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Preparation of $Fe_3O_4/TiO_2/ZnO$ Composite as a Photocatalyst for the Degradation of Methylene Blue: Optimization and Light Source Variations

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Abstract

The $Fe_3O_4/TiO_2/ZnO$ (MTZ) composite was synthesized by preparing Fe_3O_4 via the coprecipitation method, TiO_2 via the hydrothermal method, and ZnO via the precipitation method. The three oxides (Fe_3O_4, TiO_2, and ZnO) were composited using the solid-state method with varying mass ratios (1:2:1, 2:1:1, 1:1:2, and 1:1:1) and calcined at 600°C for 4 h to obtain MTZ composites. The composites were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and particle size analysis (PSA). The results indicated that the $Fe_3O_4/TiO_2/ZnO$ composite with a 1:1:2 ratio (MTZ3) exhibited the most favorable properties. MTZ3 was evaluated as a photocatalyst for methylene blue degradation under UV light, with variations in irradiation time, catalyst mass, and dye concentration. Further tests were conducted under sunlight and dark conditions using both the composite and its individual oxides (Fe_3O_4, TiO_2, and ZnO). Reuse tests assessed the stability of MTZ3 after repeated cycles. Under optimum conditions (catalyst mass 0.4 g, methylene blue concentration 20 ppm, irradiation time 60 min), MTZ3 achieved 80.4% degradation under UV light. Under sunlight, degradation efficiency reached 98.7%, while under dark conditions it was only 4.5%. Reuse tests demonstrated consistent performance over three cycles, maintaining 80.4% degradation, surpassing previous studies on Fe_3O_4–TiO_2 (1:2) composites, which achieved 67.49% degradation over two cycles. These results suggest that the MTZ3 composite is a stable and efficient photocatalyst with excellent potential for dye degradation under various light sources.

1. Introduction

Industrial development has led to an increase in dye waste being discharged into the environment, around 1– 2% during production and 1–10% during end-use [1, 2]. Dyes such as methylene blue contain toxic organic matter that contaminates soil, water, and microorganisms, and are difficult to decompose naturally due to their aromatic structure [3]. Their degradation produces aromatic compounds and amines that are carcinogenic and can cause skin irritation, cancer, and kidney dysfunction [1, 3]. Methods such as adsorption, coagulation, and filtration are still limited because they are unable to completely decompose the molecules [1]. Photocatalysis is a promising method because it is non-toxic, inexpensive, stable, and able to completely decompose dyes using photon energy and UV radiation or sunlight [1, 3, 4].

Photocatalysis can be carried out using several semiconductor photocatalyst materials. TiO_2 is considered the best semiconductor for photocatalysis applications. Furthermore, ZnO can also be used as an alternative to remove several types of contaminants in water [5]. In several studies [6, 7, 8], TiO_2/ZnO composites have been synthesized, with most of their applications being photocatalysts. This is due to the material's low-cost, environmentally friendly, and easy synthesis process, as well as its excellent chemical stability and photocatalytic properties [8, 9].

Despite its advantages, the recycling of composites is very limited because the material is difficult to extract from the reaction medium. Wang *et al.* [10] stated that conventional separation techniques are very expensive and have the potential to produce secondary pollution due to the loss of material. To overcome this, magnetic iron oxide nanoparticles are often used [11]. According to Winatapura *et al.* [5], ZnO and TiO_2 are utilized together with magnetite nanoparticles due to their ability to be easily separated in a short time using an external magnetic field. This method is said to be a practical method for separating composites simply by applying an external magnet [12]. Fe_3O_4, with its magnetic properties, allows efficient catalyst separation and recycling, while the heterojunction between TiO_2 and ZnO enhances photon absorption, charge transfer, and active surface area, thus optimizing the separation of electron-hole pairs and improving the photocatalytic performance compared to the single materials [13, 14].

TiO_2 and ZnO are n-type semiconductors with wide band gaps (~3.1 eV) that are active under UV light but are limited by high charge recombination, low response to visible light, and corrosion susceptibility in ZnO. Meanwhile, Fe_3O_4, with a smaller band gap, can absorb visible light, but shows low photocatalytic efficiency due to ineffective charge separation when used alone [15, 16, 17, 18]. Ulpa *et al.* [16] reported that Fe_3O_4/TiO_2 composites exhibited higher photoreduction activity than pure TiO_2; however, the synthesis process was time-consuming, and the distribution of titania within the pores of Fe_3O_4 was not always optimal, thereby limiting photocatalytic efficiency. Similarly, Pradipta *et al.* [19] reported that Fe_3O_4/ZnO composites still inherited the drawbacks of ZnO, including a wide band gap, a high rate of electron–hole recombination, low response to visible light, and the possibility of significant corrosion.

Therefore, the development of Fe_3O_4/TiO_2/ZnO composites is needed to overcome the limitations of each material and improve photocatalytic performance through synergy between materials. In this study, the solid-state method was employed due to its advantages of simplicity, suitability for large-scale applications, environmental friendliness, cost-effectiveness, and ability to produce high-quality composites without the need for solvents or additional chemicals [20, 21, 22]. The combination of Fe_3O_4, TiO_2, and ZnO materials in the form of a composite is expected to increase photocatalytic efficiency in the methylene blue degradation process due to the formation of a heterojunction structure that is able to accelerate the separation of electron-hole pairs and reduce charge recombination, broaden the light absorption spectrum, and enable magnetic separation of catalysts [23].

This study aims to synthesize and characterize Fe_3O_4/TiO_2/ZnO composite as a photocatalyst in the degradation process of methylene blue, and evaluate the effect of variations in light sources in dark conditions, UV light and sunlight on its photocatalytic efficiency, optimization of reaction conditions is carried out to obtain maximum degradation efficiency through variations in parameters such as catalyst mass, methylene blue concentration, and irradiation time. The resulting composite is expected to show high photocatalytic activity, good stability, and ease of separation due to the magnetic properties of Fe_3O_4, making it a promising candidate for efficient and sustainable dye wastewater treatment. This study is also expected to contribute scientifically to developing multicomponent photocatalysts and their utilization in environmentally friendly dye degradation technology.

2. Experimental

2.1. Materials and Instruments

The materials used included NaOH (Merck), universal pH, distilled water, $FeCl_3 \cdot 6H_2O$ (Merck), $FeSO_4 \cdot 7H_2O$ (Merck), NH_4OH (Merck), $Zn(CH_3COO)_2 \cdot 2H_2O$ (Merck), Titanium Tetra Isopropoxide (TTIP; $C_{12}H_{28}O_4Ti$, 97% Merck), Ethanol (C_2H_5OH; 96%, Merck) and methylene blue ($C_{16}H_{18}CIN_3S$). The instruments employed were an X-ray diffractometer (XRD; D8 Advance), a scanning electron microscope (SEM; Inspect-S50), a transmission electron microscope (TEM; HT7700), a particle size analyzer (PSA; Horiba SZ-100), and a UV- Vis spectrophotometer (Aquamate 8100).

