Integration of Mn-ZnFe₂O₄ with S-g-C₃N₄ for Boosting Spatial Charge Generation and Separation as an Efficient Photocatalyst

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Abstract: The disposal of dyes and organic matter into water bodies has become a significant source of pollution, posing health risks to humans worldwide. With rising water demands and dwindling supplies, these harmful compounds must be isolated from wastewater and kept out of the aquatic environment. In the research presented here, hydrothermal synthesis of manganese-doped zinc ferrites' (Mn-ZnFe₂O₄) nanoparticles (NPs) and their nanocomposites (NCs) with sulfur-doped graphitic carbon nitride (Mn-ZnFe₂O₄/S-g-C₃N₄) are described. The samples' morphological, structural, and bonding features were investigated using SEM, XRD, and FTIR techniques. A two-phase photocatalytic degradation study of (0.5, 1, 3, 5, 7, 9, and 11 wt.%) Mn-doped ZnFe₂O₄ NPs and Mn-ZnFe₂O₄/10, 30, 50, 60, and 70 wt.%) S-g-C₃N₄ NCs against MB was carried out to find the photocatalyst with maximum efficiency. The 9% Mn-ZnFe₂O₄ NPs and Mn-ZnFe₂O₄/50% S-g-C₃N₄ NCs exhibited the best photocatalyst efficiency in phase one and phased two, respectively. The enhanced photocatalytic activity of the Mn-ZnFe₂O₄/50% S-g-C₃N₄ NCs could be attributed to synergistic interactions at the Mn-ZnFe₂O₄/50% S-g-C₃N₄ NCs interface that resulted in a more effective transfer and separation of photo-induced charges. Therefore, it is efficient, affordable, and ecologically secure to modify ZnFe₂O₄ by doping with Mn and homogenizing with S-g-C₃N₄. As a result, our current research suggests that the synthetic ternary hybrid Mn-ZnFe₂O₄/50% S-g-C₃N₄ NCs may be an effective photocatalytic system for degrading organic pollutants from wastewater.

Keywords: integration; charge separation; degrading organic pollutants; manganese; hydrothermal technique
1. Introduction

Water contamination has attracted much attention from researchers since dye emissions from various sectors pose dangers to the public’s health and environment. Organic compounds, dissolved and suspended particles, and heavy metals are present in the complex effluents produced by the printing and textile dyeing industries [1]. About 15–50% of the azo dyes used during the dyeing process do not attach to the fabric and are washed away with the wastewater. This effluent is employed in irrigation processes, although it is terrible for crop growth and germination. Methylene blue (MB) is a basic cationic dye used in different sectors. It makes people more prone to cyanosis, tissue necrosis, shock, jaundice, vomiting, and a faster heartbeat. [2,3]. The wastewater must, therefore, unquestionably be cleaned of these colors. To treat contaminated effluents, a variety of chemical, biological, and physical methods have been used [4]. One of the green technologies for the treatment of industrial wastewater is the photocatalytic destruction of organic contaminants. Due to its incredible effectiveness and low cost, scientists have shown that photocatalytic decomposition is a suitable alternative strategy for the effective decomposition of pollutants [5,6]. The employment of alternative techniques to eliminate by-products is not required in photocatalysis procedures. Numerous nanostructured semiconductor photocatalysts have been explored, including TiO$_2$, ZnO, CuO, NiS, SnO$_2$, ZrO$_2$, and WO$_3$. Due to their significant band gaps and quick electron-hole recombination, these photocatalysts have limitations in visible-light photocatalysis [7,8].

Therefore, creating innovative visible-light-induced photocatalysts with higher activity has been a hot topic for a long time. Due to the superior cation and anion adsorption abilities, low band gap energy, and reduced electron-hole recombination, ferrite (Fe$_2$O$_4$) nanoparticles have particular relevance among photocatalysts [9]. These ferrite NPs have prospective applications in wastewater treatment, biomedicine, electrical devices, energy storage, EMR shielding, and the recording medium. They have a band gap of about 1.9 eV and are highly stable. They are also less harmful and inexpensive, have strong electronic conduction, are recyclable, and are environmentally benign. Their photocatalytic activity is unfortunately constrained for practical use by low quantum efficiency [9–11].

Many studies have shown that doping ZnFe$_2$O$_4$ with appropriate metal ions and combining it with a suitable semiconductor material improve optical and photocatalytic characteristics. Patil et al. used the co-precipitation approach to manufacture Gd$^{3+}$-doped ZnFe$_2$O$_4$ nanoparticles, demonstrating enhanced MB degradation of roughly 99% compared to pure ZnFe$_2$O$_4$ (95% degradation in 240 min.) [12]. According to Ajithkumar et al., yttrium-doped zinc ferrite made by solution combustion showed 95% MB degradation in 180 min. The photocatalytic efficiency of Y-doped ZnFe$_2$O$_4$ is greater than that of pure zinc ferrite [13]. Compared to ZnFe$_2$O$_4$, cobalt-doped zinc ferrite more effectively oxidized methylene blue under visible light. Numerous studies have found that ZnFe$_2$O$_4$ has a finite band gap energy and, as a result, may combine with S-g-C$_3$N$_4$ to create an efficient heterojunction [14]. Similarly, Savunthari et al. constructed (Cu, Bi) codoped ZnFe$_2$O$_4$ nanoparticles via the solution combustion method. The codoped NPs showed an enhanced degradation of bisphenol A compared to undoped NPs [15].

