Research Article

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Discoloration of methylene blue at neutral pH by heterogeneous photo-Fenton-like reactions using crystalline and amorphous iron oxides

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Abstract: Different iron oxides were evaluated for the discoloration of methylene blue (MB) at neutral pH by heterogeneous photo-Fenton-like reactions with a UV-LED lamp. Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, and a-FeOOH catalysts were synthesized and characterized by X-ray diffraction, scanning electron microscopy (SEM), Raman spectroscopy, Fourier transform infrared spectroscopy, and adsorption isotherms of N_2 . The results show high crystallinity and relatively low surface areas for Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$, and amorphous structure with high surface area for the case of a-FeOOH . The discoloration of MB by iron oxides as catalysts was studied using UV-Vis spectroscopy. Despite the relative high adsorption of MB for magnetite (12%) compared to the other oxides, it shows a slow discoloration kinetics. Besides, amorphous oxide (named a-FeOOH) shows a higher discoloration kinetics with negligible adsorption capacity. The pseudo first-order kinetic constant values for Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, and a-FeOOH are 5.31×10^{-3} , 6.89×10^{-3} , and $13.01 \times 10^{-3} \text{ min}^{-1}$; and the discoloration efficiencies at 120 min were 56, 60, and 82%, respectively. It was testified that low crystallinity iron oxide can be used in the efficient discoloration of MB by photo-Fenton process with a hand UV-A lamp.

Keywords: iron oxide, photo-Fenton-like, amorphous oxide, crystalline oxide, discoloration

1 Introduction

Many organic compounds are resistant to different conventional degradation treatments (physicochemical, biological, chlorination, and others) because they have high stability due to their non-biodegradable nature [1,2]. This has caused an increase in interest in the Advanced Oxidation Processes (AOPs), since these processes can convert organic compounds into carbon dioxide and water, or transform them into intermediates that can be further treated [3]. AOPs focus their operation in the generation of the hydroxyl radical ($\cdot\text{OH}$), which has a high standard oxidation-reduction potential ($E^\circ = 2.80 \text{ V}$) close to molecular fluorine ($E^\circ = 3.03 \text{ V}$) [4], which gives it high reactivity.

There are different types of AOPs (Fenton and Fenton-like oxidation, photocatalysis, plasma oxidation, ozonization, and others) that allow to obtain feasible and efficient processes for the treatment of organic pollutants in water and soil [5,6]. $\cdot\text{OH}$ radical generated by homogeneous Fenton reactions involving iron(II) salts and hydrogen peroxide (H_2O_2) are developed according to the Haber–Weiss mechanism [7]. Homogeneous systems show high degradation efficiencies for organic compounds, such as phenol, magenta methylene blue (MB), bisphenol A, naphthol blue black, sulfamethoxazole, among others, in an acid medium; and also for glyphosate, bright blue, medium yellow 10, alizarin green, phenol red, and rhodamine B in a neutral medium [8–13]. In parallel, Fenton-like reactions, using iron(III) salts and H_2O_2 , can extend the use of iron salts or minerals.

There are comparative studies for both systems, Fenton and Fenton-like. Generally, the degradation efficiencies coincide for Fenton systems at short times. However, the degree of degradation achieved at long times is similar for both the processes [14–17]. In addition, it has been shown that the Fenton and Fenton-like processes can occur simultaneously, since some intermediate compounds of oxidation promote the regeneration of Fe(III) to Fe(II) [16,18].

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Despite the vast amount of work on homogeneous Fenton and Fenton-like reaction, these reactions present some important drawbacks, such as working under acidic conditions (around pH 3), the lack of stability of the catalysts, and the presence of sludge, mainly based on iron oxyhydroxides [8,9]. An alternative to solve these problems is the use of heterogeneous catalysts based on Fe(II) and Fe(III) with H_2O_2 , since these systems can work at neutral pH.