2.2. Synthesis of Magnetite (Fe_3O_4) (M)

Fe_3O_4 was synthesized using a coprecipitation method. A total of 6 g of $FeCl_3 \cdot 6H_2O$ and 4 g of $FeSO_4 \cdot 7H_2O$ (mole ratio 3:2), each dissolved in 50 mL of distilled water. After that, the two solutions were mixed and stirred using a magnetic stirrer while heated at 70°C. The solution mixture was added with 50 mL of NH_4OH dropwise and maintained at 70°C for 3 h. The formed precipitate was separated from the filtrate using an external magnet. The resulting precipitate was washed to a neutral pH and then dried for 3 h using an oven at 100°C [24]. The material was then characterized using SEM and XRD.

2.3. Synthesis of TiO_2 Nanoparticles (T)

A total of 0.1 N TTIP was dissolved in 20 mL of ethanol and stirred for 30 min, then a few drops of distilled water were added to form a dispersion medium. The mixture was sonicated for 20 min, then transferred to an autoclave and heated at 150°C for 3 h. After cooling to room temperature, the product was washed and centrifuged using distilled water, then filtered. The precipitate was dried in an oven at 110°C for 5 h and calcined at 500°C for 2 h [25]. The material was then characterized using SEM and XRD.

2.4. Synthesis of ZnO Nanoparticles (Z)

ZnO was synthesized by the precipitation method. A total of 1.78 g of $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved in 25 mL of water while stirring at 100°C for 30 min. To the solution, 1 M NaOH was added until the pH of the solution was 12. The solution was stirred for 1 h. The white precipitate obtained was centrifuged at a speed of 4000 rpm. The precipitate was rinsed with distilled water and ethanol until the pH was neutral. The synthesized precipitate was heated in an oven at 60°C for 6 h and calcined at 600°C for 2 h [26]. The material was then characterized using SEM and XRD.

2.5. Synthesis of $Fe_3O_4/TiO_2/ZnO$ (MTZ) Composite

MTZ composites were synthesized using the solid-state method. The nanoparticles were combined at mass ratios of M:T:Z = 2:1:1, 1:2:1, 1:1:2, and 1:1:1, designated as MTZ1, MTZ2, MTZ3, and MTZ4, respectively. The resulting composites were calcined at 600°C for 4 h [26]. The best variation of MTZ composite was subsequently selected for photocatalytic testing in methylene blue degradation.

2.6. Determination of Maximum Wavelength

The absorbance of a 6 ppm methylene blue solution was measured using a UV-Vis spectrophotometer over a wavelength range of 400–800 nm to determine the maximum absorption wavelength of methylene blue.

2.7. Photocatalytic Activity of the Optimal MTZ Composite for Methylene Blue Degradation under Various Conditions

2.7.1. Catalyst Mass Variation

This procedure was carried out based on research conducted by Elshypany *et al.* [26] with modifications to the variation of catalyst mass and methylene blue concentration. A total of 0.05, 0.1, 0.2, 0.4, and 0.6 g of the best variation of MTZ composite were put into 50 mL of 20 ppm methylene blue solution, then stirred with a magnetic stirrer in a closed container while irradiated with a UV lamp for 60 min each. After that, the composite was separated using an external magnet, and the filtrate was analyzed at the maximum wavelength using a UV-Vis spectrophotometer.

2.7.2. Variation of Irradiation Time

This procedure was done based on research conducted by Elshypany *et al.* [26] with modifications to the variation of irradiation time and methylene blue concentration. The optimum mass of the selected MTZ composite was added to 50 mL of 20 ppm methylene blue solution, stirred with a magnetic stirrer in a closed container, and irradiated with UV light for 10, 20, 30, 60, and 90 min. After irradiation, the composite was separated using an external magnet, and the filtrate was analyzed at the maximum absorption wavelength using a UV-Vis spectrophotometer.

2.7.3. Variations in Methylene Blue Concentration

This procedure was adapted from Elshypany *et al.* [26] with modifications to the variation in methylene blue concentration. The optimum mass of the selected MTZ composite was added to 50 mL of methylene blue solutions at concentrations of 10, 20, 30, 40, and 50 ppm, stirred with a magnetic stirrer in a closed container, and irradiated with UV light for the optimum time. After irradiation, the composite was separated using an external magnet, and the filtrate was analyzed at the maximum absorption wavelength using a UV-Vis spectrophotometer.

2.7.4. Various Light Sources

The effect of light source variations was investigated using three conditions: dark, irradiation with a 10 W Masko UV lamp, and sunlight between 11:00 and 12:00 WITA (temperature 30°C, 73% humidity, and light intensity ranging from 55,000 to 90,000 lux). This optimization was performed on MTZ composites and the individual materials (Fe_3O_4, TiO_2, and ZnO) under previously established optimum photocatalysis conditions.

2.8. Effectiveness Test of Reuse of MTZ Composite with the Best Variation on Methylene Blue Degradation

This procedure was performed based on research conducted by Elshypany *et al.* [26] with modifications involving rinsing with distilled water and methanol to remove residual impurities. The optimal MTZ composite used in the previous photocatalytic experiments was separated from the methylene blue solution, rinsed several times with distilled water and methanol, and then dried. After drying, the composite was calcined at 600°C for 4 h. The regenerated MTZ composite was subsequently reused for methylene blue photocatalysis under the previously determined optimum conditions.

2.9. Data analysis

The % degradation value of methylene blue can be calculated using Equation 1.

$$\%\ Degradation = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

Where, C_0 is the initial concentration of dye and C_t is the concentration of dye at a certain time/final concentration.

3. Results and Discussion

3.1. Synthesis and Characterization of Fe_3O_4, TiO_2, and ZnO Nanoparticles

Fe_3O_4 was synthesized via the coprecipitation method by reacting $FeCl_3{\cdot}6H_2O$ and $FeSO_4{\cdot}7H_2O$ (molar ratio 3:2) with 25% NH_4OH at 70°C. Tukan *et al.* [27] reported that 70°C is the optimal temperature for producing Fe_3O_4 particles with suitable magnetic properties and particle size; temperatures below 70°C reduce magnetic strength, while higher temperatures can alter particle structure or form other phases such as hematite. After adding NH_4OH until the mixture reaches pH 9–10, a black precipitate of Fe_3O_4 forms, corresponding to optimal Fe^{2+} and Fe^{3+} precipitation [28].