The g-C$_3$N$_4$ semiconductor has demonstrated remarkable photocatalytic competency under visible light due to its advantageous traits, such as excellent stability and a lowered band gap energy that boosts its capacity to absorb visible radiations [16,17]. However, the rapid recombination of photoinduced $e^-/h^+$ pairs in g-C$_3$N$_4$ makes it inappropriate for use as a photocatalyst [18]. Consequently, many attempts have been undertaken to overcome this constraint, including vacancy, heterojunction creation, and combining the g-C$_3$N$_4$ with other metal oxides and nonmetals such as sulphur [19–22]. S-doping modifies the band gap of g-C$_3$N$_4$ and improves the mobility and separation of the e-h pairs by stacking its 2p orbitals on the VB of bulk g-C$_3$N$_4$ [23]. A simple molten salt approach was successfully used by Keke et al. to produce sulfur-doped g-C$_3$N$_4$. The photocatalytic performance of S-doped g-C$_3$N$_4$ toward methylene blue and tetracycline was 10 and 20 times that of bulk g-C$_3$N$_4$ [24]. Similarly, Xin et al. successfully synthesized highly active S-doped g-C$_3$N$_4$...
by employing thiourea and melamine as the precursors. The synthesized S-doped g-C₃N₄ exhibited remarkable photocatalytic efficacy against rhodamine B (Rhb) [25]. Basaleh used soft and hard templates to create ZnFe₂O₄/S-g-C₃N₄. The photocatalytic efficiency of ZnFe₂O₄/S-g-C₃N₄ against acridine orange was 4.4 and 6.3 fold that of ZnFe₂O₄ and bulk g-C₃N₄, respectively [26].

Thus, owing to the improved charge separation abilities, it is suggested to produce a metal-ZnFe₂O₄/S-g-C₃N₄ heterojunction to realize a significant photocatalytic performance. In this study, hybrid Mn-ZnFe₂O₄/S-g-C₃N₄ nanocomposites were synthesized successfully via a surfactant (PEG)-assisted hydrothermal process, and its efficiency for removing MB under sunlight was investigated. In step one, the manganese-doped zinc ferrite (Mn-ZnFe₂O₄) nanoparticles were synthesized with varying chromium percentages (0.5, 1, 3, 5, 7, 9, and 11 wt.%). The effect of Mn²⁺ substitution on the photocatalytic properties of zinc ferrite was observed. The 9% Mn-ZnFe₂O₄ sample manifested the best absorption of solar light and degradation efficiency. In step two, the 9% Mn-ZnFe₂O₄ nanoparticles were homogenized with diverse concentrations of S-g-C₃N₄ (10, 30, 50, and 70 wt.%%) to produce Mn-ZnFe₂O₄/S-g-C₃N₄ with enhanced photocatalytic activity. The 9% Mn-ZnFe₂O₄/50% S-g-C₃N₄ nanocomposite executed the best photocatalytic activity compared to pure ZnFe₂O₄, 9% Mn-ZnFe₂O₄, and S-g-C₃N₄. The results depicted that the enhanced photocatalytic activity of the 9% Mn-ZnFe₂O₄/50% S-g-C₃N₄ nanocomposite was because of the improved absorption of sunlight and better separation of e⁻/h⁺ pairs between Mn-ZnFe₂O₄ and S-g-C₃N₄. To our knowledge, the synthesis of Mn-ZnFe₂O₄/S-g-C₃N₄ heterojunctions via the hydrothermal approach has never been used.

2. Experimental

2.1. Chemicals

Thiourea (CH₄N₂S), polyvinyl pyrrolidone, methylene blue (C₁₆H₁₈ClN₃S), zinc sulphate heptahydrate (ZnSO₄·7H₂O), iron (III) chloride anhydrous (FeCl₃), manganese (II) chloride (MnCl₂), and sodium sydroxide (NaOH) were acquired from Merck and used.

2.2. Synthesis of Chromium-Doped Zinc Ferrites

A series of Mn-doped zinc ferrites (Mn-ZnFe₂O₄) with varying manganese percentages (0.5, 1, 3, 5, 7, and 9 wt.%) were produced using a surfactant-assisted hydrothermal method [6]. For the preparation of 0.5% Mn-ZnFe₂O₄, three solutions, A, B, and C, were made preceding the synthesis. The solutions, A, B, and C, were made by dispersing 0.010 g of MnCl₂·4H₂O, 1.865 g of ZnCl₂·7H₂O, and 2.435 g of FeCl₃ in 50 mL of deionized water. Then, these solutions (A, B, and C) were intermixed, and 10 mL of PVP was added as a surfactant to prevent the aggregation of nanoparticles. The pH of the solution was adjusted to 11 by adding NaOH; next, the suspension was loaded to a Teflon-lined autoclave. The autoclave was heated to 175 °C for 10 h and then cooled to ambient temperature. The resultant precipitates were separated by filtering, rinsed with deionized water and pure ethanol, and then dried at 85 °C in an oven. Other percentages of Mn-ZnFe₂O₄ (0, 1, 3, 5, 7, and 9 wt.%) were also synthesized using the same method [27].