Many structures of iron oxides and hydroxides have been studied for heterogeneous Fenton and Fenton-like reactions, such as magnetite (Fe_3O_4), hematite ($\alpha\text{-Fe}_2\text{O}_3$), goethite ($\alpha\text{-FeOOH}$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), lepidocrocite ($\gamma\text{-FeOOH}$), akaganeite ($\beta\text{-FeOOH}$), and feroxyhyte ($\delta\text{-FeOOH}$) [19–21]. Despite the importance of the crystallinity structure of these oxides in catalysis, there are many studies where a drastic increase in degradation kinetics was observed using low crystallinity or amorphous materials. For example, metallic crystals or amorphous Fe-X alloys (Si, B, Mo, B, Cu, Nb, etc.) have been studied to optimize their application in the adsorption, discoloration, and degradation of colorants such as acid orange II, blue 6, methyl orange, brilliant red 3B-A, among others [22–26].

In the same way, different iron oxides obtained from industrial waste or natural minerals have been investigated [27]. For example, we can list the use of: fly ash for the development of amorphous FeOOH catalysts and their application in the degradation of methyl orange [28]; natural hematite and siderite in the degradation of 4-chlorophenol [29]; different types of natural pyrite in the degradation of AO7 [30]; use of diatomites earth for the oxidation of orange II [31]; low-cost, high-purity goethite obtained from acid mine drainage to treat simulated petrochemical waste [32]; amorphous Fe-SiO₂ compared to crystalline goethite and hematite for efficient degradation of Reactive Blue 19 by Fenton and photo-Fenton [33], among others. These oxides can usually have partially crystalline phases; however, contrary to usual, their degradation capacity in AOPs are often better compared to crystalline materials.

In addition to the Fenton and Fenton-like methods listed above, the efficiency of photocatalytic degradation methods using UV light and iron oxides is known. For example, the photo-degradation of reagent blue is 95.08% in 56 min with Fe_2O_3 synthesized by a green pathway [34], the percent of degradation of crystal violet or MB dye (20 mg L^{-1}) using 0.1 g of Fe_2O_3 in the presence of H_2O_2 was 100% after 30 or 40 min, [35], glyphosate photodegradation with magnetite ($k_{\text{app}} = 1.2\text{ h}^{-1}$) was significantly higher than that of goethite ($k_{\text{app}} = 0.4\text{ h}^{-1}$) at pH = 7 [36], and the photodegradation of MB was close to 100% in 60 min with $\alpha\text{-Fe}_2\text{O}_3$ [37]. The main aspect in

photocatalytic processes is the separation of charges, electrons, and holes, which can dramatically improve the Fenton-like reaction. However, use of traditional UV sources such as high-pressure mercury vapor lamps present several difficulties such as energy instability due to overheating, low photon efficiency, requirement of high voltages, mercury toxicity, and short lifetime of 10^3 h [38,39]. To solve this, UV emitting diodes (UV-LED) having several advantages, such as low toxicity of their compounds (Ga, As, P, In, and N), thermal stability, directed light which generates better energy optimization, and long life of up to 10^5 h [39] have been suggested.

In this work, three iron oxides will be studied: magnetite, hematite, and amorphous iron oxo-hydroxide for the degradation of MB by heterogeneous photo-Fenton-like reactions using UV-LED lamp. MB is a cationic dye used as a comparative model due to its non-biodegradable properties and its wide usage in the textile industry. The aim of this work is the comparison of three iron oxides, namely, hematite ($\alpha\text{-Fe}_2\text{O}_3$), magnetite (Fe_3O_4), and amorphous iron(III) oxo-hydroxide hydrate (a-FeOOH) with different degrees of crystallinity and surface properties for the discoloration of MB for photo-Fenton process with a hand UV-A lamp. The results obtained in this work have great importance to encourage the efficient use of catalysts of structures with low crystallinity, since this give rise to the use of natural minerals in Fenton-like processes at neutral pH.