This method involves the precipitation and reduction of $FeO{\cdot}OH$ (iron(III) oxyhydroxide) and $Fe(OH)_2$ (iron(II) hydroxide) [29]. In the coprecipitation reaction, Fe^{3+} and Fe^{2+} ions rapidly react in a strong base (pH > 10), producing high OH^- concentrations that initiate the formation of $Fe(OH)_3$ and $Fe(OH)_2$, which spontaneously transform into magnetite (Fe_3O_4). Precipitation occurs immediately due to the high reaction rate under alkaline conditions [30]. The Fe_3O_4 synthesis reaction via coprecipitation can be expressed in Equation 2.

$$2Fe^{3+} + Fe^{2+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O \quad (2)$$

TiO_2 nanoparticles were synthesized using the hydrothermal method, beginning with the dissolution of TTIP in ethanol. Ethanol acts as an organic solvent, reducing system polarity and slowing the hydrolysis reaction, which promotes a smoother and more controlled structure [31]. A few drops of distilled water were then added to trigger TTIP hydrolysis, producing titanium hydroxide ($Ti(OH)_4$) and alcohol as a byproduct. The mixture was sonicated to disperse particles and reduce agglomeration, thereby increasing the specific surface area [32]. Ultrasonic waves during sonication also accelerate the transformation from amorphous to nanocrystalline TiO_2 [33].

During heating in an autoclave, $Ti(OH)_4$ undergoes a condensation reaction and forms Ti–O–Ti, which is a precursor to TiO_2 in amorphous or semi-crystalline form. The process ends with calcination at 500°C for 2 h, which changes the amorphous structure to crystalline. Calcination is used to synthesize nanoparticles to produce specific sizes and morphologies [34]. In addition, the calcination process is an important procedure for synthesizing TiO_2 nanoparticles, because it can affect the properties, particle size, crystallinity, crystallite size, and photocatalytic activity of TiO_2 [35, 36]. The synthesis of TiO_2 nanoparticles produces a white powder. The reaction for synthesizing TiO_2 nanoparticles using the hydrothermal method is shown in Equation 3 [31, 37].

$$Ti(OCH(CH_3)_2)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4(CH_3)_2CHOH$$

$$Ti(OH)_4 \rightarrow TiO_2\ (\text{amorphous}) + 2H_2O$$

$$TiO_2\ (\text{amorphous}) \rightarrow TiO_2 \tag{3}$$

ZnO nanoparticles were synthesized via the precipitation method by reacting $Zn(CH_3COO)_2{\cdot}2H_2O$ with NaOH. In this method, the dissolved precursor transforms into a suspended solid, which is separated by sedimentation [38]. The reaction begins with Zn^{2+} ions reacting with OH^- ions until a colloid forms. Excess OH^- then reacts with $Zn(OH)_2$ to form the $Zn(OH)_4^{2-}$ complex, which subsequently dissociates back into Zn^{2+} and OH^- ions, eventually forming ZnO [39]. After formation, the ZnO was calcined at 600°C for 2 hours. According to Azzahra *et al.* [39], calcination decomposes the Zn complex into ZnO nanoparticles; high temperatures break Zn–OH bonds on the surface, allowing rearrangement and formation of yellowish-white ZnO nanoparticles. The chemical reaction for ZnO nanoparticle synthesis via precipitation is shown in Equation 4.

$$Zn(CH_3COO)_2{\cdot}2H_2O \rightarrow Zn^{2+} + 2CH_3COO^- + 2H_2O$$

$$Zn^{2+} + NaOH \rightarrow Zn(OH)_2 + Na^+$$

$$Zn(OH)_2 + OH^- \rightarrow Zn(OH)_4^{2-}$$

$$Zn(OH)_4^{2-} \rightarrow ZnO + H_2O \tag{4}$$

Based on Figure 1, TiO_2 nanoparticles synthesized via the hydrothermal method appear as a white powder. Fe_3O_4 nanoparticles produced by the coprecipitation method form a black powder with magnetic properties; when exposed to an external magnetic field, they are strongly attracted and accumulate at the top of the container when a magnet is placed on the lid. ZnO nanoparticles synthesized using the precipitation method appear as a bone-white powder.

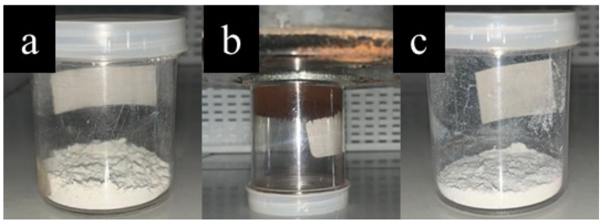


Figure 1. Synthesis results of (a) TiO_2, (b) Fe_3O_4, and (c) ZnO nanoparticles

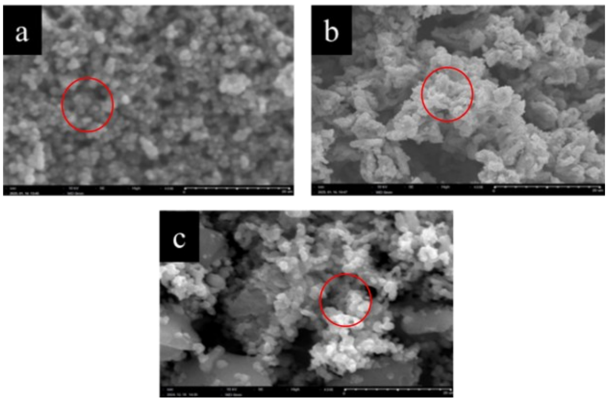


Figure 2. SEM images of (a) Fe_3O_4, (b) TiO_2, and (c) ZnO at 20,000× magnification

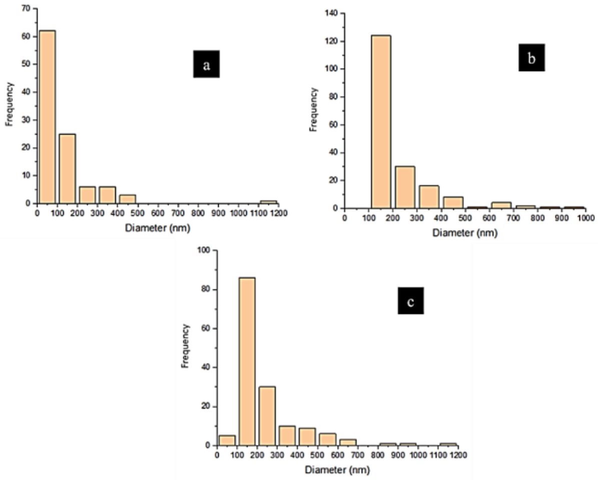


Figure 3. Particle size analysis based on SEM images of (a) Fe_3O_4, (b) TiO_2, and (c) ZnO

Fe_3O_4, TiO_2, and ZnO nanoparticles were characterized using SEM to analyze their surface morphology. As shown in Figure 2, Fe_3O_4 nanoparticles are spherical with relatively uniform sizes, although some agglomeration occurs. TiO_2 particles exhibit an uneven surface with predominantly round shapes and non-uniform sizes. ZnO nanoparticles display significant agglomeration, with small round particles adhering to the surfaces of larger particles.

