Construction of a Well-Defined S-Scheme Heterojunction Based on Bi-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ Nanocomposite Photocatalyst to Support Photocatalytic Pollutant Degradation Driven by Sunlight

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Abstract: Currently, organic dyes and other environmental contaminants are focal areas of research, with considerable interest in the production of stable, high-efficiency, and eco-friendly photocatalysts to eliminate these contaminants. In the present work, bismuth-doped zinc ferrite (Bi-ZnFe$_2$O$_4$) nanoparticles (NPs) and bismuth-doped zinc ferrites supported on sulfur-doped graphitic carbon nitride (Bi-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$) (BZFG) photocatalysts were synthesized via a hydrothermal process. SEM, XRD, and FTIR techniques were used to examine the morphological, structural, and bonding characteristics of the synthesized photocatalysts. The photocatalytic competence of the functional BZFG nanocomposites (NCs) was studied against MB under sunlight. The influence of Bi (0.5, 1, 3, 5, 7, 9, and 11 wt.%) doping on the photocatalytic performance of ZnFe$_2$O$_4$ was verified, and the 9%Bi-ZnFe$_2$O$_4$ nanoparticles exhibited the maximum MB degradation. Then, 9%Bi-ZnFe$_2$O$_4$ NPs were homogenized with varying amounts of S-g-C$_3$N$_4$ (10, 30, 50, 60, and 70 wt.%) to further enhance the photocatalytic performance of BZFG NCs. The fabricated Bi-ZnFe$_2$O$_4$/30%S-g-C$_3$N$_4$ (BZFG-30) composite outperformed ZnFe$_2$O$_4$, S-g-C$_3$N$_4$ and other BZFG NCs in terms of photocatalytic performance. The enriched photocatalytic performance of the BZFG NCs might be ascribed to a more efficient transfer and separation of photo-induced charges due to synergic effects at the Bi-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ interconnection. The proposed modification of ZnFe$_2$O$_4$ using Bi and S-g-C$_3$N$_4$ is effective, inexpensive, and environmentally safe.

Keywords: Bi; hydrothermal method; photocatalyst; MB; polluted water

1. Introduction

Water is an abiotic factor but is very important for all biotic factors, and living organisms cannot survive without it. Toxic dyes are produced and discharged directly into water bodies from homes and industries, such as the textile, dyeing, and printing industries. Therefore, water becomes contaminated and contains bacteria, viruses, and heavy metals, which cause various diseases in human beings, animals, and plants [1]. With increasing...
water demands and dwindling supplies, these harmful compounds must be isolated from wastewater and kept out of the aquatic environment. Nanotechnology and nanoparticles can be used to eliminate organic chemicals, inorganic pollutants, and microorganisms from wastewater via the photocatalytic process [2]. Photocatalytic removal of organic pollutants with semiconductor materials, such as ZnO, TiO$_2$, CdS, and ZnS, for decontamination waste products has received considerable attention during the last two decades [3,4]. However, photocatalysts (such as ZnO, TiO$_2$, CdS, and ZnS) exhibit limitations during photocatalysis under visible radiations due to their high band gap-energies and fast electron–hole recombination [5,6]. Consequently, the development of novel visible-light-induced photocatalysts with increased activity has been a hot research topic for a long time. Among photocatalysts, ferrite (Fe$_2$O$_3$) nanoparticles are of unique significance because of their excellent adsorption properties for cations and anions, low band-gap energy, and low electron–hole recombination [7–9]. These ferrite NPs have potential applications in wastewater treatment; in the biomedical field for diagnosis, drug delivery, drug release, etc.; in electronic devices, such as sensors and biosensors; energy storage; electron magnetic resonance shielding; and recording media. They are highly stable, with a band gap of approximately 1.9 eV; relatively non-toxic; cheap; highly electronically conductive; eco-friendly; and recyclable [10]. Unfortunately, their low quantum efficiency limits their photocatalytic activity for practical use. Therefore, modification has been attempted to enhance the spectral response of these UV-active oxides into the visible range by doping ZnFe$_2$O$_4$ with Bi and developing its heterojunction with S-g-C$_3$N$_4$. Many studies have shown that doping ZnFe$_2$O$_4$ with appropriate metal ions and its composite formation with another suitable semiconductor material improve optical and photocatalytic characteristics.

