Development of Sustainable Heterogeneous Catalysts for the Photocatalytic Treatment of Effluents

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Received: 25 July 2020; Accepted: 2 September 2020; Published: 9 September 2020

Abstract: The inadequate discharge of effluents from different sources without prior treatment can impact the characteristics of soil and water, which reflect serious environmental problems. Advanced oxidative processes (AOP) appear as a viable alternative for environmental remediation, including wastewater treatment. Herein, α-MoO₃ and α-Fe₂O₃ semiconductors were synthesized at low temperature by a Pechini-based method and then applied in photocatalysis. The catalytic efficiency was performed under visible light toward the degradation of an organic persistent pollutant (Rhodamine B dye, RhB), commonly present in industries wastewater. The results indicated that the synthesized α-MoO₃ or α-Fe₂O₃ photocatalysts presented a pronounced activity and promoted an efficient RhB degradation after 15 min of reaction. α-MoO₃ had a degradation efficiency of 93% and 98%, while α-Fe₂O₃ showed 67% and 100% RhB degradation without and with the addition of H₂O₂, respectively. These results suggest that the synthesized oxides have high oxi-reductive capacity, which can be used for a fast and effective photodegradation of RhB and other organic persistent pollutants to minimize environmental impacts.

Keywords: molybdenum trioxide; iron oxide; heterogeneous photocatalysis; rhodamine B; wastewater treatment; photo-Fenton process

1. Introduction

The contamination of water resources is considered as one of the major problems in developed countries and other in development. The significant amount of organic pollutants detected in water bodies (rivers, lakes and drinking water treatment plants) commonly originate from different industrial sectors (textile, food, paper, petrochemical and pharmaceutical industries). Among them, the textile industry is one of the segments that produce the most water bodies’ pollution due to the large amounts of water and synthetic dye consumption, which generates a large volume of effluents rich in organic matter, besides being heavily tinted by dyes that are not attached to the fiber of the tissues during the process [1–4].

In order to mitigate the disposal of contaminated effluents from industries and to minimize the environmental impacts caused by organic persistent pollutants in water, different water treatment...
methods have been developed. Among them, biological treatments that need long periods for effluents to reach standards’ requirements, filtration processes using membranes [5], electrochemical techniques [4], adsorption processes [6] and advanced oxidative processes (AOP) [7] can be mentioned. Particularly, heterogeneous photocatalysis, which is an advanced oxidative process, has been gaining a lot of attention in decontamination processes for being faster and more effective when compared to other processes.

During photocatalysis, a semiconductor material is irradiated by a light source with energy equal to or greater than that of its band gap. Thus, the irradiation promotes the excitation of electrons that helps to generate hydroxyl radicals (•OH) with high oxidative power, and other intermediate species (O$_2^*$, HO$_2^*$, etc.) that act on the degradation of organic pollutants, even at low concentrations (<100 ppm) [8,9]. Various wide band gap semiconductor oxides, which include TiO$_2$, SnO$_2$, ZnO and WO$_3$ [8–14], and metal chalcogenides (CdS and PbS) [15,16], have been applied as photosensitizers in the oxidation and reduction processes of organic molecules mediated by light. However, the application of high concentrations of these elements for the rapid mineralization of chemical species with environmental relevance can bring some practical inconveniences, besides being harmful to man and the aquatic ecosystem due to the short time stability. All these things make it difficult to consolidate most photocatalysts as alternatives for environmental applications [17].

Therefore, transition metal oxides such as MoO$_3$ and Fe$_2$O$_3$ are promising candidates in photo-oxidative processes; especially due to their redox properties and because they are more environmentally friendly compared to other metallic-based systems. Particularly, iron oxide (Fe$_2$O$_3$) might be highlighted as one of the most important transition metal oxides [18] due to its interesting physical and chemical properties. Hematite (α-Fe$_2$O$_3$) in its rhombohedral R3c-type phase can be readily applied in photocatalytic reactions for the degradation of contaminants in water due to its high stability [19]. Zhang et al. [20] stated that the use of α-Fe$_2$O$_3$ in photocatalysis has a great practical advantage when visible light irradiation is employed in the process due to the band gap energy value (~1.9 eV) of Fe$_2$O$_3$, which is lower than that observed for TiO$_2$ (~3.2 eV) [21]. Thus, different authors have investigated the efficiency of hematite (α-Fe$_2$O$_3$) in the Fenton and photo-Fenton process toward the degradation of different organic contaminants [20,22]. For instance, Zhang et al. [20] obtained 94.8% Rhodamine B dye (RhB) removal using Fe$_2$O$_3$/H$_2$O$_2$ after 180 min under UV and visible light irradiation. On the other hand, Xiao et al. [22] obtained a photodegradation efficiency of 98% for the Fe$_2$O$_2$/H$_2$O$_2$/vis system toward the degradation of red acid G (ARG) dye after 90 min of visible light exposure. The authors associate the catalytic properties of this material with deformations and/or defects in its crystal structure. Most iron oxides present iron cations in oxidation state +3 (Fe$^{3+}$), which is its most stable form, it is easily synthesized by ecosystems and naturally absorbed by the human body [23]. Thus, it is evident that Fe$_2$O$_3$ becomes an excellent alternative as an environmentally friendly heterogeneous catalyst for wastewater treatment.