The particle size distribution of SEM images can be seen using the Origin and ImageJ applications. In Fe_3O_4 (Figure 3a), the highest frequency is in the diameter range <100 nm, indicating that most particles are on the nanometer scale with a relatively narrow distribution. The distribution of TiO_2 and ZnO particles shows the highest frequency of particles in the diameter range of 100–200 nm.

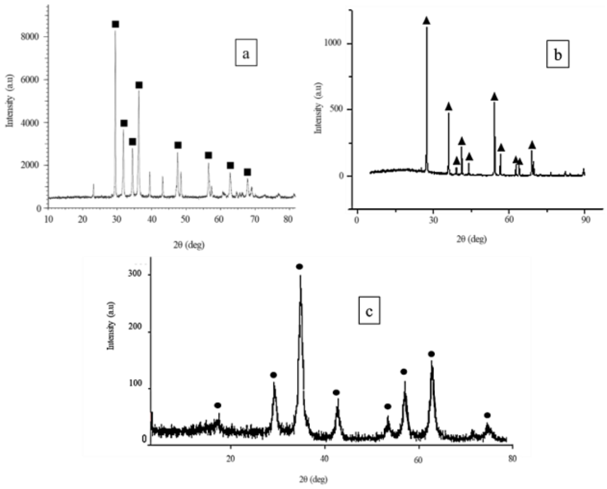


Figure 4. XRD patterns of (a) ZnO, (b) TiO_2, and (c) Fe_3O_4

Fe_3O_4, TiO_2, and ZnO nanoparticles were characterized by XRD to analyze their crystal phases. In Figure 4, the diffractogram of Fe_3O_4 shows peaks at 2θ angles of 18.59° (111), 30.38° (220), 35.62° (311), 43.56° (400), 53.85° (422), 57.30° (511), 62.90° (440) and 74.62° (533) which are in accordance with JCPDS No. 19 – 0629 for the typical angle of Fe_3O_4. In the TiO_2 diffractogram, peaks appear at 2θ angles of 27.15° (110), 35.82° (101), 38.32° (200), 41.26° (111), 43.25° (210), 54.62° (211), 57.15° (220), 62.87° (200), 63.65° (310) and 68.9° (301), indicating rutile TiO_2 and corresponding to JCPDS No. 21–1276. ZnO exhibits characteristic peaks at 31.74° (100), 34.68° (002), 36.65° (101), 47.34° (102), 56.87° (110), 63.24° (103), and 68.50° (200), in accordance with JCPDS No. 36–1451.

3.2. Synthesis of MTZ Composite

The MTZ composite was synthesized using the solid-state method by mixing the individual powders and heating them at high temperature. This method was chosen for its simplicity, low energy requirements, straightforward equipment, fast processing, and minimal material usage compared to other methods [20, 40]. MTZ composites were synthesized with different mass ratio variations of Fe_3O_4:TiO_2:ZnO (2:1:1, 1:2:1, 1:1:2, and 1:1:1), designated as MTZ1, MTZ2, MTZ3, and MTZ4, respectively. These variations were tested to determine the optimal composite composition.

In MTZ1 (higher in TiO_2) and MTZ3 (higher in ZnO), the composite appears grayish, while MTZ2 (higher in Fe_3O_4) is slightly brownish-gray. MTZ4, with equal Fe_3O_4:TiO_2:ZnO ratios, tends to be brownish. During synthesis, the materials are thoroughly ground to ensure homogeneity and facilitate contact between the components. The mixture is calcined to remove external contaminants and enhance material quality.

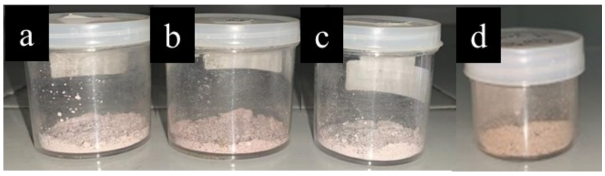


Figure 5. Synthesis results of (a) MTZ1, (b) MTZ2, (c) MTZ3, and (d) MTZ4 composites

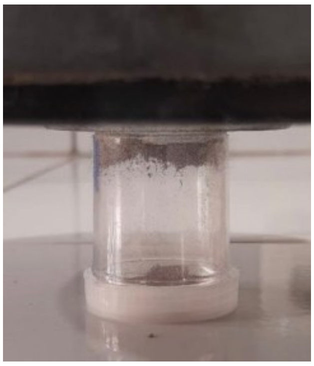


Figure 6. MTZ attraction with the external magnet

According to Febriani *et al.* [41], calcination in the solid-state method promotes reactions between basic materials, forming higher-quality products. This high-temperature process improves composite properties by developing a more regular crystal structure, eliminating impurities and volatile substances, controlling particle size and distribution, forming new phases with desired functional properties, and activating the surface to enhance performance [42, 43, 44]. Febriani *et al.* [41] also explained that in the solid-state method, reactions occur between material particles, forming a mixture of component oxides. At points of surface contact, ions migrate between pure oxides, leading to the formation of binary and ternary oxides with new structures.

The MTZ material can be attracted by an external magnetic field, confirming the presence of Fe_3O_4 and imparting magnetic properties. However, the attraction is weaker than that of pure Fe_3O_4, as indicated by part of the composite falling away from the magnet. This reduced magnetic response is due to the presence of non-magnetic components, TiO_2 and ZnO, which dilute the overall magnetic strength.

3.3. Characterization of MTZ Composites

3.3.1. Characterization of MTZ Composites Using XRD

Figure 7 shows that all composite variations have similar diffractograms, with some differences in peak intensity. In the diffactogram, the set which is a collection of magnetite phases (Fe_3O_4) appears at 2θ angles of around 29.6° (220), 43.3° (400), and 56.9° (511) and 63.03° (440) (JCPDS 19-0629), then the set for ZnO corresponds to 2θ which is around 31.8° (100), 34.5° (002), 36.3° (101), 47.5° (012), and 69.2° (201) (JCPDS 36-1451) and set for TiO_2 phase with diffraction peaks at 2θ angles around 39.5° (200), 42.7° (210), 54.4° (211), and 68.3° (301) indicating rutile phase TiO_2 (JCPDS 21-1276). From Figure 7, the % crystallinity of each composite was calculated using Origin software and is presented in Table 1 to identify the optimal composition.

