxide to form a Fe(OH)_3 gel. A concentration of 0.2 mol/L Fe(OH)_3 was used to produce nanometric hematite colloids. The suspension was heated to boiling and subsequently maintained at 60 °C under magnetic stirring (500 rpm) for 10 min to promote gel transformation. Then, 0.6 mL of 0.1 mol/L FeCl_2 solution was added as a catalyst to accelerate the gel transformation. The iron percentage in the resulting hematite was determined using a Shimadzu AA-7000 atomic absorption spectrometer. A schematic representation of the catalyst synthesis process is

shown in Fig. 2.

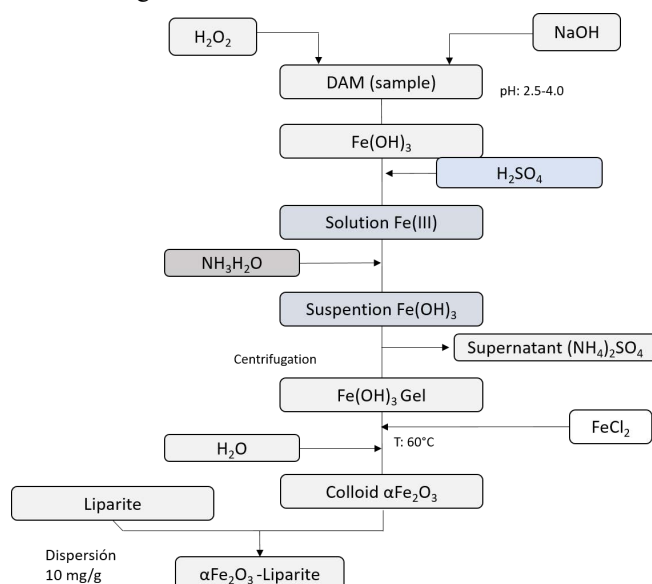


Fig. 2. Schematic diagram of hematite ($\alpha\text{-Fe}_2\text{O}_3$) synthesis from acid mine drainage and its support on liparite.

C. Experimental Setup and Operating Conditions

The synthesized hematite was supported on conditioned liparite as a granular medium at a loading of 10 mg hematite per gram of support. The liparite was washed, dried, and sieved to ensure uniform granulometry. Impregnation was performed through wet mechanical mixing to promote homogeneous distribution.

A stock solution of methylene blue (10 mg/L) was prepared using distilled water. Working solutions were freshly prepared for each experimental run. MB concentration was determined using a Spectroquant Prove 600 UV–Vis spectrophotometer at 655 nm. Calibration curves were constructed using standard solutions within the working concentration range, and linear regression was used to determine concentration values.



Fig. 3. Stainless-steel fixed-bed reactor used for continuous methylene blue degradation.

Degradation experiments were conducted in a stainless steel fixed-bed reactor (Fig. 3) with a diameter of 2.5 cm and a length of 45 cm, divided into three 15-cm sections with internal grids for proper flow distribution and sampling. The feed solution was supplied using a peristaltic pump, and flow rates of 6–10 mL/min were evaluated. The dye solution was maintained at temperatures between 40–50 °C, and hydrogen peroxide was added at concentrations ranging from 0.15–3.00 g/L. pH was adjusted to 3.5 or 5.0 using 1 N NaOH and 1 N H₂SO₄. No intentional irradiation or external light source was applied during operation. As the reactor was constructed of opaque stainless steel, the degradation process is attributed to heterogeneous Fenton-like reactions rather than photo-assisted mechanisms.

D. Analytical Methods and Experimental Design

MB concentration was determined using a Spectroquant Prove 600 UV–Vis spectrophotometer at 655 nm. Calibration curves were constructed using standard solutions within the working concentration range, and linear regression was used to determine concentration values.

Degradation efficiency (%) was calculated using:

$$\text{Degradation (\%)} = [(C_o - C_t)/C_o] \times 100 \quad (1)$$

where C_o is the initial dye concentration, and C_t is the outlet concentration.