Savunthari et al. reported the synthesis of (Cu, Bi) codoped ZnFe$_2$O$_4$ nanoparticles via a solution combustion route. The synthesized codoped NPs exhibited excellent bisphenol A degradation compared to undoped NPs [11]. Patil et al. used the coprecipitation approach to manufacture Gd$^{3+}$-doped ZnFe$_2$O$_4$ nanoparticles, demonstrating improved 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. Y-ZnFe$_2$O$_4$ has higher photocatalytic effectiveness than pure zinc ferrite. Under visible light, cobalt-doped zinc ferrite decomposed methylene blue more efficiently than ZnFe$_2$O$_4$. Many researchers have concluded that ZnFe$_2$O$_4$ has a finite band-gap energy and might form an effective heterojunction when combined with another semiconductor or metal [13–15]. The auto-combustion approach was used to synthesize visible-light-driven photocatalyst BiFe$_3$O$_4$ (BFO) nanoparticles. The 2% BFO demonstrated superior antibacterial activity against S. aureus and E. coli.) and photocatalytic efficiency against MB (81%) compared to undoped and other BFO samples [16]. Similarly, Amini et al. used BFO to remove chlorobenzene (CB). The produced BFO outperformed TiO$_2$ nanomaterial and achieved a maximum of 87.92% removal of CB under UV light [17].

The g-C$_3$N$_4$ semiconductor has shown significant photocatalytic proficiency under visible light due to its favorable characteristics, such as high stability and reduced band-gap energy, improving its capacity to absorb visible radiation [18,19]. However, the quick recombination of photoinduced e$^-$/h$^+$ pairs in g-C$_3$N$_4$ makes it unsuitable for use as a photocatalyst [18]. S-doping alters the bandgap of g-C$_3$N$_4$ and enhances the mobility and separation of e–h pairs. Hong et al. reported that the photocatalytic H$_2$ production efficiency of mesoporous S-g-C$_3$N$_4$ is 30 times that of pure g-C$_3$N$_4$. Similarly, S-g-C$_3$N$_4$ was reported to exhibit an approximately 1.38 times greater photocatalytic CO$_2$ reduction rate than that of pure g-C$_3$N$_4$ [20]. Under visible light, porous S-g-C$_3$N$_4$ had exhibited better photocatalytic degradation and adsorption of Rhodamine B dye than pure g-C$_3$N$_4$ [21]. By using a template-free chemical coprecipitation technique, Sukanya et al. effectively synthesized ZnFe$_2$O$_4@g$-C$_3$N$_4$ nanocomposites. The nanocomposite exhibited nine times better photocatalytic efficiency than pure ZnFe$_2$O$_4$ and degraded 89% RhB in 30 min under visible
light [22]. Pure and modified mesoporous TiO$_2$ nanoparticles with varying loadings of NiO (3–20.0 wt.%) were created using surfactant-assisted sol–gel technique with cetyltrimethylammonium bromide as a template. The photocatalytic performance of the as-synthesized samples was evaluated for the photodegradation of brilliant green (BG) and phenol, as well as hydrogen generation under visible light. Ten percent NiO/TiO$_2$ had resulted in the highest photocatalytic activity [23]. According to Sohier et al., a mesoporous silica/bismuth vanadate composite was created using the ultrasonication technique. The most effective photocatalytic material against MB and BG was mSiO$_2$/BiVO$_4$ with 10.0 weight percent mesoporous SiO$_2$ [24].

Motivated by the enhanced photocatalytic performance of metal-doped ZnFe$_2$O$_4$, S-g-C$_3$N$_4$, and ZnFe$_2$O$_4$/g-C$_3$N$_4$, we fabricated ZnFe$_2$O$_4$, Bi-doped ZnFe$_2$O$_4$, and Bi-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ via the hydrothermal method and examined their photocatalytic properties. S-g-C$_3$N$_4$ was synthesized by polycondensation of thiourea. The photocatalytic characteristics of synthesized materials were investigated using MB, a model dye. The study was comprised of two phases. The photocatalytic properties of (0.5, 1, 3, 5, 7, and 9 wt.%) of Bi-doped zinc ferrite (Bi-ZnFe$_2$O$_4$) NPs were examined in phase one. The 9% Bi-ZnFe$_2$O$_4$ NPs manifested the highest dye degradation efficiency. In the second phase, the 9% Bi-ZnFe$_2$O$_4$ NPs were mixed with 10, 30, 50, and 70 wt.% concentrations of S-g-C$_3$N$_4$ to produce Bi-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ NCs to further enhance the photocatalytic activity. The 9% Bi-ZnFe$_2$O$_4$/30% S-g-C$_3$N$_4$ nanocomposite exhibited the best photocatalytic activity compared to pure ZnFe$_2$O$_4$, 9% Bi-ZnFe$_2$O$_4$, and S-g-C$_3$N$_4$. To the best of our knowledge, the synthesis of Bi-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ heterojunctions via the hydrothermal approach has not been reported to date. This synthetic substance be applied in the wastewater treatment industry.

