

A Review on Photocatalytic degradation of Congo red Dye Using Graphene-BiFeO₃ Nanocomposite

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Abstract:

The increasing discharge of synthetic dyes, particularly azo dyes such as Congo red, into water bodies has become a serious environmental concern due to their toxicity, stability, and resistance to biodegradation. In this study, graphene–BiFeO₃ nanocomposites were investigated as efficient visible-light-driven photocatalysts for the degradation of Congo red dye. Pure BiFeO₃ was synthesized using a chemical route followed by annealing, and the composite was prepared by ultrasonically dispersing BiFeO₃ with graphene in a suitable solvent medium. Structural analysis confirmed the formation of rhombohedral BiFeO₃ with minor impurity phases, while morphological studies revealed that BiFeO₃ nanoparticles were uniformly anchored on graphene sheets, providing a high surface area and improved interaction with dye molecules. Photocatalytic activity was evaluated under UV–visible light irradiation using a Congo red solution, and degradation was monitored through UV–Vis spectroscopy. The results demonstrated that the graphene–BiFeO₃ nanocomposite exhibited significantly enhanced photocatalytic performance compared to pure BiFeO₃. Approximately 75% degradation of Congo red dye was achieved within 120 minutes using the composite, whereas pure BiFeO₃ showed only about 40% degradation under similar conditions. This improvement is attributed to the synergistic effects of graphene, which enhances charge separation, reduces electron–hole recombination, and increases adsorption capacity. The study confirms that graphene–BiFeO₃ nanocomposites are promising, efficient, and sustainable photocatalysts for the treatment of dye-contaminated wastewater under visible light irradiation.

Keywords: Photocatalysis; Congo red dye; Graphene–BiFeO₃ nanocomposite; Visible light

1. Introduction

The fast growth of industrialization and urbanization has resulted in the augmentation of discharge of detrimental pollutants in the aquatic environments, and synthetic dyes are especially concerning. The textile, paper, leather, and printing industries emit a lot of dye-containing wastewater into the water bodies, which leads to serious environmental pollution. Congo red (CR), a hydrophilic anionic azo dye with -N=N- bonds is a popular dye because of its high chemical stability and high color intensity. Nonetheless, this stability also renders it very unbiodegradable in nature and thus it can last long periods in water systems. Moreover, Congo red and its decomposition by-products are also toxic, mutagenic and can be cancer causing, and pose dire dangers to human health and aquatic biosphere. The traditional wastewater treatment procedures such as

adsorption, coagulation-flocculation, membrane filtration, and biological treatment are not sufficient because of incomplete decay, high operation expenses, and produces the secondary pollutants like sludge. Therefore, photocatalysis and, in general, the use of advanced oxidation processes (AOPs) have become the focus of attention as effective and environmentally friendly methods of completely mineralizing organic pollutants into harmless substances, such as carbon dioxide and water. (Z. Li et al., 2013)

The process of photocatalysis with semiconductor materials has become a promising process because it is sustainable and capable of harnessing solar energy. A visible-light-responsive photocatalyst is bismuth ferrite (BiFeO₃), which has a narrow band gap (~2.1–2.7 eV), and can effectively absorb sunlight. It also exhibits good chemical stability and multiferroic

properties. Nevertheless, it has a low photocatalytic efficiency due to the rapid recombination of electrons and holes, small surface area, and inefficient charge transport. To overcome these challenges, graphene has been included to create nanocomposites with BiFeO₃. Graphene has high electrical conductivity, high surface area and high electron mobility that promote charge separation and adsorption capacity that greatly improves the photocatalytic performance. (Fatima et al., 2020)

2. Properties Of Congo Red Dye

Congo red (CR) is a synthetic azo dye anionic dye that is commonly used in textile, paper, rubber, and

printing industries whose chemical formula is C₃₂H₂₂N₆O₆S₂.2Na. It has two azo (-N=N-) linkages between aromatic rings and sulfonate (RSO₃⁻) functional groups. These structural attributes result in its strong red color, high solubility in water and chemical stability in aqueous environments. The existence of a large conjugated 5-electron chain of phenomena allows the Congo red to be used as a” potent light absorber, which is why it is a useful dye and a pH indicator. Its attraction to cellulose fibres further increases its usability in textile dyeing. But these desirable properties also render Congo red very persistent after entering the environment. (Dryaz et al., 2021)