All experiments were performed according to a Taguchi L8 orthogonal array (Table 2) using Minitab 18, and average values were reported.

Table 2. Orthogonal arrangement for the experimental matrix

Exp.	pH	Temperature (°C)	H ₂ O ₂ (g/L)	Flow Rate (mL/min)
1	3.5	40	0.15	6
2	3.5	40	0.15	10
3	3.5	50	3.00	6
4	3.5	50	3.00	10
5	5.0	40	3.00	6
6	5.0	40	3.00	10
7	5.0	50	0.15	6
8	5.0	50	0.15	10

IV. RESULT AND DISCUSSION

A. Synthesis of Hematite

The high iron concentration in the AMD confirms its suitability as a precursor for the recovery of iron and the subsequent synthesis of iron oxides. During neutralization, the predominance of dissolved iron favors the formation of ferric hydroxides, which constitute a critical intermediate for hematite production. The synthesized samples exhibited iron contents ranging from 46.84% to 52.83% (Table 3), values that are consistent with hematite obtained from AMD or other non-pure industrial precursors. Samples with higher iron content indicate a more effective thermal transformation toward crystalline hematite, whereas lower values may be associated with minor residual mineral phases or variations during washing and calcination.

Similar iron contents have been reported for catalysts derived from industrial residues, where the recovered iron is effectively transformed into active phases for pollutant degradation [5]. These findings reinforce the suitability of

AMD as a viable and sustainable source of iron for catalyst synthesis.

Table 3. Iron content (%) in hematite synthesized from acid mine drainage

Exp.	% Fe
1	52.75
2	49.42
3	46.84
4	51.2
5	48.04
6	52.83
7	47.51
8	51.11

From a mechanistic standpoint, the iron content achieved ensures the presence of sufficient active sites to sustain redox reactions at the solid–liquid interface. Moreover, the moderate compositional variability inherent to AMD-derived materials may introduce structural defects and surface heterogeneity, which are known to enhance catalytic behavior by facilitating electron transfer and hydrogen peroxide activation. Consequently, the chemical composition of the hematite reflects both the nature of the AMD precursor and its functional suitability for heterogeneous Fenton-like applications. This type of behavior has also been observed in iron-based materials supported by mineral matrices, where structural heterogeneity contributes to improved catalytic efficiency [4]. Although advanced physicochemical characterization techniques such as X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), or Scanning Electron Microscopy (SEM) were beyond the scope of the present study, the synthesis procedure employed follows well-established precipitation and thermal transformation routes widely reported for the formation of α -Fe₂O₃ from iron hydroxide precursors. The consistency between the obtained iron content and the catalytic performance observed later suggests the successful formation of active iron oxide phases, as reported in previous studies on heterogeneous Fenton-like catalysts [2, 3]. The measured iron content and the reproducible catalytic performance under heterogeneous Fenton-like conditions are consistent with the formation of active iron oxide phases. The primary objective of this work was to evaluate catalytic efficiency and operational optimization using AMD-derived materials in a continuous system. Nevertheless, complementary structural and morphological analyses will be addressed in future studies to further elucidate phase composition and surface characteristics.

B. Methylene Blue Degradation

Table 4 shows the methylene blue degradation percentages, demonstrating the high efficiency of the hematite/liparite catalyst under heterogeneous Fenton-like conditions. The most favorable conditions corresponded to Experiment 3, which resulted in 90.3% degradation. This behavior is consistent with studies indicating that acidic pH optimizes the surface reduction of Fe(III)/Fe(II) and promotes the generation of hydroxyl radicals in hematite-based catalysts [9, 10]. Likewise, moderately high temperatures accelerate the decomposition kinetics of H₂O₂, while a lower flow rate improves the contact time between the reagent and the catalytic bed. The least favorable conditions occurred at pH 5.0 with a high H₂O₂ concentration (3 g/L) and a high flow rate (10 mL/min), where the