2. Experimental Section

2.1. Materials

Iron (III) nitrate nonahydrate Fe(NO$_3$)$_3$·9H$_2$O (99.99%), Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) (98%), bismuth nitrate pentahydrate Bi(NO$_3$)$_3$·5H$_2$O (99%), polyvinylpyrrolidone (PVP), sodium hydroxide (NaOH) (98%), thiourea (CH$_4$N$_2$S) (99.99%), and methylene blue (C$_{16}$H$_{18}$ClN$_3$S) were purchased from Merck and used as received.

2.2. Synthesis of Bismuth-Doped Zinc Ferrites

The hydrothermal method was used to synthesize ZnFe$_2$O$_4$ and Bi-ZnFe$_2$O$_4$ NPs [25]. Briefly, to synthesize ZnFe$_2$O$_4$ NPs, 1.61 g of Fe(NO$_3$)$_3$·9H$_2$O (0.2 M) and 1.19 g of Zn(NO$_3$)$_2$·6H$_2$O (0.2 M) were combined in a beaker, to which 50 mL water was added. The mixture was then allowed to stir for about 1 h, at which point 10 mL of PVP solution (1%) was added and stirred. Once the pH of the reaction mixture reached a constant of 11–12, NaOH solution (6 M) was gradually added to the reaction mixture on a magnetic stirrer. Then, the reaction mixture was placed into an autoclave with a Teflon coating and baked for about 16 h at 180 °C. The reaction mixture was filtered, rinsed several times in distilled water, dried in an oven at 100 °C for roughly four hours, and crushed after the autoclave had been running for 16 h. The orange–brown NPs were collected. For the synthesis of Bi-doped zinc ferrites varying weight percentages (0.5%, 1%, 3%, 5%, 7%, 9%, and 11%) of Bi(NO$_3$)$_3$·5H$_2$O were used. For the synthesis of 0.5% Bi-doped zinc ferrite NPs, 0.24 g of Bi(NO$_3$)$_3$·5H$_2$O was dissolved in a beaker containing 100 mL of 0.2 M Fe(NO$_3$)$_3$·9H$_2$O and 0.2 M of Zn(NO$_3$)$_2$·6H$_2$O mixture and stirred for 1 h. The next steps of the synthesis of Bi-ZnFe$_2$O$_4$ were the same as those for ZnFe$_2$O$_4$ NPs. The same procedure was followed during the synthesis of other (1%, 3%, 5%, 7%, 9%, and 11%) Bi-ZnFe$_2$O$_4$ NPs.

2.3. Synthesis of Sulfur-Doped Graphitic Carbon Nitride

In order to prepare sulfur-doped graphitic carbon nitride, 8 g of thiourea was added to an alumina crucible and covered with a lid. The thiourea was heated to 550 °C for about 5 h at a rate of 5 °C/min. a muffle furnace. The prepared sulfur-doped graphitic carbon nitride was then allowed to cool, crushed, and stored for further use [26].
2.4. Synthesis of Bi-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ Nanocomposites

A series of Bi-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ nanocomposites was made by incorporating 9% Bi-ZnFe$_2$O$_4$ with varying concentrations of S-g-C$_3$N$_4$ (10, 30, 50, 60, and 70 wt.%) via a surfactant-assisted hydrothermal process (Figure 1). For the preparation of 9% Bi-ZnFe$_2$O$_4$/10% S-g-C$_3$N$_4$, 0.19 g of S-g-C$_3$N$_4$, 1.61 g of Fe(NO$_3$)$_3$·9H$_2$O, 1.19 g of Zn(NO$_3$)$_2$·6H$_2$O, and 0.24 g of Bi(NO$_3$)$_3$·5H$_2$O were combined in a beaker and dissolved in 100 mL of water. This mixture was allowed to stir on a magnetic stirrer for 1 h with the addition of 10 mL of PVP solution. Finally, orange-brown precipitates were obtained by following the same steps as those described in Section 2.2. The detailed composition of Bi-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ with corresponding catalytic efficiency is presented in Table 1.

![Figure 1. Schematic representation of the synthesis of Bi-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$.](image)

Table 1. Composition of Bi-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ nanocomposites and their corresponding photocatalytic activities.

