

Photocatalytic Degradation of Malachite Green in Simulated Textile Dyeing Wastewater Using Fe₃O₄/SiO₂/ZnO

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Abstract. Malachite Green (MG) is a triphenylmethane-based textile dye that is toxic and difficult to degrade. Various methods for textile wastewater treatment containing textile dyes have been developed, one of which involves using composites based on magnetite (Fe₃O₄) coated with silica (SiO₂) and ZnO as a photocatalyst. This study aims to synthesize and characterize the Fe₃O₄/SiO₂/ZnO composite, test its ability to reduce MG concentration in a textile wastewater simulator, and evaluate the reusability of the composite. FTIR spectra showed absorption peaks at 651.94 cm⁻¹ and 941.26 cm⁻¹, corresponding to Zn-O and Si-O-Zn bonds, confirming the presence of ZnO and SiO₂ in the synthesized composite. The XRD diffractogram showed diffraction patterns consistent with Fe₃O₄/SiO₂/ZnO, with diffraction peaks observed at 31.89°, 34.53°, 36.25°, 47.65°, 57.45°, and 67.85°, measured at 2θ angles. SEM-EDX analysis identified the presence of Fe, O, Si, and Zn elements, the average of composite particle size is 67.636 nm. Performance tests for MG removal demonstrated that the Fe₃O₄/SiO₂/ZnO composite effectively reduced MG concentration of textile waste simulated sample, under UV irradiation at 366 nm for 8 hours, with a removal capacity of 0.5084 mg MG/g composite. Reusability tests showed that in the first cycle, the composite reduced MG concentration by 0.4880 mg/g, while in the second and third cycles, the removal capacities were 0.4863 mg/g and 0.4809 mg/g, respectively. The synthesized Fe₃O₄/SiO₂/ZnO composite successfully degraded Malachite Green (MG) in the textile wastewater simulation under UV 366 nm irradiation. The composite was able to degrade MG over multiple reuse cycles, the performance decline is 2%

1 Introduction

Dyes are essential components in the textile industry as they provide color and characteristics to fabrics. One such dye is Malachite Green (MG), a cationic triphenylmethane compound that is difficult to degrade and toxic. The dyeing and finishing processes in the textile industry require large amounts of water and produce wastewater containing detergents, dyes, and other chemicals [1].

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Wastewater containing Malachite Green (MG) can pollute the environment due to its intense color, which blocks light penetration in water, and its toxic and carcinogenic properties [2].

The treatment of dye-containing textile wastewater requires a careful and meticulous approach due to its complex chemical composition. Various methods have been developed, including a combination of adsorption and degradation techniques [3].

Adsorbents can capture dye molecules on their surfaces. The adsorption method is preferred for its simplicity, efficiency, and safety, but it carries the risk of pollutant release when the adsorbent is disposed of. The combination of adsorption and degradation, particularly through photocatalytic degradation, can break down dye molecules into simpler compounds with the assistance of light and a catalyst, resulting in a more efficient and environmentally friendly process [4].

The use of silica-coated magnetite adsorbents combined with metals as photocatalysts has been widely studied and shows great potential. The $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite exhibits high photocatalytic activity in degrading dyes such as Acid Blue 161 and methylene blue [5], [6] However, previous studies were limited to dye-containing water and have not been tested on wastewater simulators with more complex matrices that better represent actual textile effluents.

Textile wastewater is highly complex, containing dyes, heavy metals, surfactants, salts, and other organic substances. Dyeing wastewater can be simulated using a mixture of synthetic dyes, starch ($(\text{C}_6\text{H}_{10}\text{O}_5)_n$), NH_4Cl , KH_2PO_4 , Na_2SO_4 , and NaHCO_3 as a formula representing actual conditions [7].

Analyzing the performance of adsorbents in degrading MG using a wastewater simulator allows for assessment close to real textile wastewater conditions. The controlled composition of the simulator enables specific analysis of the photocatalyst's effect on MG and prediction of its performance in actual textile effluents. This article presents the synthesis and characterization of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite and evaluates its performance in reducing dye concentration in simulated textile wastewater.

2 Method

2.1 Materials

There are two categories of materials used in this study, synthesis materials: $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ p.a and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ p.a., ammonium hydroxide (NH_4OH) p.a., ethanol p.a. ($\text{C}_2\text{H}_5\text{OH}$, 96%), tetraethyl orthosilicate (TEOS) p.a., NaOH solid p.a., zinc acetate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$) p.a. simulator materials: malachite green (MG) solid p.a., amyllum p.a. ($(\text{C}_6\text{H}_{10}\text{O}_5)_n$), ammonium chloride p.a. (NH_4Cl), potassium dihydrogen phosphate p.a. (KH_2PO_4), sodium sulfate p.a. (Na_2SO_4), and sodium bicarbonate p.a. (NaHCO_3) and water.

2.2 Synthesis of Magnetite (Fe_3O_4)

Magnetite composite (Fe_3O_4) was synthesized from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.379 g) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1.7376 g), each dissolved in 50 mL of distilled water. The solutions were then mixed, stirred, and heated at 90 °C. The mixture was reacted with NH_4OH at a constant temperature under stirring, then allowed to cool to room temperature. The precipitate was separated using an external magnet, decanted, washed with distilled water to achieve a neutral pH, and dried in an oven at 60 °C for 3–4 hours. The synthesized product was characterized using XRD and FTIR

2.3 Synthesis of $\text{Fe}_3\text{O}_4/\text{SiO}_2$

Silica-coated magnetite was prepared using TEOS as the silica source. One gram of magnetite composite was dispersed in 200 mL of ethanol and 35 mL of distilled water, followed by the addition of 15 mL NH_4OH to create a basic medium and 3 mL of TEOS. The mixture was stirred for 2 hours and sonicated for 10 minutes. The precipitate was separated using an external magnet, and the coating process was repeated three times. The precipitate was washed with ethanol until the solution reached

neutral pH, then treated in a water bath at 60 °C for 2 hours, magnetically separated, and dried in an oven at 60 °C for 4 hours. The resulting material was characterized using XRD , FTIR, and SEM-EDX [8].

2.4 Synthesis of Fe₃O₄/SiO₂/ZnO

Fe₃O₄/SiO₂ was modified with ZnO by dispersing 1 g of Fe₃O₄/SiO₂ composite into a solution containing 100 mL of ethanol and 1 g of Zn(Ac)₂·2H₂O. The mixture was ultrasonicated at 60 °C for 15 minutes, followed by the dropwise addition of 20 mL of 0.25 M NaOH. Ultrasonication was continued at 60 °C for 4 hours. The resulting mixture was cooled to room temperature, separated using an external magnet, and washed several times with distilled water and ethanol until it reached neutral pH. The precipitate was dried at 60 °C and calcined at 200 °C. The Fe₃O₄/SiO₂/ZnO composite was characterized using FTIR (Shimadzu IR Prestige 21) to analyze the composite's spectral character , XRD (PANalytical X'Pert PRO) to analyze the structure of the composite, and SEM-EDX (FEI Inspect-S50) to analyze the composite's morphology [5].

2.5 Performance Evaluation of Fe₃O₄/SiO₂/ZnO Composite for the Removal of Malachite Green from Simulated Textile Dyeing Wastewater

One gram of the Fe₃O₄/SiO₂/ZnO composite was dispersed in 40 mL of a simulated wastewater solution containing 15 ppm malachite green (MG). The simulated wastewater was prepared by dissolving starch, NH₄Cl, KH₂PO₄, Na₂SO₄, and NaHCO₃ in distilled water, followed by the addition of solution at the desired concentration. Degradation was carried out at room temperature under UV light irradiation ($\lambda = 366$ nm) for 4, 6, 8, and 12 hours to determine the optimum exposure time. The procedure was repeated with various composite masses (0.25, 0.375, 0.5, 0.75, and 1 g) to determine the optimum adsorbent dose for maximum MG removal under the optimal time condition. The adsorbent was separated from the solution using an external magnet, and the supernatant was decanted for spectrophotometric analysis of MG concentration. Prior to the determination of MG concentrations, a calibration curve was established with different concentrations of MG (2, 4, 6, 8, and 10 ppm) measured at λ_{\max} using a Genesys 20 Visible spectrophotometer.