2 Methods

2.1 Chemicals

Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), iron(II) chloride hexahydrate ($\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$), hydrazine sulfate ($\text{NH}_2\text{NH}_2\text{H}_2\text{SO}_4$), sodium hydroxide (NaOH), and ethanol ($\text{C}_2\text{H}_5\text{OH}$) were supplied from Sigma-Aldrich. Iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), ammonium hydroxide (NH_4OH), and hydrogen peroxide (30% v/v) were supplied by Merck. Ultrapure water was supplied by Purelab Classic Elga. For the synthesis of iron oxides and oxo-hydroxides, all reagents were of analytical grade unless otherwise specified.

2.2 Synthesis of iron oxides and hydroxides

Magnetite nanoparticles were synthesized by a co-precipitation method [40], starting from iron precursors prepared separately in an inert atmosphere of nitrogen. The

molar ratio of the precursor ($\text{Fe}^{2+}/\text{Fe}^{3+}$) solutions was 1:2 and NaOH solution was added rapidly until $\text{pH} = 11$ was reached. For nucleation and growth, it was stirred for 40 min under nitrogen atmosphere. Nanoparticles were washed with ultrapure water, followed by a magnetic separation, and dried for 12 h at 50°C .

The hematite nanoparticles were synthesized by a chemical precipitation method [41]. It was started with 0.05 mol L^{-1} of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution at 80°C for 30 min under constant magnetic stirring and 2.0 mol L^{-1} of NH_4OH solution was added dropwise until $\text{pH} = 11$ (orange precipitate) was reached. After this, the system was heated to 80°C for an interval of 3 h under constant magnetic stirring. The final precipitate was washed with ultrapure water and separated from the aqueous phase by centrifugation. Finally, it was calcined at 700°C for 4 h in a muffle.

Iron oxo-hydroxide hydrate, named $\alpha\text{-FeOOH}$, was synthesized from the dissolution of 7.5 g of hydrazine sulfate in a 0.1 mol L^{-1} of ferric nitrate solution, under magnetic stirring and heating at 90°C for 1 h. The pH was adjusted to 3 by dropwise addition of a 1.5 mol L^{-1} of NaOH solution. The precipitate formed was washed with ultrapure water and separated from the aqueous phase by centrifugation. Finally, the product obtained was dried at 100°C for 12 h.

2.3 Characterizations

2.3.1 Physicochemical characterizations

Diffraction patterns of the samples were obtained using the PANalytical Aeris X-ray diffractometer with a $\text{CuK}\alpha$ source of $1.5418 \text{ \AA}$. The data were obtained in the range of $20\text{--}80^\circ$ at a scan speed of $0.001^\circ \text{ s}^{-1}$. Scanning electron microscopy (SEM) images were analyzed through a KYKY-EM3200 25 kV microscope. The surface properties of the oxides were determined with Micromeritics Gemini VII 2390t by physical nitrogen adsorption at 77 K. Raman spectra were obtained using Horiba Scientific equipment, with a 532 nm laser and a power of 10%. Fourier transform infrared spectra (FTIR) were obtained with the Digilab Excalibur equipment, FTS 3000 series, with a transmission spectral range of $40,000\text{--}400 \text{ cm}^{-1}$ and a resolution of 4 cm^{-1} .

2.4 Adsorption and degradation of MB by heterogeneous Fenton-like process

In this work, MB was used as a pollutant model since its discoloration can be easily monitored by UV-Vis

spectroscopy. To determine the amount of MB that is adsorbed in 20 mg of catalyst, 15 mL of 25 mg L^{-1} of MB solution was placed under constant stirring for 120 min prior to the experiments. To quantify MB concentration, a Genesys UV-Vis, 1DS, ThermoScientific spectrophotometer was used and the wavelength of maximum absorbance at 664 nm was selected. The discoloration analysis by UV-Vis spectroscopy was started from the addition of H_2O_2 . Moreover, to evaluate the effect of hydrogen peroxide on discoloration with $\alpha\text{-FeOOH}$, different volumes of H_2O_2 at 30% by weight (1.5, 2.0, and 2.5 mL) were used for 15 min and 20 mL of 100 mg L^{-1} of MB solution, these experiments were performed without and with time of adsorption of 120 min (Figure S1 in the supplementary information).