2.3. Synthesis of S-g-C₃N₄

Thiourea was heated to 560 °C for 6 h at a rate of 5 °C per minute in a muffle furnace to form S-g-C₃N₄. After cooling to ambient temperature, the resulting yellowish S-g-C₃N₄ was stored [17,28].

2.4. Synthesis of Mn-ZnFe₂O₄/S-g-C₃N₄

Using a surfactant-assisted hydrothermal technique, 9% Mn-ZnFe₂O₄ was combined with various amounts of S-g-C₃N₄ (10, 30, 50, 60, and 70 wt.%) to produce a range of Mn-ZnFe₂O₄/S-g-C₃N₄ nanocomposites. For the preparation of 9% Mn-ZnFe₂O₄/10%S-g-C₃N₄, firstly, four solutions, A, B, C, and D, were made by dispersing 0.185 g of manganese chloride in 50 mL of water (Solution A), 1.706 g of zinc chloride in 50 mL of water (Solution
B), 2.435 g of FeCl$_3$ in 50 mL of water (Solution C), and 0.18 g of S-g-C$_3$N$_4$ in 50 mL of water (Solution D). Then, three solutions, A, B, and C, were added to solution D and homogenized for 1 h along with the addition of 10 mL of PVP as a surfactant. The following steps were the same as for the synthesis of Mn-ZnFe$_2$O$_4$ NPs. Moreover, the same process was repeated to synthesize the 9% Mn-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ containing 30, 50, 60, and 70 wt.% of S-g-C$_3$N$_4$. The schematic diagram (Scheme 1) depicts the synthesis procedure for Mn-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ NCs, and Table 1 lists the precise composition.

Table 1. Composition of the synthesized Mn-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ composites.

| Sr. No. | Nanocomposites | Manganese Chloride | Zinc Chloride | Ferric Chloride | S-Doped g-C$_3$N$_4$ |
|---------|-----------------|--------------------|---------------|----------------|---------------------|
| 1       | Mn-ZnFe$_2$O$_4$| 0.185 g            | 1.706 g       | 2.435 g        | -                   |
| 2       | S-g-C$_3$N$_4$  | -                  | -             | -              | 0.52 g              |
| 3       | 9% Mn-ZnFe$_2$O$_4$/10S-g-C$_3$N$_4$ | 0.185 g | 1.706 g | 2.435 g | 0.17 g |
| 4       | 9% Mn-ZnFe$_2$O$_4$/30S-g-C$_3$N$_4$ | 0.185 g | 1.706 g | 2.435 g | 0.52 g |
| 5       | 9% Mn-ZnFe$_2$O$_4$/50S-g-C$_3$N$_4$ | 0.185 g | 1.706 g | 2.435 g | 0.87 g |
| 6       | 9% Mn-ZnFe$_2$O$_4$/70S-g-C$_3$N$_4$ | 0.185 g | 1.706 g | 2.435 g | 0.94 g |

2.5. Photocatalytic Activity

The photocatalytic activity of zinc ferrites, Mn-doped zinc ferrites, sulphur-doped graphitic carbon nitride, and nanocomposites was studied under solar light irradiation. The aqueous solution of an organic dye, methylene blue, was used as the standard contaminant. Then, 0.2 g of each photocatalyst was added to the beaker in which 100 mL of MB solution (10 mg L$^{-1}$) was added and allowed to stir in the dark for about 45 min to attain the adsorption–desorption equilibrium. After that, the suspension was positioned under solar light in an open atmosphere, and aliquots of 5 mL were collected after every 30 min. A UV-Vis spectrophotometer was used to evaluate the photocatalytic activity of the collected samples after centrifugation [29].
2.6. Characterization

The structure of the synthesized catalysts was determined by applying XRD (Bruker AXS, D8-54, Madison, WI, USA) using Cu Kα radiation \((k = 1.54056 \text{ Å})\) at 40 kV and 30 mA at room temperature, whereas elemental content and morphology were found using SEM-EDS (Hitachi, S-4800, Tokyo, Japan). The UV-visible and photocatalytic absorption spectra were measured using a UV-Vis-NIR spectrophotometer (UV-770, Jasco, Tokyo, Japan) from 800 nm to 200 nm wavelengths. Using a transmission electron microscope, the surface morphologies of the photocatalysts were examined (TEM, JEOL-JEM-1230, Peabody, MA, USA). FTIR spectrometers measured functional groups in the 4000–400 cm\(^{-1}\) range with a resolution of 1 cm\(^{-1}\) (Perkin 400 FTIR, Waltham, MA, USA).