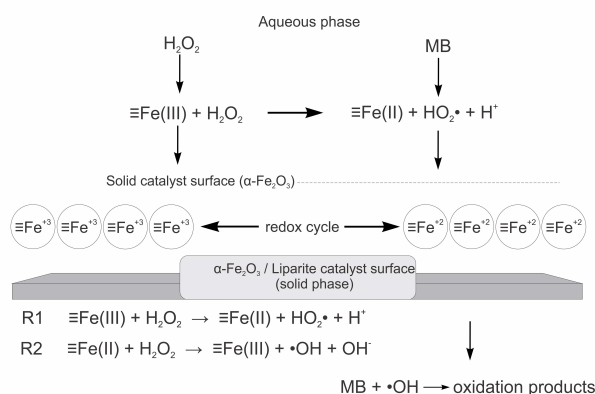
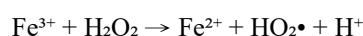
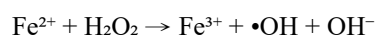
degradation decreased to 72.5%. This may be attributed to reduced residence time, partial surface deactivation due to excess oxidant, or lower stability of the redox cycle under near-neutral conditions. These effects have been previously described in Fenton-like catalysts derived from clays, incinerated sludge, and natural minerals [17, 24, 26].

Table 4. Methylene blue degradation results

Exp.	pH	Temp. (°C)	H ₂ O ₂ (g/L)	Flow rate (mL/min)	MB Degradation (%)
1	3.5	40	0.15	6	88.9
2	3.5	40	0.15	10	84.4
3	3.5	50	3.00	6	90.3
4	3.5	50	3.00	10	85.7
5	5.0	40	3.00	6	78.8
6	5.0	40	3.00	10	72.5
7	5.0	50	0.15	6	82.6
8	5.0	50	0.15	10	76.9

It is important to clarify that dye removal in heterogeneous catalytic systems may involve an initial adsorption step before oxidative degradation. Although partial adsorption of methylene blue onto the hematite/liparite surface may occur during early contact stages, the magnitude of removal observed in this study (up to 90.3%) and its strong dependence on pH, hydrogen peroxide concentration, and temperature indicate that oxidative degradation is the dominant mechanism. The significant effect of acidic conditions and oxidant availability supports hydroxyl radical generation through Fe(III)/Fe(II) redox cycling at the catalyst surface rather than dye retention. Therefore, adsorption is considered a preliminary surface interaction rather than an independent primary removal process under the studied conditions.

The heterogeneous Fenton-like mechanism occurring on the hematite surface involves redox cycling between Fe(III) and Fe(II) species at the solid–liquid interface. Under acidic conditions, hydrogen peroxide interacts with surface Fe(III) sites, leading to the formation of Fe(II) and hydroperoxyl radicals (HO₂•). Subsequently, Fe(II) reacts with H₂O₂ to generate highly reactive hydroxyl radicals (•OH), following the classical Fenton pathway:

Fig. 4. Proposed redox mechanism of the heterogeneous Fenton-like process on $\alpha\text{-Fe}_2\text{O}_3$ /liparite.

The generated hydroxyl radicals attack the aromatic structure of methylene blue, promoting chromophore

cleavage, structural destabilization, and progressive mineralization. In the present system, these reactions are proposed to occur predominantly at the catalyst surface, where iron species act as active sites for peroxide activation. The enhanced degradation observed at pH 3.5 is consistent with improved stability of the Fe(III)/Fe(II) redox cycle and more efficient radical generation under acidic conditions. Furthermore, the positive effects of increased temperature and adequate hydrogen peroxide dosage support a reaction pathway in the process. A schematic representation of the proposed heterogeneous Fenton-like mechanism is presented in Fig. 4.