Molybdenite (α-MoO$_3$) is another important oxide with great technological interest, especially in catalysis for hydrogen evolution, oxygen evolution, and fuel cells [24,25]. α-MoO$_3$ is a non-toxic semiconductor oxide material with high chemical stability. This oxide has a band gap energy in the range of 3.0–4.0 eV [26], which makes it useful in UV-mediated photocatalysis. In spite of this, few studies have been dedicated to the use of α-MoO$_3$ as photocatalysts for environmental remediation, since this material presents a low quantum yield that restricts its practical applications [25,27,28]. However, Huang et al. [27] evaluated the photocatalytic activity of α-MoO$_3$ toward Rhodamine B dye (RhB) degradation and observed that the catalyst presented a good performance after 160 min under UV exposure.

Several methods have already been used to synthesize α-Fe$_2$O$_3$- and α-MoO$_3$-based materials, such as the sol–gel method [29], micro-wave assisted hydrothermal [30], and solvothermal methods [31], among others, but little is described about the synthesis of these oxides by a Pechini-based method, also known as the polymerizing complex method [32]. This method stands out from others because of its simplicity and low cost, besides presenting a good control of the desired phase, particle size and...
In this context, this work aimed to produce sustainable materials based on rhombohedral iron oxide (α-Fe$_2$O$_3$) and orthorhombic molybdenum trioxide (α-MoO$_3$) using a Pechini-based method to be applied in visible-light-driven heterogeneous photocatalysis for the degradation of Rhodamine B (RhB) dye. RhB dye was used as a target molecule commonly present in wastewater. RhB dye is a persistent organic pollutant compound widely used in agate dyeing industries, animal feed industries and textile industries. Moreover, RhB is also used as a fluorescent tracer in water and employed in the production of cartridges inkjet and laser printers [27–36]. It is also important mentioning that the visible light photocatalytic performance of α-Fe$_2$O$_3$ and α-MoO$_3$ synthesized by the Pechini method has not been investigated toward Rhodamine B or any other organic dye compounds yet.

2. Experimental Procedure

2.1. Synthesis and Characterization of the Photocatalysts

α-Fe$_2$O$_3$ and α-MoO$_3$ oxides were synthesized by the Pechini-based method [37], using stoichiometric amounts of ammonium molybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_2$$_7$·4H$_2$O NEON, 83.0%), citric acid monohydrate (C$_{2}$H$_{8}$O$_{7}$·H$_2$O NEON, 99.8%), iron nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O SIGMA-ALDRICH, 98.0%) and ethylene glycol (C$_2$H$_6$O$_2$ DINÁMICA, 99.5%). The precursor solutions were prepared by dissolving stoichiometric amounts of metal salts into citric acid (AC) solution in a proportion of 3 moles of AC to 1 mol of the metal to ensure the metal chelating. The mixing solution was maintained under constant stirring and heating at a temperature of approximately 65 °C. After the complete dissolution of the metal salts and AC, ethylene glycol (EG) with a mass ratio of 40% of EG to 60% of AC was added and the temperature was raised to 90 °C to promote the polymerization and then to form a polymeric resin. This polymeric resin has a clear and characteristic color of the precursor salt. Each resin was calcined at 300 °C for 2 h with a heating rate of 5 °C min$^{-1}$ to obtain the precursor powders. The precursor powders of α-MoO$_3$ and α-Fe$_2$O$_3$ were deagglomerated in a mortar and pestle, sieved through a 200-mesh sieve and calcined at 550 °C for 2 h at the heating rate of 5 °C min$^{-1}$. The calcination temperature was optimized based on the formation of the desired crystalline phase of α-MoO$_3$ (as described in the Discussion Section). Further details about the synthesis can be found in previous works [32,33].

The quality of the obtained α-MoO$_3$ and α-Fe$_2$O$_3$ samples were investigated by X-ray powder diffraction (XRD) using a Shimadzu XRD 6000 diffractometer (Shimadzu Corporation, Tokyo, Japan) equipped with a KCu$_{x$_{α1}}$ radiation source. The short-range structural ordering was investigated by infrared (IR) spectroscopy using a Shimadzu IR Prestige-21 spectrophotometer (Shimadzu Corporation, Tokyo, Japan), and Raman spectroscopy using a Renishaw inVia confocal Raman microscope (Renishaw plc, Wotton-under-Edge, UK) that is equipped with an Ar laser. The morphology of the photocatalyst particles were evaluated by scanning electron microscopy (SEM) using a Shimadzu SSX 550 microscope (Shimadzu Corporation, Tokyo, Japan). The specific surface areas of the oxides were evaluated by ultraviolet–visible (UV–vis) absorption spectroscopy using a Shimadzu UV-3600 spectrometer (Shimadzu Corporation, Tokyo, Japan), and the optical band gap values ($E_g$) were determined using Wood and Tauc’s method [38]. The optical properties of the oxides were evaluated by ultraviolet–visible (UV–vis) absorption spectroscopy using a Shimadzu EDX 720 spectrophotometer (Shimadzu Corporation, Tokyo, Japan). The optical properties of the oxides were evaluated by ultraviolet–visible (UV–vis) absorption spectroscopy using a Shimadzu UV-3600 spectrometer (Shimadzu Corporation, Tokyo, Japan), and the optical band gap values ($E_g$) were determined using Wood and Tauc’s method [38]. The specific surface areas of Brunauer–Emmett–Teller (S$_{BET}$) [39] were measured by N$_2$ adsorption/desorption measurements using a BEL Japan BELSORP-mini II analyzer (BEL Japan Inc., Tokyo, Japan), while the particle sizes distribution was measured using laser light scattering performed on Malvern Mastersizer 2000 analyzer (Malvern Panalytical Instruments, Malvern, UK).
2.2. Photocatalysis and Adsorption Test

The photocatalytic efficiency of the $\alpha$-Fe$_2$O$_3$ and $\alpha$-MoO$_3$ systems was evaluated toward the photodegradation of Rhodamine B (RhB) dye solution. The experiments were conducted in a custom-built photoreactor, containing a visible light irradiation source ($\lambda = 500$–800 nm, 160 W) placed on the top. The distance of 15 cm between the lamp and dye solution was maintained during the reactions. For the experiments, 10.0 mg of the oxide was dispersed in a petri dish containing 15.0 mL of the RhB stock solution previously prepared in a concentration of 5.0 mg L$^{-1}$.