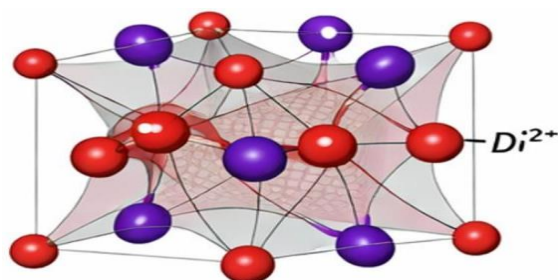


Figure 1: Structure of Congo Red Dye

The ability to be readily dispersed by its high solubility in water because of sodium sulfonate groups and the difficulty in eliminating it in wastewater is one of the major properties of Congo red. Its structure features azo bonds (-N=N-), which are very stable and difficult to break down through biodegradation resulting in “long-term environmental retention. Also, in some circumstances, Congo red may break down to form aromatic amines, which are more toxic and maybe carcinogenic than the original substance. Its growth in water bodies inhibits the passage of light to the water surface and hence interferes with photosynthesis and adversely impacts aquatic life. These characteristics also indicate the need to have effective treatment techniques, like photocatalysis, to guarantee total degradation and environmental protection. (Alarifi et al., 2021)

3. BiFeO₃ As A Photocatalyst

Bismuth ferrite (BiFeO₃) has become one of the promising semiconductors photocatalysts, owing to its special multiferroic behavior, which is both a ferroelectric and antiferromagnetic material. This combination of properties coupled with its attractive electronic structure renders BiFeO₃ very viable to visible-light-driven photocatalytic applications, especially in the degradation of organic pollutants like dyes. A key strength lies in its comparatively small band gap (~2.1–2.7 eV), allowing it to absorb visible light efficiently, as compared to traditional photocatalysts, such as TiO₂, which can only effectively absorb ultraviolet light. This is due to its visible-light activity, which increases its feasibility in the solar-driven wastewater treatment process, thereby rendering it an environmentally friendly and energy-efficient material. (Daub et al., 2021)



BiFeO₃ Crystal Structure

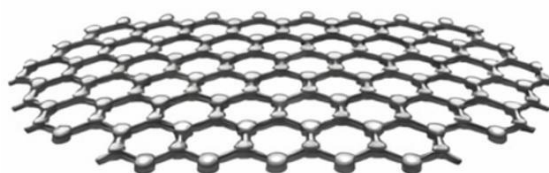
Figure 2: BiFeO₃ Crystal Structure

In addition, BiFeO₃ also exhibits sufficient chemical and thermal stability, non-toxicity, and affordable nature, which is preferable in large-scale environmental uses. Along with these benefits, there are a number of intrinsic limitations that prevent the practical performance of BiFeO₃. The fast recombination between the generated photogenerated electron-holes pairs greatly decreases the photocatalytic efficiency since it reduces the supply of active charge particles to participate in the redox reaction. Moreover, its low surface area limits the active sites of adsorption and interaction with pollutant molecules. The moderate photocatalytic performance is also because of poor charge mobility and lack of optimal light utilization. In order to overcome such problems, several modification methods have been devised, such as elemental doping, formation of heterojunctions, and fabrication of nanocomposites using carbon-based materials like graphene. These strategies promote charge separation, raise surface area, and boost the

overall photocatalytic performance.(Wang et al., 2018)

4. Role Of Graphene In Nanocomposites

A two-dimensional (2D) carbon nanomaterial, graphene, which comprises a single layer of sp² - hybridized carbon atoms in a hexagonal structure has gained tremendous interest in nanotechnology because of its remarkable properties in physics, chemistry and its electronics. Its integration into photocatalytic systems based on semiconductors including BiFeO₃ has been found to be very successful in improving the overall photocatalytic functionality. Graphene has special properties that predispose it to be an excellent ingredient in the fabrication of new nanocomposites that can be used in ecological cleanup. The delocalized π -electron system of graphene is one of the most important properties of this material as it gives the material an incredibly high electrical conductivity. (Wu et al., 2021)



Graphene

Figure 3: Structure of Graphene

This enables the use of graphene as an effective electron donor and carrier in combination with semiconductor materials. Photogenerated electrons on the surface of BiFeO₃ can be quickly transferred to the graphene surface during the photocatalysis process, which will decrease the recombination rate of the electron-hole pairs. This enhanced charge

separation which is directly related to the increase in photocatalytic activity. The second significant characteristic of graphene is that it has a high specific surface area that can be as high as 2630 m²/g. This large surface area offers a large number of active sites where the dye molecules like Congo red can be adsorbed. Adsorption is enhanced, which

allows closer contact between the pollutant and the reactive species produced during the photocatalysis process and enhances the degradation. Also, a planar structure of graphene allows uniform dispersion of semiconductor nanoparticles to prevent agglomeration and keep them highly reactive. Graphene also has a high electron mobility, which allows charge carriers to move quickly across its surface. This property also increases the separation and movement of photogenerated charges, which improves the overall efficiency of photocatalytic process. Beyond that, graphene is capable of indirectly extending light absorption through the application of this material as a photosensitizer in certain applications, which is why it is a crucial material in the development of advanced photocatalytic systems.(Sun et al., 2021)