From a comparative perspective, the degradation efficiency achieved in this study places the hematite/liparite system within the upper range of performance reported for iron-based heterogeneous Fenton-like catalysts derived from both synthetic and waste-based precursors. This performance is comparable to values reported for waste-derived Fenton-like catalysts and composite materials, where removal efficiencies close to or above 90% have been achieved under optimized conditions [5]. In addition, photocatalytic systems have reported higher efficiencies (up to 99.35%) using modified bentonite/ Fe_3O_4 -based materials [1], although under batch and light-assisted conditions. Unlike many studies conducted under batch conditions, the present work demonstrates that high removal efficiencies can be sustained under continuous-flow operation, which better reflects practical wastewater treatment scenarios. In this context, the present results highlight that comparable degradation efficiencies can be achieved in continuous systems, emphasizing the importance of residence time and hydrodynamic control in fixed-bed reactors. This highlights the relevance of residence time and hydrodynamic control in fixed-bed systems and underscores the potential of AMD-derived hematite as a competitive and scalable catalyst for dye degradation.

C. Effects of Variables

Fig. 5 demonstrates that pH is the most influential factor affecting methylene blue degradation, with significantly higher efficiencies achieved at pH 3.5 compared to pH 5.0. This result confirms that acidic conditions are required for optimal performance of the heterogeneous Fenton-like process. Temperature also exhibits a positive, although less pronounced, effect on degradation efficiency, indicating enhanced reaction kinetics at higher operating temperatures. This behavior is consistent with the widely reported optimal pH range (approximately 3–4) for Fenton and Fenton-like systems, where iron species remain more active, and hydrogen peroxide is more efficiently converted into hydroxyl radicals [2, 3].

The influence of pH can also be interpreted by considering the surface charge properties of hematite. The Point of Zero Charge (PZC) of $\alpha\text{-Fe}_2\text{O}_3$ is typically reported in the range of 7–9, depending on its origin and preparation method [37, 38]. Since the experiments were conducted at pH 3.5 and 5.0, both values are below the PZC, indicating that the catalyst surface was predominantly positively charged under the studied conditions. Considering that methylene blue is a cationic dye, electrostatic attraction is not favored in this pH range. Therefore, the enhanced degradation observed at acidic pH

cannot be attributed primarily to electrostatic adsorption but rather to the increased stability of the Fe(III)/Fe(II) redox cycle and more efficient generation of hydroxyl radicals. This analysis supports the conclusion that oxidative degradation, rather than surface charge-driven adsorption, governs methylene blue removal in the present system. Accordingly, the removal mechanism is dominated by catalytic oxidation processes at the catalyst surface rather than by electrostatic interactions.

From a mechanistic perspective, acidic conditions favor the stability of the Fe(III)/Fe(II) redox cycle at the catalyst surface, minimizing radical scavenging and promoting sustained hydroxyl radical generation. The observed temperature effect is associated with faster hydrogen peroxide decomposition and increased molecular mobility, which together accelerate oxidation reactions. These mechanisms are consistent with established interpretations of iron-based advanced oxidation processes and support the experimental trends observed.

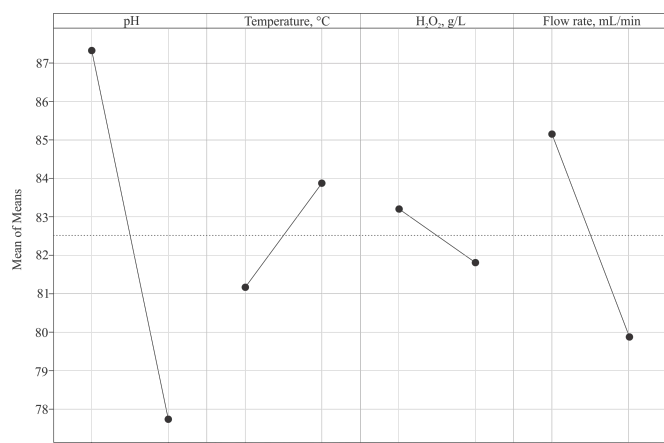


Fig. 5. Main effects plot for means on MB degradation.

The interactions (Fig. 6) confirm that pH 3.5 maximizes degradation regardless of flow rate, but a low flow rate (6 mL/min) amplifies efficiency at all H₂O₂ levels, and a higher temperature improves performance, especially when the oxidant is at its maximum concentration. This suggests that the process kinetics are strongly determined by residence time and the effective availability of the catalyst, consistent with previous studies in fixed-bed reactors for heterogeneous Fenton [31–33]. This observation also aligns with continuous heterogeneous Fenton systems, where the hydraulic residence time is a key parameter controlling degradation efficiency and overall treatment performance [39].