Table 1. Crystallinity % values of MTZ1, MTZ2, MTZ3 and MTZ4 composites

Composite	Crystallinity %
MTZ1	58.9
MTZ2	60.1
MTZ3	70
MTZ4	76

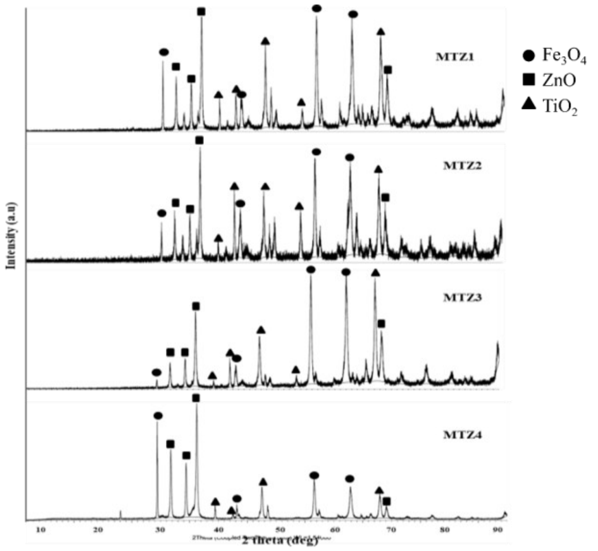


Figure 7. X-ray diffractogram of MTZ1, MTZ2, MTZ3, and MTZ4 composites

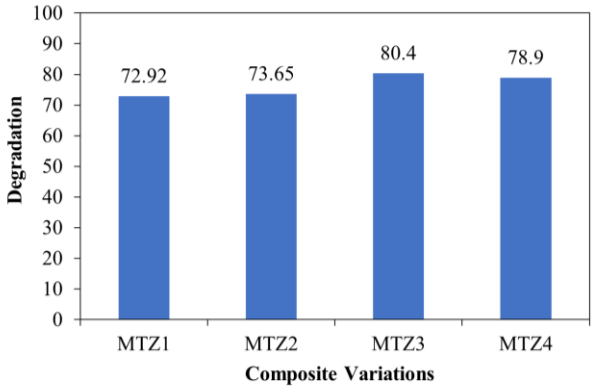


Figure 8. Methylene blue degradation (%) using MTZ1, MTZ2, MTZ3, and MTZ4 composites

According to Zaiyar [45], materials with high crystallinity values have a more regular molecular arrangement, whereas irregular structures result in lower crystallinity. Based on Table 1, the crystallinity values of all composite variations are relatively similar, especially the crystallinity values of MTZ3 and MTZ4. To select for the best variation material, MTZ1, MTZ2, MTZ3, and MTZ4 were subjected to photocatalytic tests for methylene blue degradation, allowing comparison of their photocatalytic efficiency and identification of the most effective composite. The tests were conducted using 0.4 g of catalyst with 20 ppm methylene blue for 60 min. The results are presented in Figure 8.

Based on Figure 8, the MTZ3 composite shows the highest % degradation of methylene blue compared to MTZ1, MTZ2, and MTZ4. Although MTZ4 exhibited the highest % crystallinity, MTZ3 demonstrated superior photocatalytic activity. This result is thought to be due to the higher ZnO composition in the MTZ3 composite. Increased crystallinity is believed to enhance electron–hole separation and suppress charge recombination, while the presence of UV-sensitive ZnO promotes electron–hole pair generation. Together, these factors improve light absorption efficiency, enlarge the active surface area, enhance stability, and ultimately boost photocatalytic performance [46, 47, 48].

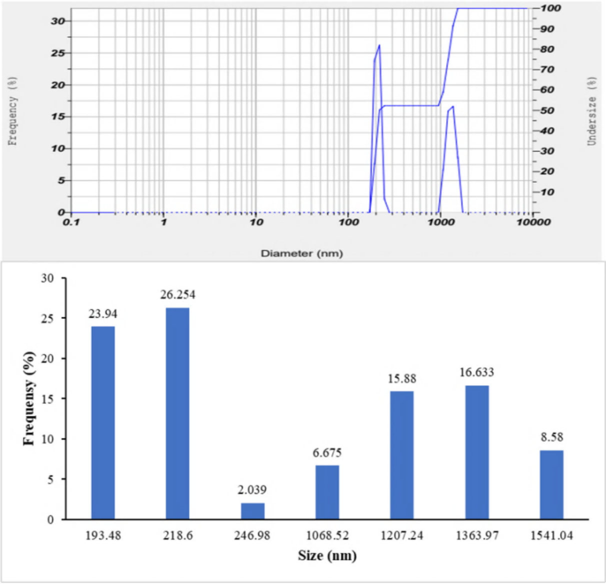


Figure 9. Particle size distribution of MTZ3

Amanda *et al.* [49] reported ZnO photocatalytic activities of 94% and 97% in methylene blue degradation under sunlight using zinc acetate dihydrate and zinc nitrate hexahydrate precursors, respectively. Therefore, in this study, the MTZ3 composite with a higher ZnO composition (1:1:2) was selected as the photocatalyst for further photocatalysis testing.

3.3.2. Characterization of MTZ3 Composite Using PSA

The MTZ3 composite was characterized using PSA to evaluate particle size, uniformity, and distribution. As shown in Figure 9, the average particle size distribution of MTZ3 is 365 nm, with sizes ranging from 193.48 nm to 1541.04 nm. The particle size with the lowest frequency is 246.98 nm, while the most frequent size is 218.6 nm. This indicates that the MTZ3 material has a tendency for sizes ranging from 193 to 246 nm with a fairly large frequency. Sizes greater than 1000 nm indicate inhomogeneity, and the large size of MTZ3 is suspected to form aggregates or agglomerates [50].

Based on Figure 9, the results of the particle size distribution analysis show that the MTZ3 composite has a significantly larger particle size and a broader distribution compared to its constituent materials (Fe_3O_4, TiO_2, and ZnO), as shown in Figure 3. This difference suggests a tendency for particle aggregation during the synthesis process. The presence of particle sizes around 200 nm still reflects a relationship with the sizes of Fe_3O_4, TiO_2, and ZnO. However, according to Vasquez *et al.* [51] particles measuring less than 1000 nm in composites can be categorized as nano-sized particles. Therefore, the MTZ3 composite remains classified as nano-sized.