3. Results and Discussion

3.1. TEM and EDX Analyses

The size, shape, and distribution of the particles and the elemental components of the as-prepared materials were disclosed by TEM, SEM, and EDX spectra. Due to their large surface area due to their nanoscale size and solid magnetic interaction, undoped ZnFe\(_2\)O\(_4\) and Mn-doped ZnFe\(_2\)O\(_4\) nanoparticles were observed to be crystalline and included agglomerated, irregular, spherical nanoparticles with an average size of 20–38 nm (Figure 1a,b). The proper exposure to different hosts made possible by the efficient synthesis of Mn-ZnFe\(_2\)O\(_4\) at the nanoscale also guaranteed the single-domain character of the particles for the increase in magnetic remanence and decrease in magnetic coercivity. The S-g-C\(_3\)N\(_4\) specimen had some creases and a beehive-like shape (Figure 1c,d). This supramolecular complex was synthesized using a mixture of three different precursors, and the pyrolysis of the complex resulted in the formation of wrinkles. These wrinkles facilitated high interfacial contact between S-g-C\(_3\)N\(_4\) and other components, which improved the transfer and separation of charge carriers in the NCs. The 9% Mn-ZnFe\(_2\)O\(_4\)/50% S-g-C\(_3\)N\(_4\) NCs’ TEM pictures showed that several Mn-ZnFe\(_2\)O\(_4\) nanoparticles seemed to be incorporated in the S-g-C\(_3\)N\(_4\) matrix. As shown in Figure 1e, it was clear that S-g-C\(_3\)N\(_4\) had firmly encircled several Mn-ZnFe\(_2\)O\(_4\) NPs. The 9% Mn-ZnFe\(_2\)O\(_4\)/50% S-g-C\(_3\)N\(_4\) NCs had sheet-like clusters with O, Zn, Fe, C, N, and Mn as their primary components, according to EDX mapping in Figure 1f, for the 9% Mn-ZnFe\(_2\)O\(_4\)/50% S-g-C\(_3\)N\(_4\) binary hybrid photocatalyst.

3.2. FTIR Analysis

In the wave number range of 4000–450 cm\(^{-1}\), the FTIR spectra of the produced photocatalysts were compared (Figure 2). The observed FTIR spectrum of ZnFe\(_2\)O\(_4\) confirmed the presence of the M-O bond at 879 cm\(^{-1}\) and the absence of all functional groups. The peak at 3335 cm\(^{-1}\) was due to the O-H bond stretching while the peak at 1696 cm\(^{-1}\) was due to the bending of the O-H bond (Figure 2a) [5]. When the FTIR spectrum of 9% Mn-ZnFe\(_2\)O\(_4\) was compared to pure ZnFe\(_2\)O\(_4\), there was little difference in the peak positions. The effective production of Mn-doped ZnFe\(_2\)O\(_4\) was confirmed by the modest shift in peak positions (Figure 2b) [30,31]. The FTIR spectrum of S-g-C\(_3\)N\(_4\) exhibited a broad band at 3178 cm\(^{-1}\) due to O-H bond stretching; the peaks between 1500 and 2000 cm\(^{-1}\) were due to the stretching vibrations of C=N, and peaks between 1500 and 1000 cm\(^{-1}\) were due to C-N bond stretching, as shown in Figure 2c [32]. A peak at 805 cm\(^{-1}\) indicated the triazine unit. The FTIR spectrum of the composite contained the peaks corresponding to both Mn-ZnFe\(_2\)O\(_4\) and S-g-C\(_3\)N\(_4\), signifying that the Mn-ZnFe\(_2\)O\(_4\)/S-g-C\(_3\)N\(_4\) composite was formed successfully (Figure 2d) [33–36].
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3.3. XRD Analysis

The X-ray diffractogram of the samples of ZnFe$_2$O$_4$, 9% Mn-ZnFe$_2$O$_4$, S-g-C$_3$N$_4$, and 9% Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ is shown in Figure 3. In the XRD spectra of pure ZnFe$_2$O$_4$, seven peaks were observed with crystal facets (220), (311), (400), (422), (511), (440), and (533) at 2$\theta$ = 30°, 34.8°, 42.6°, 53°, 56°, 61.8°, and 73.2°, which fitted well with the pattern of standard zinc ferrites with JCPDS file 22-1012 [12,30,31,37,38]. The distinctive peaks of zinc ferrites in the XRD spectra of Mn-ZnFe$_2$O$_4$ showed that the structure of zinc ferrite does not significantly alter when Mn metal is doped into it. Two characteristic peaks were detected in the XRD pattern of S-g-C$_3$N$_4$; the crystal plane (002) was attributed to the interlayer assembling of aromatic systems, and the plane (100) was ascribed to the interplanar arrangement of aromatic systems (JCPDS file # 00-087-1526) [39,40]. The crystal phase of Mn-ZnFe$_2$O$_4$ remained intact after coupling with S-g-C$_3$N$_4$, and the (002) crystal plane of S-g-C$_3$N$_4$ was indicated in the composite systems. In 9%Mn-ZnFe$_2$O$_4$/50%S-g-C$_3$N$_4$ composites, owing to the high crystallinity of Mn-ZnFe$_2$O$_4$, the characteristic peaks of Mn-ZnFe$_2$O$_4$ were prominent. The emergence of the distinct peaks of Mn-ZnFe$_2$O$_4$ and S-g-C$_3$N$_4$ in composites demonstrated the successful production of Mn-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ composites [34,35,41,42].