2.5 Photo-Fenton-like discoloration of MB

Photocatalytic degradation of MB was investigated by taking 15 mL of 25 mg L^{-1} of MB solution, $\text{pH} = 6.5$, with 1.0 mL of hydrogen peroxide (30% v/v) in the presence of 20 mg of iron oxides, and 120 min of interaction time. The suspension was stirred to ensure that all the active sites of the catalysts are in contact with the MB. Then, the sample was illuminated with a UV-LED hand lamp (365 nm) positioned at a perpendicular distance of $\sim 4 \text{ cm}$ on the surface of the reaction solution (Figure S2 in the supplementary information). The irradiation was interrupted in regular intervals to take electronic spectra on the UV-Vis spectrophotometer until no more changes in the characteristic band of MB was observed.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussions

3.1 Characterizations of iron oxides and hydroxides

Figure 1 shows the SEM of the synthesized iron oxides. Magnetite and hematite nanoparticles have a spherical and ovoid shape, respectively (Figure 1a and b). A small number of spherical particles in the medium and large agglomerates are evident for $\alpha\text{-FeOOH}$ (Figure 1c). Histograms obtained for magnetite show a size of 30 nm in

diameter and hematite show an average size of 85 nm (Figure S3 in the supplementary information), while that of amorphous iron oxo-hydroxide show a mixture of large agglomerated particles and small particles of about 20–50 nm (Figure 1c).

Figure 1: SEM images for the three iron oxides: (a) magnetite, (b) hematite, and (c) a-FeOOH.

The X-ray diffraction patterns of three synthesized oxides are shown in Figure 2. The standard magnetite pattern (JCPDS card no. 19-0629, blue asterisks in Figure 2) shows coincidence of six characteristic peaks at 2θ angles of 30.1° , 35.5° , 43.2° , 53.5° , 57.0° , and 62.8° which are attributed to the planes of (220), (311), (400), (422), (511), and (440) [42]. The standard hematite pattern (JCPDS card no. 33-664, red asterisks in Figure 2) matches with peaks at angles 24.16° , 33.12° , 35.63° , 40.64° , 49.57° , 54.08° , 57.42° , 62.51° , 64.12° , 72.07° , and 75.50° , which are attributed to planes (012), (104), (110), (113), (024), (116), (018), (214), (300), (119), and (220). All the detectable peaks in this pattern can be assigned to the hexagonal structure of α - Fe_2O_3 and the high intensity of the spectral peaks shows a high crystallinity of hematite [43]. On the other hand, in the case of iron hydroxide, its amorphous structure is evident, due only the spectral lines around 35.5° are slightly visible presenting a height value at the middle of the FWHM peak quite high compared to the standard of goethite diffraction pattern (JCPDS card no. 29-07131) [44].

Furthermore, iron oxides Raman shifts are shown in Figure S4 and Table S1, it demonstrated the reverse spinel structure for magnetite. Besides, α - Fe_2O_3 structure for hematite is confirmed and the amorphous a-FeOOH material coincide with structures of the goethite (α -FeOOH) and lepidocrocite (γ -FeOOH).

FTIR spectra of magnetite, hematite, and a-FeOOH are shown in Figure 3, and it is observed that magnetite and a-FeOOH have common bands near $3,400$ and $1,632\text{ cm}^{-1}$, corresponding to the vibration bands of adsorbed water [45]. Also, the appearance of two bands at 515 and 430 cm^{-1} in the IR spectrum of hematite, can be attributed to the bending and stretching vibrations of the

Figure 2: X-ray diffractograms of hematite, magnetite, and amorphous oxide, a-FeOOH. On each diffraction plane, the plane corresponding to the JCPDS pattern is placed with asterisks for each oxide.