3.3.3. Characterization of MTZ Composites with SEM and TEM

SEM characterization was performed to examine the surface morphology of the MTZ composites. As shown in Figure 10, MTZ1 (a) exhibits irregularly shaped particles with a rough surface and layered structure. MTZ2 (b) displays a granular morphology with semi-angular to irregular shapes and visible pores between particles.

MTZ3 (c) shows denser and more homogeneous particles with several morphologies, including spherical, rod-like, cylindrical, and tubular shapes. This sample presents the most uniform morphology with a highly porous surface, which is expected to enhance the photocatalytic active area. In contrast, MTZ4 (d) demonstrates quasi-spherical particles with a poorly defined surface structure and suboptimal particle distribution. Siregar *et al.* [52] reported Fe_3O_4/ZnO particles as spherical and needle-like. Kustiningsih *et al.* [33] also mentioned that Fe_3O_4 particles adhere to and surround TiO_2 surfaces, causing aggregation and rougher surfaces. Similarly, Siwińska-Stefańska *et al.* [53] showed that the particles were round and had a high tendency to agglomerate.

To analyze the internal structure, the best composite variation, MTZ3, was characterized using TEM. As shown in Figure 11, TEM images at 20,000× magnification with scales of 50, 100, and 200 nm reveal spherical particles stacked on one another. This result is similar to the research of Barua et al. [12], which reported that the characterization results of TiO_2-ZnO-Fe_3O_4 showed a particle shape that was not very clear but tended to be round and oval with agglomeration. Similarly, Upadhyay *et al.* [9] reported the morphology of TiO_2/ZnO showed spherical particles, while Elshypany *et al.* [26] reported cubic and spherical morphologies in Fe_3O_4/ZnO composites.

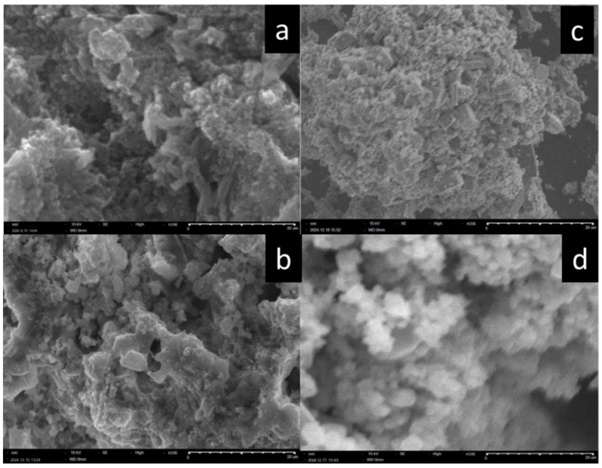


Figure 10. SEM images of (a) MTZ1, (b) MTZ2, (c) MTZ3 and (d) MTZ4 at 20,000× magnification

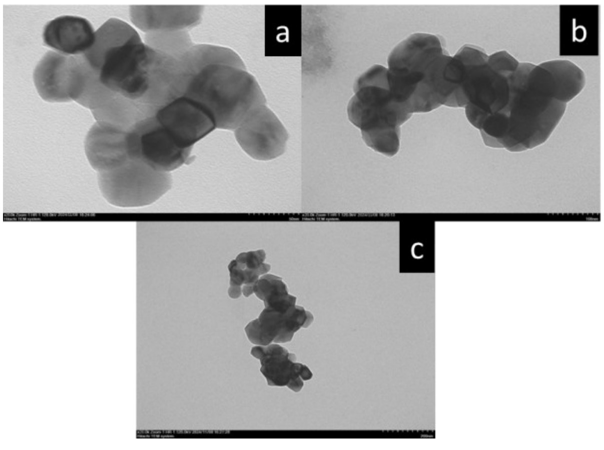


Figure 11. TEM images of MTZ3 at 20,000× magnification with scales of (a) 50 nm, (b) 100 nm, and (c) 200 nm

3.4. Activity of MTZ3 as a Photocatalyst in Degrading Methylene Blue

3.4.1. Catalyst Mass Variation

The MTZ3 catalyst mass was optimized (0.05, 0.1, 0.2, 0.4, and 0.6 g) using a 10 W UV lamp for 60 min with 20 ppm methylene blue solution to determine the optimal mass for photocatalysis. As shown in Figure 12, % degradation increases with catalyst mass. According to Wildan and Mutiara [54], increasing the catalyst mass causes an increase in the contact time between the catalyst and the target compound (dye), thus causing degradation. Additionally, more catalyst produces more hydroxyl radicals (•OH) and electrons to reduce metal ions, further promoting dye degradation. However, beyond a certain point, increasing catalyst mass no longer improves degradation; for example, 0.6 g exhibited lower % degradation than 0.4 g. Wang *et al.* [2] attributed this to catalyst agglomeration, which reduces light penetration and inhibits the photocatalytic process. In this optimization, 0.4 g was taken as the optimum mass of catalyst for photocatalytically degrading methylene blue.

3.4.2. Variation of Irradiation Time

The irradiation time for photocatalytic degradation of methylene blue using MTZ3 was optimized with a catalyst mass of 0.4 g and 20 ppm methylene blue solution, using a 10 W UV lamp for 10, 20, 30, 60, and 90 min. Based on Figure 12, % degradation increases with irradiation time, reaching an optimum at 60 minutes. Longer irradiation produces more hydroxyl radicals (•OH), which act as strong oxidants to degrade dyes into simpler compounds such as CO_2 and H_2O [55, 56, 57]. However, degradation does not increase indefinitely with time; beyond the optimum, further irradiation yields negligible improvement [58, 59].

In Figure 12, the irradiation time from 60 to 90 min did not experience a significant increase and tended to stagnate. According to Vifta *et al.* [60], prolonged irradiation can saturate the photocatalyst, reduce its activity, and cause accumulation of adsorbed products, hindering contact between the catalyst, UV light, and dye, thereby decreasing photodegradation efficiency.

3.4.3. Variation of Methylene Blue Concentration

Optimization of methylene blue concentration variations (10, 20, 30, 40, and 50 ppm) was carried out using an optimum catalyst mass of 0.4 g and an optimum irradiation time of 60 min. In Figure 12, % degradation increased from 10 to 20 ppm and decreased from 20 to 50 ppm, indicating an optimum concentration of 20 ppm. At 10 ppm, it was suspected that the number of methylene blue molecules was not sufficient to react optimally with the catalyst surface, and electron-hole recombination occurred before reacting with methylene blue [59, 61]. Hariani *et al.* [62] stated that high initial dye concentrations can hinder light penetration and absorption by the catalyst, while excess dye molecules may block active sites, reducing the generation of reactive oxygen species (ROS) necessary for degradation.