All the tests were performed in triplicate at pH 5.0 (natural pH of the RhB dye solution in a concentration of 5.0 mg L$^{-1}$). A photolysis test was carried out under the same conditions without the presence of a photocatalyst, while an adsorption test was performed in the dark using the same methodology as described in our previous report [40].

To investigate the role of the hydroxyl radicals (OH•) on the photocatalysis, 0.5 mL of hydrogen peroxide (H$_2$O$_2$, 30%) was added to the reaction vessel. Based on the literature reports, 0.5 mL of H$_2$O$_2$ is sufficient to increase the formation of further hydroxyl radicals (OH•) to improve the photocatalytic activity of materials.

Therefore, to evaluate photolysis, an adsorption capacity and photocatalytic efficiency of the oxides with or without the presence of H$_2$O$_2$, an aliquot of the solution, was collected from the petri dish after 15 min of reaction, centrifuged and then filtered. After that, the resulting solution was analyzed by UV–vis absorption spectroscopy using a Shimadzu UV-1800 spectrophotometer, with a wavelength scanning between 400 and 800 nm. Thus, by monitoring the maximum absorption band of RhB at 553 nm, the final concentration of the solution can be calculated using the equation 1 as suggested by Rahman et al. [41] and Chantelle et al. [33]:

$$\text{Degradation rate (\%) } = \left( \frac{C_0 - C}{C_0} \right) \times 100 \quad (1)$$

where $C_0$ is the initial concentration at the time 0 min and $C$ is the variable concentration at time $t$, respectively.

It is important mentioning that the maximum absorption of RhB is attributed to the chromophore group, which is responsible for the dye coloring [41,42] and the decrease in this band after photocatalysis indicates the photodegradation of the dye.

3. Result and Discussion

3.1. Characterization of the Photocatalysts

3.1.1. X-Ray Diffraction (XRD)

Figure 1 shows the XRD patterns of the MoO$_3$ and Fe$_2$O$_3$ photocatalysts synthesized in the present work. To evaluate the crystallization process and the formation of the desired phase for MoO$_3$, the sample was calcined at different temperatures and then analyzed by XRD (Figure 1a,b). The XRD patterns of MoO$_3$ (Figure 1a,b) show that a long-range disordered phase was observed at 300 °C. The beginning of the sample crystallization occurred only at 350 °C as indicated by the presence of a few diffraction peaks in the XRD patterns of this sample (Figure 1a). A long-range structural ordering was achieved for the MoO$_3$ sample calcined at 550 °C as indicated by the appearance of highly intense and well defined peaks in XRD (Figure 1b). All these diffraction peaks were then indexed to the orthorhombic Pbmn crystal structure (ICDD 05-0508) of $\alpha$-MoO$_3$, which is in good agreement with the XRD results reported by Layegh et al. [43].
The infrared spectra of the $\alpha$-MoO$_3$ and $\alpha$-Fe$_2$O$_3$ samples are illustrated in Figure 2a,b, respectively, and the assignments of the main vibration bands are summarized in Tables 1 and 2.

Figure 1. XRD patterns: (a), (b) $\alpha$-MoO$_3$ and (c) $\alpha$-Fe$_2$O$_3$ photocatalysts.

In addition, it is possible to observe well defined and narrow diffraction peaks in the XRD patterns of Fe$_2$O$_3$ (Figure 1c). All the diffraction peaks were indexed to the rhombohedral-type structure with $R3c$ symmetry (ICDD 33-0664), characteristic of the hematite mineral ($\alpha$-Fe$_2$O$_3$), which is the most stable phase of iron oxide. This behavior agrees with other reported work [44]. Maggi et al. [45] observed the $\beta$-, $\gamma$- and $\alpha$-phase transition of Fe$_2$O$_3$ when it is subjected to calcinations above 500 $^\circ$C. Similarly, Mathevula et al. [29] synthesized hematite nanoparticles ($\alpha$-Fe$_2$O$_3$) by the sol–gel method employing two-step heat treatments of 300 and 600 $^\circ$C and observed the formation of the hematite phase after calcinations at 500 $^\circ$C.

It is also important to mention that no peak related to any secondary phase was observed in the XRD patterns of the samples synthesized in this work. As a result, the proposed synthesis conditions and the calcination temperature of 550 $^\circ$C contributed to the formation of well crystallized and single phase $\alpha$-MoO$_3$ and $\alpha$-Fe$_2$O$_3$ samples in their thermodynamically stable structures.

3.1.2. Infrared Spectroscopy

The infrared spectra of the $\alpha$-MoO$_3$ and $\alpha$-Fe$_2$O$_3$ samples are illustrated in Figure 2a,b, respectively, and the assignments of the main vibration bands are summarized in Tables 1 and 2.
In Figure 1a, the bands observed in the region between 1000 and 400 cm$^{-1}$ refer to the three band stretching vibration patterns of the orthorhombic structure of $\alpha$-MoO$_3$. The well-defined and narrow band at 997 cm$^{-1}$ is attributed to the vibration bond $\nu$(Mo=O) that involves the terminal oxygen atoms. Bands at 852 and 817 cm$^{-1}$ are attributed to the angular deformation vibration of two-coordinated oxygens (Mo–O–Mo). The broad band at 592 cm$^{-1}$ and the shoulder at 487 cm$^{-1}$ are attributed to the vibrations of symmetrical Mo–O bonds that comprise the molybdenum and oxygen atoms. Some authors [46,47] observed similar band frequencies for the Mo–O group in comparison to that found in the present study (Table 1). As result, the formation of $\alpha$-molybdenite crystallites is confirmed after calcination at 550 °C, which is in accordance with XRD data.