Beyond the observed interactions, these results have important implications for reactor design and process scalability. In fixed-bed heterogeneous Fenton-like systems, hydrodynamic control directly influences oxidant utilization efficiency and catalyst performance. The ability to sustain high degradation at lower flow rates demonstrates that continuous systems can be effectively optimized through residence time management, highlighting a key advantage over batch configurations commonly reported in the literature.

Fig. 7 illustrates the interaction between temperature and H₂O₂ concentration, showing that maximum methylene blue degradation is achieved at 50 °C and 3 g/L H₂O₂. The elevated temperature enhances peroxide decomposition and

accelerates hydroxyl radical generation, while the higher H₂O₂ concentration increases the availability of oxidizing species without causing inhibition within the studied concentration range. At 40 °C, efficiency improves with increasing oxidant concentration, but does not reach the levels obtained at 50 °C, confirming that thermal activation and adequate H₂O₂ supply act synergistically to enhance the Fenton-like process. Hydrogen peroxide concentration strongly influences degradation efficiency, as increasing the oxidant dosage enhances radical generation up to an optimal level. However, excessive hydrogen peroxide may lead to scavenging effects, reducing the availability of hydroxyl radicals for pollutant degradation, as reported in continuous Fenton systems [39].

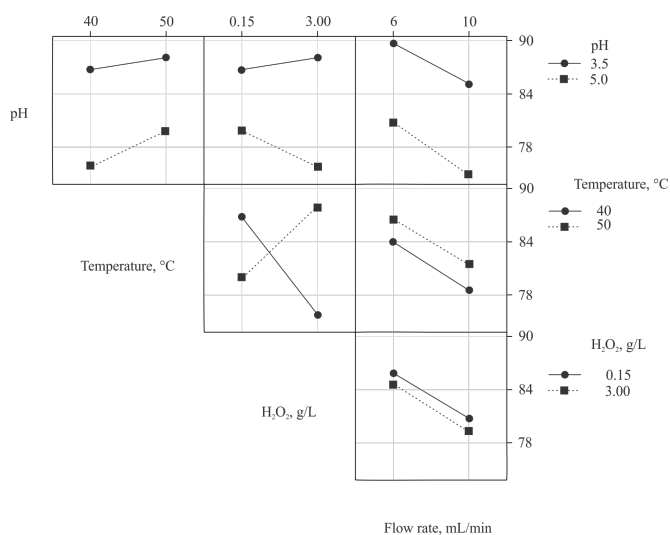


Fig. 6. Interaction plot for MB degradation.

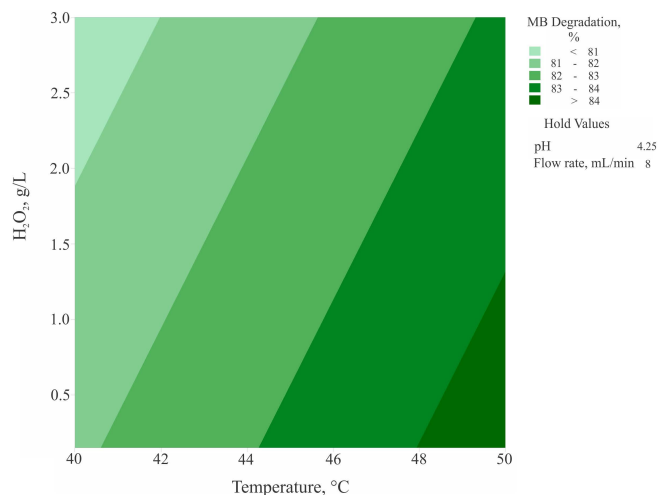


Fig. 7. Contour plot of MB degradation vs H₂O₂; Temperature.