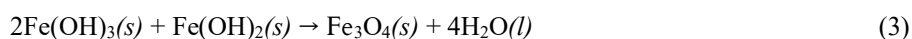
2.6 Reusability

The Fe₃O₄/SiO₂/ZnO composite was used for a single adsorption cycle was washed 20 times with distilled water and 6 times with ethanol, then dried in an oven at 60 °C for 2 hours. The recovered Fe₃O₄/SiO₂/ZnO composite was reused for the second degradation process of malachite green in the simulated textile wastewater.

3 Result and Discussion

3.1. Synthesis Magnetite (Fe₃O₄)

The synthesis of Fe₃O₄ was carried out using the co-precipitation method based on the simultaneous precipitation of Fe²⁺ and Fe³⁺ ions in a basic solution. The reaction equation is as follows:



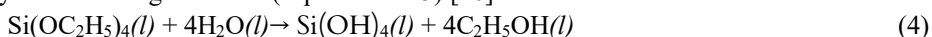
The synthesized product was obtained as a dense black powder. Based on visual observation, the color of the synthesized powder theoretically correspond to that of iron oxide in the magnetite (Fe_3O_4) phase. The synthesized Fe_3O_4 was characterized using FTIR to identify the absorption peaks present in the magnetite composite. The FTIR spectrum of Fe_3O_4 is shown in Fig.2a. The spectrum shows that a peak at 632.65 cm^{-1} , which corresponds to the Fe–O stretching vibration of Fe_3O_4 [9].

3.2 Synthesis of $\text{Fe}_3\text{O}_4/\text{SiO}_2$

Magnetite tends to easily undergo agglomeration, which can reduce its magnetic properties. Therefore, surface modification through coating is necessary. Silica (SiO_2) possesses good chemical stability and can prevent agglomeration; hence, it is commonly used as a coating material for Fe_3O_4 . The modification also serves to prevent electrical contact and direct interaction between the magnetic core and the photocatalyst layer. The SiO_2 layer, acting as an intermediary, can be applied between the magnetic core and the photocatalytic layer [10].

The surface modification of magnetite with silica utilizes tetraethyl orthosilicate (TEOS), which is frequently used as a binder or coating agent due to its excellent adhesion and relatively low toxicity, making it safer for laboratory use. Through this modification, siloxane (Si–O–Si) groups on the magnetite surface can form silane polymers. These polymers establish covalent bonds with hydroxyl groups, protecting the magnetic core from oxidation and agglomeration [11].

The Stöber method was employed to coat magnetic particles with a SiO_2 layer. This method involves the stepwise hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in an alcoholic medium in the presence of ammonia (NH_4OH) as a catalyst. The formation mechanism can be represented by the following reactions (Equations 4–5) [10]:



The synthesis of magnetite coated with silica derived from TEOS produced a black powder that could be attracted by an external magnet.

Referring to Fig. 2b, FTIR's spectrum of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ shows the peaks observed at 1107.14 cm^{-1} indicates the presence of asymmetric Si–O–Si stretching vibrations, while the peak at 939.33 cm^{-1} corresponds to the Si–O bond. The appearance of these two peaks confirms the presence of siloxane and silanol groups within the silica structure, the peak at 3321.42 cm^{-1} correlates to the stretching vibration of hydroxyl (-OH) groups, originating from the absorption of water molecules during the coating of magnetite with silica.

3.3 Synthesis of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$

The synthesized $\text{Fe}_3\text{O}_4/\text{SiO}_2$ was subsequently composited with ZnO as a photocatalyst, which has the potential to enhance dye degradation efficiency in simulated wastewater. In this composite synthesis, $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ was used as the Zn source precursor. The gradual addition of the precipitating agent NaOH induced the formation of $\text{Zn}(\text{OH})_2$, as shown in reaction (6), which was then converted into ZnO upon heating at $200\text{ }^\circ\text{C}$ according to reaction (7) [5]. The synthesis produced a brown-colored composite, as shown in Fig. 1, which was further characterized using FTIR, XRD, and SEM-EDX.



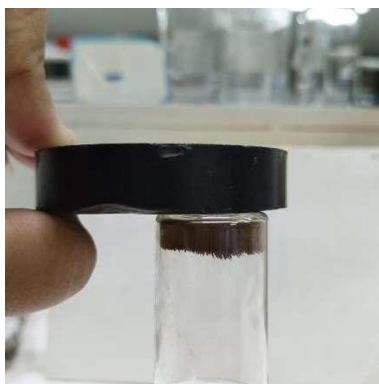


Fig. 1. $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ synthesis results

As shown in Fig. 2c, the FTIR's spectrum of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$, absorption have some peaks at 651.94 cm^{-1} correlates to the Zn-O bond of ZnO , peak at 941.26 cm^{-1} correlates to the vibrational mode of the Si-O-Zn bond, which is characteristic of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite [12].

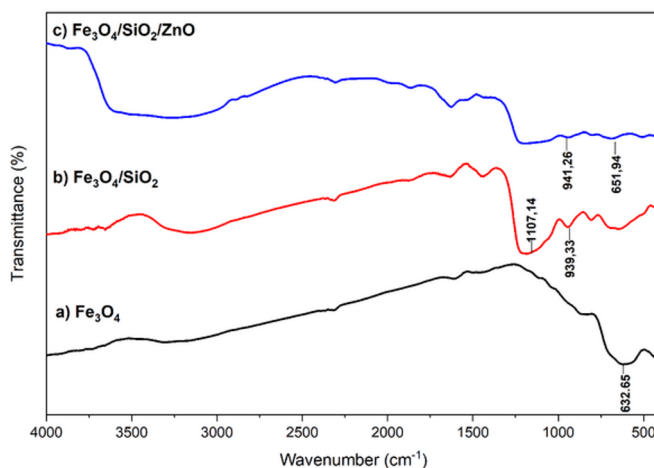


Fig. 2. FTIR Spectra of (a) Fe_3O_4 ; (b) $\text{Fe}_3\text{O}_4/\text{SiO}_2$; (c) $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$

Based on the XRD diffractogram shown in Fig. 3a, the synthesized Fe_3O_4 particles exhibited diffraction peaks at 2θ angles of 18.43° , 30.31° , 35.71° , 43.25° , 53.89° , 57.05° , 62.81° , and 74.57° , corresponding to the (111), (220), (311), (400), (422), (511), (440), and (533) planes, respectively. These peaks are consistent with the reference data from COD Card No. 00-101-1032 and align with previous studies reporting similar peak positions at 18.23° , 30.24° , 35.57° , 43.19° , 53.58° , 57.14° , 62.77° , and 74.23° [8]. Meanwhile, in Fig. 3b, no sharp peaks were observed for silica, indicating that SiO_2 exists in an amorphous or non-crystalline form, typically characterized by a broad hump in the 2θ range of approximately 20° – 30° [5].

The $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite displayed a diffraction pattern (Fig. 3c) similar to that of Fe_3O_4 , with additional peaks at $2\theta = 31.89^\circ$, 34.53° , 36.25° , 47.65° , 57.45° , and 67.85° , corresponding to the (100), (002), (101), (102), (110), and (112) planes, respectively, in agreement with the COD Card No. 00-036-1451 for the ZnO crystal structure [13].

