

Article

Homogeneous and Heterogeneous Photo-Fenton-Based Photocatalytic Techniques for the Degradation of Nile Blue Dye

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Abstract

In this study, the degradation of Nile Blue dye was investigated using homogeneous and heterogeneous photocatalytic methods based on the photo-Fenton reaction. More specifically, for homogeneous photocatalysis, the classical photo-Fenton (UV/Fe²⁺/H₂O₂) and modified photo-Fenton-like (UV/Fe²⁺/S₂O₈^{2−}) systems were studied, while for heterogeneous photocatalysis, a commercial MOF catalyst, Basolite F300, and a natural ferrous mineral, goethite, were employed. Various parameters—including the concentrations of the oxidant and catalyst, UV radiation, and pH—were investigated to determine their influence on the reaction rate. In homogeneous systems, an increase in iron concentration led to an enhanced degradation rate of the target compound. Similarly, increasing the oxidant concentration accelerated the reaction rate up to an optimal level, beyond which radical scavenging effects were observed, reducing the overall efficiency. In contrast, heterogeneous systems exhibited negligible degradation in the absence of an oxidant; however, the addition of oxidants significantly improved the process efficiency. Among the tested processes, homogeneous techniques demonstrated a superior efficiency, with the conventional photo-Fenton process achieving complete mineralization within three hours. Kinetic analysis revealed pseudo-first-order behavior, with rate constants ranging from 0.012 to 0.688 min^{−1} and correlation coefficients (R²) consistently above 0.90, confirming the reliability of the applied model under various experimental conditions. Nevertheless, heterogeneous techniques, despite their lower degradation rates, also achieved high removal efficiencies while offering the advantage of operating at a neutral pH without the need for acidification.



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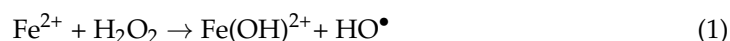
Keywords: Nile blue; AOPs; photocatalysis; photo-Fenton; MOF; goethite; hydrogen peroxide; persulfate

1. Introduction

The extensive use of synthetic dyes in industrial applications, including textiles, cosmetics, leather processing, and biotechnology, has emerged as a significant environmental challenge in recent decades [1]. These compounds, characterized by their chemical stability and resistance to conventional biological treatment methods, demonstrate remarkable persistence in aquatic environments [2,3]. Epidemiological studies have linked prolonged exposure to synthetic dyes with an increase in respiratory disorders and a significant elevation in thyroid dysfunction cases among textile industry workers [4,5]. Additionally, a

series of scientific reports showed that certain azo and azine dyes can cause tumor development in different animal species (mainly rats) [6–8]. Repeated inhalation of dyes can also cause various disorders, such as damage to the liver, nervous system, thyroid problems, and tissue necrosis [9,10]. Nile Blue ($C_{20}H_{20}N_3O \cdot Cl$), an azine dye with a complex heterocyclic structure, presents particular challenges due to its high water solubility, resistance to photodegradation, and tendency to form stable complexes with metal ions in aqueous solutions [11,12]. These properties not only enhance its persistence in the environment, but also complicate conventional treatment approaches. Apart from health issues, the intense color of water imparted by dyes inhibits the access of sunlight to the interior of aqueous bodies and, thus, limits the photosynthesis process of aquatic plants, putting aquatic species at risk [5,13].

There are many different treatment methods used for the removal of dyes. These include conventional methods such as biological processes, membrane filtration, coagulation/flocculation, precipitation, and adsorption, as well as electrochemical and photocatalytic methods [14]. Biological methods often face limitations in treating dyes due to the antimicrobial characteristics of these compounds, which hinder removal efficiencies. Other conventional methods have also the main drawback of low removal efficiencies. Conversely, Advanced Oxidation Processes (AOPs) demonstrate a remarkable efficacy across diverse domains, including environmental applications [15], medical treatment, energy production, and organic synthesis [16]. Among AOPs, the photo-Fenton process is recognized for its ability to produce high reactive hydroxyl radicals ($\bullet OH$, $E^\circ = 2.8$ V) along with other oxidative species, facilitating the transformation of organic pollutants into fully mineralized forms [17,18], as illustrated as follows (Equations (1) and (2)):



The classical photo-Fenton process, employing iron (Fe) as a catalyst and hydrogen peroxide (H_2O_2) as an oxidant, has demonstrated considerable success in environmental remediation [18]. However, alternative modifications and catalysts have been explored to enhance the process's efficiency, reduce costs, improve pollutant degradation under milder conditions, and alter several limitations that hinder its widespread application.

One major limitation is the rapid decomposition of hydrogen peroxide, which requires continuous replenishment to maintain high radical generation, leading to higher operational costs. On the other hand, persulfate ($S_2O_8^{2-}$) has emerged as a promising alternative oxidant in advanced oxidation processes due to its unique ability to generate reactive oxygen species (ROS) such as sulfate radicals ($\bullet SO_4^-$) upon activation [19]. These sulfate radicals are highly reactive and can effectively degrade a wide range of organic contaminants, including those resistant to hydroxyl radicals. One significant advantage of persulfate over traditional oxidants is its stability at neutral to slightly alkaline pHs, making it more versatile and suitable for a broader range of environmental conditions. Additionally, persulfate can be activated by a variety of methods, including UV light and transition metal catalysts, providing flexibility in process design. The combination of persulfate with UV light and iron-based materials can enhance the generation of sulfate radicals, resulting in more efficient pollutant degradation. Moreover, the use of persulfate reduces the need for continuous chemical replenishment, as its activation can be controlled more effectively, offering a more sustainable and cost-effective approach compared to conventional hydrogen peroxide-based systems.

Additionally, the homogeneous nature of the classical process, where iron acts in solution, poses challenges such as catalyst recovery and potential iron leaching, which can

complicate treatment and lead to secondary contamination. Furthermore, the efficiency of the classical photo-Fenton process can be affected by factors such as pH, where acidic conditions are required to maintain iron in its active ferrous state, limiting its applicability to a narrower range of environmental conditions [20].

To overcome these drawbacks, the use of heterogeneous catalysts such as Fe-based metal–organic frameworks (MOFs) and iron-rich minerals in the photo-Fenton process offers a promising alternative [20]. MOFs, often referred to as porous coordination polymers, are porous materials made of organic linkers and metal-containing nodes [21]. Fe-MOFs, with their high surface area, tunable pore structure, and ability to incorporate metal ions, have shown significant potential in enhancing the efficiency of the photo-Fenton process by providing a stable catalytic support, improving the activation of hydrogen peroxide or peroxydisulfate, and minimizing metal leaching. Fe-MOFs are one of the many documented MOFs with a wide range of catalytic uses across a broader pH range, including neutral or near-neutral conditions.

Goethite (α -FeOOH), a naturally abundant iron-bearing mineral, offers an eco-friendly and cost-effective alternative to homogeneous iron catalysts, providing a robust platform for heterogeneous Fenton reactions [22]. It exhibits a combination of properties essential for various applications, including resistance to photocorrosion, a wide operational pH range, and negligible iron leaching into the solution [23]. Additionally, it can serve as a source of iron and, consequently, as a catalyst in heterogeneous photocatalysis systems designed to facilitate photo-Fenton reactions [24].

Although there has been considerable advancement in the field of dye degradation, the use of photo-Fenton processes for the degradation of Nile Blue has not been thoroughly investigated. This specific dye poses distinct challenges, mainly because of its pH-dependent properties ($pK_a = 9.5$) and the formation of reactive intermediates during the degradation process [25]. These complexities present an opportunity to further develop and improve advanced oxidation processes that are based on the photo-Fenton reaction.

Furthermore, this study contributes a novel perspective by systematically evaluating the performance of two widely used oxidants—hydrogen peroxide and persulfate—applied separately but under identical conditions across both homogeneous (Fe^{2+}) and heterogeneous (Basolite F300 and goethite) photo-Fenton systems. Notably, the application of goethite for persulfate activation under photo-Fenton conditions has not, to the best of our knowledge, been previously reported. This comparative analysis provides deeper mechanistic and performance-based insights into radical generation efficiency, mineralization potential, and operational sustainability—extending the current understanding beyond traditional single-catalyst or single-oxidant approaches.

To fill this gap, the current study systematically investigates the degradation of Nile Blue using both homogeneous and heterogeneous methods based on the photo-Fenton reaction. The research has the following three primary objectives: (1) to evaluate the effect of operational parameters such as oxidant concentration, catalyst dosage, and pH; (2) to evaluate the effectiveness of the traditional photo-Fenton process ($UV/Fe^{2+}/H_2O_2$) and modified systems that use persulfate ($S_2O_8^{2-}$, PS) as an alternative oxidant; and (3) to assess the performance of novel heterogeneous catalysts, specifically Basolite F300 (MOF) and goethite in combination with oxidants, as environmentally sustainable options for dye removal in heterogeneous Fenton-based photocatalytic systems. By bridging laboratory findings with practical applications, this study seeks to contribute to the development of more efficient and environmentally sustainable solutions for industrial wastewater treatment.

2. Materials and Methods

2.1. Reagents and Materials

The Nile Blue dye ($C_{20}H_{20}N_3O \cdot Cl$) used in this research was obtained from Sigma-Aldrich (Darmstadt Germany). Hydrogen peroxide (H_2O_2 , 30% *w/v*) was purchased from Panreac (Barcelona, Spain) and sodium persulfate ($S_2O_8^{2-}$) was procured in the factory of Merck in Darmstadt Germany. Basolite F300, a metal–organic framework with a specific surface area of 1300–1600 m^2/g and a bulk density of 0.16–0.35 g/cm^3 (as verified by BET analysis) (Fe-BTC, Iron 1,3,5-benzenetricarboxylate; CAS Number:1195763–37–1), was purchased from Sigma Aldrich/Merck (Darmstadt Germany) and produced by BASF (Germany).