<table>
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<th>Sr. No</th>
<th>Nanocomposites</th>
<th>Wt. in gm.</th>
<th>Photocatalytic Activity</th>
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<td></td>
<td></td>
<td>S-g-C$_3$N$_4$</td>
<td>Fe(NO$_3$)$_3$</td>
</tr>
<tr>
<td>1</td>
<td>9% Bi-ZnFe$_2$O$_4$/10% S-g-C$_3$N$_4$</td>
<td>0.19</td>
<td>1.61</td>
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<td>2</td>
<td>9% Bi-ZnFe$_2$O$_4$/30% S-g-C$_3$N$_4$</td>
<td>0.58</td>
<td>1.61</td>
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<td>0.96</td>
<td>1.61</td>
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<td>4</td>
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<td>1.61</td>
</tr>
<tr>
<td>5</td>
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<td>00</td>
</tr>
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<td>6</td>
<td>9% Bi-ZnFe$_2$O$_4$</td>
<td>00</td>
<td>1.61</td>
</tr>
</tbody>
</table>

2.5. Photocatalytic Activity

The photocatalytic activities of zinc ferrites, Bi-doped zinc ferrites, sulfur-doped graphitic carbon nitride, and nanocomposites were studied under solar light irradiation. An
aqueous solution of an organic dye, methylene blue, was used as the standard contaminant. An amount of 0.2 g of each photocatalyst was added to a beaker, to 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. Then, the suspension was positioned under solar light in an open atmosphere, and aliquots of 5 mL were collected every 30 min. A UV-Vis spectrophotometer was used to evaluate the photocatalytic activity of the collected samples after centrifugation.

2.6. Characterization

The XRD (Bruker AXS, D8-S4, Billerica, MA, USA) pattern was determined by applying Cu Kα radiation (\(k = 1.54056 \text{ Å}\)) at 40 kV, and 30 mA at room temperature was used to identify the structure of catalysts, whereas SEM-EDS detected the morphology (Hitachi, S-4800, Tokyo, Japan) and the elements present. A UV-vis-NIR spectrophotometer measured the photocatalytic and UV-visible absorption spectra in the wavelength range of 800 nm to 200 nm (UV-770, Jasco, Tokyo, Japan). FT-IR spectrometers measured functional groups in the 4000–400 cm\(^{-1}\) range with a resolution of 1 cm\(^{-1}\) (Perkin 400 FT-IR, Peterborough, England). The surface morphologies of the photocatalysts were examined using a transmission electron microscope (TEM, JEOL-JEM-1230, Tokyo, Japan).

3. Results and Discussion

3.1. XRD Analysis

Figure 2 shows the X-ray diffractograms of ZnFe\(_2\)O\(_4\), 9% Bi-ZnFe\(_2\)O\(_4\), S-g-C\(_3\)N\(_4\), and 9% Bi-ZnFe\(_2\)O\(_4\)/30% S-g-C\(_3\)N\(_4\) samples. Seven peaks were observed in the case of pure ZnFe\(_2\)O\(_4\) 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\(^\circ\), respectively, that fit well with the pattern of standard zinc ferrites with JCPDS file 01-077-0011 [12,27]. The characteristic peaks of zinc ferrites were also present in bismuth-doped zinc ferrite, indicating that no significant change in the structure of zinc ferrite occurred when it was doped with bismuth metal. Two characteristic peaks at \(2\theta = 13.1^\circ\) and 27.4\(^\circ\) were observed in the XRD pattern of S-g-C\(_3\)N\(_4\); the crystal plane (002) was attributed to the interlayer assembly of aromatic systems, and the (100) plane was ascribed to the interplanar arrangement of aromatic systems (JCPDS file # 00-087-1526) [28,29]. After coupling with S-g-C\(_3\)N\(_4\), the crystal phase of Bi-ZnFe\(_2\)O\(_4\) remained unchanged, and the (002) crystal plane of the S-g-C\(_3\)N\(_4\) (weak) was indicated in the composite systems. In 9%Bi-ZnFe\(_2\)O\(_4\)/30% S-g-C\(_3\)N\(_4\) composites, owing to the high crystallinity of Bi-ZnFe\(_2\)O\(_4\), the characteristic peaks of Bi-ZnFe\(_2\)O\(_4\) are prominent. The appearance of the characteristic peaks of both Bi-ZnFe\(_2\)O\(_4\) and S-g-C\(_3\)N\(_4\) in composites indicates the successful fabrication of Bi-ZnFe\(_2\)O\(_4\)/S-g-C\(_3\)N\(_4\) composites [30,31].

3.2. TEM and EDX Analyses

The form, size, and distribution of the particles in the as-prepared nanomaterials, as well as their elemental makeup, were disclosed by TEM profiles with EDX spectra. As shown in Figure 3a, pure S-g-C\(_3\)N\(_4\) has an uneven, wrinkled, sheet-like shape. Figure 3b depicts the nanoparticles of ZnFe\(_2\)O\(_4\), which range in size from 24 to 38 nm. With particle sizes ranging from 17 to 26 nm, Bi-ZnFe\(_2\)O\(_4\) is visible as a spherical nanoparticle agglomerated structure (Figure 3c). TEM was conducted as described in Figure 3d to further demonstrate the heterojunction of Bi-ZnFe\(_2\)O\(_4\)/S-g-C\(_3\)N\(_4\). The S-g-C\(_3\)N\(_4\) nanosheets were completely covered by spherical Bi-ZnFe\(_2\)O\(_4\) NPs with equal distribution, as shown in the TEM image of the NCs. The sheet-like S-g-C\(_3\)N\(_4\) 2D materials aid in enhancing photo-absorption, improving electron transport capabilities, and facilitating longer lifetimes for photo-excited charge carriers.
3.2. TEM and EDX Analyses