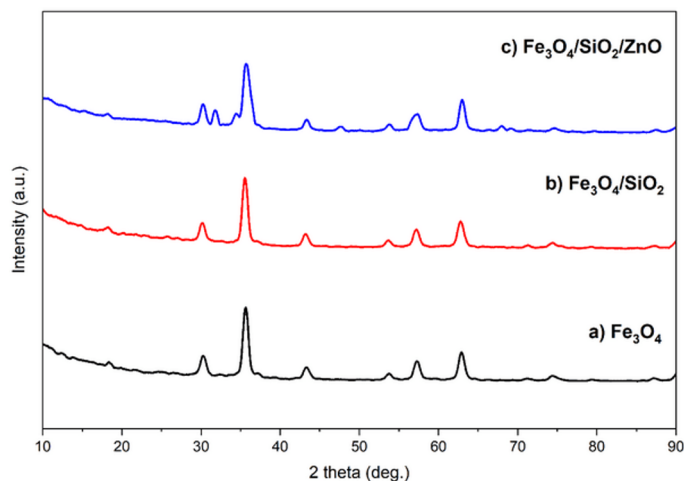


Fig. 3. XRD diffractogram of (a) Fe_3O_4 (b) $\text{Fe}_3\text{O}_4/\text{SiO}_2$ (c) $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$

The morphological and elemental characteristics of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite were examined using SEM–EDX analysis, as shown in Fig. 4 and Fig. 5. The average particle size distribution was determined using the ImageJ software, yielding an average diameter of approximately 67.636 nm. The presence of the main constituent elements—Fe, Si, Zn, and O—indicating the successful formation of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite, as supported by the EDX results presented in Table 2.

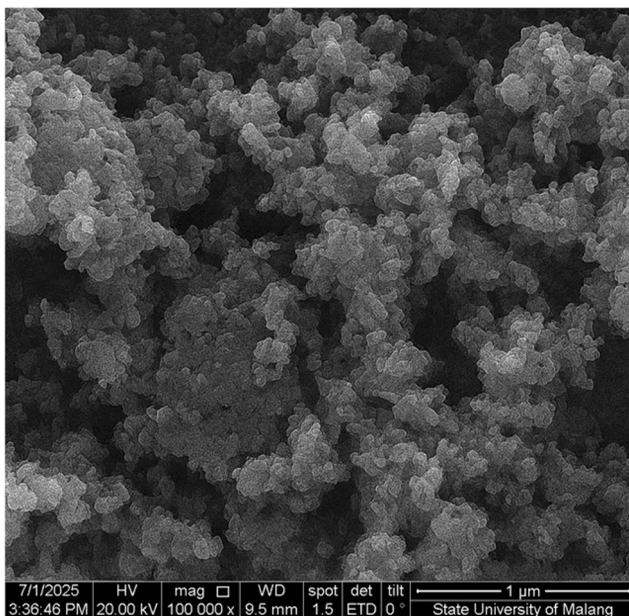


Fig. 4. Morphology of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$

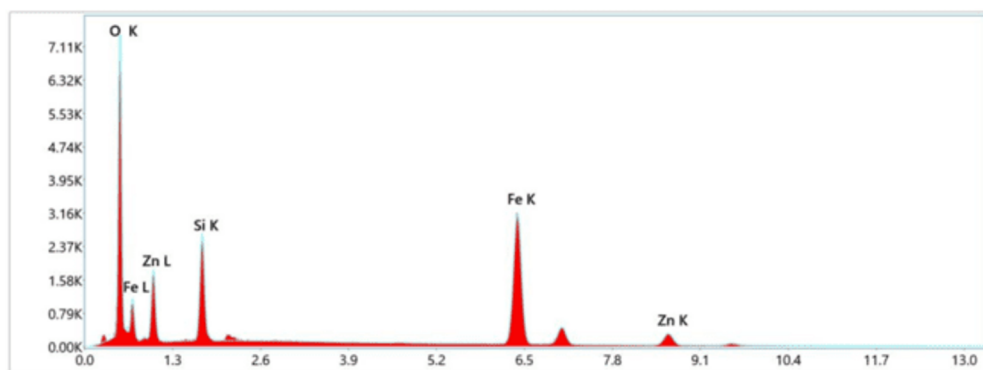


Fig. 5. EDX curve data $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$

Table 1. EDX data of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite

Element	Weight %	Atomic %
O	3.47	65.13
Si	8.97	8.89
Fe	43.98	21.90
Zn	9.58	4.07

The magnetic properties of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite were characterized using a vibrating sample magnetometer (VSM). As shown in Fig. 8, the composite exhibited a saturation magnetization value of 39.7 emu/g at room temperature. This value is relatively lower than that of pure Fe_3O_4 , which is typically reported to have a saturation magnetization of around 80 emu/g [5], [10]. The reduction in magnetization can be attributed to the presence of non-magnetic SiO_2 and ZnO layers, which decrease the fraction of magnetic Fe_3O_4 contributing to the overall magnetization.

Previous studies have also reported that $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composites exhibit lower magnetization values, typically in the range of 55–65 emu/g [14]. The addition of a ZnO layer onto the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ composite further reduced the magnetization to 39.7 emu/g in the present study. This result is consistent with earlier reports indicating that $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composites possess magnetization values around 41 emu/g [5]. Therefore, the VSM results confirm that the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite was successfully synthesized with sufficiently strong magnetic properties for magnetic separation applications, while the observed decrease in magnetization serves as evidence of the successful coating of Fe_3O_4 cores with SiO_2 and ZnO layers.

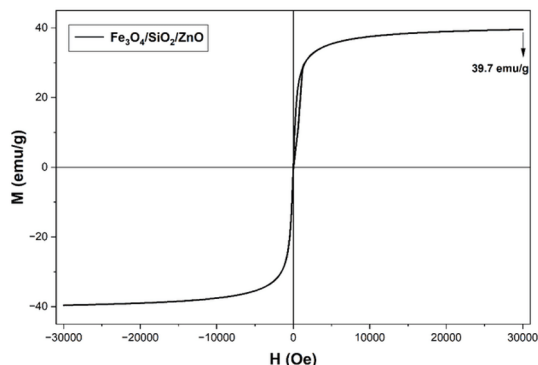


Fig. 6. Magnetization curve of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite.

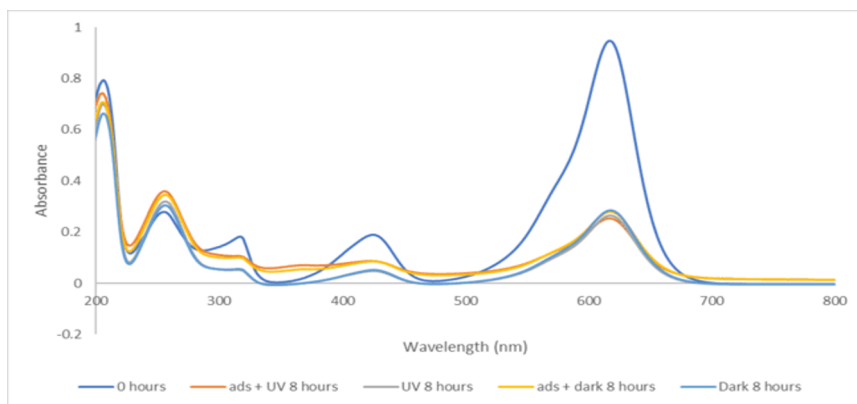


Fig. 7. Comparison of the absorption curves of Malachite Green solution in simulated wastewater at 0 hours and after various treatment conditions.

The UV–Vis analysis results, illustrated in Fig. 7, show a decrease in the absorption peak intensity of malachite green after several treatments, both under UV irradiation and in dark conditions, with or without the addition of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite. The significant reduction in the absorption peak intensity of malachite green compared to the initial condition indicates a decrease in dye concentration in the simulated wastewater. However, when comparing the different treatments (UV, dark, with or without the adsorbent), the reduction in absorbance did not differ significantly.

The main mechanism responsible for this behavior is presumed to involve a decrease in absorbance intensity due to adsorption processes on the composite surface and a simple photocatalytic degradation process that partially breaks the chromophore bonds of malachite green. This interpretation is supported by the absence of new peaks in the UV–Vis spectra, suggesting that the main molecular structure of the dye remained intact and no new colored degradation products were formed. The appearance of a new absorption band around 350 nm is likely associated with the initial breakdown of the polyaromatic ring structure, followed by demethylation of $-\text{N}$ groups and the formation of intermediate compounds lacking conjugated structures.