Figure 2 shows the characteristic IR pattern of the rhombohedral structure of $\alpha$-Fe$_2$O$_3$. The high intensity vibration bands at 532 and 449 cm$^{-1}$ were attributed to the stretching Fe–O bonds of the hematite, which agreed with other studies. For instance, Wang et al. [48] observed three patterns of band vibration for the same material, one at 578 cm$^{-1}$, and two at 485 cm$^{-1}$ and 380 cm$^{-1}$ and the authors correlated these bands with the size, shape, and internal structure of the Fe$_2$O$_3$ particles. Žic et al. [49] investigated the influence of nitrate anions on the properties of hematite particles ($\alpha$-Fe$_2$O$_3$) and obtained four vibration modes at 571, 461, 397 and 343 cm$^{-1}$ associated to Fe–O stretching vibrations. Grigorie et al. [50], from the transformation of the maghemite phase ($\gamma$-Fe$_2$O$_3$) into hematite ($\alpha$-Fe$_2$O$_3$), found two vibration bands at 542 and 488 cm$^{-1}$ associated with the Fe–O bond vibrations. Therefore, all the IR results obtained in this work confirm the local structure vibrations of the synthesized oxides, which agree with the literature. A comparison of the IR modes observed in this work with the literature data is summarized in Table 2.

Table 1. Band positions and attributions of the IR absorption spectrum of $\alpha$-MoO$_3$.

<table>
<thead>
<tr>
<th>Band Position (cm$^{-1}$)</th>
<th>This Work</th>
<th>Seguin et al. [46]</th>
<th>Jiebing et al. [47]</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>997</td>
<td>990</td>
<td>995</td>
<td>$\nu$(Mo=O)</td>
<td></td>
</tr>
<tr>
<td>852</td>
<td>876</td>
<td>868</td>
<td>$\delta$(Mo–O–Mo)</td>
<td></td>
</tr>
<tr>
<td>817</td>
<td>818</td>
<td>818</td>
<td>$\nu$(Mo=O)</td>
<td></td>
</tr>
<tr>
<td>592</td>
<td>603</td>
<td>557</td>
<td>$\nu$(Mo–O)</td>
<td></td>
</tr>
<tr>
<td>487</td>
<td>509</td>
<td>513</td>
<td>$\nu$(Mo–O)</td>
<td></td>
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</table>
symmetry mode characteristics of the iron oxide vibrations of sustainability 2020 and rhombohedral (both the crystal (free rotations or translations of the molecule), and the latter two are attributed to internal structure with $R3c$ unit, while the bands at 244 and 217 cm$^{-1}$ are attributed to the scissor-type vibrations of the oxygen atom doubly coordinated with two Mo, and the weak band at 473 cm$^{-1}$ is related to the wagging vibration of the oxygen atom $O(1)$ in the $O_{3(2)} - Mo - O(3)$ unit. The band at 283 cm$^{-1}$ is related to the wagging vibration of the oxygen atom $O(1)$ in the $\delta_{O(3)} = Mo - O(3)$ unit, while the bands at 244 and 217 cm$^{-1}$ are attributed to scissor-type vibrations of the oxygen atom $O(2)$ in $\delta_{O(2)} = Mo - O(2)$. Finally, the bands observed below 200 cm$^{-1}$ correspond to the stretching, deformation and translational modes of the molybdenum oxide network [51].

For the hematite structure ($\alpha$-Fe$_2$O$_3$), the spectrum (Figure 3b) presented the allowed Raman modes of the $R3c$ symmetry. The band at 219 cm$^{-1}$ is attributed to the $A_{1g}$ mode, and the others at 237, 286, 401 and 602 cm$^{-1}$ are attributed to the $E_g$ symmetry mode characteristics of the iron oxide structure with $R3c$ symmetry [52–54]. The first two frequencies correspond to external vibrations of the crystal (free rotations or translations of the molecule), and the latter two are attributed to internal vibrations. The band at 489 cm$^{-1}$ represents the $A_{1g}$ transition mode. All these results confirm that both $\alpha$-MoO$_3$ and $\alpha$-Fe$_2$O$_3$ samples synthesized in the present work are purely orthorhombic (Pbnm) and rhombohedral (R3c), respectively, without the presence of any other coexisting phase. All these results are in good agreement with XRD and IR data.

### Table 2. Band positions and attributions of the IR absorption spectrum of $\alpha$-Fe$_2$O$_3$.

<table>
<thead>
<tr>
<th>Band Position (cm$^{-1}$)</th>
<th>This Work</th>
<th>Wang et al. [48]</th>
<th>Žic et al. [49]</th>
<th>Grigorie et al. [50]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>532</td>
<td>578</td>
<td>571</td>
<td>542</td>
<td>Fe–O stretching mode</td>
</tr>
<tr>
<td>449</td>
<td>485</td>
<td>461</td>
<td>488</td>
<td>Fe–O stretching mode</td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>397</td>
<td></td>
<td>$\alpha$-Fe$_2$O$_3$</td>
</tr>
</tbody>
</table>

3.1.3. Raman Spectroscopy

The Raman spectra of the $\alpha$-MoO$_3$ and $\alpha$-Fe$_2$O$_3$ photocatalysts are shown Figure 3a,b, respectively.