Figure 1. TEM profiles of (a) ZnFe$_2$O$_4$, (b) 9% Mn-ZnFe$_2$O$_4$, (c) SEM profile of S-g-C$_3$N$_4$, (d) TEM image of S-g-C$_3$N$_4$, and (e) 9% Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ NCs. (f) EDX of 9% Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ NCs.

Figure 2. FTIR spectrum of composites of ZnFe$_2$O$_4$ (a), S-g-C$_3$N$_4$ (b), 9% Mn-ZnFe$_2$O$_4$ (c), and 9% Mn-ZnFe$_2$O$_4$/50%S-g-C$_3$N$_4$ (d).
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The X-ray diffractogram of the samples of ZnFe$_2$O$_4$, 9% Mn-ZnFe$_2$O$_4$, S-g-C$_3$N$_4$, and 9% Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ is shown in Figure 3. In the XRD spectra of pure ZnFe$_2$O$_4$, seven peaks were observed with crystal facets (220), (311), (400), (422), (511), (440), and (533) at $2\theta = 30^\circ$, 34.8$^\circ$, 42.6$^\circ$, 53$^\circ$, 56$^\circ$, 61.8$^\circ$, and 73.2$^\circ$, which fitted well with the pattern of standard zinc ferrites with JCPDS file 22-1012 [12,30,31,37,38]. The distinctive peaks of zinc ferrites in the XRD spectra of Mn-ZnFe$_2$O$_4$ showed that the structure of zinc ferrite does not significantly alter when Mn metal is doped into it. Two characteristic peaks were detected in the XRD pattern of S-g-C$_3$N$_4$; the crystal plane (002) was attributed to the interlayer assembling of aromatic systems, and the plane (100) was ascribed to the inter-planar arrangement of aromatic systems (JCPDS file # 00-087-1526) [39,40]. The crystal phase of Mn-ZnFe$_2$O$_4$ remained intact after coupling with S-g-C$_3$N$_4$, and the (002) crystal plane of S-g-C$_3$N$_4$ was indicated in the composite systems. In 9%Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ composites, owing to the high crystallinity of Mn-ZnFe$_2$O$_4$, the characteristic peaks of Mn-ZnFe$_2$O$_4$ were prominent. The emergence of the distinct peaks of Mn-ZnFe$_2$O$_4$ and S-g-C$_3$N$_4$ in composites demonstrated the successful production of Mn-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ composites [34,35,41,42].

![Figure 3. XRD spectrum of ZnFe$_2$O$_4$, 9% Mn-ZnFe$_2$O$_4$, S-g-C$_3$N$_4$, and 9% Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$.](image)

3.4. Photocatalytic Degradation Study

The photocatalytic activity of synthesized samples was detected in two phases. The photocatalytic activities of ZnFe$_2$O$_4$ and Mn-ZnFe$_2$O$_4$ NPs were first examined in the presence of sunlight using an aqueous methylene blue solution (Figure 4a). The rate of dye disintegration was monitored using a UV-Vis spectrophotometer with a wavelength range of 200–800 nm (Figure 4a). According to the degradation contours (Figure 4b) and percentile degradation graphs (Figure 4c), when we increased the Mn$^{2+}$ doping (0.5 to 9 wt. %), there was a gradual improvement in the photocatalytic activity of Mn-doped zinc ferrite nanoparticles. Since the Mn$^{2+}$ doping decreased the band gap of ZnFe$_2$O$_4$ and facilitated the enhanced generation of the e$^-$/h$^+$ pair, the photocatalytic efficiency of Mn-ZnFe$_2$O$_4$ was better than ZnFe$_2$O$_4$. It was observed that the insertion of various metal ions into the pure ferrite can affect its optical and structural properties, which can enhance
the ferrite's photocatalytic ability [43]. When the concentration of doped Mn$^{2+}$ ions was increased beyond this point (<9 wt.%), the photocatalytic activity of Mn$_{x}$Zn$_{1-x}$Fe$_{2}$O$_{4}$ NPs was reduced (Figure 5a,b). This Mn (9 wt.%) is the optimum doping concentration for Mn-ZnFe$_{2}$O$_{4}$ NPs. The observed degradation efficiencies of Mn-ZnFe$_{2}$O$_{4}$ catalysts with different manganese concentrations (0, 0.5, 1, 3, 5, 7, and 9 wt.%) were 71%, 78%, 81%, 86%, 92%, 91%, 95%, and 89%, respectively, after 210 min of sunlight irradiation. Thus, the 9% Mn-ZnFe$_{2}$O$_{4}$ NPs exhibited the maximum photocatalytic efficiency compared to other nanoparticles (Figure 4c).