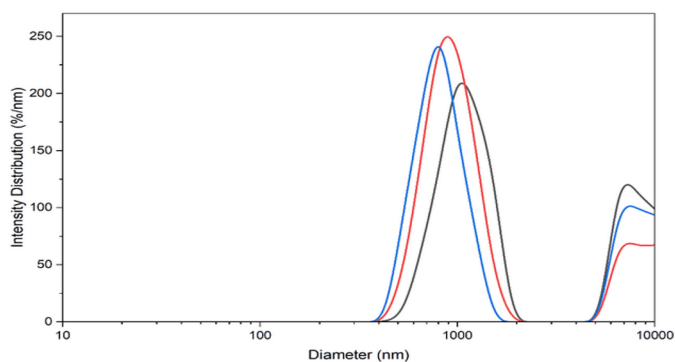


Fig. 8. The intensity size distribution of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ versus particle diameter in nanometers

Fig. 8 depicts the particle size analyzer (PSA) results of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite. The average of three repeated measurements shows a mean peak intensity value of 1349.0 nm. The obtained Z-average of 1349 nm (1.349 μm) with a polydispersity index (PDI) of 0.143 indicates a relatively homogeneous particle size distribution, although not completely monodisperse. The relatively large average size, approximately 1.3 μm , suggests the occurrence of agglomeration, which is commonly observed in metal oxide materials due to intermolecular interactions. Therefore, despite

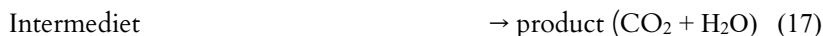
the tendency of particles to agglomerate to the micrometer scale, their size distribution remains fairly uniform, as reflected by the obtained PDI value.

3.4 Adsorption–Photocatalytic Degradation Mechanism

The adsorption and photocatalytic degradation mechanisms occur simultaneously through the Fe₃O₄/SiO₂/ZnO composite to reduce the concentration of malachite green in simulated textile wastewater. During the degradation process, ZnO absorbs UV light and generates electron–hole pairs (e⁻/h⁺) within the conduction band (CB) and valence band (VB), as illustrated in Equation (7). The photogenerated holes and the active radical species formed simultaneously facilitate the degradation of dye molecules adsorbed on the composite surface.

The e⁻/h⁺ pairs migrate to the ZnO surface and participate in redox reactions as shown in Equations (8–10). The holes (h⁺) react with water molecules and hydroxide ions to produce hydroxyl radicals (•OH), while electrons (e⁻) react with molecular oxygen (O₂) to form superoxide radical anions (O₂^{•-}) and hydrogen peroxide (H₂O₂), which subsequently generate additional hydroxyl radicals (•OH) (Equations 10–13). Hydrogen peroxide also reacts with superoxide radicals to produce more hydroxyl radicals (Equations 14–15).

The hydroxyl radicals (•OH) produced act as strong oxidizing agents that attack the adsorbed pollutant molecules on the SiO₂ surface, rapidly forming intermediate compounds (Equation 16). These intermediates are eventually mineralized into simpler and environmentally benign products such as CO₂ and H₂O (Equation 17). The photocatalytic degradation reactions under UV irradiation can be summarized as follows [15]:



The degradation mechanism of MG through the photocatalytic process involves a series of reactions that ultimately lead to its breakdown into simpler and more environmentally benign compounds such as CO₂ and H₂O. The degradation process begins with a substitution reaction between a hydrogen atom (H) attached to the central carbon atom (C) of the malachite green molecule and a hydroxyl radical (•OH). Subsequently, the central carbon atom of malachite green is attacked by hydroxyl radicals, forming intermediate compounds, which is evidenced by the gradual fading of the dye's

characteristic color. In the final stage, these intermediates undergo mineralization, yielding simple and non-toxic products such as CO₂ and H₂O.

In addition to the degradation process, adsorption also plays a crucial role in this mechanism. The silica (SiO₂) component within the Fe₃O₄/SiO₂/ZnO composite acts as an adsorptive agent for malachite green molecules. The presence of surface hydroxyl (–OH) groups on silica is essential for the adsorption process. This adsorption occurs primarily due to electrostatic interactions between the silanol groups (Si–OH) on the SiO₂ surface and the positively charged malachite green molecules.

It is proposed that during the photocatalytic degradation of MG, several processes occurred, including hydroxylation, demethylation, oxidation, deamination, and deformation of the benzene ring as a result of aromatic ring cleavage. As illustrated in Fig. 11, several intermediates were identified, including 4,4'-(dimethylamino)phenyl[(phenyl)methylidene] (m/z = 315), 4-(dimethylamino)phenyl (m/z = 301), 4-(methylamino)benzophenone (m/z = 211), 4-(dimethylamino)benzophenone (m/z = 225), 1-(4-aminophenyl)ethan-1-one (m/z = 135), and 1-phenylethan-1-one (m/z = 119). In previous studies, the final product propan-2-one (m/z = 57 g/mol) was detected, indicating benzene ring cleavage from 1-phenylethan-1-one. The series of intermediate degradation products suggests that the aromatic rings are opened, forming simpler and less toxic molecules. Further degradation may lead to complete mineralization, leaving no residual organic compounds [39].

ZnO photocatalysts generally possess a wide band gap (approximately 3.37 eV), which allows optimal activation only under UV light with wavelengths ≤385 nm. Under visible light irradiation, the photon energy is insufficient to overcome this band gap, thus limiting electron excitation and the formation of reactive radical species. Nevertheless, ZnO can be modified through various approaches—such as metal doping or coupling with other materials—to extend its spectral response into the visible region.

3.5 Performance Evaluation of Fe₃O₄/SiO₂/ZnO Composite for the Removal of Malachite Green from Simulated Textile Dyeing Wastewater

3.5 Reduction of Malachite Green Concentration in Simulated Textile Wastewater Using Fe₃O₄/SiO₂/ZnO

3.5.1 Determination of Optimum Irradiation Time

The reduction of MG concentration in simulated textile wastewater began with determining the optimum irradiation time. The decreased MG concentration was monitored under varying irradiation durations using a 366 nm UV lamp and under non-irradiated (dark) conditions. The simulated wastewater contained 15 ppm of MG along with several components—such as starch, NH₄Cl, KH₂PO₄, Na₂SO₄, and NaHCO₃—which represent typical constituents of textile industry effluents.

The determination of the optimum irradiation time aimed to evaluate the duration required for the Fe₃O₄/SiO₂/ZnO composite to achieve maximum removal of MG from the simulated wastewater. The experiment was conducted using 40 mL of simulated wastewater containing 15 ppm of MG under two conditions: (1) UV irradiation at 366 nm and (2) dark (non-UV) conditions, with irradiation times of 4, 6, 8, and 12 hours.

The selection of a maximum irradiation time of 12 hours was intended to simulate the duration of natural sunlight exposure during a full day in tropical climates. This approach allows evaluation of the practical operational limits of the UV-A–based photocatalytic system, since the 366 nm wavelength used in this study corresponds to the dominant component of solar UV radiation reaching the Earth's surface.