Goethite (α -FeOOH), a natural iron mineral with an orthorhombic structure, was obtained from Fluka (Buchs, Switzerland), and it contains 35%Fe ($FeHO_2$). Sulfuric acid (H_2SO_4 , 98%) was purchased from Sigma-Aldrich (Darmstadt Germany), and deionized water (resistivity 18.2 $M\Omega \cdot cm$) was prepared using a Millipore Milli-Q system.

2.2. Experimental Setup

The photocatalytic experiments were conducted in a batch reactor setup, as depicted in Figure 1. A UVA lamp (power: 9 W) was used as the radiation source, positioned inside the reactor. The setup included a Pyrex cylindrical vessel with a 1 L capacity, chosen for its high transparency to UV radiation, ensuring efficient exposure to the 400 nm UV source. The vessel was equipped with a magnetic stirrer to maintain uniform mixing of the reaction medium and prevent sedimentation of the heterogeneous catalyst. The temperature was approximately 25–26 degrees and was kept steady by using a water-cooling circuit. The experimental setup was selected for its simplicity and allowed for the control for the key parameters, including pH, catalyst concentration, and oxidant levels. Furthermore, the incorporation of a magnetic stirrer eliminated mass transfer limitations and ensured steady mixing and reliable results in all experiments.

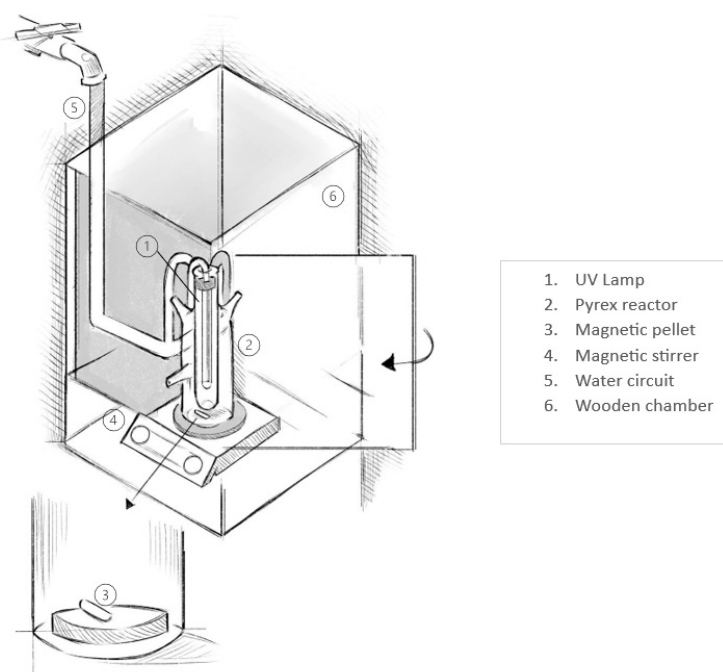


Figure 1. The experimental setup used for the degradation of Nile Blue dye.

2.3. Experimental Procedures

Homogeneous Photo-Fenton Reactions: The conventional photo-Fenton method, using UV light, Fe^{2+} ions, and hydrogen peroxide, was carried out at $pH = 3$, where Fe^{2+} ions

exhibit their highest solubility, resulting in an enhanced production of hydroxyl radicals, which play a crucial role in the degradation process [18]. Experiments were conducted using hydrogen peroxide at concentrations ranging from 100 to 500 mg L⁻¹ or varying Fe²⁺ concentrations of between 1 and 5 mg L⁻¹. More specifically, the homogeneous photocatalysis procedure consisted of the following steps: (i) the preparation of the sample with pH adjustment by adding a concentrated solution of hydrochloric acid (HCl, 1M), (ii) the placement of the sample (100 mL) into the reactor and the addition of Fe(II), (iii) the placement of the UV lamp in the reactor, (iv) the addition of oxidants and turning the lamp on ($t = 0$ min), and (v) taking samples at regular time intervals. On the other hand, for the modified photo-Fenton method, sodium persulfate was used instead of hydrogen peroxide, at concentrations ranging from 100 to 500 mg L⁻¹.

Heterogeneous Photo-Fenton Reactions: The concentrations of goethite and Basolite F300 used as catalysts were set at 100 mg L⁻¹ to enhance the degradation of Nile Blue dye by achieving an optimal balance between providing a sufficient surface area and ensuring proper dispersion. The oxidants were added in different concentration levels ranging between 100 and 500 mg L⁻¹. Additionally, for the goethite/H₂O₂ system, experiments with different catalyst concentrations (100–500 mg L⁻¹) and different pH values (pH = 3 and pH = 7) were also investigated.

Control Experiments: Control experiments were also conducted to evaluate (i) the impact of photolysis, using only UV light, (ii) adsorption on the catalysts' surface, by leaving the dye solution in the dark in the presence of the catalyst, and (iii) the photocatalytic efficiency of the catalysts without the addition of oxidants. These control tests allowed for the isolation of each factor's specific contribution to the degradation process.

2.4. Analytical Processes

The degradation of Nile Blue dye was examined using a UV–Vis spectrophotometer. Absorbance readings were recorded at the dye's specific maximum wavelength, $\lambda_{\max} = 636$ nm, to track the reaction's progress. The kinetic parameters were evaluated as follows [26]:

$$k = -\frac{\ln(C_t/C_0)}{t}$$

$$t_{1/2} = \frac{\ln 2}{k}$$

The starting concentration of Nile Blue is referred to as C_0 , and C_t indicates the concentration at a specific time, t . The pseudo-first-order rate constant (k) was determined from the slope of the linear graph that plots $\ln(C_t/C_0)$ against time. This method facilitated a straightforward evaluation of the dye degradation kinetics over time.

Regarding the mineralization of the dye, the COD values were measured. The Chemical Oxygen Demand (COD) quantifies the oxygen required to oxidize organic matter into CO₂ and water, as well as certain inorganic compounds such as nitrite and ammonia [27].

In this study, the COD values of the dye solutions were determined by a heated digestion process, which facilitated the oxidation of the organic matter in the sample within a predetermined time period of two hours. During digestion, hexavalent chromium in the reagent was reduced to trivalent chromium. The amount of reduced chromium was then measured colorimetrically, with the intensity of color being determined by a compatible photometer and the COD concentration displayed in mg L⁻¹ O₂.

The COD results were considered a key parameter in evaluating the feasibility of the photochemical process for the mineralization of Nile Blue Chloride dye. The equation used for this purpose is as follows:

$$\% \text{ mineralization} = \frac{COD_0 - COD}{COD_0} \times 100$$

COD_0 = initial COD of the dye solution and COD = final COD of the dye solution [28].

The COD of the dye solution was estimated before and after treatment. Samples were withdrawn at an interval of 60 min consistently for 3 h.

The determination of the amount of iron leaching in the solution during the photocatalytic treatment with the MOF or goethite was performed by inductively coupled plasma mass spectroscopy (ICP-MS) (model Thermo Scientific, Fisher Scientific, Ottawa, Canada) with Qtegra™ Intelligent Scientific Data Solution™ Software version 2.7 (further analytical details can be found elsewhere [29]).

3. Results

3.1. Preliminary/Comparative Experiments

3.1.1. Photolysis

A photolysis experiment was conducted to assess whether Nile Blue undergoes degradation under UV irradiation in the absence of catalysts or oxidizing agents. Indicatively, within one hour, the degradation of the dye by photolysis alone reached only 12.7%, confirming that direct photolysis contributes minimally to the overall removal process.

3.1.2. Photolysis with $H_2O_2/S_2O_8^{2-}$

As observed, the effect of UV radiation was ineffective for dye degradation within the prescribed application time (1 h). Therefore, the effect of adding oxidizing agents on the photodegradation of Nile Blue dye was studied, utilizing the following two broadly utilized oxidizing reagents: hydrogen peroxide (HP) and persulfate ions (PS). These preliminary experiments were carried out using 200 mg L^{-1} of oxidant and the results are presented in Figure 2.

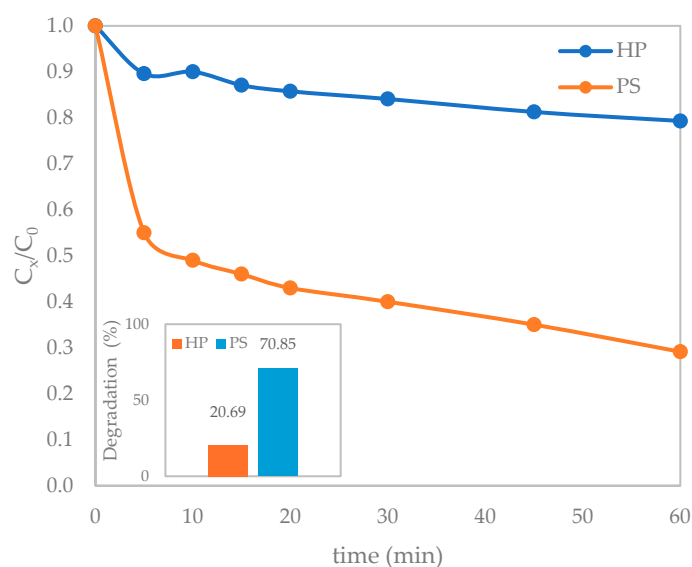


Figure 2. Photolytic degradation of Nile Blue dye in the presence of H_2O_2 (HP) and $S_2O_8^{2-}$ (PS). Inset: % degradation achieved after 1 h of treatment ($C_0 = 15 \text{ mg L}^{-1}$, $C_{\text{oxidant}} = 200 \text{ mg L}^{-1}$).

It is evident that with the addition of an oxidant, the degradation of the dye was faster compared to the effect of radiation alone. Over a period of one hour, the degradation efficiency of the dye reached 21% in the presence of H_2O_2 , while in the presence of $\text{S}_2\text{O}_8^{2-}$, it increased to 71%.