Figure 3: FTIR spectra of hematite, magnetite, and amorphous oxide, a-FeOOH.

Fe–O bond [41]. Similarly, in the spectra of magnetite and a-FeOOH, the peaks of 540 and 589 cm^{-1} are observed, respectively, which are the characteristics of Fe–O vibrations for a goethite-type structure (α -FeOOH). And, peaks at 787 and 878 cm^{-1} are associated with out-of-plane deformational (δ) modes of hydroxyls in goethite [46]. Finally, additional peaks of 1,185 and 1,007 cm^{-1} can be associated with the vibrations of the Fe–OH bonds, which could be attributed to a structure of the type

lepidocrocite (γ -FeOOH) [45,47]. Therefore, different peaks in a-FeOOH are related to vibrations associated with structures of the α -FeOOH, γ -FeOOH, and ferrihydrite.

Study of iron oxide surfaces were performed by adsorption and desorption isotherm shown in the Figure 4a. Table 1 tabulates the parameters such as surface area ($\text{m}^2 \text{g}^{-1}$), pore volume ($\text{cm}^3 \text{g}^{-1}$), and pore size (nm) obtained according to the BET model. Magnetite and a-FeOOH present relatively high surface area values of 91.7 and $119.4 \text{ m}^2 \text{g}^{-1}$, respectively, and hematite has a low surface area of $10.7 \text{ m}^2 \text{g}^{-1}$. These values obtained for magnetite and a-FeOOH will influence the adsorption and degradation processes by Fenton processes [48].

Fe_3O_4 and a-FeOOH exhibited a N_2 adsorption-desorption isotherm of type IV with the hysteresis loops H3 and H4, respectively, typical of catalytic mesoporous solids, while hematite showed a pure type III isotherm according to IUPAC classes (Figure 4a) [49]. In the Figure 4b, the BJH graph obtained from magnetite leads to explain a large amount of mesoporous that favor the adsorption of MB. On the other hand, the results obtained from hematite shows an insignificant presence of porous associated with its high crystallinity shown in Figure 2. In the case of amorphous oxide, a-FeOOH, the low adsorption of MB is associated with the small amount and small size of the pores.

Figure 4: (a) Adsorption and desorption isotherms for the synthesized iron oxides and (b) pore diameter distribution according to the BJH model for synthesized iron oxides.

Table 1: Summary of results of surface area ($\text{m}^2 \text{g}^{-1}$), pore volume ($\text{cm}^3 \text{g}^{-1}$), and pore size (nm) obtained according to the BET model

Iron oxide	BET		
	Superficial area BET ($\text{m}^2 \text{g}^{-1}$)	Pore volume BJH ¹ ($\text{cm}^3 \text{g}^{-1}$)	Pore size BJH (nm)
Fe_3O_4	91.7	0.319	12.16
$\alpha\text{-Fe}_2\text{O}_3$	10.7	0.031	10.92
a-FeOOH	119.4	0.109	6.180

3.2 Photo-Fenton catalytic discoloration of MB

Figure 5a shows the discoloration curves of MB (C_t/C_0) as a function of time, initially considering a Fenton process and then a photo-Fenton process with UV-A light irradiation. In the initial 120 min during the adsorption-desorption equilibrium, MB adsorption is approximately 5% ($C_t/C_0 = 0.95$) and 12% ($C_t/C_0 = 0.88$) for hematite and magnetite, respectively. While for a-FeOOH, it does not present significant adsorption, despite that it has the highest surface area of $119.4 \text{ m}^2 \text{g}^{-1}$ (Table 1). The discrepancy between the surface area of the oxides and their adsorption shows that point of zero charge (PZC), porosity,