The form, size, and distribution of the particles in the as-prepared nanomaterials, as well as their elemental makeup, were disclosed by TEM profiles with EDX spectra. As shown in Figure 3a, pure S-g-C3N4 has an uneven, wrinkled, sheet-like shape. Figure 3b depicts the nanoparticles of ZnFe2O4, which range in size from 24 to 38 nm. With particle sizes ranging from 17 to 26 nm, Bi-ZnFe2O4 is visible as a spherical nanoparticle agglomerated structure (Figure 3c). TEM was conducted as described in Figure 3d to further demonstrate the heterojunction of Bi-ZnFe2O4/S-g-C3N4. The S-g-C3N4 nanosheets were completely covered by spherical Bi-ZnFe2O4 NPs with equal distribution, as shown in the TEM image of the NCs. The sheet-like S-g-C3N4 2D materials aid in enhancing photo-absorption, improving electron transport capabilities, and facilitating longer lifetimes for photo-excited charge carriers.

3.3. FTIR and XPS Analyses

A comparison between FT-IR spectra of prepared photocatalysts is shown in the wavenumber range 4000–450 cm\(^{-1}\). The FT-IR spectrum of ZnFe2O4 confirms the absence of all functional groups and the presence of an M-O bond. The peak at 3452 cm\(^{-1}\) is the result of O-H bond stretching, whereas the peak at 1488 cm\(^{-1}\) is the result of bending of the O-H bond. The peak at 534 cm\(^{-1}\) confirms M-O bond stretching [32]. The FT-IR spectrum of 9% Bi-ZnFe2O4 shows a small change in peaks compared to pure ZnFe2O4. This slight variation in peak positions confirms the successful formation of Bi-doped ZnFe2O4.

In S-g-C3N4, the broadband at 3172 cm\(^{-1}\) is the result of O-H bond stretching, the peaks between 1500–2000 cm\(^{-1}\) are the result of the stretching vibrations of C=N, and the peaks between 1500 and 1000 cm\(^{-1}\) are due to C-N bond stretching [33]. The peak at 805 cm\(^{-1}\) indicates the triazine unit. The FT-IR spectrum of Bi-ZnFe2O4/S-g-C3N4 contains peaks corresponding to both Bi-ZnFe2O4 and S-g-C3N4, confirming the successful formation of the composite (Bi-ZnFe2O4/S-g-C3N4) [34]. Bi-ZnFe2O4/S-g-C3N4 was analyzed using XPS (Figure S1) to determine its chemical makeup and the electronic states of each of its constituent components. XPS analysis confirmed that Bi-ZnFe2O4/S-g-C3N4 contains Bi, ZnFe2O4, and S-g-C3N4, as also indicated by TEM and EDX.
3.3. FTIR and XPS Analyses

A comparison between FT-IR spectra of prepared photocatalysts is shown in the wavenumber range 4000–450 cm\(^{-1}\) (Figure 4). The FT-IR spectrum of ZnFe\(\text{O}_4\) confirms the absence of all functional groups and the presence of an M-O bond. The peak at 3452 cm\(^{-1}\) is the result of O-H bond stretching, whereas the peak at 1488 cm\(^{-1}\) is the result of bending of the O-H bond. The peak at 534 cm\(^{-1}\) confirms M-O bond stretching [32]. The FT-IR spectrum of 9% Bi-ZnFe\(\text{O}_4\) shows a small change in peaks compared to pure ZnFe\(\text{O}_4\). This slight variation in peak positions confirms the successful formation of Bi-doped ZnFe\(\text{O}_4\). In S-g-C\(\text{N}_4\), the broadband at 3172 cm\(^{-1}\) is the result of O-H bond stretching, the peaks between 1500–2000 cm\(^{-1}\) are the result of the stretching vibrations of C=N, and the peaks between 1500 and 1000 cm\(^{-1}\) are due to C-N bond stretching [33]. The peak at 805 cm\(^{-1}\) indicates the triazine unit. The FT-IR spectrum of Bi-ZnFe\(\text{O}_4\)/S-g-C\(\text{N}_4\) contains peaks corresponding to both Bi-ZnFe\(\text{O}_4\) and S-gC\(\text{N}_4\), confirming the successful formation of the composite (Bi-ZnFe\(\text{O}_4\)/S-g-C\(\text{N}_4\)) [34]. Bi-ZnFe\(\text{O}_4\)/S-g-C\(\text{N}_4\) was analyzed using XPS (Figure S1) to determine its chemical makeup and the electronic states of each of its constituent components. XPS analysis confirmed that Bi-ZnFe\(\text{O}_4\)/S-g-C\(\text{N}_4\) contains Bi, ZnFe\(\text{O}_4\), and S-g-C\(\text{N}_4\), as also indicated by TEM and EDX.