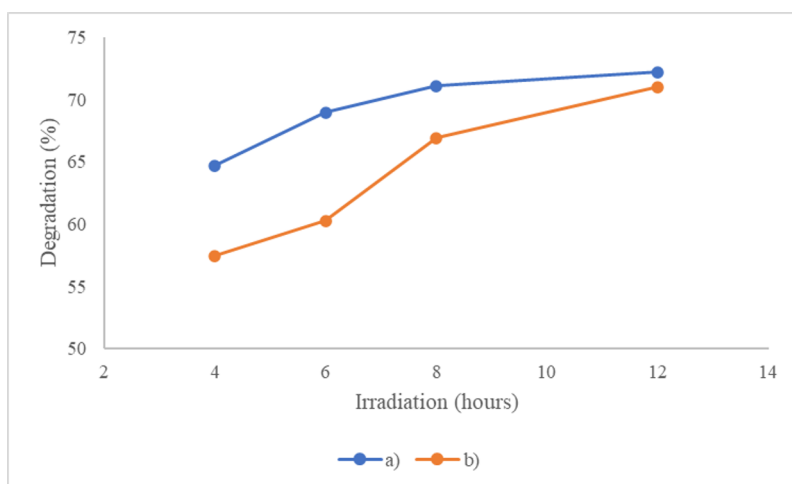


Fig. 9 Reduction of 40 mL of 15 ppm MG solution in simulated wastewater over various time intervals: (a) under the influence of 366 nm UV light, (b) in dark conditions (non-UV).

The MG solution in the simulated textile wastewater, in the absence of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite, exhibited a decrease in concentration or an increase in the percentage of degradation under both UV irradiation (366 nm) and dark conditions, as shown in Fig. 12. With increasing irradiation time, the degradation percentage rose from 64.67% at 4 hours to 68.95% at 6 hours, 71.1% at 8 hours, and 72.2% at 12 hours. Under dark conditions, as depicted in Fig. 12b, the degradation percentage also increased but remained lower than under UV irradiation, with values of 57.46% at 4 hours, 60.26% at 6 hours, and 66.9% and 71.01% at 8 and 12 hours, respectively.

The more significant degradation observed under UV irradiation can be attributed to the absorption of light energy by malachite green molecules, leading to electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). This process facilitates the formation of superoxide radicals ($\text{O}_2^{\bullet-}$), as the HOMO energy level of malachite green is suitable for the reduction of molecular oxygen (O_2). Although photocatalytic reactions generally produce hydroxyl radicals ($\bullet\text{OH}$) from water, the HOMO level of malachite green is too high to directly oxidize H_2O to $\bullet\text{OH}$. Therefore, the formation of $\bullet\text{OH}$ radicals in this system primarily occurs indirectly through secondary reactions involving superoxide radicals rather than direct oxidation of water.

MG can undergo photocatalytic degradation under light irradiation through the generation of hydroxyl radicals ($\bullet\text{OH}$) from O_2 and H_2O_2 . These radicals attack the dimethylamino groups, central carbon atoms, and aromatic rings of the dye molecules, initiating oxidative reactions that yield specific intermediate compounds. The sequence of these reactions can be represented by the following equations



Meanwhile, under dark conditions, the concentration of malachite green also decreased, although the reduction was not as significant as that observed under UV irradiation. This phenomenon can be attributed to the inherent instability and high solubility of malachite green in water, causing gradual fading over time. In addition, this effect may also result from the presence of certain components in the simulated wastewater, particularly starch, which can act as a weak adsorbent by physically adsorbing a portion of the malachite green molecules. Starch has been reported as an environmentally friendly adsorbent material suitable for water purification applications.

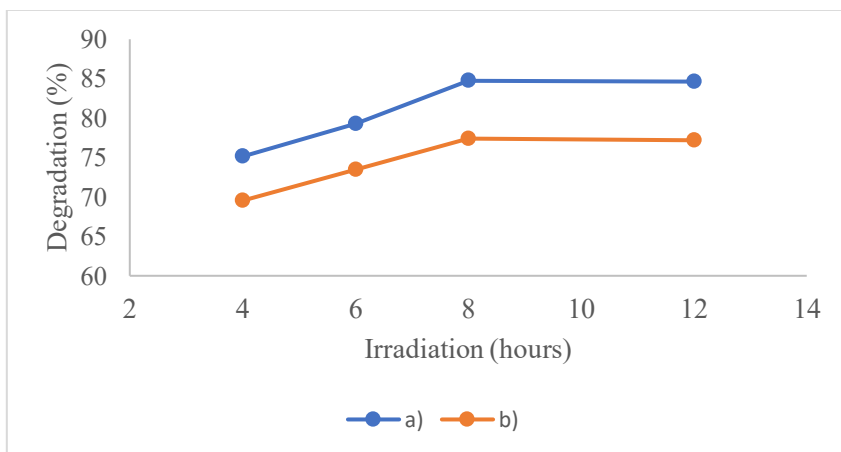


Fig. 10. Percentage degradation of 15 ppm Malachite Green solution in 40 mL simulated wastewater after contact with $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ over various time intervals: (a) under 366 nm UV light, (b) in dark conditions (non-UV).

Based on Fig. 11, the percentage degradation of MG in the simulated wastewater increased with longer UV irradiation time. Under UV-irradiated conditions (Fig. 13a), the degradation percentage reached 75.13% after 4 hours with a removal capacity of 0.4508 mg MG/g composite, which increased to 79.26% after 6 hours and 84.73% after 8 hours, corresponding to removal capacities of 0.4756 mg MG/g and 0.5084 mg MG/g composite, respectively. Beyond this point, the degradation trend became nearly constant, with 84.6% degradation and a removal capacity of 0.5076 mg MG/g composite after 12 hours. These results indicate that the maximum degradation capacity was achieved after 8 hours of UV irradiation, suggesting that the system had reached its optimal photocatalytic performance, as most MG molecules had already degraded through simultaneous photodegradation and adsorption processes.

This process is driven by the excitation of electrons within the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ photocatalyst, forming electron-hole pairs. The excited electrons react with dissolved oxygen to produce superoxide radicals ($\bullet\text{O}_2^-$), while the holes participate in the oxidation of water to generate hydroxyl radicals ($\bullet\text{OH}$). Both radicals are highly reactive and play key roles in the cleavage of MG's structural bonds.

In contrast, under dark conditions (Fig. 11b), degradation still occurred but with lower effectiveness compared to the UV-irradiated system. The degradation percentage increased from 69.53% at 4 hours (removal capacity: 0.4172 mg MG/g composite) to 73.46% at 6 hours (0.4408 mg MG/g composite), and 77.4% at 8 hours (0.4644 mg MG/g composite). After 12 hours, the degradation reached 77.2% with an adsorption capacity of 0.4636 mg MG/g composite, showing no significant increase. The lower degradation rate in dark conditions suggests that only adsorption took place, as no UV light was available to activate ZnO for photocatalytic degradation. Therefore, the optimum irradiation time was determined to be 8 hours, since beyond this duration, no notable improvement in degradation percentage or capacity was observed.

The degradation results indicate that the addition of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ adsorbent still contributed positively to MG removal, although the improvement was not highly significant. After 8 hours of UV exposure, the photocatalytic degradation efficiency began to decline, which can be attributed to several factors. At longer irradiation times, the photocatalytic system tends to experience increased recombination of electron–hole (e^-/h^+) pairs, reducing the number of active radicals ($\bullet\text{OH}$ and $\text{O}_2\bullet^-$) available for attacking MG molecules. As most MG is degraded, its concentration decreases, making the generated radicals less effective and more likely to recombine or react with stable intermediate products.

The presence of starch in the simulated wastewater contributes to solution turbidity. Suspended starch particles can scatter UV light, limiting its penetration throughout the reaction volume and reducing the light intensity reaching the photocatalyst surface, thereby decreasing the formation of reactive species. Moreover, prolonged UV exposure may also lead to degradation or inactivation of the photocatalyst surface due to structural changes in the crystal lattice or blockage of active sites by intermediate products.

3.5.2 Determination of Optimum Catalyst Mass

The reduction of malachite green concentration in simulated textile wastewater using the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite began with determining the maximum wavelength (λ_{max}) of malachite green and constructing a calibration curve. The λ_{max} of malachite green was obtained by measuring the absorbance of a 5 ppm standard solution within the wavelength range of 470–700 nm. The maximum absorbance was observed at $\lambda = 617$ nm, as shown in Fig. 12.