The UV/ H_2O_2 method was more effective than simple photolysis in decomposing the dye due to the generation of reactive hydroxyl radicals. On the other hand, the UV/ $\text{S}_2\text{O}_8^{2-}$ approach proved to be even more effective. The superior efficiency of this process, as indicated by the steep decline in the curve shown in Figure 2, can be attributed to the high oxidizing activity of the sulphate radicals ($E^0 = 2.5\text{--}3.1\text{ V}$), since they are stronger oxidants than hydroxyl radicals ($E^0 = 1.89\text{--}2.72\text{ V}$), especially at a neutral pH [30]. Furthermore, the higher degradation rates may be also attributed to the O-O bond energy of H_2O_2 and $\text{S}_2\text{O}_8^{2-}$ which is estimated to be $33.5\text{ kcal mol}^{-1}$ for persulfate, while for hydrogen peroxide, it is 51 kcal mol^{-1} . This suggests that the former is more easily decomposed than the latter, and, thus, the resulting sulfate radicals can be formed more easily and rapidly than the corresponding hydroxyl radicals [31].

3.2. Homogeneous Photocatalysis

3.2.1. Photo-Fenton and Photo-Fenton-like

Preliminary Study

First, a preliminary experiment was carried out to determine whether the photo-Fenton technique is effective at degrading the target dye. The experiment was carried out in the presence of $2\text{ mg L}^{-1}\text{ Fe}^{2+}$ and $200\text{ mg L}^{-1}\text{ H}_2\text{O}_2$ and the results are presented in Figure 3A.

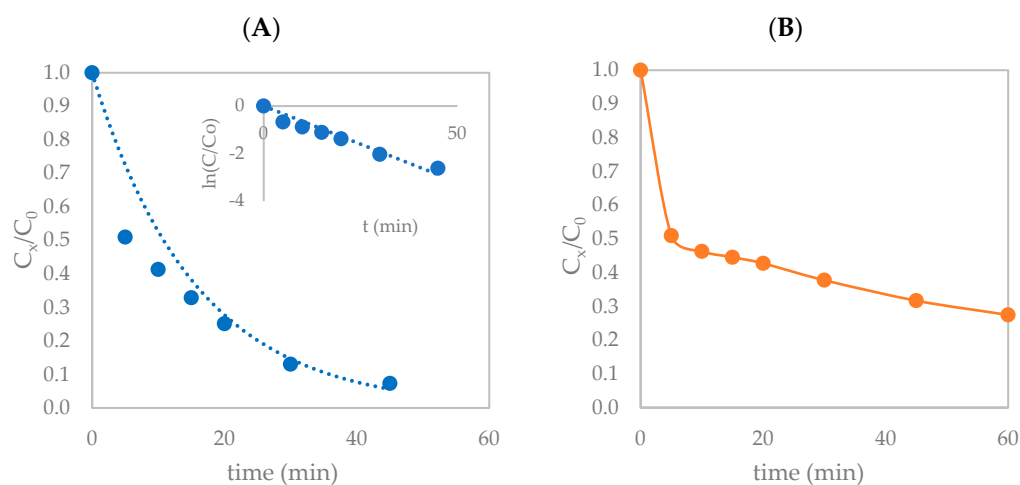
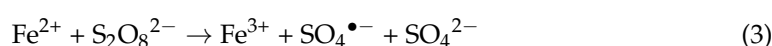
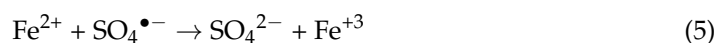
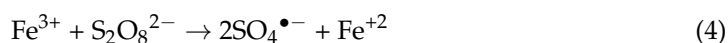


Figure 3. Photocatalytic degradation of Nile Blue dye in the presence of Fe^{+2} and (A) H_2O_2 and (B) $\text{S}_2\text{O}_8^{2-}$ ($C_0 = 15\text{ mg L}^{-1}$, $C_{\text{Fe}^{+2}} = 2\text{ mg L}^{-1}$, $C_{\text{oxidant}} = 200\text{ mg L}^{-1}$).

As can be observed, within 45 min, the dye was degraded by 93.8%, which highlights the photo-Fenton technique as an excellent technique for the degradation of Nile Blue dye. Based on the experimental data, a plot of $\ln(C_0/C)$ as a function of time was constructed, yielding a straight line with an excellent fit ($R^2 = 0.94$) (inset of Figure 3). This indicates that the degradation process follows first-order kinetics. Consequently, the rate constant (k) was calculated to be 0.064 min^{-1} . The good linearity of the $\ln(C_0/C)$ vs. time plots further supports that the reaction follows pseudo-first-order kinetics under these conditions.

As for the photo-Fenton-like reaction, the application of this system is similar to that of the traditional photo-Fenton process. The differences lie in the oxidant used and the radicals produced, as shown in the following relevant reactions (Equations (3)–(5)) [32]:





In order to determine whether this technique can effectively degrade the dye, a preliminary experiment was conducted in the presence of $2 \text{ mg L}^{-1} \text{ Fe}^{2+}$ catalyst and $200 \text{ mg L}^{-1} \text{ S}_2\text{O}_8^{2-}$ oxidant. The results are shown in Figure 3B.

In Figure 3B, we observe a sharp decrease, which indicates an immediate increase in the rate of dye degradation. Particularly, in the first five minutes, the calculated degradation rate equals 49%. Hence, the photo-Fenton-like process is considered effective. However, the sharp decrease of the curve does not allow for kinetic study of the reaction, as it does not follow first-order kinetics.

Effect of Oxidant Concentration

With the aim of studying the effect of different oxidant concentrations on the photo-Fenton and photo-Fenton-like process, experiments were conducted at four different concentrations of hydrogen peroxide and $\text{S}_2\text{O}_8^{2-}$, respectively ($100, 200, 300$, and 500 mg L^{-1}). The selected concentrations were based on values commonly reported in the literature for similar photo-Fenton systems, ensuring both relevance and comparability with previous studies [32–34]. Furthermore, all experiments involving the classical and modified photo-Fenton process were conducted at pH 3, where Fe^{2+} is most soluble and active. Experiments at a neutral pH were not performed, as the process is known to be inefficient under such conditions due to Fe^{3+} precipitation and poor hydroxyl radical formation [35]. The photodegradation rates of the dye were calculated over a period of one hour and the results are depicted in Figure 4.

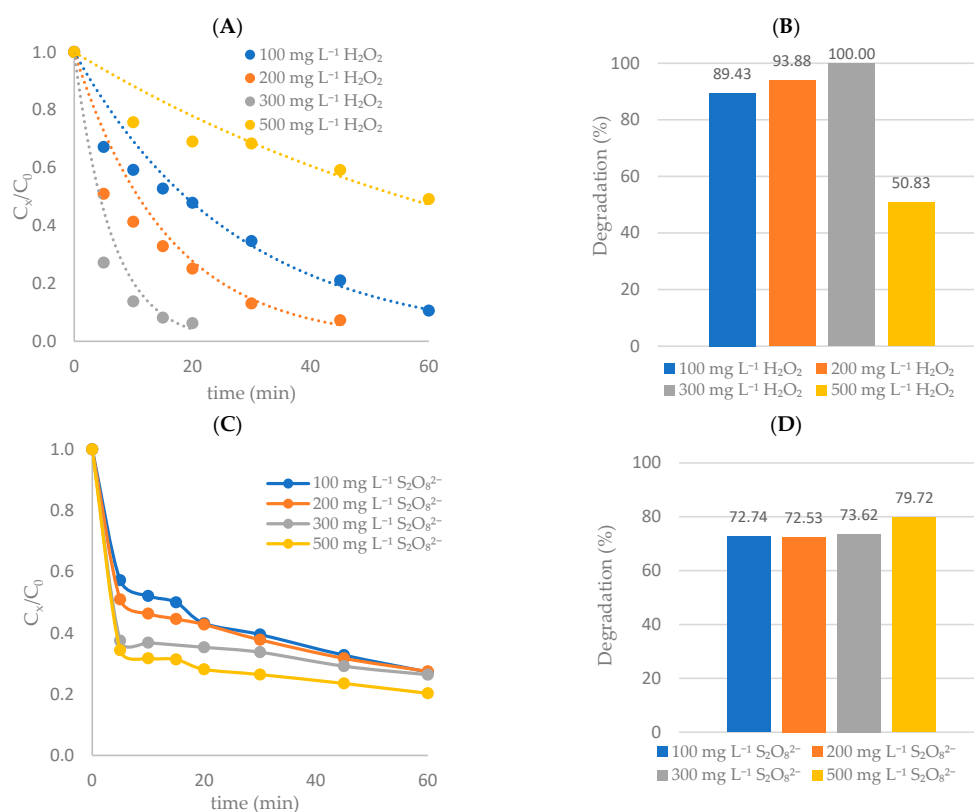


Figure 4. (A) Photocatalytic degradation of Nile Blue and (B) % degradation achieved after 60 min, in the presence of Fe^{2+} and different H_2O_2 concentrations, (C) photocatalytic degradation of Nile Blue and (D) % degradation achieved after 60 min, in the presence of Fe^{2+} and different concentrations of $\text{S}_2\text{O}_8^{2-}$ ($C_0 = 15 \text{ mg L}^{-1}$, $C_{\text{Fe}^{2+}} = 2 \text{ mg L}^{-1}$, $C_{\text{oxidant}} = 100, 200, 300, 500 \text{ mg L}^{-1}$).

From Figure 4A,B, it can be observed that increasing the concentration of hydrogen peroxide up to 300 mg L⁻¹ increases the degradation rate of the dye. However, above 300 mg L⁻¹, a significant decrease is observed due to the scavenging effect of the oxidant according to the following reactions (Equations (6)–(8)):



The calculated rate constants for 100, 200, 300, and 500 mg L⁻¹ of oxidant were 0.037, 0.064, 0.159, and 0.012 min⁻¹, respectively. Additionally, the calculated R² values (0.90–0.96) confirm that the degradation kinetics under varying H₂O₂ concentrations followed a pseudo-first-order model.