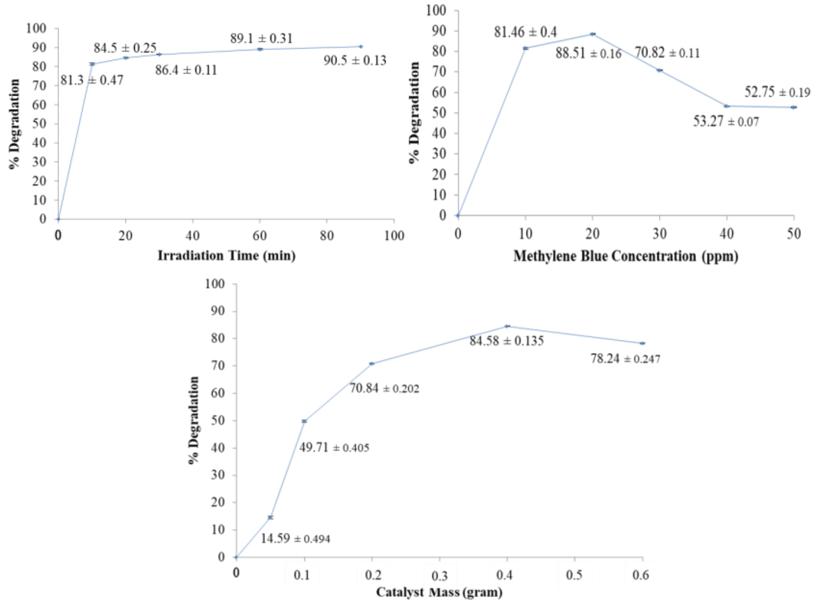


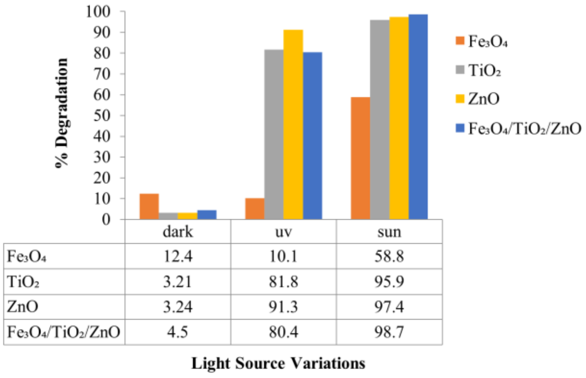
Figure 12. Methylene blue degradation (%) for different catalyst masses, irradiation times, and methylene blue concentrations

3.5. Activity of Fe_3O_4, TiO_2, ZnO and MTZ3 Composite as Photocatalysts in Different Light Sources

3.5.1. Dark Conditions

The application of the MTZ3 composite as a photocatalyst for methylene blue degradation was further evaluated under sunlight and dark conditions, alongside comparison with UV light. Additionally, individual catalysts (Fe_3O_4, TiO_2, and ZnO) were tested to assess their performance under different light sources. These experiments aimed to identify the most effective light condition and to compare the photocatalytic efficiency of each catalyst. Degradation tests under dark conditions were conducted using the optimum parameters: 0.4 g of catalyst, 20 ppm methylene blue solution, and 60 minutes of reaction time.

Based on Figure 13, the Fe_3O_4 catalyst achieved the highest % degradation under dark conditions compared to the other catalysts. According to Elshypany *et al.* [26], Fe_3O_4 can produce reactive species via redox reactions even in the absence of light, allowing these species to react with the dye and degrade it through a non-photocatalytic pathway.



	dark	uv	sun
Fe_3O_4	12.4	10.1	58.8
TiO_2	3.21	81.8	95.9
ZnO	3.24	91.3	97.4
$Fe_3O_4/TiO_2/ZnO$	4.5	80.4	98.7

Figure 13. Effect of catalyst type on methylene blue degradation (%) under dark, UV, and sunlight conditions at optimum parameters

Under dark conditions, the TiO_2 and ZnO catalysts exhibited low % degradation because they are semiconductors that require light activation to generate electron–hole pairs for redox reactions, which drive dye degradation. Without light, these activation processes do not occur, and their degradation efficiency is limited [63, 64]. Additionally, the band gaps of TiO_2 and ZnO are optimal for UV light, further reducing their effectiveness in the dark [53]. In contrast, the composite catalyst achieved slightly higher % degradation than TiO_2 or ZnO alone. Dalvi *et al.* [65] and Kadhim *et al.* [66] reported that combining Fe_3O_4 with other semiconductors increases dye adsorption and the available surface area, providing more active sites for reactions and improving degradation performance.

3.5.2. UV Light

Photocatalytic tests under UV light were conducted using a 10 W Masko UV lamp (365 nm) with Fe_3O_4, TiO_2, ZnO, and composite catalysts under optimum conditions: 0.4 g of catalyst, 20 ppm methylene blue solution, and 60 min of reaction time. As shown in Figure 13, Fe_3O_4 exhibited the lowest % degradation, likely because it is not an effective photocatalyst and is prone to oxidation. Therefore, combining Fe_3O_4 with other materials is necessary to enhance its stability and photocatalytic performance [67].

The % degradation values for TiO_2 and ZnO indicate that both are effective photocatalysts under UV light. TiO_2 and ZnO have band gaps of approximately 3.2 eV and 3.37 eV, respectively, allowing them to absorb UV light and generate electron–hole pairs. The excited electrons react with water to produce hydroxyl radicals (·OH), which degrade dyes [68, 69, 70]. ZnO exhibited a higher % degradation than TiO_2, which Raganata *et al.* [71] attributed to its higher quantum efficiency, enabling the production of more hydroxyl radicals and more effective dye degradation.

The composite catalyst exhibited a lower % degradation than the individual TiO_2 and ZnO catalysts. Although the MTZ composite was expected to enhance photocatalytic activity, the UV photocatalytic results did not meet expectations. Kustiningsih *et al.* [33] and Elshypany *et al.* [26] suggested that incorporating Fe_3O_4 into the TiO_2–ZnO matrix alters the band gap, reducing UV light absorption. Consequently, the generation and efficiency of excited electron–hole pairs are lower than in single TiO_2 or ZnO, limiting photocatalytic performance.

3.5.3. Sunlight

Variations in light sources using sunlight were carried out under optimum conditions: 0.4 g of catalyst, 20 ppm methylene blue, and 60 min of reaction time. The tests were performed between 11:00 and 12:00 WITA, with sunlight intensity ranging from 55,000 to 90,000 lux, temperature at 30°C, and humidity at 73%. As shown in Figure 13, % degradation under sunlight was higher than under UV light. According to Wardiyati *et al.* [72] and Yuningrat *et al.* [73], this is because sunlight provides a broader spectrum, including both UV and visible light, which enhances photocatalytic activity. Moreover, sunlight's intensity and wavelength range (310–2300 nm) exceed those of UV light (200–380 nm), further improving degradation efficiency [59].