Fig. 8 shows that the most efficient combination is 50°C and 6 mL/min, indicating that residence time is crucial for maximizing degradation. At high flow rates (10 mL/min), contact between the contaminant and the catalyst decreases, reducing efficiency even under favorable thermal conditions. Conversely, low flow rates promote diffusion, adsorption, and interaction with the generated radicals. Temperature enhances this effect by accelerating the activation kinetics of hydrogen peroxide (H₂O₂). Thus, the figure confirms that the simultaneous optimization of hydrodynamics and temperature is crucial for achieving degradation rates exceeding 90%.

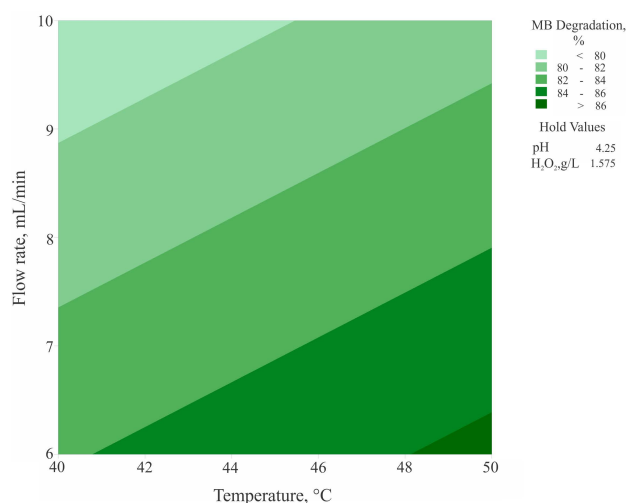


Fig. 8. Contour plot of MB degradation vs Flow rate; Temperature.

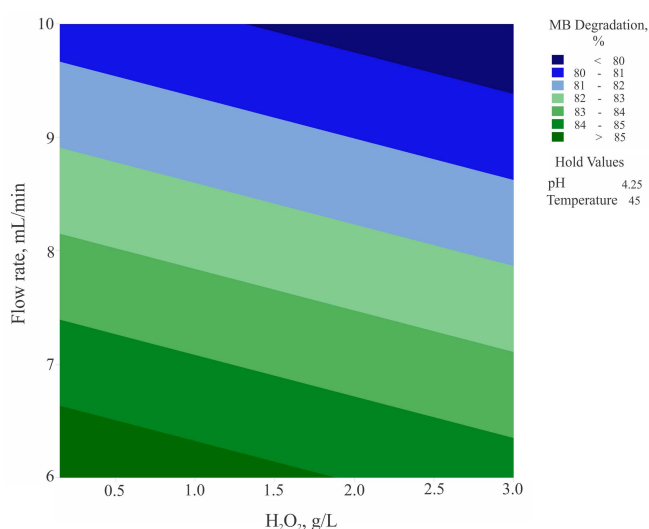
Fig. 9. Contour plot of MB degradation vs. flow rate; H_2O_2 .

Fig. 9 shows that the highest yield is obtained with 3 g/L of H_2O_2 and 6 mL/min, reinforcing the combined role of the oxidant and the flow rate. Efficiency decreases at high flow rates due to the shorter contact time, while low H_2O_2 concentrations limit radical generation. At 3 g/L, the availability of oxidants allows for sustained high production of hydroxyl radicals ($\bullet\text{OH}$), but maximum performance is only achieved at low flow rates. Overall, the figure confirms that oxidative kinetics (H_2O_2 concentration) and flow dynamics (flow rate) must be adjusted together to ensure efficient degradation in heterogeneous Fenton-like systems. The Taguchi analysis further indicates that pH and flow rate are the most influential parameters affecting degradation efficiency, highlighting the importance of simultaneously optimizing both chemical conditions and hydrodynamic behavior in continuous systems [2, 3].

The contour plots collectively demonstrate that optimal degradation occurs within a well-defined operational domain where temperature, oxidant concentration, and flow rate act synergistically. The identification of this domain provides practical guidance for process optimization and potential scale-up. The convergence of optimal conditions across multiple variable combinations confirms the robustness of the catalytic system and supports its applicability in continuous wastewater treatment scenarios.