On the contrary, Figure 4C,D illustrate that an increase in the concentration of persulfate ions leads to an accelerated degradation rate of the target compound. This is attributed to the enhanced generation of sulfate radicals (SO₄^{•-}) as the concentration of S₂O₈²⁻ increases. However, the variation in the degradation achieved is not substantial, as a portion of the additional radicals produced may undergo self-recombination, as demonstrated in (Equation (9)) [36], as follows:



Photo-Fenton: Effect of Fe⁺² Concentration

In order to study the effect of the iron concentration on the photo-Fenton process, experiments were carried out at four different Fe⁺² concentrations (1, 2, 3, and 5 mg L⁻¹). The H₂O₂ concentration was set at 200 mg L⁻¹ and the dye concentration was set at 15 mg L⁻¹. The results of these experiments are presented in Figure 5A,B.

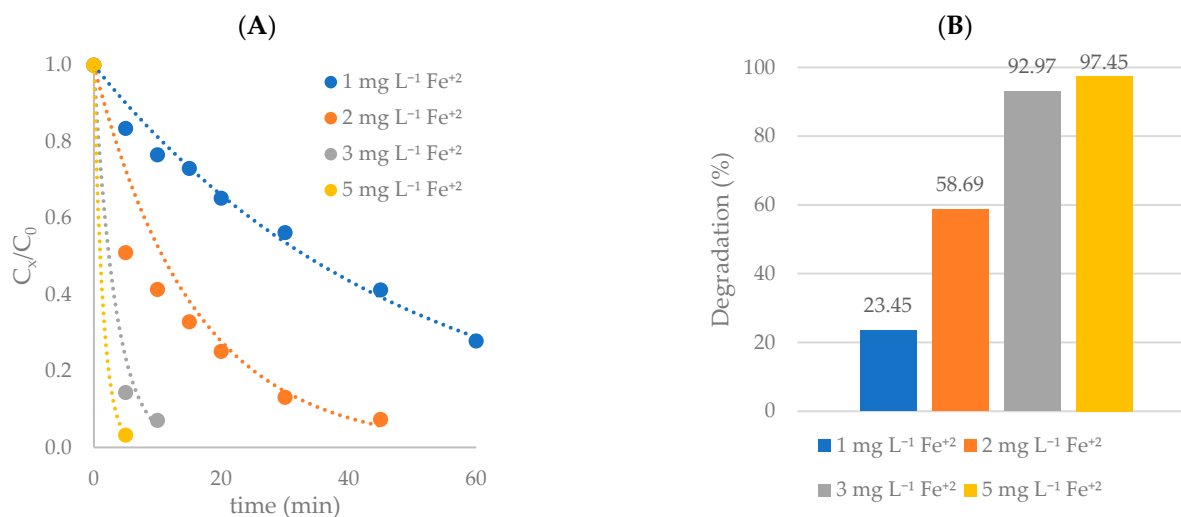


Figure 5. (A) Photocatalytic degradation of Nile Blue dye and (B) % degradation achieved after 10 min, ($C_0 = 15 \text{ mg L}^{-1}$, $C_{\text{oxidant}} = 200 \text{ mg L}^{-1}$, $C_{\text{Fe}^{+2}} = 1, 2, 3, 5 \text{ mg L}^{-1}$).

Increasing the iron concentration from 1 to 5 mg·L⁻¹ clearly results in a significant rise in the reaction rate constant from 0.021 to 0.688 min⁻¹ ($R^2 = 0.95\text{--}0.99$). This indicates that higher Fe⁺² concentrations enhance the reaction rate by promoting the production of hydroxyl radicals, as indicated by (Equations (1) and (2)) [37].

Effect of Ultraviolet Radiation

In order to study the effect of UV radiation on the Fenton and modified Fenton reaction, a catalytic and photocatalytic treatment experiment was carried out for a total duration of 90 min (Figure 6). The first treatment took place for 60 min in the dark, while for the next 30 min, the UV lamp was turned on.

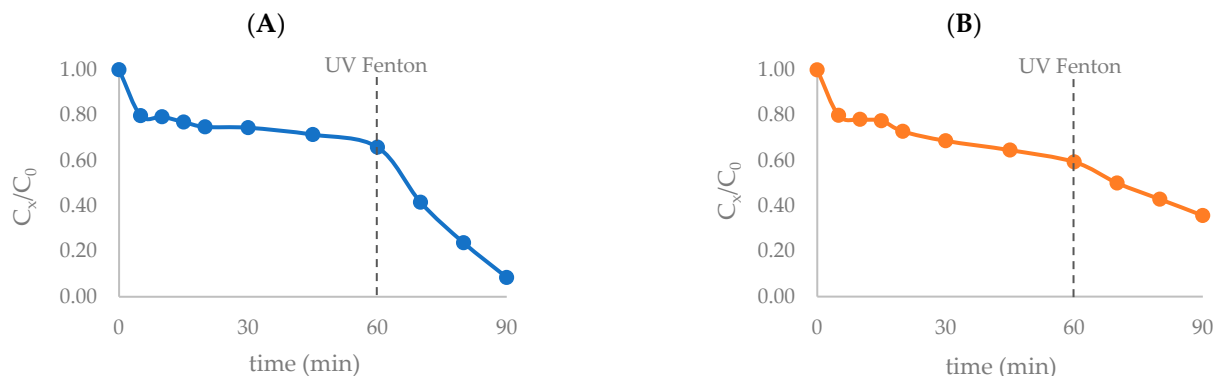
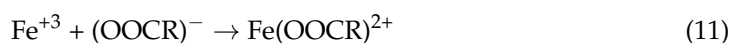
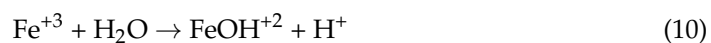


Figure 6. Degradation of Nile Blue dye in the presence of Fe^{2+} and (A) H_2O_2 and (B) $S_2O_8^{2-}$ in dark and irradiated conditions ($C_0 = 15 \text{ mg L}^{-1}$, $C_{\text{oxidant}} = 100 \text{ mg L}^{-1}$, $C_{Fe^{2+}} = 2 \text{ mg L}^{-1}$).

In Figure 6A, it is evident that the presence of light significantly influences the degradation rate of the dye by accelerating the reaction. In the absence of light, degradation proceeds very slowly and remains virtually constant after the initial few minutes of the reaction. Therefore, the presence of UV radiation enhances the reaction rate without the need for additional reagents, as it facilitates the continuous reduction of Fe^{3+} to Fe^{2+} , thereby sustaining a photocatalytic cycle that results in the ongoing generation of hydroxyl radicals. In contrast, in the conventional Fenton process, the reaction rate declines over time due to the complete oxidation of Fe^{2+} to Fe^{3+} [32,33].

Figure 6B displays a slightly different trend, with the degradation of Nile Blue continuing throughout the dark phase, albeit at a relatively slow rate, ultimately reaching 40.6% removal after one hour. This can be attributed to the reaction between the Fe^{2+} and the $S_2O_8^{2-}$ oxidant, which gradually slows over time. As in the case of hydrogen peroxide, the decline in reaction rate is primarily due to the deactivation of Fe^{3+} through the formation of hydroxo- and organic complexes (Equations (10) and (11)), preventing its reduction back to Fe^{2+} . Consequently, as Fe^{2+} is consumed, the overall reaction rate decreases.



On the other hand, in the presence of light, the reaction proceeds slightly faster, as Fe^{+3} iron is continuously photo-reduced to Fe^{+2} .

3.3. Heterogeneous Photocatalysis

3.3.1. Basolite F300 (MOF)

Preliminary Study

Initially, a simple photocatalytic experiment on the Nile Blue dye in the presence of Basolite F300 was carried out in order to evaluate the catalyst's efficiency. Prior to illumination, the dye solution was kept in the dark with the catalyst in order to assess its absorbance on the catalyst's surface. A 15.4% removal was recorded in the dark and, subsequently, the lamp was turned on and the photocatalytic degradation of the dye was monitored. The results are demonstrated in Figure 7.

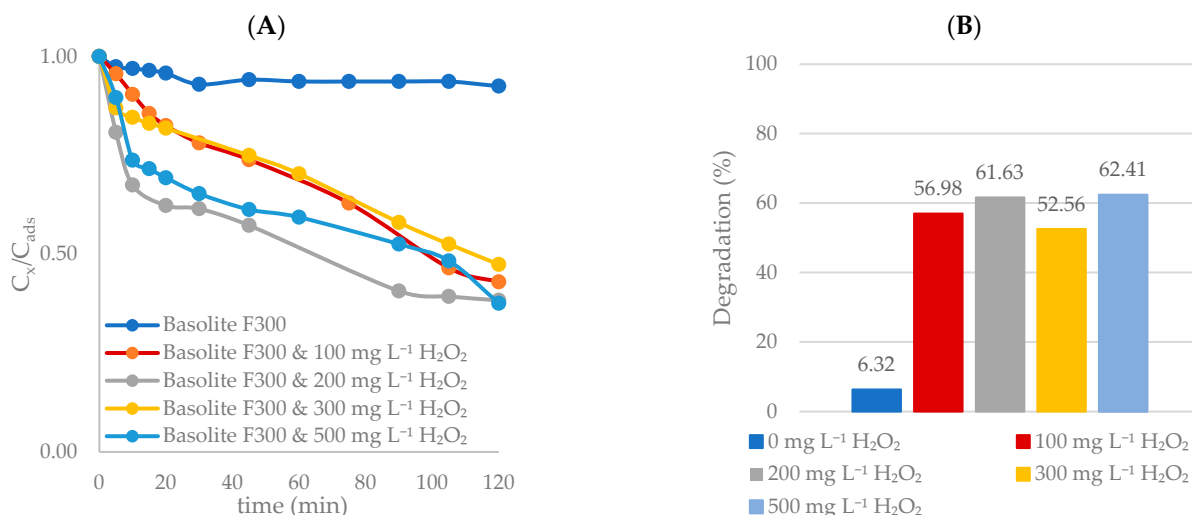


Figure 7. (A) Photocatalytic degradation of Nile Blue and (B) % degradation achieved after 120 min, in the presence of Basolite F300 catalyst and different H₂O₂ concentrations (120 min) ($C_0 = 15 \text{ mg L}^{-1}$, $C_{\text{catalyst}} = 100 \text{ mg L}^{-1}$, $C_{\text{oxidant}} = 100, 200, 300, 500 \text{ mg L}^{-1}$).