![Raman spectra](image_url)

**Figure 3.** Raman spectra: (a) $\alpha$-MoO$_3$ and (b) $\alpha$-Fe$_2$O$_3$ photocatalysts obtained at 550 °C/2 h.

The spectrum of each material resulted from a sum of four spectra scanned in the frequency range between 100 and 1000 cm$^{-1}$ acquired at different points in the samples. Well defined peaks related to the Raman active modes of $\alpha$-MoO$_3$ and $\alpha$-Fe$_2$O$_3$ structures are observed in the spectra. Based on Raman results obtained for the molybdite phase ($\alpha$-MoO$_3$) (Figure 3a), high frequency and narrow bands positioned at 994 cm$^{-1}$ and 818 cm$^{-1}$ are observed. These bands are attributed to asymmetric vibrations of ($\nu_{as} Mo = O(1)$) and symmetrical elongation modes ($\nu_{s} Mo - O(3) - Mo$) of the terminal oxygen $O(1)$ atoms, unshared and doubly $O(3)$ coordinated, respectively. The defined band centered at 665 cm$^{-1}$ is attributed to the asymmetric stretching vibration ($\nu Mo - O(2) - Mo$) of the oxygen atom doubly coordinated with two Mo, and the weak band at 473 cm$^{-1}$ is characteristic of the $O_{3(2)} - Mo$ unit. The bands between 377 and 336 cm$^{-1}$ are assigned to the vibration modes of the oxygen atoms $O(2)$ in $\nu_{O_{2}} = Mo = O(2)$ and the deformation of the oxygen atoms $O(3)$ in $\delta O_{3} = Mo - O(3)$. The band at 283 cm$^{-1}$ is related to the wagging vibration of the oxygen atom $O(1)$ in the $\delta O_{1} = Mo = O(1)$ unit, while the bands at 244 and 217 cm$^{-1}$ are attributed to scissor-type vibrations of the oxygen atom $O(2)$ in $\delta O_{2} = Mo - O(2)$. Finally, the bands observed below 200 cm$^{-1}$ correspond to the stretching, deformation and translational modes of the molybdenum oxide network [51].
3.1.4. Microstructure Characteristics and Elemental Analysis

SEM images of the photocatalysts are displayed in Figure 4. The elemental composition obtained by X-ray dispersive energy (EDX) analysis is listed in Table 3.

![SEM images](image)

**Figure 4.** SEM images: (a,c) α-MoO₃ and (b,d) α-Fe₂O₃ photocatalysts calcined at 550 °C/2 h.

**Table 3.** Chemical composition of the synthesized photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MoO₃</td>
</tr>
<tr>
<td>α-MoO₃</td>
<td>83</td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>100</td>
</tr>
</tbody>
</table>

A difference in the particles morphology was observed for α-MoO₃ (Figure 4a,c) and α-Fe₂O₃ (Figure 4b,d) and it might be associated with the creation of different types of nucleation sites as a function of the composition. The orthorhombic α-MoO₃ photocatalyst exhibited particles with a well-defined and unoriented plate-like morphology (Figure 4a,c). A similar result was observed by Chen et al. [55] who synthesized α-MoO₃ nanoplates using inorganic–organic hybrids molybdate-based precursors, which were formed from the reaction of molybdic acid (MoO₃·H₂O) and n-octylamine at room temperature. The EDX results (Table 3) confirmed that the molybdenum ion is the major element present in the orthorhombic oxide structure. However, the presence of the volatile (SO₃) in the α-MoO₃ sample arises from the decomposition of the starting precursor [56], and insignificant traces of other elements resulting from the preparation process (Table 3).

Analyzing the SEM images of the hematite α-Fe₂O₃ (Figure 4b,d), an undefined morphology is observed, and aggregates composed by these unevenly distributed particles is also observed. Such morphology might be due to the thermal treatment that induces the particles sintering. Li et al. [57] observed similar morphological arrangements for hematite films deposited on Au and Ti. The results of X-ray spectroscopy by dispersive energy (EDX) for this system (Table 3) indicated a majority presence of iron metal confirming that the target composition was achieved for the α-Fe₂O₃ photocatalyst.
3.1.5. UV–Visible Spectroscopy

The UV–visible spectra of the samples are displayed in Figure 5. The band gap energy (Eg) values were estimated using the Wood and Tauc’s method [38] by extrapolating the linear part to the photon energy axis. The calculated Eg values are indicated in the graph.

\[ E_g = \alpha \times h\nu - b \]

\[ E_g = 2.79 \text{ eV} \quad \text{(a-MoO}_3) \]

\[ E_g = 1.89 \text{ eV} \quad \text{(α-Fe}_2\text{O}_3) \]

Figure 5. UV–vis absorption spectra: (a) α-MoO3 and (b) α-Fe2O3 photocatalysts calcined at 550 °C/2h.

The N2 adsorption–desorption isotherms of the photocatalysts (α-MoO3 and α-Fe2O3) were collected and the textural characteristics of the samples were investigated by the Brunauer–Emmett–Teller (BET) method [39]. The isotherms are illustrated in Figure 6. It was observed that the materials exhibited type II and III isotherm profiles with the absence of the hysteresis phenomenon, which is able to define the structures containing multilayer adsorption. From the BET measurements (Table 4), it was also possible to observe distinct textural features and the relatively small values for a specific surface area, pore diameter and pore volume distribution in both samples. These differences are due to the different nuclei sites and larger particle growth observed for α-MoO3 in comparison to the α-Fe2O3 system as evidenced in SEM images (Figure 4). The smaller values found for the pore diameters could classify the catalytic powders as mesoporous [61], however, the observed pores in these systems exist because of the interparticle domains.
Figure 6. N₂ adsorption–desorption isotherms: (a) α-MoO₃ and (b) α-Fe₂O₃ calcined at 550 °C/2 h.