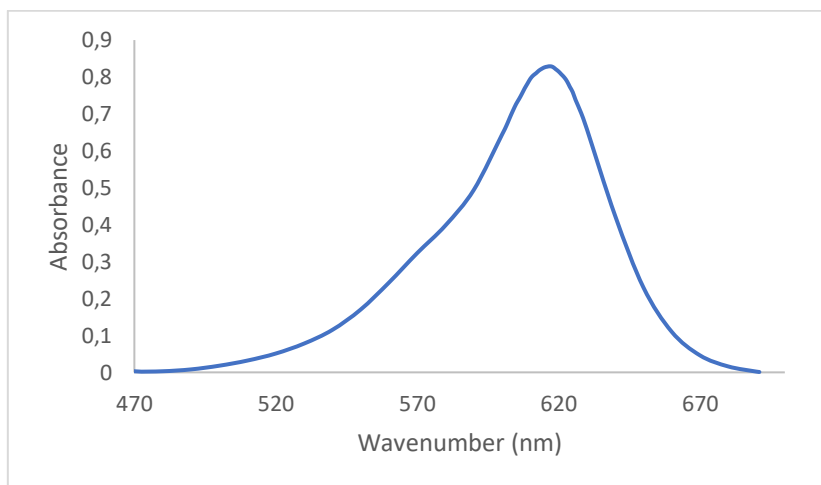


Fig. 11. Maximum wavelength curve of Malachite Green.

The $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite was employed as an adsorbent to evaluate its performance in reducing the concentration of malachite green in simulated textile dyeing wastewater. The adsorbent was applied to the malachite green solution under simulated wastewater conditions. The composite mass was varied at 0.25, 0.375, 0.5, 0.75, and 1.0 g, and each experiment was conducted under UV irradiation ($\lambda = 366$ nm) for 8 hours, which was previously determined as the optimum irradiation time.

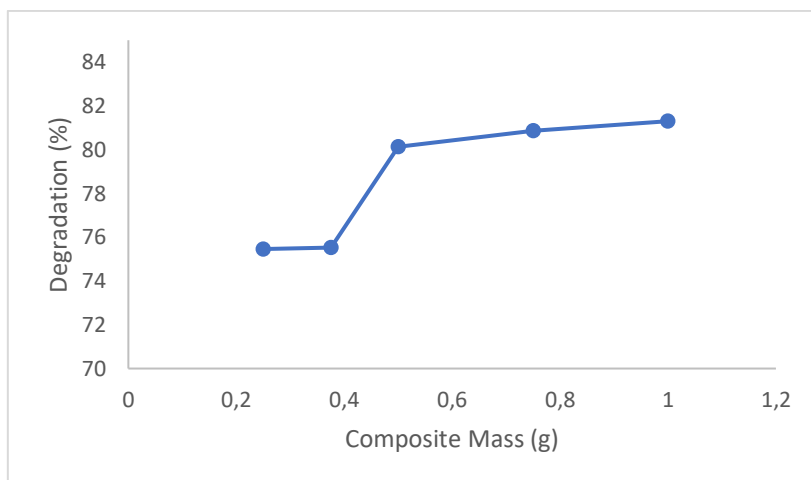


Fig. 12. Percentage reduction of 40 mL of 15 ppm MG solution in simulated wastewater using $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ over 8 hours under 366 nm UV light with varying adsorbent masses.

Based on Fig. 15, it can be observed that increasing the mass of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ adsorbent is directly proportional to the increase in the percentage of MG degradation. At adsorbent masses of 0.25 g and 0.375 g, the degradation percentages were relatively low and showed no significant difference, approximately 75.46% and 75.53%, respectively. This may be attributed to the limited number of active sites, preventing all dye molecules from interacting effectively with the catalyst surface, resulting in suboptimal adsorption and photocatalytic decomposition. Furthermore, photon absorption by the catalyst was not yet maximized, leading to a low generation of electron-hole (e^-/h^+) pairs, and consequently, the photocatalytic reaction proceeded less efficiently.

However, as the adsorbent mass increased to 0.5 g, the degradation percentage rose significantly to 80.13%, and further to 80.86% at 0.75 g. This improvement indicates that increasing the amount of adsorbent enhances the contact surface area, providing more active sites and thereby increasing the probability of oxidative reactions through reactive oxygen species such as $\bullet\text{OH}$ and $\bullet\text{O}_2^-$, which play a key role in the photocatalytic degradation process. With more available active sites, a greater number of MG molecules can interact with the composite surface, resulting in a more efficient degradation process.

When the adsorbent mass reached 1 g, the degradation percentage continued to increase but at a slower rate, achieving 81.3%. This behavior suggests that the system had reached a saturation point where further increases in adsorbent mass no longer significantly improved degradation efficiency. This phenomenon may result from particle aggregation at higher adsorbent concentrations, which reduces the effective active surface area and inhibits UV light penetration into the photocatalytic system. As shown in Fig. 15, the maximum degradation of malachite green by the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite in textile wastewater simulation was achieved at an optimum adsorbent mass of 1 g, corresponding to a removal capacity of 0.4880 mg of Malachite Green per gram of composite.

3.5.3 Reusability Study of $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ Composite

The reusability of an adsorbent is a critical aspect in its development, as it determines the feasibility of industrial application. The reusability study of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite was conducted to

evaluate the stability and efficiency of the photocatalytic adsorbent after repeated use in multiple degradation cycles of malachite green (MG) in simulated textile wastewater.

To assess the reusability performance, the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ particles were recovered after each photocatalytic test using an external magnetic field, then washed, dried, and reused for up to three consecutive cycles under the same optimal conditions. This approach aimed to evaluate the structural stability, photocatalytic durability, and recovery efficiency of the magnetic $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite, highlighting its potential as a sustainable, cost-effective, and easily recoverable photocatalyst for textile wastewater treatment.

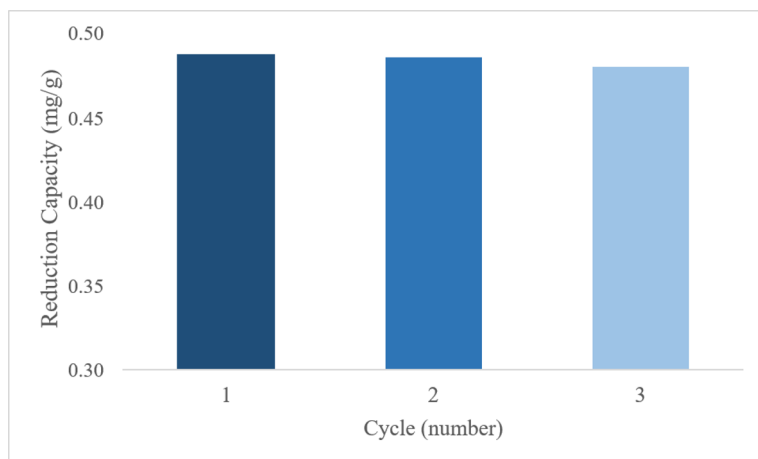


Fig. 13. Reuse of the composite for reducing 40 mL of 15 ppm MG in simulated wastewater using $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ over 8 hours under 366 nm UV light.

The reusability test of the composite was conducted under optimum conditions 15 ppm with a solution volume of 40 mL, and irradiated with a 366 nm UV lamp for 8 hours. The reusability results indicated that the ability of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite to remove MG gradually decreased during the second and third cycles. The first use exhibited a removal capacity of 0.4880 mg MG/g composite, which slightly decreased to 0.4863 mg MG/g in the second use and 0.4809 mg MG/g in the third.

This decline in performance is likely due to the partial blockage of active sites by MG molecules that were not completely desorbed during the washing process [10]. Consequently, the number of available active sites for adsorption and photodegradation reactions was reduced in subsequent cycles. As shown in Fig. 16, the effectiveness of the composite in degrading malachite green decreased by 0.35% from the first to the second cycle, and by 1.11% from the second to the third cycle. This relatively small decrease indicates that the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite maintains good stability and efficiency in reducing malachite green levels even after multiple reuse cycles.