As can be observed, the degradation of the Nile blue dye proceeds very slowly in the presence of the MOF catalyst, achieving only a 6.3% reduction after one hour of irradiation. The slow rate of dye degradation can be attributed to the rapid recombination of photogenerated holes and electrons [34].

All experiments with Basolite F300 were conducted at a neutral pH without additional acidification.

Effect of H₂O₂ Concentration

Due to the slow rate of dye decomposition by simple photocatalysis in the presence of the Basolite F300 catalyst, the experiments were performed with oxidant addition, so as to achieve the following:

- To limit the hole–electron recombination.
- To produce additional active radicals from self-activation of the oxidant by radiation.
- To achieve, apart from the heterogeneous photocatalytic process, a photo-Fenton reaction, as the catalyst is an iron-based MOF.

Figure 7 presents the photocatalytic degradation of the target compound in the presence of four different H₂O₂ concentrations (100, 200, 300, and 500 mg L⁻¹) and the Basolite F300 catalyst.

The addition of the oxidant clearly enhances the photocatalytic degradation of the dye. Furthermore, the degradation rate increases with an increasing H₂O₂ concentration up to 200 mg L⁻¹. However, beyond this concentration, a decline in the degradation rate is observed. As mentioned before, this may be due to the action of hydrogen peroxide as a scavenger of hydroxyl radicals, as already mentioned in Equations (6)–(8).

In order to evaluate if a synergistic effect takes place, meaning that the combination of the catalyst and the oxidant results in a greater performance than the sum of the contributions of the standalone systems [38], the following equation is used:

$$\frac{\% \text{removal by Basolite F300} / \text{H}_2\text{O}_2}{\% \text{removal by Basolite F300} + \% \text{removal by H}_2\text{O}_2} = \frac{60.68}{6.32 + 20.69} \% = 2.25 > 1$$

The resulting value significantly exceeding unity ($2.25 > 1$) clearly indicates the presence of a synergistic effect. This suggests that the combined system of Basolite F300 and H₂O₂ does not merely add their individual efficiencies, but they rather interact in a way that

amplifies the overall photocatalytic degradation of the dye. Such a synergistic interaction can be attributed to the enhanced generation of reactive species, improved electron–hole separation, or the catalytic activation of H_2O_2 by Basolite F300, all of which contribute to the markedly improved performance observed.

Effect of $\text{S}_2\text{O}_8^{2-}$ Concentration

Accordingly, in order to study the effect of the $\text{K}_2\text{S}_2\text{O}_8$ oxidant on the photocatalytic degradation of the studied dye with the Basolite F300 catalyst, experiments were also carried out with four different concentrations of $\text{S}_2\text{O}_8^{2-}$ (100, 200, 300, and 500 mg L^{-1}). The results are presented in Figure 8.

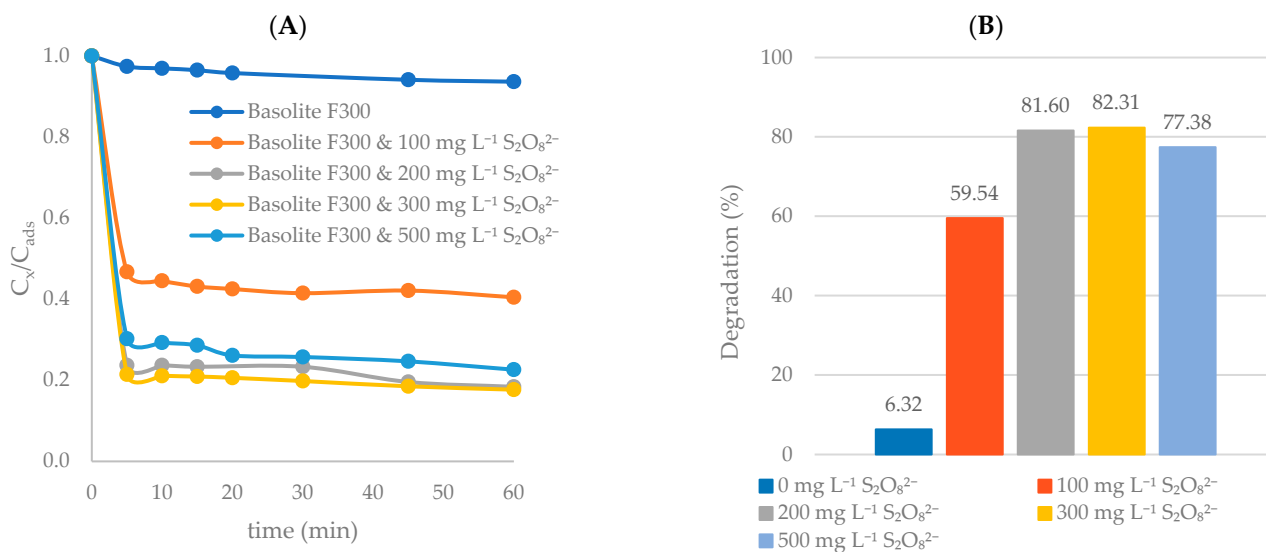


Figure 8. (A) Photocatalytic degradation of Nile Blue and (B) % degradation achieved after 60 min, in the presence of Basolite F300 catalyst and different concentrations of $\text{S}_2\text{O}_8^{2-}$. ($C_0 = 15 \text{ mg L}^{-1}$, $C_{\text{catalyst}} = 100 \text{ mg L}^{-1}$, $C_{\text{oxidant}} = 100, 200, 300, 500 \text{ mg L}^{-1}$).

As observed, the addition of the oxidant strongly enhances the degradation of the target compound. An increase in the concentration of persulfate also causes the enhancement of the degradation rate up to 300 mg L^{-1} . Above the optimum concentration, scavenging effects may occur, reducing the reaction rate.

To evaluate the interaction between the Basolite F300 catalyst and persulfate ions, the following equation is applied:

$$\frac{\% \text{removal by Basolite F300} / \text{S}_2\text{O}_8^{2-}}{\% \text{removal by Basolite F300} + \% \text{removal by S}_2\text{O}_8^{2-}} = \frac{81.60}{6.32 + 70.85} \% = 1.1$$

This ratio being greater than 1 indicates a synergistic effect between Basolite F300 and persulfate ions. However, the synergy is less pronounced compared to that observed with hydrogen peroxide. In this case, the overall efficiency of the combined system is only marginally higher than the sum of the individual contributions. This limited enhancement is likely due to the high efficiency of UV-induced persulfate activation, which dominates the degradation process and diminishes the relative contributions of additional activation pathways, such as those facilitated by the MOF catalyst.

Consequently, Basolite F300 facilitates oxidant activation through surface Fe(III)/Fe(II) redox cycling. Moreover, the presence of oxidants such as H_2O_2 and persulfate helps to suppress the recombination of photogenerated electron–hole pairs, enhancing radical formation. With H_2O_2 , this results in increased hydroxyl radical ($\bullet\text{OH}$) production via

photo-Fenton-like reactions, while with persulfate, it promotes sulfate radical ($\text{SO}_4^{\bullet-}$) generation, albeit to a lesser extent due to strong UV activation. Although a small amount of iron leaching is observed (less than 0.1 mg L^{-1}), which may contribute to a minor homogeneous Fenton reaction, the overall degradation is still governed predominantly by the heterogeneous photocatalytic process. Overall, Basolite F300 works synergistically with the oxidants to boost radical generation and accelerate degradation kinetics.

3.3.2. Goethite

Preliminary Study

In order to evaluate the photocatalytic efficiency of the goethite, a photocatalytic experiment was conducted without the presence of oxidizing agents. The results are demonstrated in Figure 9. Blank experiments in the dark, prior to illumination, revealed that 16% of the target dye was adsorbed on the mineral's surface.

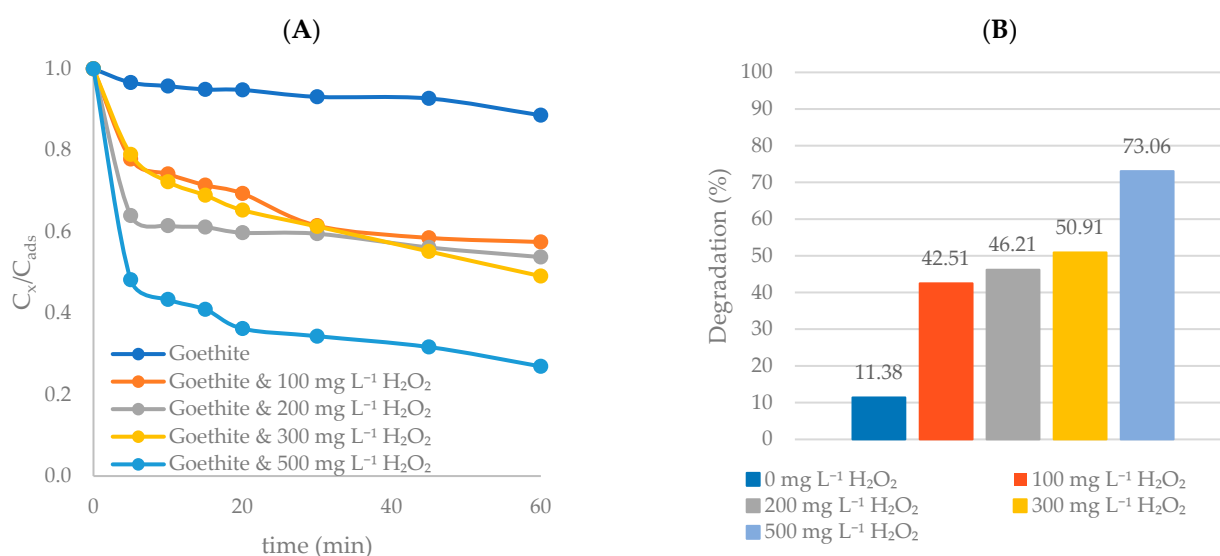


Figure 9. (A) Photocatalytic degradation of Nile Blue and (B) % degradation achieved in 60 min, in the presence of Goethite catalyst and different H_2O_2 concentrations ($C_0 = 15 \text{ mg L}^{-1}$, $C_{\text{catalyst}} = 100 \text{ mg L}^{-1}$, $C_{\text{oxidant}} = 100, 200, 300, 500 \text{ mg L}^{-1}$).