Table 4. Specific surface area, average pore diameter and pore volume of the synthesized photocatalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S\textsubscript{BET} (m² g⁻¹)</th>
<th>Pore Diameter (nm)</th>
<th>Pore Volume (cm³ g⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>α-MoO₃</td>
<td>3.24</td>
<td>5.80</td>
<td>4.70 × 10⁻³</td>
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<tr>
<td>α-Fe₂O₃</td>
<td>8.23</td>
<td>7.39</td>
<td>1.52 × 10⁻²</td>
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</tbody>
</table>

Figure 7a, b show the curves of the equivalent spherical diameter values of the particles as a function of the cumulative mass of the photocatalysts. It was observed that the samples have a mean particle diameter (D\textsubscript{50}) between 10 and 50 μm. For the molybdenite (α-MoO₃) photocatalyst (Figure 7a), one can be observed that half of its volume is composed by particles with diameters smaller than 37.96 μm. In addition, 50% of the hematite (α-Fe₂O₃) volume is composed of particles with diameters smaller than 16.65 μm. These results indicate that small particles of the samples tend to agglomerate after calcination and it is consistent with the morphology observed by microscopic analysis (Figure 4).

Figure 7. Particle size distribution and mean particle diameter (D\textsubscript{50}): (a) α-MoO₃ and (b) α-Fe₂O₃ photocatalysts calcined at 550 °C/2 h.
3.2. Photocatalytic Experiments

3.2.1. Photolysis

In order to evaluate the photo-stability of the RhB dye under visible light irradiation, a photolysis test (control reaction) was performed in the absence of the photocatalyst. The UV–vis spectra of the RhB solution before and after photolysis are shown in Figure 8a.

![Figure 8a](image1.png)

Figure 8. (a) UV–vis absorption spectra of the Rhodamine B dye (RhB) before and after the photolysis under visible irradiation; and (b) the emission spectrum of the visible light source.

After 15 min of irradiation, no meaningful decrease in the maximum absorption band of the RhB dye was observed. The maximum absorption at 553 nm (E = 2.24 eV) is characteristic of the chromophore group that is responsible for the dye coloring [41,42]. The low decrease in this band after photolysis corresponds to approximately 5.8% of the dye discoloration.

According to the UV–vis spectrum of the light source employed in the experiment (Figure 8b), the highest emission occurs in the wavelength range of λ = 600–750 nm (E = 2.07–1.65 eV). This energy is not sufficiently high to promote the direct degradation of the dye without catalysts. Some authors have also evidenced the photo-stability of RhB dye under irradiation, especially under UV light, even after a long period of exposure [62]. All this confirms that RhB has great stability under irradiation.

3.2.2. Photocatalytic Activity and Possible Mechanism

Given the photo-stability of the RhB dye, the use of photocatalysts to promote the complete degradation of the dye is necessary. In this context, α-MoO$_3$ and α-Fe$_2$O$_3$ were investigated for the photodegradation of RhB dye solution (5 mg L$^{-1}$, pH 5) under visible light for 15 min.

The literature reports two distinct mechanisms to describe photocatalysis, the direct mechanism and the indirect one. In the direct mechanism, there is an electron transfer from the catalyst to the compound to be oxidized, while, in indirect photocatalysis, strong oxidizing agents are generated on the surface of the catalysts. These oxidizing agents can react homogeneously with the organic material degrading them [63,64]. For the indirect mechanism to occur, the adsorption of the dye molecules onto the catalyst is necessary. Thus, to better understand this, adsorption tests were also performed as shown in Figure 9a. It was observed that an adsorption of approximately 33.9% of the RhB dye was attained when the molybdenite (α-MoO$_3$) is used, while 10.2% of the adsorption was achieved for the hematite (α-Fe$_2$O$_3$) sample. The different adsorption behavior observed for α-MoO$_3$ and α-Fe$_2$O$_3$ might be especially due to the different types of defects present on the surface of the catalysts, since the low specific surface area observed for both materials seems to not play an important role in the process (Table 4), whereas we can suggest that the indirect mechanism is probably the most important way for the photodegradation of RhB to occur in the presence of these catalysts.
When α-MoO$_3$ and α-Fe$_2$O$_3$ are used in the photocatalytic degradation of RhB under visible light, a pronounced decrease in the maximum UV–vis absorption band of the dye at 553 nm was observed after 15 min (Figure 9b). This indicates that a 93.3% and 67.2% degradation of RhB were achieved for molybdite (α-MoO$_3$) and hematite (α-Fe$_2$O$_3$), respectively (Figure 9d).

![Figure 9](image)

**Figure 9.** (a) Adsorption tests in the dark. The inset indicates the adsorption capacity of the catalysts. (b) UV–visible absorption spectra of RhB before and after photocatalysis in the presence of α-MoO$_3$ and α-Fe$_2$O$_3$. (c) UV–visible absorption spectra of RhB before and after photocatalysis in the presence of α-MoO$_3$/H$_2$O$_2$ and α-Fe$_2$O$_3$/H$_2$O$_2$. (d) Degradation rate of the RhB solution in the presence of light (photolysis), catalysts/light and catalysts/light/H$_2$O$_2$.