For the TiO_2 and ZnO catalysts, % degradation increased under sunlight compared to UV light. While both catalysts are effective under UV, the UV component in sunlight is sufficient to initiate photocatalysis [74]. Additionally, conducting the process outdoors allows excited electrons to react with oxygen more readily, generating reactive species such as superoxide radicals that efficiently degrade dyes [75]. The % degradation of methylene blue under sunlight was higher with the ZnO catalyst than with TiO_2, as ZnO can absorb a broader spectrum of light, including visible wavelengths, enhancing its photocatalytic efficiency [74].

The highest % degradation was observed using the composite catalyst because the Fe_3O_4 component facilitates electron transfer from TiO_2 and ZnO, reducing charge carrier recombination and allowing more reactive species to form for effective dye degradation [33, 65]. Under sunlight, the $Fe_3O_4/TiO_2/ZnO$ composite achieved 98.7% degradation of methylene blue, while under UV light it reached only 80.4%. According to Gebrezgiabher *et al.* [76] and Barua *et al.* [12], the difference arises because Fe_3O_4 can absorb visible light, increasing the composite's overall light absorption. Additionally, incorporating Fe_3O_4 reduces the composite's band gap, enabling it to utilize a broader spectrum of sunlight, including visible wavelengths that TiO_2 or ZnO alone cannot efficiently exploit [26, 33, 65].

The MTZ3 composite exhibits a dominant particle size distribution of 193–218 nm, covering approximately 50% of the total particle population (Figure 8). These nanosized particles provide a high specific surface area, increasing the number of active sites available for photocatalytic reactions [77]. This increased surface area contributes directly to higher degradation efficiency, as demonstrated by the sunlight-driven photocatalytic degradation of methylene blue, which reached 98.7%.

Research by Kiziltaş *et al.* [4] reported that the use of MTZ composite photocatalysts with particle sizes in the range of 210–240 nm achieved 100% photodegradation in 105 min, supporting the correlation between particle size and photocatalytic activity observed in this study. The synergy between the constituent materials of the composite in this study also strengthens photocatalytic activity. The presence of Fe_3O_4 provides magnetic properties that facilitate post-reaction catalyst separation, while TiO_2 and ZnO act as active semiconductors that are able to absorb UV light and some visible light. Together, these three materials form a heterojunction structure that accelerates electron–hole separation, suppresses charge recombination, and improves overall photocatalytic efficiency [14].

The reduction of methylene blue dye in this study was possible due to the synergistic effect between the adsorption and photocatalysis processes. This is in line with the research of Mohammad Shafiee *et al.* [78], which showed that the degradation of dyes takes place effectively through the synergy between the adsorption and photocatalysis processes. That adsorption is identified as an important initial stage in the photocatalytic process. The data indicate that increasing the surface area and porosity of the material enhances adsorption capacity, while a narrow band gap promotes the formation of electron–hole pairs, enabling the subsequent degradation of adsorbed dye molecules. Thus, a strong adsorption process functions as an essential preliminary stage, and the synergy between adsorption and photocatalysis results in a more effective and efficient system for dye degradation.

3.6. Effectiveness Test of Reusing MTZ3 Composite Catalyst in Degrading Methylene Blue

In this procedure, a reuse test was conducted to determine the composite's ability to degrade the methylene blue dye after repeated photocatalysis cycles. The test was performed under optimum conditions, using a catalyst mass of 0.4 g and a 20 ppm methylene blue solution for 60 min, with the composite reused up to three times in the photodegradation process.

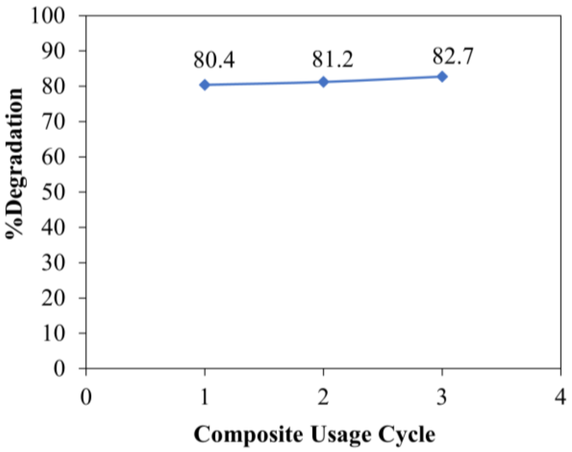


Figure 14. Methylene blue degradation (%) by MTZ3 composite in the reuse test

Based on Figure 14, the % degradation of methylene blue by the MTZ3 composite over the first three uses did not decrease and even showed a slight increase. This value indicates that the MTZ3 composite has good photocatalytic activity even though it has been used repeatedly. The increase in degradation is likely due to changes in the catalyst properties during the initial photocatalytic reactions, such as enhanced crystallinity and improved light absorption. Additionally, Sorathiya *et al.* [79] reported that beneficial modifications can occur on the photocatalyst surface during reuse, including increased surface area and more active sites.

However, repeated use beyond three cycles may reduce the photocatalyst's effectiveness. Długosz *et al.* [80] observed decreased dye degradation efficiency after three reuses due to reduced dye adsorption and accumulation of residues on the catalyst surface. Similarly, Quy *et al.* [81] found that chitosan/ZnO–Fe_3O_4 photocatalytic activity declined after four cycles. Feng *et al.* [82] stated that while photocatalyst activity was maintained for three cycles, signs of photocorrosion and loss of Fe_3O_4 or ZnO could potentially reduce efficiency with more frequent reuse.

4. Conclusion

The characterization of the $Fe_3O_4/TiO_2/ZnO$ (MTZ) composite revealed that the XRD diffractogram exhibits peaks corresponding to magnetite (Fe_3O_4), ZnO, and rutile TiO_2 phases. PSA analysis of MTZ3 (1:1:2) revealed an average particle size of 365 nm, mostly 193–246 nm. SEM images indicated spherical, rod-like, and tubular morphologies forming aggregates, while TEM confirmed stacked spherical particles. Among the composites, MTZ3 was identified as the best variant for photocatalysis, achieving 80.4% methylene blue degradation under optimum conditions (0.4 g catalyst, 20 ppm, 60 min). The highest photocatalytic efficiency was observed under sunlight (98.7%), compared to UV light (80.4%) and dark conditions (4.5%). Reuse tests demonstrated that MTZ3 maintained stable photocatalytic performance over three cycles, with degradation efficiency reaching 81.4%.

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