As can be observed, the degradation rate of Nile Blue dye reaches 11.4% after one-hour irradiation. Obviously, the mineral demonstrates low photocatalytic activity that leads to high e^-/h^+ pair recombination due to its positive conduction band potential (2.2 eV) and inability to reduce molecular oxygen [39,40].

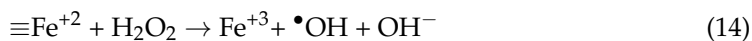
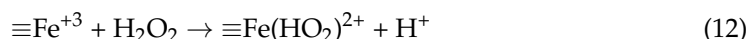
Effect of H_2O_2 Concentration

Due to the slow rate of dye decomposition by simple photocatalysis in the presence of the goethite catalyst, experiments were carried out with the addition of an oxidant for the reasons mentioned in the section Effect of H_2O_2 Concentration in the presence of MOF catalyst.

Experiments at four different oxidant concentrations (100, 200, 300, and 500 mg L^{-1}) were conducted and the results are presented in Figure 9. In this specific system (UV/Goethite/ H_2O_2), there are three possible sources of iron, including Fe^{+2} , Fe^{+3} , and FeOOH , while two possible mechanisms for hydroxyl radical generation can occur:

The first mechanism is similar to that occurring in homogeneous Fenton reactions, due to the presence of iron ions leached from the catalyst through its reductive dissolution. These ions react with hydrogen peroxide, resulting in the formation of hydroxyl radicals [41].

The second mechanism refers to the surface adsorption and redox reaction with hydrogen peroxide. The main process of hydroxyl radical formation takes place at the goethite–water interface and is described by the following reactions (Equations (12)–(14)) [41]:



In Figure 9, we observe that increasing the concentration of hydrogen peroxide increases the degradation of the dye, which is due to the increased production of hydroxyl radicals by the mechanisms mentioned above. The increased degradation rates are indicative of catalyst activation, assisted by H_2O_2 , and the possibility of a heterogeneous photo-Fenton reaction taking place between the Fe atoms contained in the catalyst and H_2O_2 .

Finally, the experimental results indicate a synergistic effect in the applied process. This is evidenced by the following calculation:

$$\frac{\% \text{removal by Goethite} / \text{H}_2\text{O}_2}{\% \text{removal by Goethite} + \% \text{removal by H}_2\text{O}_2} = \frac{46.21}{11.38 + 20.69} \% = 1.44 > 1$$

A ratio greater than one confirms that the combined use of goethite and hydrogen peroxide leads to a more efficient degradation of the dye than when each component is applied individually. This synergistic interaction suggests that goethite may play a catalytic role.

Effect of $\text{S}_2\text{O}_8^{2-}$ Concentration

Accordingly, in order to evaluate the effect of persulfate, experiments were carried out at four different concentrations of $\text{S}_2\text{O}_8^{2-}$ (100, 200, 300, 300, and 500 mg L^{-1}). The results are presented in Figure 10. It is obvious that the rate of dye degradation increases with a rising concentration of persulfate ions. This enhancement is attributed to the greater generation of sulfate radicals, as previously discussed [36].

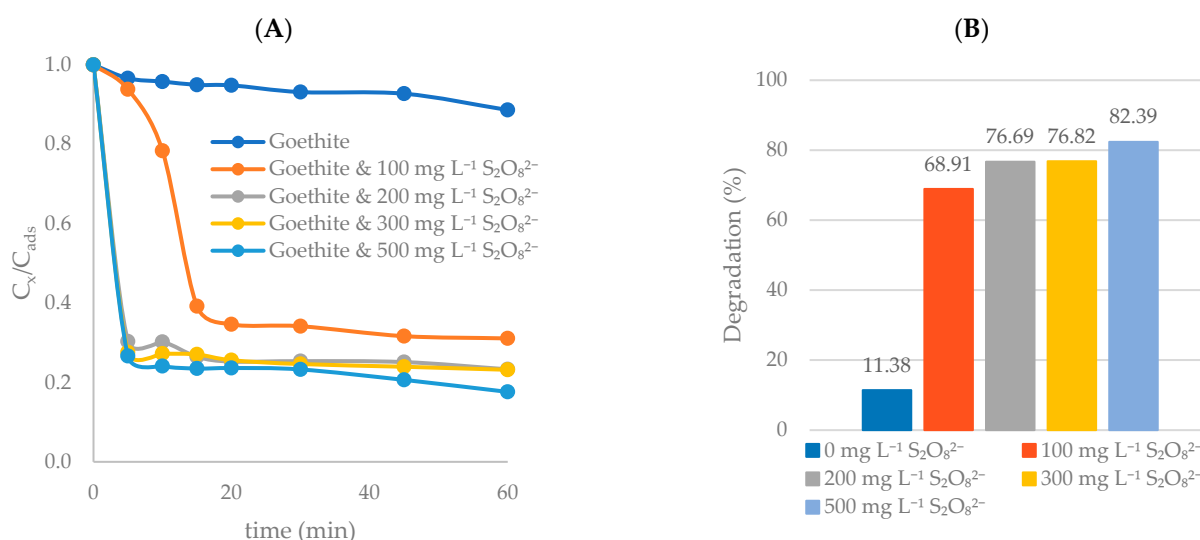


Figure 10. (A) Photocatalytic degradation of Nile Blue and (B) % degradation achieved in 60 min, in the presence of Goethite catalyst and different concentrations of $\text{S}_2\text{O}_8^{2-}$ ($C_0 = 15 \text{ mg L}^{-1}$, $C_{\text{catalyst}} = 100 \text{ mg L}^{-1}$, $C_{\text{oxidant}} = 100, 200, 300, 500 \text{ mg L}^{-1}$).

A comparison between Figures 2 and 10A shows that the rate of dye degradation is not different from that found in the presence of the oxidant alone. Therefore, the catalyst does not further enhance the formation of active radicals, and the decomposition of the dye is primarily due to the action of the oxidant.

This can be confirmed by the following equation:

$$\frac{\% \text{removal by Goethite} / \text{S}_2\text{O}_8^{2-}}{\% \text{removal by Goethite} + \% \text{removal by } \text{S}_2\text{O}_8^{2-}} = \frac{76.69}{11.38 + 70.85} \% = 0.93 < 1$$

The above underscores that goethite does not contribute to enhancing the production of active radicals compared to that produced by the exclusive use of the $\text{S}_2\text{O}_8^{2-}$ oxidant. Thus, there is no synergistic effect between goethite and persulfate ions. Therefore, the following experiments were carried out using only hydrogen peroxide as an oxidant.

Consequently, goethite exhibits limited photocatalytic activity alone due to rapid electron–hole recombination, linked to its conduction band position. In the presence of H_2O_2 , it catalyzes hydroxyl radical generation via both leached iron ions (homogeneous Fenton-like reactions) and surface-mediated redox processes, leading to enhanced dye degradation and a clear synergistic effect. Conversely, with persulfate, goethite shows no synergistic interaction, indicating a minimal catalytic contribution beyond direct oxidant activation. A small amount of iron leaching is detected during the reaction, with concentrations remaining below 0.2 mg L^{-1} . While this minor leaching may contribute slightly to homogeneous Fenton processes, it does not alter the predominantly heterogeneous nature of the photocatalytic system. Thus, goethite acts primarily as a heterogeneous photo-Fenton catalyst when combined with hydrogen peroxide.

Effect of Goethite Concentration

Given the high efficiency of the system comprising goethite and hydrogen peroxide in degrading the target dye, it was subjected to further investigation. Consequently, experiments were carried out at four different goethite concentrations (100, 200, 300, and 500 mg L^{-1}) (Figure 11).