Different factors may contribute to the photocatalytic performance of materials. For instance, crystal structure and surface defects as well as particle sizes and surface area are important parameters that affect the interaction of the dye molecules with catalysts for the photocatalysis to occur [33]. The higher photocatalytic activity observed for α-MoO$_3$ might be attributed to either the presence of structural defects that are inherent to the material or due to the presence of ionic defects in the material as suggested by Raman results. As a result, a high interaction between dye molecules and the α-MoO$_3$ surface occurs, which leads to an increased adsorptive capacity observed for this oxide (Figure 9) despite its low surface area (Table 4). In addition to that, the particle morphology and band gap energy may also favor the photogeneration of the ($e_{CB}^{-}$/h$_{VB}^{+}$) pairs to promote RhB photodegradation in this system.

Zheng et al. [10] reported a higher degradation rate of RhB (95.0%) for α-MoO$_3$ after only 60 min of visible light exposure. Similarly, Xi et al. [28] observed a photocatalytic performance of 90.2% for α-MoO$_3$ toward the degradation of RhB after 30 min under visible light. On the other hand, Huang et al. [27] obtained a photocatalytic efficiency for α-MoO$_3$ of 91.57% and 91.98 % toward the
degradation of RhB dye under visible and UV light during 160 min, respectively. The different photocatalytic efficiency among the catalysts prepared by these authors and the α-MoO₃ synthesized in our study might be due to the different morphological and electronic features of the samples, reflecting the differences in the synthesis conditions.

In relation to the hematite (α-Fe₂O₃) catalyst, the observed photocatalytic performance might be attributed to the low band gap value and the high recombination rate of the electron–hole pairs ($e_{CB}^-/h_{VB}^+$) generated in the process that affect the amount of oxidizing species promoting RhB photodegradation. Some authors reported the lower photocatalytic efficiencies of Fe₂O₃ in comparison to that for the α-Fe₂O₃ catalyst synthesized in our work. For instance, Wang et al. [65] reported that the hematite (α-Fe₂O₃) presented a reasonable efficiency of 42.0% for the degradation of methyl orange dye, after 180 min of reaction under visible light, and the authors attributed it to the morphology of the catalyst particles. A lower degradation rate of 15.4% was achieved by Luo et al. [66] for the degradation of RhB dye after 60 min of reaction using hematite (α-Fe₂O₃) as a photocatalyst. These authors attributed the catalytic efficiency to the redox property of iron cations ($Fe^{2+} \leftrightarrow Fe^{3+}$) that favored the recombination of the photogenerated electron–hole pairs ($e_{CB}^-/h_{VB}^+$).

Taking into account what was mentioned before and based on the adsorption capacity evaluated (Figure 9a), the photocatalytic behavior of both materials prepared in this work can be understood considering the possible indirect mechanism for the photodegradation of RhB.

According to Honorio et al. [67] and Ong et al. [68], the mechanism involves the reactions represented in the following equations (Equations (2)-(12)). In summary, the photogenerated electrons may interact with O₂ to produce superoxide anionic radicals ($\cdot $O₂⁻) and finally hydroxyl radicals $\cdot OH$.

On the other hand, the photogenerated holes ($h_{VB}^+$) react with the water of the medium to give rise hydroxyl radicals $\cdot OH$*. The resulting hydroxyl radicals will attack the dye molecules adsorbed on the surface of the photocatalyst to rapidly produce intermediate compounds, which will consequently be converted into environmentally acceptable green compounds as CO₂ and H₂O (Equations (11) and (12)):

$$\text{photocatalyst} \rightarrow \text{hν} \rightarrow \text{photocatalyst} \left( e_{CB}^- (h_{VB}^+) \right)$$

$$\text{photocatalyst} (h_{VB}^+) + H_2O \rightarrow \text{photocatalyst} + H^+ + \text{OH}^*$$

$$\text{photocatalyst} (h_{VB}^+) + \text{OH}^- \rightarrow \text{photocatalyst} + \text{OH}^*$$

$$\text{photocatalyst} (e_{VB}^-) + O_2 \rightarrow \text{photocatalyst} + O_2^*$$

$$O_2^* - + H^+ \rightarrow \text{HO}^*$$

$$\text{HO}^* + \text{HO}^* \rightarrow H_2O_2 + O_2$$

$$\text{photocatalyst} (e_{CB}^-) + H_2O_2 \rightarrow \text{OH}^* + \text{OH}^-$$

$$H_2O_2 + O_2^* \rightarrow \text{OH}^* + \text{OH}^- + O_2$$

$$H_2O_2 + \text{hv} \rightarrow 2\text{OH}^*$$

$$\text{Organic compounds} + \text{OH}^* \rightarrow \text{Intermediaries}$$

$$\text{Intermediaries} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$

3.2.3. Increased Photocatalytic Activity

According to Xiao et al. [22] and Miklos et al. [69], the combination of hydrogen peroxide (H₂O₂) and ultraviolet (UV) radiation has been applied to oxidize numerous organic pollutants, since H₂O₂ can increase the formation of hydroxyl radicals ($\cdot OH$*) to promote photodegradation. However, the formation kinetics of these radicals using only H₂O₂ and UV radiation can be limited. In this sense, to
enhance the generation of hydroxyl radicals (OH•) from the photocatalysts and therefore, improve the photodegradation of RhB, the photo-Fenton process was used.