In the next phase, the Mn-ZnFe$_{2}$O$_{4}$/S-\(\gamma\)-C$_{3}$N$_{4}$ NCs were produced by mixing 9% Mn-ZnFe$_{2}$O$_{4}$ NPs with diverse amounts of S-\(\gamma\)-C$_{3}$N$_{4}$ (as given in Table 1). Then, the photocatalytic activity of the produced NCs was checked every 15 min. The samples were placed in the dark to establish adsorption–desorption equilibrium between the dye and the fabricated NCs before sunlight exposure, as described by Mudassar et al. [44]. According to Figure 5b, the photocatalysts absorbed modest amounts of MB. After that, the samples were exposed to sunlight, and the 9% Mn-ZnFe$_{2}$O$_{4}$/50\% S-\(\gamma\)-C$_{3}$N$_{4}$ NCs exhibited the largest dye degradation relative to the other samples (Figure 5a). It was evident from the degradation contours (Figure 5a) and percent degradation plots (Figure 5b) that the dye degradation increased as the concentration of S-\(\gamma\)-C$_{3}$N$_{4}$ and 9% Mn-ZnFe$_{2}$O$_{4}$/0–50\% S-\(\gamma\)-C$_{3}$N$_{4}$ NCs up to 50% and then dropped for ZnFe$_{2}$O$_{4}$/S-\(\gamma\)-C$_{3}$N$_{4}$ NCs containing S-\(\gamma\)-C$_{3}$N$_{4}$ contents >50%. After 120 min of exposure to sunlight, the measured degradation efficiencies of S-\(\gamma\)-C$_{3}$N$_{4}$ and 9% Mn-ZnFe$_{2}$O$_{4}$/0–50\% S-\(\gamma\)-C$_{3}$N$_{4}$ NCs were 51%, 54%, 65%, 89%, 100%, and 85%, respectively. Better charge separation and transportation via Mn-ZnFe$_{2}$O$_{4}$ and S-\(\gamma\)-C$_{3}$N$_{4}$ coupling, as well as improved visible light absorption due to Mn doping in ZnFe$_{2}$O$_{4}$, might be responsible for the enhanced photocatalytic efficiency of 9% Mn-ZnFe$_{2}$O$_{4}$/50\% S-\(\gamma\)-C$_{3}$N$_{4}$ NCs [41,42,45]. Figure 5b depicts the percentage of photocatalytic degradation of MB by the corresponding NCs.

The Langmuir–Hinshelwood model was applied to understand the kinetics of Mn-ZnFe$_{2}$O$_{4}$ (Supplementary Materials: Figure S1) and Mn-ZnFe$_{2}$O$_{4}$/S-\(\gamma\)-C$_{3}$N$_{4}$ NCs, and Figure 5c shows the resultant graph [38]. Figure 5c exhibits that the dye degradation by the NCs under sunlight was fit to pseudo-first-order kinetics. The rate constant (k) values of Mn-ZnFe$_{2}$O$_{4}$/S-\(\gamma\)-C$_{3}$N$_{4}$ NCs are summarized in Table 2. Therefore, the highest and lowest calculated “k” values were found for ZnFe$_{2}$O$_{4}$/50\% S-\(\gamma\)-C$_{3}$N$_{4}$ NCs (0.0142 min$^{-1}$) and S-\(\gamma\)-C$_{3}$N$_{4}$ (0.00515 min$^{-1}$), respectively. The ZnFe$_{2}$O$_{4}$/50\% S-\(\gamma\)-C$_{3}$N$_{4}$ NCs completely decolorized the MB in 120 min, and its “k” value was 2.1 and 2.75 times more than that of ZnFe$_{2}$O$_{4}$ and S-\(\gamma\)-C$_{3}$N$_{4}$ respectively. The rate of dye degradation increased as the concentration of S-\(\gamma\)-C$_{3}$N$_{4}$ increased from 10% to 50% in ZnFe$_{2}$O$_{4}$/50\% S-\(\gamma\)-C$_{3}$N$_{4}$ NCs but then declined for NCs with a greater concentration of S-\(\gamma\)-C$_{3}$N$_{4}$ (<50%). Accordingly, the observed optimal concentration for ZnFe$_{2}$O$_{4}$/S-\(\gamma\)-C$_{3}$N$_{4}$ NCs is 50% S-\(\gamma\)-C$_{3}$N$_{4}$. A further rise in the concentration of S-\(\gamma\)-C$_{3}$N$_{4}$ could result in the formation of e−/h+ pair combination centers, which would gradually reduce the photocatalytic efficiency of NCs [32,44]. A preliminary study is required to conduct a more in-depth analysis of this justification. According to Table 3, the photocatalytic efficiency of ZnFe$_{2}$O$_{4}$/50\% S-\(\gamma\)-C$_{3}$N$_{4}$ NC was noticeably superior to that of several previously reported studies [46–48]. The better photocatalytic efficiency of the NC might be due to the development of good heterojunctions between ZnFe$_{2}$O$_{4}$ and S-\(\gamma\)-C$_{3}$N$_{4}$ as compared to the previously reported composites. The Mn atoms may also facilitate the transportation and separation of the e−/h+ in the composite [21,28,29]. Because the ZnFe$_{2}$O$_{4}$/50\% S-\(\gamma\)-C$_{3}$N$_{4}$ NC was the most efficient photocatalyst, it was used in the recycling study.
Figure 4. Degradation rate (a), degradation contours (b), and % degradation of MB (c) by Mn-ZnFe$_2$O$_4$ NPs.
Table 2. The rate constant (k) values of the 9% Mn-ZnFe₂O₄/50% S-g-C₃N₄ nanocomposites.