![Figure 4. FTIR spectra of composites of ZnFe\(\text{O}_4\), S-gC\(\text{N}_4\), 9% Bi-ZnFe\(\text{O}_4\), and 9% Bi-ZnFe\(\text{O}_4\)/30S-gC\(\text{N}_4\).](image-url)

3.4. Photocatalytic Degradation Study

Two stages were employed to determine the photocatalytic activity of synthesized samples in sunlight. In the presence of light, an aqueous methylene blue solution was used to examine the photocatalytic activity of pure and Bi-doped zinc ferrite NPs (0, 0.5, 1, 3, 5, 7, 9, and 11 wt.\%). A UV-Vis spectrophotometer with a wavelength of 200–800 nm was used to track the dye degradation rate. Among the prepared nanoparticles, 9% Bi-ZnFe\(\text{O}_4\) showed the highest degradation of MB dye in sunlight and exhibited 65% dye degradation within 150 min (Figure S2 and Figure 5a). There was a gradual increase in photocatalytic activity of Bi-ZnFe\(\text{O}_4\) NPs up to 9% Bi doping, which may have occurred because Bi-
doping decreased the bandgap of ZnFe$_2$O$_4$ and facilitated e$^-$/h$^+$ pair generation, inhibiting e$^-$/h$^+$ pair recombination. 9% Bi doping was determined as the optimal concentration of Bi$^{3+}$ ions. Increasing the Bi$^{3+}$ ion concentration beyond this <9 wt.%. leads to a decrease in photocatalytic activity of Bi-ZnFe$_2$O$_4$ NPs (Figure 5a,b). The observed photocatalytic activity of all the Bi-ZnFe$_2$O$_4$ NPs was better than that of ZnFe$_2$O$_4$ NPs (Figure 5b) [11]. A linear relationship was observed between the radiation period and ln (C/Co) for Bi-(containing 30% S-g-C$_3$N$_4$)

In the next step, the 9% Bi-ZnFe$_2$O$_4$ NPs were homogenized with varying amounts of S-g-C$_3$N$_4$ (as shown in Table 2) to develop Bi-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ NCs, the photocatalytic activity was determined in 15 min intervals. The constructed NCs were placed in the dark before exposure to sunlight to induce an equilibrium between dye adsorption and desorption on the ZF, BZFG10, BZFG30, BZFG50, and BZFG70 catalysts. The corresponding amounts of MB adsorbed on the catalysts are shown in Figure 6a.

The graph shown in Figure 6a unequivocally demonstrates that the samples absorbed only modest amounts of dye. Samples were exposed to sunshine, and the BZFG30 NCs exhibited maximum dye degradation compared to other samples (Figure 6b). According to the % degradation plots (Figure 6c) and degradation contours (Figure 6d), upon enhancement of SG contents in the BZFG NCs, dye degradation was increased to BZFG30 (containing 30% S-g-C$_3$N$_4$) and decreased for BZFG50 and BZFG70 (<30% S-g-C$_3$N$_4$). The observed degradation efficiencies of SG, Bi-ZnFe$_2$O$_4$, BZFG10, BZFG30, BZFG50, and BZFG70 catalysts were 41%, 58%, 63%, 99%, 81%, and 72%, respectively, after 120 min of sunlight irradiation.

**Table 2.** Rate constant (k) values of the 9% Bi-ZnFe$_2$O$_4$/S-g-C$_3$N$_4$ nanocomposites.

<table>
<thead>
<tr>
<th>Sr. No.</th>
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<th>k (min$^{-1}$)</th>
<th>Nanocomposite Code</th>
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<td>1</td>
<td>S-g-C$_3$N$_4$</td>
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<td>SG</td>
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</tr>
<tr>
<td>2</td>
<td>9% Bi-ZnFe$_2$O$_4$</td>
<td>-</td>
<td>0.0088</td>
<td>BZF</td>
<td>0.941</td>
</tr>
<tr>
<td>3</td>
<td>9% Bi-ZnFe$_2$O$_4$/105-g-C$_3$N$_4$</td>
<td>10</td>
<td>0.0095</td>
<td>BZFG10</td>
<td>0.974</td>
</tr>
<tr>
<td>4</td>
<td>9% Bi-ZnFe$_2$O$_4$/305-g-C$_3$N$_4$</td>
<td>30</td>
<td>0.0169</td>
<td>BZFG30</td>
<td>0.986</td>
</tr>
<tr>
<td>5</td>
<td>9% Bi-ZnFe$_2$O$_4$/508-g-C$_3$N$_4$</td>
<td>50</td>
<td>0.0156</td>
<td>BZFG50</td>
<td>0.989</td>
</tr>
<tr>
<td>6</td>
<td>9% Bi-ZnFe$_2$O$_4$/705-g-C$_3$N$_4$</td>
<td>70</td>
<td>0.0129</td>
<td>BZFG70</td>
<td>0.978</td>
</tr>
</tbody>
</table>