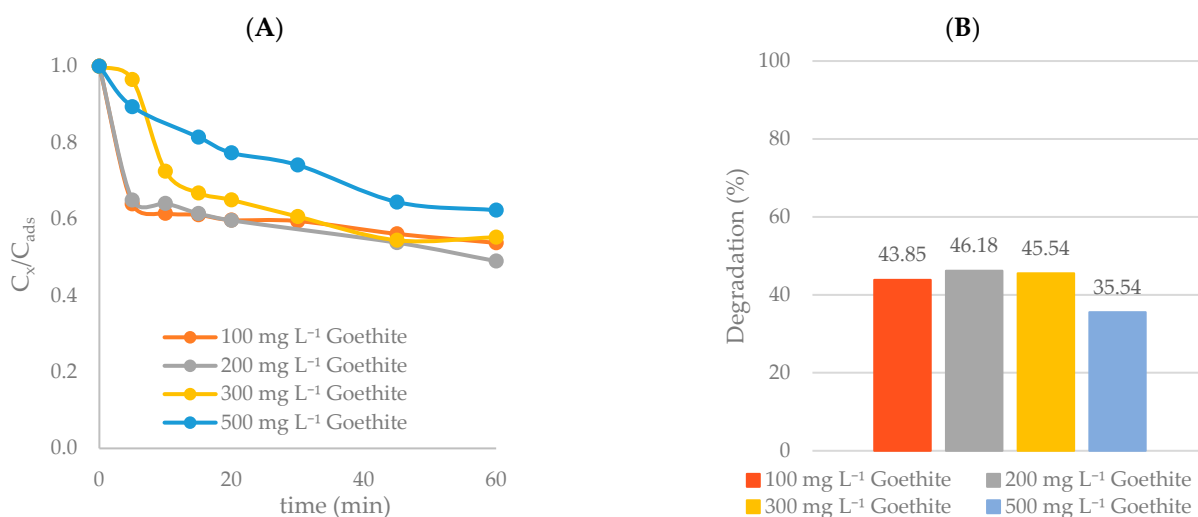


Figure 11. (A) Photocatalytic degradation of Nile Blue and (B) % degradation achieved in 60 min, in the presence of H_2O_2 and different concentrations of Goethite ($C_0 = 15 \text{ mg L}^{-1}$, $C_{\text{oxidant}} = 200 \text{ mg L}^{-1}$, $C_{\text{catalyst}} = 100, 200, 300, 500 \text{ mg L}^{-1}$).

In Figure 11, we observe that as the catalyst concentration increases up to 200 mg L^{-1} , the degradation rate of the dye increases. This may be attributed to the increase in the

specific surface area of the catalyst. Consequently, more active sites on the mineral's surface are now available for the oxidant and the dye, increasing the reaction rate.

However, at higher catalyst concentrations, a decrease in the degradation rate is observed due to possible agglomeration of the goethite, which results in a reduction in the specific surface area available for the reaction in the treated solution. Furthermore, as the concentration of the catalyst increases, hydrogen peroxide tends to undergo excessive reaction with goethite, resulting in an unproductive consumption of the oxidant. This undesirable side reaction, characteristic of the heterogeneous Fenton process, significantly accelerates the depletion of H_2O_2 and diminishes the overall efficiency of the system [41].

Finally, at higher catalyst concentrations, a visible color change in the solution is observed, shifting from blue to green. This alteration may be attributed to the increased leaching of iron ions into the solution, which could interact with the dye or influence light absorption, thereby imparting a darker, greenish hue (Figure S1) [42].

Effect of pH

In order to overcome the disadvantages of the Fenton reaction, such as $\text{pH} \approx 3$ regulation and sludge production, the effect of pH on the UV/Goethite/ H_2O_2 process was explored. Experiments at neutral and acidic pHs were carried out at the optimum concentration conditions of H_2O_2 oxidant and goethite catalyst based on previous series of experiments (Figure 12).

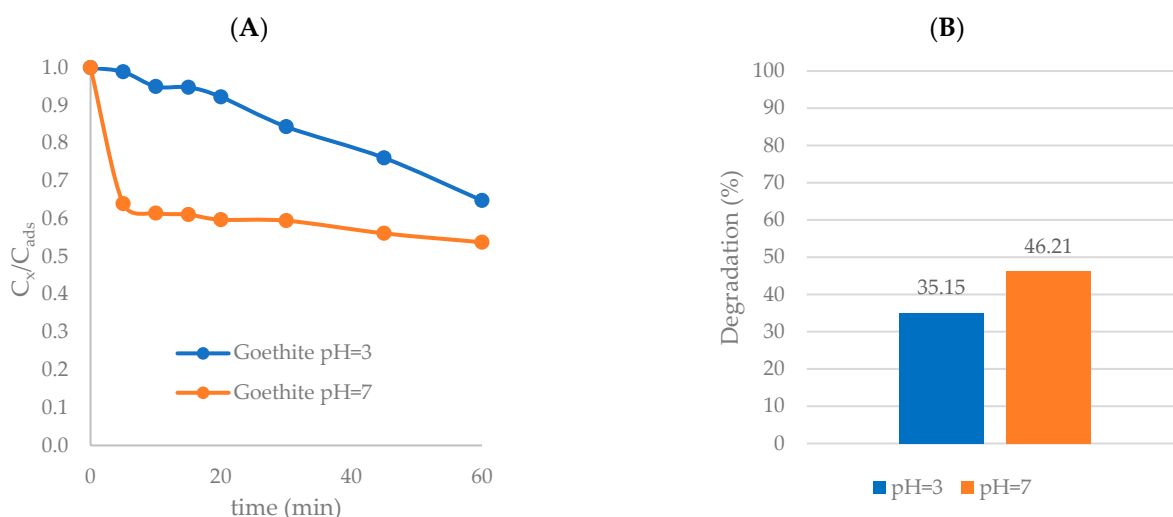


Figure 12. (A) Photocatalytic degradation of Nile Blue and (B) % degradation achieved in 60 min, in the presence of Goethite and H_2O_2 at different pH values ($C_0 = 15 \text{ mg L}^{-1}$, $C_{\text{oxidant}} = 200 \text{ mg L}^{-1}$, $C_{\text{catalyst}} = 100 \text{ mg L}^{-1}$, $\text{pH} = 3, 7$).

Comparing the results at acidic and neutral pHs, it can be concluded that the photocatalytic degradation of the target dye is more efficient at $\text{pH} = 7$. More specifically, under acidic conditions, where the pH is below the point of zero charge ($\text{pH}_{\text{pzc}} = 7.5$), goethite exhibits a positive z potential due to the protonation of surface $\equiv\text{Fe-OH}$ groups, forming positively charged $\equiv\text{Fe-OH}^+$ groups, whose number increases as the pH decreases. Although acidic conditions ($\text{pH} < \text{pzc}$) may promote the leaching of iron ions from the goethite surface, potentially increasing hydroxyl radical production, the overall degradation efficiency is reduced. This is primarily due to electrostatic repulsion between the positively charged goethite surface and the protonated, cationic form of Nile Blue, which hinders dye adsorption onto the catalyst. At a neutral pH ($\text{pH} \approx 7$), the surface charge of goethite is closer to neutral, reducing repulsive interactions and enhancing dye adsorption, thereby improving the photocatalytic degradation performance [43,44].

A trial experiment was also conducted under alkaline conditions. However, a noticeable change in the color of the solution was observed (Figure S2), which can be attributed to the structural changes that Nile Blue undergoes at high pH values. Although the color intensity decreased rapidly during photocatalysis—suggesting, based on visual observation, that the dye was effectively degraded—the inherent instability of Nile Blue at alkaline pHs complicates interpretation. As a result, its degradation curve was considered unreliable and was, therefore, excluded from the comparative diagrams and not further investigated.

3.4. Comparison of Homogeneous and Heterogeneous Techniques

Figure 13 summarizes the degradation efficiency of the optimum homogeneous and heterogeneous photocatalytic techniques applied, as well as the results obtained from the experiments conducted only in the presence of an oxidant (H_2O_2 and $\text{S}_2\text{O}_8^{2-}$).

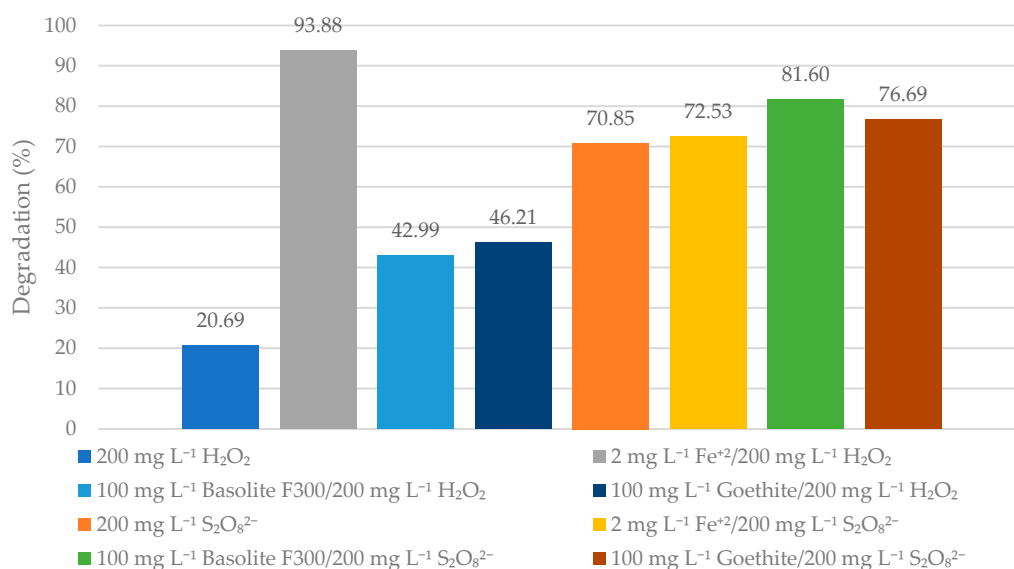


Figure 13. The % degradation of Nile Blue dye, with different homogeneous and heterogeneous photocatalytic techniques after 60 min of treatment ($C_0 = 15 \text{ mg L}^{-1}$, $C_{\text{Fe}^{2+}} = 2 \text{ mg L}^{-1}$, $C_{\text{catalyst}} = 100 \text{ mg L}^{-1}$, $C_{\text{oxidant}} = 200 \text{ mg L}^{-1}$).

As observed from the results, the conventional photo-Fenton system demonstrates the highest efficiency in degrading the target dye. Nevertheless, this does not diminish the effectiveness of heterogeneous photocatalytic techniques—particularly when combined with persulfate ions—which successfully address the key limitations commonly associated with homogeneous systems. These include the requirement for highly acidic conditions (typically around pH3) and the problematic formation of iron-containing sludge during the reaction [45]. Furthermore, solid catalysts not only exhibit excellent photocatalytic activity, often comparable to their homogeneous counterparts, but also offer additional advantages such as reusability and ease of separation from the treated solution. Their confirmed recyclability reinforces their potential for sustainable and practical applications in wastewater treatment processes [46].