3.6 Effect of Simulator Components

MG in the simulated wastewater system can interact with various chemical components that form the reaction environment, so the degradation efficiency is strongly influenced by the composition of the medium. Each component in the simulator—such as starch, NH_4Cl , KH_2PO_4 , Na_2SO_4 , and NaHCO_3 —may contribute differently to the MG degradation process, either through pH modification or through the formation of reactive radicals. However, the exact extent of each component's contribution, whether individually or in combination, has not been fully elucidated. Therefore, it is necessary to

analyze each component separately to determine its specific role in enhancing or inhibiting the degradation process.

NH_4Cl was included to represent inorganic nitrogen species that typically originate from additives used in dyeing or printing processes. Na_2SO_4 simulates the presence of sulfate ions, commonly employed as dye-fixation agents. KH_2PO_4 serves as a phosphate source, which may derive from detergent or washing residues, while NaHCO_3 represents bicarbonate ions used for pH adjustment or formed as intermediates during treatment processes.

To elucidate the contribution of each simulator component to the degradation of Malachite Green (MG), a series of systematic tests were performed by selectively eliminating or adding specific components. Separate analyses of each component's influence were conducted by comparing the MG absorbance values across different solution variations, both with and without the adsorbent, under UV irradiation and in the absence of light. The decrease in absorbance was measured spectrophotometrically at the maximum wavelength of MG (617 nm). The aim of this analysis was to identify which components play the most significant role in MG degradation and to evaluate potential synergistic or inhibitory effects caused by the presence of other components.

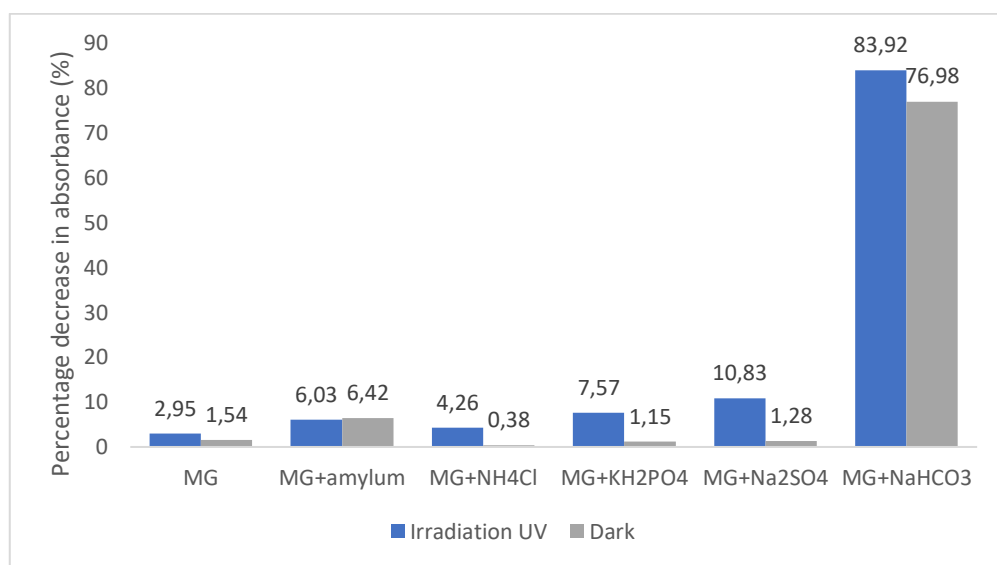


Fig. 14. Percentage reduction of MG absorbance with various single components of the simulator over 8 hours under UV and non-UV conditions.

Based on Fig. 15, the simulated system for MG degradation demonstrated that the effectiveness of MG removal strongly depends on the chemical composition present in the medium. In the absence of additional components, MG degradation remained low under both UV irradiation and dark conditions, with absorbance reductions of only 2.95% and 1.94%, respectively, as observed in the MG control solution. This indicates that natural photodegradation or spontaneous decomposition of MG in aqueous media occurs very slowly.

Components such as NH_4Cl , KH_2PO_4 , and Na_2SO_4 exhibited relatively low contributions to MG degradation. The addition of NH_4Cl caused the solution pH to decrease to a moderately acidic level (approximately pH 5). Na_2SO_4 , due to the chemical stability of sulfate ions (SO_4^{2-}), behaved as an inert species, contributing negligibly to both chemical and photocatalytic reactions. The natural polymer starch is chemically neutral and showed no intrinsic chemical activity toward degradation, although it may slightly enhance MG removal through weak physical adsorption or partial surface interaction.

Several studies have reported that the presence of common anions such as Cl^- and SO_4^{2-} tends to slightly inhibit the photocatalytic degradation efficiency of Malachite Green (MG), whereas HCO_3^- has the opposite effect, enhancing the degradation rate. This improvement is attributed to the increase in pH caused by HCO_3^- , which promotes the formation of superoxide radicals ($\bullet\text{O}_2^-$), thereby increasing the oxidative capacity of the system. Although HCO_3^- can also generate carbonate radicals ($\bullet\text{CO}_3^-$)—which are less reactive than hydroxyl radicals ($\bullet\text{OH}$)—the mildly basic conditions resulting from NaHCO_3 addition remain favorable for the overall MG degradation process.

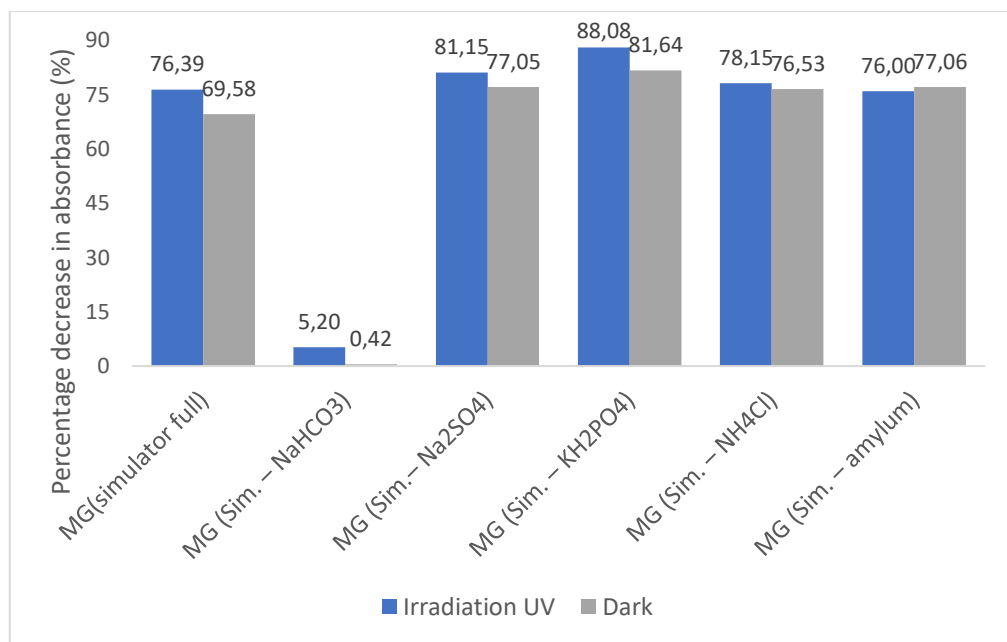


Fig. 15. Percentage reduction of MG absorbance in the simulator with each component removed over 8 hours under UV and dark conditions.

Consistent with previous studies, the addition of NaHCO_3 to the system exerted a highly significant impact on the reduction of Malachite Green (MG) absorbance, even in the absence of UV irradiation. As shown in Fig. 16, the MG solution containing NaHCO_3 exhibited a decrease in absorbance of 83.95% under UV illumination and 76.98% under dark conditions, indicating that NaHCO_3 plays a crucial role in enhancing MG degradation. This finding is further supported by experiments conducted on modified simulators with the selective removal of components.