| Sr. No. | Nanocomposites | S-g-C₃N₄ (wt.%) | % Degradation | k (min⁻¹)  |
|---------|----------------|-----------------|---------------|-----------|
| 1       | S-g-C₃N₄       | 100             | 51            | 0.00515   |
| 2       | ZnFe₂O₄        | -               | 54            | 0.00673   |
| 3       | 9% Mn-ZnFe₂O₄/10%S-g-C₃N₄ | 10  | 65            | 0.00721   |
| 4       | 9% Mn-ZnFe₂O₄/30%S-g-C₃N₄ | 30  | 89            | 0.00838   |
| 5       | 9% Mn-ZnFe₂O₄/50% S-g-C₃N₄ | 50  | 100           | 0.0142    |
| 7       | 9% Mn-ZnFe₂O₄/70% S-g-C₃N₄ | 70  | 85            | 0.0096    |

The produced Mn-ZnFe₂O₄/50% S-g-C₃N₄ NCs are shown in Figure 6a throughout their stability cycles and photocatalyst reuse. The recycling and stability test was used to gauge how well the material as prepared performed in real-world applications. Six sequential cycles of MB dye degradation under direct sunshine irradiation were used to test the photocatalyst’s stability. After six cycles of the photocatalytic MB elimination test, Mn-ZnFe₂O₄/50% S-g-C₃N₄ NCs’ crystallographic alterations were also examined using XRD, and the relevant findings are shown in Figure 6b. The stability of the crystal structure of Mn-ZnFe₂O₄/50% S-g-C₃N₄ NCs is shown by the lack of noticeable change in the XRD curves before and after the photocatalytic test, as shown in Figure 6b.
Table 3. Comparison of photocatalytic efficiency of the Mn-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ NCs with some previous works.

| Sr. No. | Photocatalyst                  | Contaminant | Light Source | Radiation Time (min.) | Degradation % | Ref. |
|---------|--------------------------------|-------------|--------------|-----------------------|---------------|------|
| 1       | ZnFe$_2$O$_4$@metyle cellulose | Metronidazole | Xe lamp      | 120                   | 92.65         | [49] |
| 2       | Bi$_2$WO$_6$/CoFe$_2$O$_4$     | Bisphenol A  | Solar        | 120                   | 92            | [50] |
| 3       | ZnNd$_x$Fe$_{2-x}$O$_4$        | Rhodamine B  | Xe lamp      | 180                   | 98            | [51] |
| 4       | ZnFe$_2$O$_4$                 | Toluene      | Xe lamp      | 300                   | 57.2          | [52] |
| 5       | ZnO/Fe$_2$O$_4$/g-C$_3$N$_4$   | MO           | Visible      | 150                   | 97.87         | [53] |
| 6       | Pt-BiFeO$_{3}$                | MG           | Solar        | 240                   | 96            | [54] |
| 7       | Mn-ZnO/RGO                    | RhB          | Visible      | 140                   | 99            | [55] |
| 8       | ZnFe$_2$O$_4$@ZnO             | MO           | Visible      | 240                   | 240           | [56] |
| 9       | Mn-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ | MB           | Solar        | 120                   | 100           | Present Work |