3.5. Mineralization

To ensure a more comprehensive study, the mineralization of the dye was examined in the two homogeneous techniques that proved to be the most effective. The reduction in the COD values of the treated dye solution indicates the mineralization of dye molecules along with color removal. In Figure 14, a substantial decrease is observed in the COD of the solution with time.

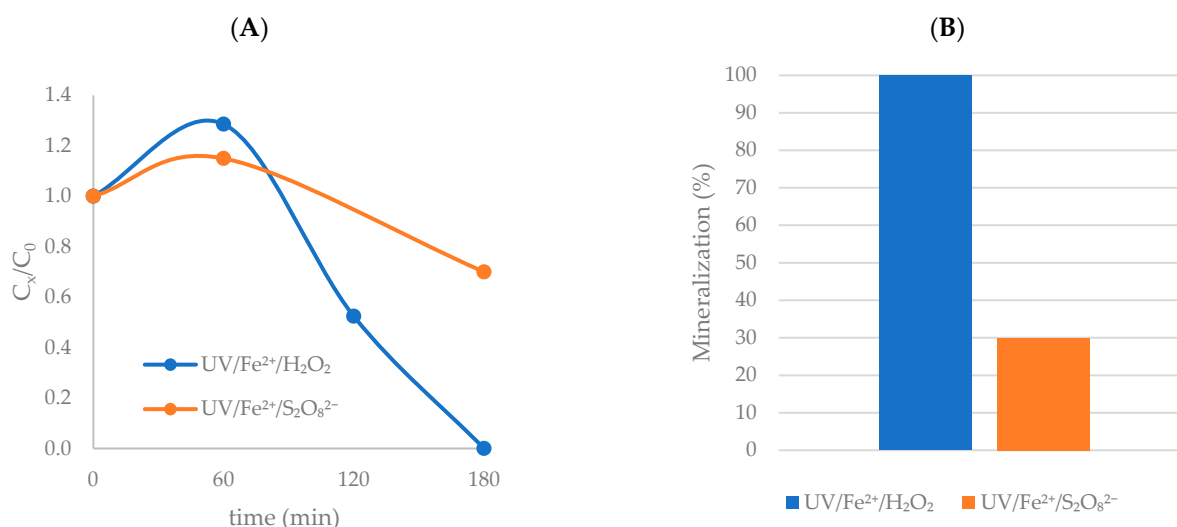


Figure 14. (A) COD reduction and (B) mineralization (%) of Nile Blue, in the presence of the UV/Fe²⁺/H₂O₂ and the UV/Fe²⁺/S₂O₈²⁻ systems.

In the UV/Fe²⁺/H₂O₂ system, the chemical oxygen demand (COD) is completely reduced from 20 mg L⁻¹ to 0 mg L⁻¹, indicating 100% mineralization of the organic compounds. This high efficiency can be attributed to the enhanced generation of reactive hydroxyl radicals (•OH), which is promoted not only by the continuous regeneration of Fe²⁺ ions via the photoreduction of Fe³⁺ ions under UV light, but also by the direct activation of hydrogen peroxide through UV irradiation [47]. The slight increase observed at the beginning may be due to the fact that the dye does not degrade instantly into CO₂ and water, but produces intermediates that require oxygen for further breakdown, thus temporarily increasing the COD. Additionally, if a portion of the added oxidant remains unreacted during the initial stages of the treatment, it may contribute to an apparent increase in the COD value, as it can consume dissolved oxygen in the solution.

In the case of the UV/Fe²⁺/S₂O₈²⁻ system, the COD is reduced by only 30% (from 20 to 14 mg L⁻¹) relative to its initial value, indicating that the process is less efficient than the conventional photo-Fenton reaction. This lower performance may be due to the slower generation rate of reactive sulfate radicals (SO₄•⁻) compared to hydroxyl radicals (•OH), as well as the more complex activation mechanism of persulfate, which typically requires longer reaction times to achieve complete mineralization [48].

4. Discussion

The comparison between the two homogeneous photocatalytic techniques revealed that both hydrogen peroxide and persulfate achieved high removal efficiencies, demonstrating their potential as effective oxidants in advanced oxidation processes. While hydrogen peroxide exhibited slightly higher degradation rates and enabled complete decolorization within 60 min of treatment, persulfate also showed a strong performance, contributing significantly to pollutant removal. The observed differences may be attributed to variations in radical generation mechanisms and reactivity, with hydrogen peroxide producing hydroxyl radicals and persulfate generating sulfate radicals. Both radicals are highly reactive, yet their efficiency may vary depending on the specific conditions and target compounds involved. Overall, the results indicate that both oxidants are capable, with hydrogen peroxide offering a marginal advantage in terms of treatment speed and completeness.

The comparison between homogenous and heterogenous techniques demonstrated that homogeneous Fenton processes exhibited a higher degradation efficiency, likely due to the rapid generation of hydroxyl radicals in the homogeneous phase, leading to more

immediate and effective dye breakdown. However, despite their lower efficiency, heterogeneous Fenton processes offer notable advantages, particularly in terms of operational simplicity and environmental compatibility. One significant benefit of the heterogeneous system is the elimination of the stringent pH regulation typically required for the homogeneous reaction to proceed efficiently. This not only simplifies the treatment process, but also reduces the need for additional chemical inputs and subsequent neutralization steps, making heterogeneous Fenton techniques a sustainable and cost-effective alternative for practical wastewater treatment applications. Nonetheless, various challenges remain in Fenton-based systems, such as Fe^{2+} /persulfate activation, particularly in terms of cost-effectiveness and environmental sustainability, which are key considerations for future large-scale applications.

Regarding economic feasibility and environmental impact, the activation of persulfate with transition metal ions, particularly iron, offers several advantages from both economic and environmental standpoints, including enhanced degradation and mineralization rates of contaminants and operation under mild conditions. However, several limitations must be acknowledged. One of the primary challenges lies in the declining efficiency and increased cost associated with the repeated use of metal catalysts, especially in systems where catalyst recovery is difficult. Additionally, the release of metal ions into treated water can lead to secondary pollution, necessitating further treatment steps and thus raising the overall operational cost [49].

From a broader perspective, while notable progress has been made in the development and optimization of PS activation techniques, most studies to date have focused on the degradation of single-component pollutants under controlled laboratory conditions, although that wastewater is typically characterized by a complex and variable composition. As a result, there is a lack of research on PS-based treatment systems operating at full scale, with only few pilot-scale studies available in the literature [50,51]. In terms of sustainability, the formation of toxic intermediates is possible, and, therefore, it is essential to monitor and mitigate the generation of harmful residues with appropriate pre- and post-treatment processes. In fact, bioassay findings from various studies suggest that $\text{S}_2\text{O}_8^{2-}$ exhibits a significantly greater toxicity than its decomposition product, SO_4^{2-} , primarily due to the strong oxidative nature of persulfate [52]. Consequently, efforts should be directed toward developing economically viable and sustainable methods that enable industrial-scale implementation.

5. Conclusions

The photocatalytic degradation of Nile Blue dye was comprehensively investigated using various homogeneous and heterogeneous Fenton-based photocatalytic techniques. The experimental results demonstrated that UV radiation alone led to a relatively slow degradation rate of the dye. However, the introduction of oxidants—particularly hydrogen peroxide (H_2O_2) and persulfate ions ($\text{S}_2\text{O}_8^{2-}$)—significantly enhanced the degradation process, with persulfate proving to be the most effective in facilitating dye removal.

In homogeneous systems, the conventional photo-Fenton process exhibited the highest degradation efficiency. The reaction rate was strongly influenced by both the iron and oxidant concentrations. An increase in H_2O_2 concentration improved the degradation up to an optimal value of 300 mg L^{-1} , beyond which efficiency declined, likely due to scavenging effects. Conversely, higher concentrations of Fe^{2+} ions consistently enhanced the degradation rate, with no inhibitory effects observed within the tested range. A similar trend was noted in the photo-Fenton-like process, where increasing the oxidant concentration further accelerated the reaction. Importantly, UV irradiation played a critical role in enhancing the degradation efficiency in both homogeneous systems.

In heterogeneous photocatalytic systems, the catalyst alone showed limited activity in degrading the dye. However, the addition of oxidants—particularly hydrogen peroxide—significantly improved the process performance, with an optimal concentration at approximately 200 mg L⁻¹. Beyond this threshold, a decrease in degradation efficiency was observed. When persulfate ions were used, a lower degree of synergism between the catalyst and oxidant was noted, yet effective dye degradation was still achieved.

Comparative analysis of the investigated techniques revealed the superior performance of homogeneous systems, especially the classical photo-Fenton process, which also resulted in complete mineralization of the target compound. Nevertheless, the potential of heterogeneous techniques should not be overlooked. These methods provide efficient dye removal without the need for rigorous pH adjustments—commonly required in homogeneous processes—and eliminate the generation of iron-containing sludge. Moreover, solid catalysts offer significant practical advantages, including a high photocatalytic performance, reusability, and easy separation from the treated solution, making them promising candidates for sustainable wastewater treatment applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/app15147917/s1>, Figure S1: Discoloration of Nile Blue dye solution in the presence of H₂O₂ and Goethite at time t = 0, t = 45 and t = 60 min respectively (C₀ = 15 mg L⁻¹, C_{oxidant} = 200 mg L⁻¹, C_{catalyst} = 500 mg L⁻¹), Figure S2: Nile Blue dye solution in the presence of Goethite at (A) pH = 3, (B) pH = 7, (C) pH = 10 (C₀ = 15 mg L⁻¹, C_{oxidant} = 200 mg L⁻¹, C_{catalyst} = 100 mg L⁻¹).

Author Contributions: G.P.: investigation, formal analysis, data curation, writing—original draft; E.E.: formal analysis, methodology, visualization, writing—review and editing; D.L.: conceptualization; supervision, project administration; funding acquisition, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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