The produced nanocomposite sample contains both S-g-C$_3$N$_4$ and Bi-ZnFe$_2$O$_4$ NPs, as the improvement of the photocatalytic active sites and an increase in capacitive nature.
The reduced photocatalytic efficacy of S-g-C₃N₄ sheets, which resemble structured catalysts, is caused by the photocatalyst being lost during the recycling process. The catalytic activity is increased by integrating the magnetic NPs into the S-g-C₃N₄ layer structure. As a result of the robust contact between the NPs, whereby the electrons are diffused in the trap state, the photo-induced electron in the Bi-ZnFe₂O₄ was transported to S-g-C₃N₄. To encourage the transition of electron holes from one NP to another and to stop photo-excited electron–hole pairs from recombining, the composite creates a heterojunction. Contrary to pure materials, the heterojunction between the particles contributes to the improvement of the photocatalytic active sites and an increase in capacitive nature. The produced nanocomposite sample contains both S-g-C₃N₄ and Bi-ZnFe₂O₄ NPs, as shown by the TEM images. The EDX spectrum (Figure 3e) evidences that Zn and Fe, as well as Bi, S, O, and C, are present in the nanocomposite. Improved charge separation and transfer via Bi-ZnFe₂O₄ and S-g-C₃N₄ coupling, as well as increased visible light absorption due to Bi doping in ZnFe₂O₄, may account for the improved degradation by BZFG [35–37]. Figure 6b depicts the % photocatalytic degradation of MB by NCs.

The Langmuir–Hinshelwood model was applied to explain the kinetics [37]. It is evident that the dye degradation by the NCs under sunlight is fit to pseudo-first-order kinetics (Figure 6c). The calculated values of the rate constant (k) of each are shown in Figure S4. BZFG30 (0.0169 min⁻¹) and SG (0.0063 min⁻¹) had the highest and lowest “k” values, respectively. The BZFG30 NCs completely decolorized the MB within 120 min, with a “k” value 1.92 and 2.7 times that of Bi-ZnFe₂O₄ (0.0088 min⁻¹) and SG (0.0063 min⁻¹), respectively. As the S-g-C₃N₄ concentration increases from 10% to 30% in BZFG NCs, dye degradation also enhances before reducing in association with concentrations of more than
30%. Thus, 30% S-g-C3N4 is the ideal concentration for BZFG NCs to exhibiting maximum photocatalytic activity. Furthermore, an increase in S-g-C3N4 concentration (<30%) might produce e-h pair combination centers, successively decreasing the photocatalytic efficiency [35,38]. To further analyze this rationalization, a preliminary investigation is required. The photocatalytic efficiency of BZFG50 NC is significantly higher than that reported in previous research, as shown in Table 3.

Table 3. Comparison of photocatalytic efficiency of the Bi-ZnFe2O4/S-g-C3N4 NCs with those reported in previous works.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Photocatalyst</th>
<th>Contaminant</th>
<th>Light Source</th>
<th>Radiation Time (min.)</th>
<th>Degradation %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TiO2</td>
<td>MB</td>
<td>Xe lamp</td>
<td>120</td>
<td>99</td>
<td>[39]</td>
</tr>
<tr>
<td>2</td>
<td>FeOOH-LDO</td>
<td>MB</td>
<td>Xe lamp</td>
<td>180</td>
<td>92</td>
<td>[40]</td>
</tr>
<tr>
<td>3</td>
<td>AgTiO2</td>
<td>MB</td>
<td>UV</td>
<td>200</td>
<td>97.1</td>
<td>[41]</td>
</tr>
<tr>
<td>4</td>
<td>ZnS</td>
<td>MB</td>
<td>Xe lamp</td>
<td>120</td>
<td>77.2</td>
<td>[42]</td>
</tr>
<tr>
<td>5</td>
<td>Bi3SbO4</td>
<td>MB</td>
<td>Xe lamp</td>
<td>10 h</td>
<td>96.7</td>
<td>[43]</td>
</tr>
<tr>
<td>6</td>
<td>TiO2/GO</td>
<td>MB</td>
<td>Solar</td>
<td>140</td>
<td>97.5</td>
<td>[44]</td>
</tr>
<tr>
<td>7</td>
<td>MgS/Ag2MoO4</td>
<td>MB</td>
<td>Visible</td>
<td>200</td>
<td>90</td>
<td>[45]</td>
</tr>
<tr>
<td>8</td>
<td>Cu2O/BiVO4</td>
<td>MB</td>
<td>Visible</td>
<td>180</td>
<td>73</td>
<td>[46]</td>
</tr>
<tr>
<td>9</td>
<td>Bi-ZnFe2O4/S-g-C3N4</td>
<td>MB</td>
<td>Solar</td>
<td>120</td>
<td>97</td>
<td>Present Work</td>
</tr>
</tbody>
</table>