and particle size of the oxides are the key parameters for MB adsorption [50,51]. To explain these adsorption values, we must consider the PZC of oxides, since oxide surface exhibits a positive charge at pH lower than the PZC and a negative charge at a pH higher than the PZC. PZC of magnetite reported previously ranged from pH 6.5 to 7.3 [52], and for hematite, goethite, and lepidocrocite theoretical PZC varies between 7.1 and 8.5. Other works show highest PZC values obtained for goethite from 7.3 to 10. In contrast, magnetite and hematite show low values of 3.2 and 4.2, respectively [53]. Further, these theoretical PZC values depend on the synthesis method, purity, crystallinity, degree of hydration, and the measurement method [54]. In this sense, we can infer a positive surface charge on a-FeOOH, and this explains the non-adsorption of MB because this is a cationic dye and would repel in the presence of a-FeOOH. On the other hand, magnetite can have a negative surface charge that favors the adsorption of MB during photo-discoloration experiments carried out in a system at a natural pH of 6.5. Hematite is a particular case because according to the theoretical data its surface charge can be negative and positive, therefore a low adsorption of MB is justified.

Also, according to the shape of adsorption isotherms (Figure S5, supplementary information), only for Fe_3O_4

Figure 5: (a) MB discoloration in iron oxide catalysts with 120 min of adsorption, 60 min of Fenton reaction followed by 90 min of photo-Fenton reaction for a system containing 20 mg of catalyst, 15 mL of 25 mg L^{-1} of MB and 1 mL of H_2O_2 30% by weight. Linear regression of the MB photo-Fenton-like discoloration for: (b) Fenton and (c) photo-Fenton reaction.

oxide, the adsorption fit to Langmuir model ($R^2 = 0.9995$) obtaining a $Q_{\max}$ of 9.08 mg g^{-1} . For $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-FeOOH}$ oxides, the adsorption isotherm did not follow a regular Langmuir model. The adsorption amount of MB in these oxides decreased with the increase in the initial concentration, this could be due to the different solubilities of these oxides affect the adsorption process. Besides, previous works show a low adsorption capacity of MB on iron oxides (between 5 and 30 mg g^{-1} , Table S2) [55–57]. These results indicated that the discoloration of MB on iron oxides is highly related to Fenton and Photo-Fenton processes.

Figure 5 shows that Fenton processes (from 0 to 60 min) are kinetically slow for $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 (linear regression in Figure 5b) which shows a discoloration of 4.4 and 6.4%, respectively. In contrast to this, it can be seen that $\alpha\text{-FeOOH}$ presents a degradation of 28.8% in the 60 min of Fenton reaction. To understand Fenton processes on the surface of oxides, Lin and Gurol raised the reactions (1–5) that explain the interaction of iron oxides and H_2O_2 [58]:

In the case of $\alpha\text{-Fe}_2\text{O}_3$, only Fe^{III} is present in its structure. Therefore, the kinetics is slow because only reactions (1–3) generated the formation of the reactive species $\bullet\text{OH}$. In addition, the surface area of the hematite is $10.7 \text{ m}^2 \text{ g}^{-1}$ which implies a smaller surface for the interaction between $\equiv\text{Fe}^{\text{III}}$ and H_2O_2 . In the case of $\alpha\text{-FeOOH}$, the high discoloration is possibly due to the presence of species that include FeOOH , Fe^{2+} , and Fe^{3+} during the addition of H_2O_2 and since it has a high surface area of $119.4 \text{ m}^2 \text{ g}^{-1}$. Fe^{2+} could be formed from dissolution of the iron oxo-hydroxo (FeOOH) structure that is present in goethite, lepidocrocite, and/or akaganeite-like [28], according to the following reaction:

The surface coordination model explains the dissolution of oxides. The main reactions for how Fe can be released from solid Fe oxides are: protonation, reduction, and complexation (reactions 7–9) [53]:

Thus, we propose two pathways to generate $\bullet\text{OH}$ radicals. The first pathway is related to heterogeneous reactions (1–5), and the second pathway is related to homogeneous reactions of Fe^{2+} or Fe^{3+} with H_2O_2 shown in reactions (6) and (10–12) (analogous to reactions 1–5), and which may be due to the dissolution of $\equiv\text{Fe}^{\text{III}}$ from the oxide structure [59,60].