As illustrated in Fig. 16, the elimination of NaHCO_3 completely inhibited the degradation process, whereas the removal of other components such as NH_4Cl , Na_2SO_4 , or even KH_2PO_4 did not significantly affect degradation efficiency. Interestingly, when KH_2PO_4 was excluded from the system, the degradation process proceeded more effectively than in the complete simulator, suggesting a possible inhibitory role of phosphate species. These observations imply that the other components act only as minor contributors, serving primarily as buffering agents or ionic stabilizers, which may support system stability but do not play a central role in the chemical transformation of Malachite Green.

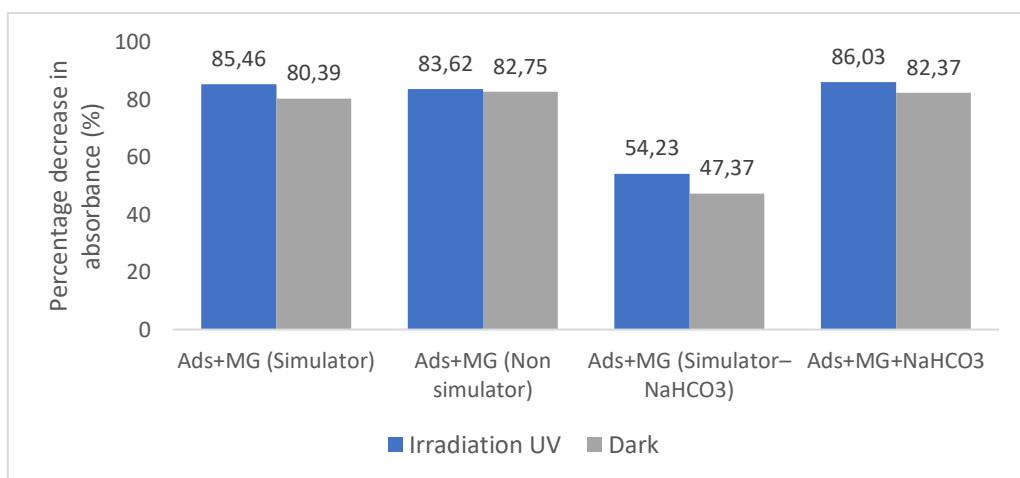


Fig. 16. Percentage reduction of MG absorbance with the adsorbent in various systems over 8 hours under UV and non-UV conditions.

An enhancement in degradation efficiency was also observed when the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ adsorbent was introduced, both in the presence and absence of simulator components. The $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite effectively adsorbed Malachite Green (MG) from the solution through combined physical and chemical interactions. As illustrated in Fig. 17, the combination of the adsorbent with NaHCO_3 resulted in a marked decrease in MG absorbance—86.03% under UV irradiation and 82.37% under dark conditions—indicating a synergistic effect between adsorption and photocatalytic degradation.

The adsorbent provides an extensive surface area that facilitates active-site interactions, while NaHCO_3 establishes favorable chemical conditions for the generation of oxidative radical species. In systems containing the adsorbent, the initial MG absorbance values were relatively higher but decreased substantially after 8 hours under both UV and dark conditions when NaHCO_3 was present in the complete simulator. This phenomenon remained consistent even in the absence of the adsorbent, where degradation efficiency still improved when NaHCO_3 was the only additive, in both simulator and non-simulator systems. These findings confirm that NaHCO_3 contributes directly to MG degradation, even without the presence of the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite.

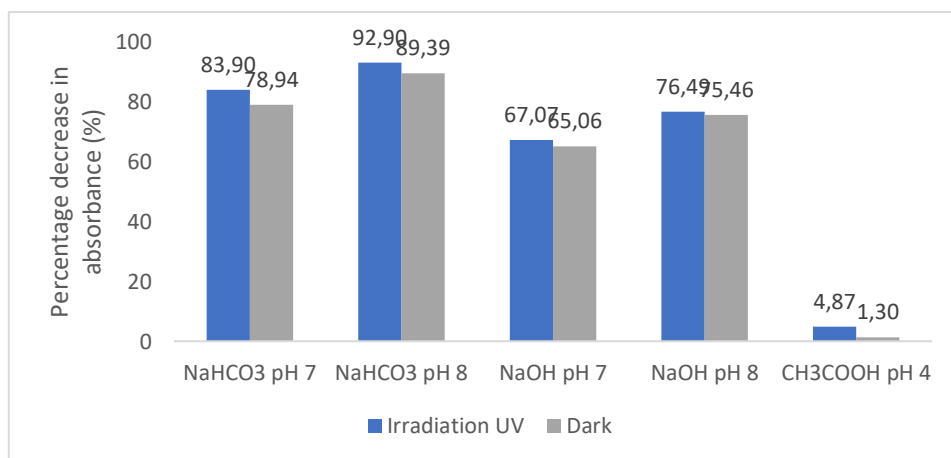


Fig 17. Percentage reduction of MG absorbance in various pH-adjusted systems under UV and dark conditions.

As shown in Fig. 16, the degradation system was examined at various pH levels adjusted using NaHCO_3 , NaOH , and CH_3COOH to determine whether the observed effect originated from pH regulation or from the intrinsic influence of NaHCO_3 itself. The results demonstrated that neutral to mildly basic conditions ($\text{pH} \approx 8$) adjusted with NaHCO_3 produced the highest reduction in MG absorbance. In contrast, acidic conditions ($\text{pH} 4$) adjusted with CH_3COOH resulted in negligible degradation of Malachite Green (MG).

Malachite Green is a cationic dye that carries a positive charge; therefore, its degradation is less favorable under acidic conditions due to the high concentration of H^+ ions. The excess of positive charges in the medium enhances electrostatic repulsion between MG molecules and the positively charged environment, thereby suppressing adsorption and hindering the overall degradation process.

The addition of NaHCO_3 facilitates the formation of carbonate radicals ($\text{CO}_3^{\bullet-}$) through the reaction between hydroxyl radicals ($\bullet\text{OH}$) and bicarbonate ions (HCO_3^-). The $\text{CO}_3^{\bullet-}$ radical is a selective one-electron oxidant capable of attacking electron-rich organic sites such as amine ($-\text{N}$), sulfhydryl ($-\text{S}$) groups, and aromatic rings, which are structural features present in the MG molecule. The combination of its buffering capacity, ability to generate selective oxidative species, and support for oxidation reactions makes NaHCO_3 the most critical component in enhancing the degradation efficiency of MG within this system.

4 Conclusion

A $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite was successfully synthesized and characterized. FTIR analysis revealed absorption bands at 651.94 cm^{-1} and 941.26 cm^{-1} , corresponding to the Zn–O stretching and Si–O–Zn vibration bonds, respectively, confirming the composite structure. XRD characterization indicated that the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite exhibited diffraction patterns consistent with Fe_3O_4 , along with additional peaks at $2\theta = 31.89^\circ, 34.53^\circ, 36.25^\circ, 47.65^\circ, 57.45^\circ, \text{ and } 67.85^\circ$, which matched the reference data (COD Card No. 00-036-1451) for ZnO. SEM–EDX analysis confirmed the presence of four constituent elements—Fe, O, Si, and Zn—with an average particle diameter of approximately 67.636 nm and a magnetization value of 39.7 emu/g.

Photocatalytic degradation experiments demonstrated that under UV irradiation (366 nm) for varying durations of 4, 6, 8, and 12 hours, the optimum degradation of Malachite Green (MG) was achieved after 8 hours, with a removal capacity of 0.5084 mg MG/g composite. From the variation of adsorbent mass, the optimum capacity was obtained at 0.4880 mg MG/g composite with an optimum mass of 1 g. Furthermore, the $\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{ZnO}$ composite maintained its performance over multiple reuse cycles, with a degradation capacity of 0.4863 mg MG/g composite in the second cycle and 0.4809 mg MG/g composite in the third cycle, demonstrating good stability and reusability in simulated textile wastewater treatment.

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