The UV–vis spectra of the dye solution (RhB) after the photocatalysis in the presence of H2O2 are illustrated in Figure 9c. The results of the photodegradation in the presence of H2O2 are shown in Figure 9d. It is possible to observe that after 15 min of photocatalysis using catalysts/H2O2/visible light, a satisfactory increase in the degradation percentage of the dye was observed in comparison to the tests performed in the absence of H2O2 (Figure 9b). It is also possible noting that, without photocatalysts (H2O2/visible light), a low degradation rate of RhB was achieved (Figure 9b). This result may be associated with the low amount of hydroxyl radicals (OH•) produced during the process, which indicates a limitation of the hydrogen peroxide activity in Fenton methodology.

When the molybdenite (α-MoO3) is combined with Fenton reagent (H2O2) and visible light (Figure 9c), an increase in 5.1% in the photodegradation rate of the dye was observed compared to that seen for the α-MoO3/visible light system (Figure 9b). In this case, the presence of the photocatalyst enhances the H2O2 decomposition and consequently, produced more hydroxyl radicals (OH•) to promote dye degradation. The results indicate that the α-MoO3 synthesized in our work presents a promising Fenton and photon-Fenton efficiency as compared to the results reported for α-MoO3 by other authors [70–72].

For the α-Fe2O3 sample, a higher efficiency was achieved after 15 min, reaching 100% of the photodegradation of RhB (Figure 9d). The catalytic efficiency obtained for α-Fe2O3 in the presence of H2O2 is much higher than that observed without H2O2 (Figure 9d). This result can be attributed an improvement of hydroxyl radicals (OH•) generated by the decomposition of H2O2 promoted by the Fe2+ cation, which is regenerated by the reaction between Fe3+ and the photogenerated electrons (e−CB) and from the reaction of holes (h+V) with the water molecules present on the catalyst surface. According to the literature, hydrogen peroxide can also be catalyzed by the Fe3+ ion, but the degradation of organic pollutants by the photon-Fenton reagent (Fe3+/H2O2) is much slower than Fe2+/H2O2 reagent, due to the lower reactivity of iron (III) with respect to H2O2 [66,69]. Different authors have also investigated the efficiency of the Fenton and photo-Fenton process toward the degradation of different organic contaminants using hematite [20,22]. For instance, Zhang et al. [20] obtained a 94.8% RhB degradation using Fe2O3/H2O2 after 180 min under irradiation. Xiao et al. [22] obtained a photodegradation efficiency of 98% of red acid G (ARG) dye using α-Fe2O3/H2O2/vis system after 90 min of light exposure. According to these authors, the high percentage yield observed for the α-Fe2O3/H2O2/vis system resulted from a synergistic effect existing among H2O2, photocatalyst and irradiation, besides the high surface area of the catalyst that led in an increase in large amount of active sites exposed on the surface.

Based on what was mentioned above, the use of H2O2 is one of the main factors to increase the photogenerated hydroxyl radicals (OH•) and then enhance the photodegradation rate of the organic dye. Therefore, we evidenced that the recombination of the electron–hole pairs in this work was effectively suppressed and more oxidizing radicals (OH•) were produced in the dye/catalysts/H2O2/visible irradiation (Figure 9c) in comparison to the common photocatalysis dye/catalysts/visible light (Figure 9b). Additionally, the combination of all these results showed that a significant improvement of the photocatalytic properties of the synthesized oxide materials was achieved.

4. Conclusions

α-MoO3 and α-Fe2O3 catalysts were successfully synthesized at a low temperature using a Pechini method, showing to be effective for the preparation of different materials. Monophased and well crystallized samples were obtained after calcinations at 550 °C, with different structural symmetries (orthorhombic Pbnm for α-MoO3, and rhombohedral R3c-type for α-Fe2O3) as indicated by XRD results and confirmed by Raman and IR spectroscopy. The particles morphology, specific surface areas and band gap energies (evidenced by BET, granulometric analysis and UV–vis spectroscopy) differed according to the composition and strongly affected the photocatalytic properties. A higher catalytic activity toward RhB photodegradation was observed for α-MoO3 (93.3%) in the absence
of H₂O₂. However, the addition of H₂O₂ to the photocatalytic systems promoted a faster RhB photodegradation, especially for α-Fe₂O₃ with 100% of efficiency after 15 min of reaction. The efficiency of the photocatalytic processes was strongly related to the mechanism that involves heterogeneous photocatalysis, the indirect mechanism. Our findings suggest that the visible light-driven photocatalysis using the α-Fe₂O₃ as catalyst might be considered more advantageous in comparison to other processes reported in the literature due to its economic viability and environmental sustainability, since the sun light can be readily applied in the process. In addition to that, the photocatalytic process can promote the complete degradation of organic pollutants (mineralization of these compounds in environmentally acceptable green compounds, CO₂ and H₂O), decreasing their toxicity. As a consequence, the studied systems are promising candidates for the rapid treatment of wastewater contaminated by persistent organic pollutants.


**Funding:** This work was funded by Coordenação de Aperfeiçoamento de Pessoa de Nível Superior (CAPES—PNPD/UFCG), grant 88882.314956/2019-01.

**Acknowledgments:** The authors acknowledge the Brazilian research funding agencies (Coordenação de Aperfeiçoamento de Pessoa de Nível Superior—CAPES, Conselho Nacional de Desenvolvimento Científico e Tecnológico—CNPq, and UFCG for the support). H.B.S. would like to thank to PNPD/CAPES (grant 88882.314956/2019-01), LaNano-IPFB for the BET measurements and NPE-LACOM for the photocatalysis resources. R.R.M. Would like to thank CNPq (308822/2018-8 and 420004/2018-1). A.L.M.O acknowledges PNPD/CAPES (grant 88882.317938/2019-01).

**Conflicts of Interest:** The authors declare no conflict of interest.

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