Figure 6. (a) Cyclic stability of the Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ NCs through the sixth cycle. (b) The structural stability of Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ NCs was determined by comparing XRD patterns obtained before the first cycle and after the sixth recycling experiment. (c) EIS Nyquist plots of ZnFe$_2$O$_4$, Mn-ZnFe$_2$O$_4$, and Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ NCs and (d) transient photocurrent responses of ZnFe$_2$O$_4$, S-g-C$_3$N$_4$, Mn-ZnFe$_2$O$_4$, and Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ NCs in visible-light irradiation.
The improvements in the Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ photocatalyst’s photocatalytic MB removal ability were further examined using Figure 6c. The transient photocurrent responses of the ready photocatalysts are shown in Figure 6c. The law of transient photocurrent responses and the photocatalytic MB elimination efficiency of the various photocatalysts may be compared using the photocatalytic test results shown in Figure 6c. The photocurrent density of Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ NCs is was highest, indicating the material’s best optical responsiveness and output capacity of photogenerated carriers during the photocatalytic reaction. ZnFe$_2$O$_4$, Mn-ZnFe$_2$O$_4$, and Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ NCs’ EIS spectra are shown in Figure 6d. The outstanding photogenerated carrier migration and separation efficiency of Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ NCs is shown by the fact that their EIS curve’s arc is noticeably lower than that of ZnFe$_2$O$_4$. Furthermore, the PL was measured using a 330 nm excitation wavelength to assess the charge transfer and separation effectiveness of ZnFe$_2$O$_4$, Mn-ZnFe$_2$O$_4$, and Mn-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ heterojunctions, as shown in Figure S3.

3.5. Scavenging Activity

The primary active species for the decomposition of organic pollutants in water are typically superoxide radicals (•O$_2$), hydroxyl radicals (•OH), and photogenerated holes (h$^+$) [46]. Therefore, the active species-generating capacity was examined by incorporating the appropriate scavengers into the suspensions of the MB degradation in the presence of the Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ photocatalyst. In particular, isopropanol (IPA) was specifically utilized to trap •OH, EDTA-2Na to trap holes (h$^+$), and benzoquinone (BQ) to trap •O$_2$. After adding benzoquinone, the efficiency of MB degradation was lowered by 90%. IPA and EDTA-2Na, on the other hand, only suppressed the degradation rates of MB by 61% and 37%, respectively. The effect of trapping chemicals on the dye degradation reaction is depicted in Figure 7. The outcomes demonstrated that •OH and •O$^-_2$ are the main reactive species involved in photocatalytic dye degradation rather than the holes (h$^+$).

![Figure 7](image-url)

Figure 7. Role of radical scavengers in the photocatalytic degradation of MB with Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$. 
4. Photocatalytic Degradation Mechanism

The accelerated degradation of methylene blue by photocatalysts may be attributed to the production of $e^-/h^+$ pairs in the synthesized photocatalysts as predicted via a schematic sketch (Figure 8). Both Mn-ZnFe$_2$O$_4$ and S-g-C$_3$N$_4$ were excited and $e^-/h^+$ pairs were produced on their respective conduction bands (CB) and valence bands (VB) when solar light was irradiated on Mn-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ [47]. Based on the CB/VB edge potentials, the photo-induced electrons easily migrated from the conduction band (CB) of Mn-ZnFe$_2$O$_4$ to the CB of S-g-C$_3$N$_4$ since the CB of Mn-ZnFe$_2$O$_4$ was lower in potential than that of S-g-C$_3$N$_4$. In addition, the holes that were created in the VB of S-g-C$_3$N$_4$ had the potential to migrate to Mn-ZnFe$_2$O$_4$ [48]. In the hybrid composite, the presence of Mn atoms not only lowered the value of $E_g$ but also served as the facilitator for the transit of electrons from S-g-C$_3$N$_4$ to ZnFe$_2$O$_4$. Therefore, by increasing the separation of photoexcited $e^-/h^+$ pairs, doping could significantly lower the chance of charge recombination. The produced $e^-/h^+$ pairs combined with the oxygen and water molecules taken up on the surface of the photocatalyst to generate (•OH and •O$_2^-$) the reactive oxygen species (ROS) [1]. Then, the generated radicals were consumed in the degradation of MB via an oxidative mechanism.

![Figure 8. A schematic MB sunlight catalytic degradation mechanism over the Mn-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ NCs.](image)

5. Conclusions

In summary, ZnFe$_2$O$_4$, Mn-ZnFe$_2$O$_4$ nanoparticles, and a series of Mn-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ nanocomposites were developed via a straightforward hydrothermal technique. XRD, TEM, EDX, and FTIR techniques were used to investigate the structure and purity of the samples. The degradation of MB at room temperature was carried out using ZnFe$_2$O$_4$, Mn-ZnFe$_2$O$_4$, and Mn-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$. The synthesized samples were tested photocatalytically against MB, and it was discovered that the 9%Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ had a very high catalytic efficiency. It was established through the radical scavenging experiment that the 9%Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ utilized electrons, holes, and ROS for MB degradation. For six sequential catalytic cycles, the nanocomposites showed exceptional stability and continuously high levels of MB degradation. The separation and mobility of photoinduced $e^-/h^+$ pairs in 9%Mn-ZnFe$_2$O$_4$/50% S-g-C$_3$N$_4$ may be considerably enhanced by the fine interfaces produced and the synergistic effect between Mn and ZnO as supported by transient photocurrent responses. Both for NPs and NCs, it was found that...
a rate constant for the dye reduction reaction was pseudo-first order. As a result, the 9% Mn-ZnFe₂O₄/50% S-g-C₃N₄ heterojunction is a promising contender and may find use in the photocatalytic destruction of organic pollutants to purify water.

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