Overall, the results demonstrate that hematite synthesized from AMD and supported on liparite exhibits strong catalytic activity under heterogeneous Fenton-like conditions. The integration of waste-derived materials with continuous-flow operation not only enhances degradation performance but also addresses key challenges related to sustainability and practical implementation. These findings position the current system as a promising alternative to iron-based catalytic materials recovered from AMD for the treatment of dye-contaminated wastewater.

D. Optimization of Operating Conditions

The Taguchi experimental design not only allowed the evaluation of individual and interaction effects but also enabled the identification of optimal operating conditions for methylene blue degradation. The analysis of both Signal-to-Noise (S/N) ratios using the “larger-is-better” criterion and mean response values consistently indicated that pH is the dominant factor influencing degradation efficiency, followed by volumetric flow rate, temperature, and hydrogen peroxide concentration.

Based on the response analysis, the optimal combination of operating parameters was determined as pH 3.5, temperature 50 °C, hydrogen peroxide concentration of 3 g/L, and volumetric flow rate of 6 mL/min. Under these conditions, the highest experimental degradation efficiency reached 90.3%.

The optimal levels of each factor and the corresponding degradation efficiency are summarized in Table 5. The agreement between the S/N ranking and mean response analysis confirms the robustness of the experimental design and demonstrates that the selected conditions maximize both degradation efficiency and process stability. These results validate the predictive capability of the Taguchi methodology and provide clear operational guidance for scaling up the continuous heterogeneous Fenton-like process.

Under less favorable conditions, such as higher pH, higher flow rate, and excess hydrogen peroxide, degradation efficiency decreased to approximately 72.5%, which can be attributed to reduced residence time and less efficient Fe(III)/Fe(II) redox cycling.

Despite these variations, the catalyst maintained relatively high performance across all tested conditions, demonstrating its stability and operational robustness. Compared to batch systems commonly reported in the literature, the continuous configuration used in this study offers advantages in terms of process control, scalability, and potential real-world application [39].

Table 5. Optimal operating conditions predicted by Taguchi design

Factor	Optimal Level
pH	3.5
Temperature	50°C
H_2O_2	3 g/L
Flow rate, mL/min	6 mL/min
MB Degradation	90.3%

V. CONCLUSION

This study demonstrated that iron recovered from acid mine drainage can be successfully transformed into hematite and applied as an efficient heterogeneous Fenton-like catalyst

in a continuous fixed-bed reactor for methylene blue degradation. Under optimized conditions (pH 3.5, 50 °C, 3 g/L H₂O₂, and 6 mL/min), degradation efficiencies reached 90.3%, with Taguchi analysis confirming that pH and flow rate were the dominant operational parameters. The originality of this work lies in integrating AMD valorization with continuous-flow catalytic oxidation and statistical optimization, providing a sustainable and scalable approach for dye-contaminated wastewater treatment.

The results also highlight that temperature plays a secondary but relevant role in enhancing degradation performance, emphasizing the combined influence of chemical conditions and hydrodynamic factors in continuous systems.

In addition, the use of AMD as an iron source represents an effective strategy for the valorization of mining waste, contributing to the development of low-cost and environmentally sustainable catalytic materials.

Furthermore, the ability of the system to achieve high degradation efficiencies under continuous-flow operation, in contrast to the batch configurations commonly reported in the literature, underscores its potential for practical wastewater treatment applications.

While advanced structural characterization techniques were beyond the scope of the present study, the catalytic performance and iron content analysis support the formation of active iron oxide phases. Future research should focus on detailed physicochemical characterization, catalyst stability and reusability, long-term continuous operation, and the evaluation of the catalyst against other organic pollutants in complex industrial effluents. These efforts will further validate the applicability of AMD-derived catalysts in practical environmental remediation systems.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Elizabeth C. Oré conducted the research; Dante M. García analyzed the data; Elizabeth C. Oré and Dante M. García wrote the paper; all authors approved the final version.

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