Thus, the lack of crystallinity, the high surface area, and the presence of species of FeOOH , Fe^{2+} , and Fe^{3+} during the addition of H_2O_2 , can be associated with the high degradation efficiency of $\alpha\text{-FeOOH}$ compared to the other iron oxides. In addition, previous works describe that the homogeneous reaction between Fe^{2+} or Fe^{3+} (from the salts FeSO_4 , FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$, and FeCl_2) and H_2O_2 generate nanoparticles of $\text{Fe}_2\text{O}_3\text{-FeO}(\text{OH})$ behaving as a Lewis acid in the Fenton process. This can verify that the structures of $\text{FeO}(\text{OH})$ and Fe_2O_3 are the main species for the Fenton reaction [61], this is congruent with results obtained for the Fenton process in the darkness. Also, it should be noted that pH in this work was neutral, so the degradations are slow at short times of Fenton process.

Also, in Figure 5a, the UV lamp was turned on after 60 min of Fenton reaction. It can be seen that even in the presence of only H_2O_2 , the increase in discoloration is considerable (Table S3, Figure 5b and c). This is due to the fact that the generation of $\bullet\text{OH}$ radicals occurring for H_2O_2 photolysis help in MB discoloration, which mainly occurs with UV light at wavelengths less than 365 nm [62], following reaction (13):

Also, a significant increase in MB discoloration is observed for Fe_2O_3 and $\alpha\text{-FeOOH}$; however, for Fe_3O_4 , there is no substantial change in degradation. This may be related to the irradiation with UV light generating electrons ($\text{e}_{(\text{cb})}^-$) and holes ($\text{h}_{(\text{vb})}^+$) on the surface of iron oxides and according to the band gap values shown in the literature for hematite, goethite, akaganeite, lepidocrocite, and magnetite that are 2.20, 2.10, 2.12, 2.06, and 0.1 eV, respectively [63,64]. In this sense, oxo-hydroxo-type structures and hematite present a generation of the electron-hole pair with theoretical band gaps greater than 2.0 eV, whereas magnetite due to the low value of

its band gap will present an electron-hole pair easy to recombine. The generation of the pair $[e_{(cb)}^-; h_{(vb)}^+]$ and successive reactive species, such as $OH^\bullet$ and $O_2^{\bullet-}$, can help the discoloration of MB, as shown in reactions (14–19) [35,65,66]. Furthermore, in reaction (16), it is evidenced that the electrons generated in the conduction band can reduce $\equiv Fe^{III}$ to $\equiv Fe^{II}$, helping both hematite and α -FeOOH to generate $OH^\bullet$, as shown in the reaction (3).

To carry out the kinetic study of MB discoloration, the data obtained in Figure 6a were taken. In these experiments, adsorption-desorption was performed for an equilibrium time of 120 min, and after this time the iron oxide catalyst was irradiated with UV light for 120 min observing efficient discoloration of MB for α -FeOOH and

α -Fe₂O₃ (Figure 6c). Besides, although the Fe₃O₄ has a relatively high MB adsorption, it shows the same percentage of discoloration as that obtained for H₂O₂ after 120 min. The latter is explained since at neutral pH, the magnetite can present complexation of Fe³⁺ or inhibition of the $OH^\bullet$ radical [67–69]. In addition to that, there is an immediate recombination of the electron-hole pair in the magnetite. Finally, to better understand the behavior of α -FeOOH, an experiment was carried out with 20 mg of Fe₂SO₄ (0.12 mmol of Fe²⁺) in the same conditions and observed an immediate discoloration of MB. However, when the volume of H₂O₂ is reduced to 0.5 mL, the percent of discoloration was only 45 and 60% after 5 min without and with UV light, respectively. Besides, α -FeOOH showed a highest discoloration of 90% after 40 min with UV light (Figure S6). This is evidence of the synergic effect of dissolution of $\equiv Fe^{III}$ from the α -FeOOH structure and the generation of the pair $[e_{(cb)}^-; h_{(vb)}^+]$ with successive reactive species in this amorphous oxide.