The stability of the BZFG NCs was investigated by the gradual degradation of MB five times. The obtained findings demonstrate effective MB breakdown; even after the fifth recycling, the percentage was still above 92 percent (Figure 7a). Possible explanations for the small decrease in catalytic effectiveness include partial blockage of active sites. Therefore, the BZFG NC catalysts might function as reliable, effective, and reusable NCs. Figure 7b, which represents the first and fifth cycles of dye photodegradation assessments, shows the XRD patterns of BZFG NCs. Stability analysis revealed that the crystal phase structure of the BZFG NCs did not change noticeably before or after the organic pollutant recycling investigations, demonstrating chemical structural robustness.

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4. Photocatalytic Degradation Mechanism

The photocatalytic degradation mechanism follows the same step scheme (S-scheme) as that shown in the schematic sketch in Figure 8. The enhanced degradation of methylene...
The formation and purity of samples were examined using XRD, EDX, and FTIR characterizations. The photocatalytic efficiency of the fabricated samples was examined by degrading MB at ambient temperature under sunlight. In a comparative investigation of the photo-ZnFe₂O₄ nanoparticles, as well as a series of Bi-ZnFe₂O₄/S-g-C₃N₄ nanocomposites. The pseudo-first-order rate constant. The 9%Bi-ZnFe₂O₄/30%S-g-C₃N₄ NCs completely mineralized the MB within 120 min, with a “k” 3.5 times that of ZnFe₂O₄. Therefore, the heterojunction of 9 percent Bi-ZnFe₂O₄ and 30 percent S-g-C₃N₄ is a viable option for the photocatalytic removal of organic pollutants from contaminated waste.

5. Conclusions

In this study, we used a simple hydrothermal approach to produce ZnFe₂O₄ and Bi-ZnFe₂O₄ nanoparticles, as well as a series of Bi-ZnFe₂O₄/S-g-C₃N₄ nanocomposites. The formation and purity of samples were examined using XRD, EDX, and FTIR characterizations. The photocatalytic efficiency of the fabricated samples was examined by degrading MB at ambient temperature under sunlight. In a comparative investigation of the photocatalytic effectiveness of the synthesized samples against MB, 9%Bi-ZnFe₂O₄/30%S-g-C₃N₄ exhibited maximum catalytic efficiency, and dye degradation was found to have a pseudo-first-order rate constant. The 9%Bi-ZnFe₂O₄/30%S-g-C₃N₄ NCs completely mineralized the MB within 120 min, with a “k” 3.5 times that of ZnFe₂O₄. Therefore, the heterojunction of 9 percent Bi-ZnFe₂O₄ and 30 percent S-g-C₃N₄ is a viable option for the photocatalytic removal of organic pollutants from contaminated waste.

**Figure 8.** Schematic representation of the MB sunlight catalytic degradation mechanism over the BZFG NCs.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal12101175/s1, Figure S1: High-resolution XPS spectra of BZFG NCs; (a) Zn 2p, (b) O 1s, (c) Fe 2p, (d) Bi 4f, (e) C 1s and (f) N 1s; Figure S2: Photodegradation of MB by Bi-ZnFe2O4 NPs at 10 minutes (a) and after 150 minutes (b) of sunlight irradiation (Degradation contours); Figure S3: First-order kinetics plot of S-g-C3N4, Bi-ZnFe2O4 Ns, Bi-ZnFe2O4/S-g-C3N4 NCs; Figure S4: Photodegradation rate constant k (min⁻¹) of Methylene Blue by S-g-C3N4, Bi-ZnFe2O4 NPs, Bi-ZnFe2O4/S-g-C3N4 NCs.

Author Contributions: Conceptualization, writing-original draft Preparation, M.L. and M.J.; methodology, K.J.; software, resources, S.T.; validation, project administration, writing and editing, S.I., G.L. and W.B.K.; writing review and editing, M.A.Q.; investigation, H.A.; resources, R.A.P.; data curation, E.A.; writing-original draft preparation, A.-E.F. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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

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