The kinetic discoloration of MB by photo-Fenton-like reaction is studied through a kinetic model of pseudo first order, according to equation (1):

$$\ln \frac{C_t}{C_0} = -k_1 t, \quad (1)$$

Figure 6: (a) MB photo-Fenton-like discoloration on iron oxide catalysts with 120 min of adsorption for a system containing 20 mg of catalyst, 15 mL of 25 mg L⁻¹ of MB and 1 mL of H₂O₂ 30 wt%, (b) linear regression of the MB photo-Fenton-like discoloration on different iron oxides from (a), and (c) photographs of MB discoloration at the end of the experiment.

Table 2: Kinetic constants for pseudo first-order kinetics in the photo-Fenton-like discoloration of MB

Catalyst	k (min^{-1})
H_2O_2	6.11×10^{-3}
Fe_3O_4	5.31×10^{-3}
$\alpha\text{-Fe}_2\text{O}_3$	6.89×10^{-3}
a-FeOOH	13.01×10^{-3}

where C_0 and C_t (mg L^{-1}) are the initial concentration and concentration at time t (min^{-1}), respectively and the pseudo first-order constant is represented by k_1 (min^{-1}). In Figure 6b it is shown that the pseudo first-order model fits satisfactorily for MB discoloration for all three iron oxides. Therefore, the rate constant for discoloration on Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, a-FeOOH and H_2O_2 are 5.31×10^{-3} , 6.89×10^{-3} , 13.01×10^{-3} , and $6.11 \times 10^{-3} \text{ min}^{-1}$, respectively. All these data are summarized in Table 2.

To delve into the discoloration of MB by a-FeOOH, reuse experiments of a-FeOOH were carried out for three cycles, as shown in Figure 7a. The discoloration efficiencies indicate reuse stability for the first two cycles, while for the third cycle around 20% decrease in the discoloration efficiency is observed, which can be associated to a

loss of mass of catalyst in cycles one and two due to a-FeOOH dissolution in the photo-Fenton process [70]. Furthermore, after the third cycle, a change is observed in the FTIR spectra of the a-FeOOH catalyst (Figure 7b). Before the photo-Fenton-like reaction, it was possible to identify the characteristic goethite bands (marked in red in Figure 7b) and the pronounced bands in 1,185 and $1,007 \text{ cm}^{-1}$ related to the presence of lepidocrocite. These last two bands decreased after the third reuse cycle of MB discoloration. Therefore, a transformation between groups associated with goethite and lepidocrocite can be evidenced, which influences the discoloration efficiency.

4 Conclusion

Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, and a-FeOOH catalysts were synthesized and used as heterogeneous photo-Fenton catalysts for the discoloration of MB in neutral medium (pH 6.5). Adsorption of MB on a-FeOOH was insignificant, and for $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 was 5 and 12%, respectively. The oxide a-FeOOH showed the highest value of the kinetic constant of $13.01 \times 10^{-3} \text{ min}^{-1}$ due to the presence of OH groups on the surface of Fe(III), charge separation by

Figure 7: (a) MB discoloration efficiency after 120 min of photo-Fenton-like reaction for 3 consecutive cycles of reuse of a-FeOOH and (b) FTIR spectra of the catalyst a-FeOOH before and after the photo-Fenton-like reaction.

irradiation with UV-A light, and high surface area compared to magnetite and hematite. At the same time, the magnetite and hematite presented a value of the kinetic constant of 5.31×10^{-3} and $6.89 \times 10^{-3} \text{ min}^{-1}$, respectively. Finally, discoloration efficiencies of MB in a-FeOOH were around 80 and 60% for the second and third reuse cycles, respectively.

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