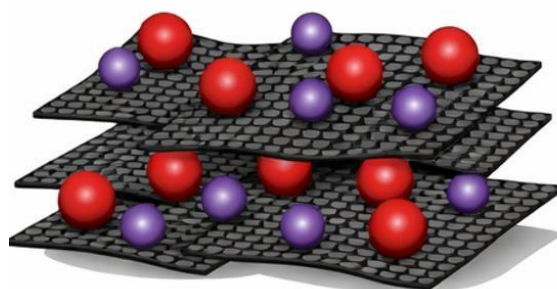
5. Graphene–BiFeO₃ Nanocomposite

5.1 Synthesis Methods

The production of graphene-BiFeO₃ nanocomposites is a key determinant of their structural, morphological and photocatalytic characteristics. There are several preparation methods that have been devised to attain uniform dispersion of BiFeO₃ nanoparticles on the graphene sheets, which will improve the overall performance of the composite.(T. Li et al., 2013)

Common synthesis techniques include:

- Sol-gel method
- Hydrothermal synthesis
- Co-precipitation
- Ultrasonic-assisted methods



Graphene–BiFeO₃ Nanocomposite

Figure 4: Graphene–BiFeO₃ Nanocomposite

One of the most common techniques that are used is the sol-gel technique because it is simple and can also be used to form highly homogeneous materials. This involves a reaction of metal precursors with hydrolysis and condensation reaction to form a gel, which is then subjected to calcination to form the nanocomposite. Particle size and composition can be well controlled using this method.

Another effective method is hydrothermal synthesis that occurs in a sealed autoclave at high temperature and pressure. It helps to form well-crystallized nanoparticles with a controlled morphology and good interaction between graphene and BiFeO₃ leading to a high photocatalytic efficiency.

In the co-precipitation process, metal ions are co-precipitated as a solution and dried and calcinated. This method is inexpensive and can be used with high production volumes, but it might not provide as much control of particle uniformity.

Ultrasonic-assisted techniques make use of ultrasonic waves to improve mixing and dispersion, avoiding agglomeration of the particles and leading to improved dispersion of graphene with BiFeO₃.

The synthesis method greatly influences particle size, surface area, morphology, and, eventually, the photocatalytic efficiency of the nanocomposite.(P. Li et al., 2017)

6. Photocatalytic Mechanism

of the photogenerated charge carriers are the main forces behind the photocatalytic degradation of Congo red by graphene-BiFeO₃ nanocomposites. Exposing the nanocomposite to visible light, BiFeO₃ absorbs light owing to its narrow bandgap, and the electrons in the valence band (VB) are

The visible light irradiation and effective separation excited to the conduction band (CB). It creates pairs of electrons and holes with the negatively charged electrons (e⁻) being excited to the CB leaving positively charged holes (h⁺) in the VB. (Z. Li et al., 2014)

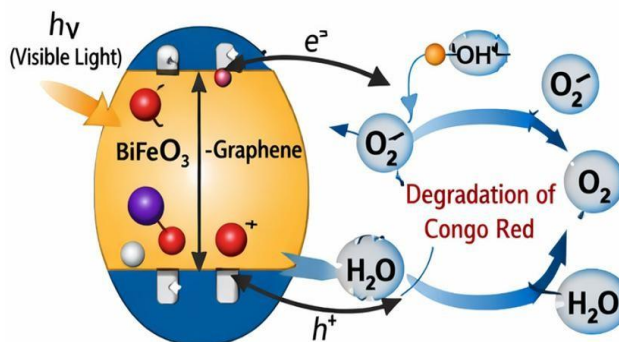
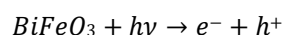


Figure 5: Photocatalytic Mechanism

Light absorption

- BiFeO₃ absorbs visible light → electron excitation



Charge separation

- Electrons transfer to graphene
- Recombination suppressed

Reactive species formation

- $e^- + O_2 \rightarrow O_2^{\bullet -}$
- $h^+ + H_2O \rightarrow \bullet OH$

Dye degradation

- Reactive radicals break Congo red into CO₂ and H₂O

One of the key drawbacks with pure BiFeO₃ is the short recombination of these electron-hole pairs, which lowers the photocatalytic efficiency. However, in the graphene-BiFeO₃ nanocomposite, graphene plays a crucial role as an electron acceptor and transporter. The excited electrons of the conduction band of BiFeO₃ are quickly moved to the sheets of the graphene because it has high electrical conductivity and high electrons mobility. This transfer is effective to suppress the recombination of electron-hole" pairs and consequently increase the lifetime of charge

carriers and increase photocatalytic activity.

The charge carriers that have been separated are then involved in redox reactions at the catalyst surface. The dissolved oxygen (O₂) reacts with the charge concentration of the electrons on the graphene to produce "superoxide radicals (O₂^{•-}) and the holes in the valence band react with water (H₂O) or hydroxide ions (OH⁻) to form very reactive hydroxyl radicals (OH[•]). They are reactive oxygen species that are potent oxidizing agents that can degrade the complex molecular structure of Congo red dye. (Koe et al., 2020)

7. Factors Affecting Photocatalytic Activity

Several parameters of operation have an effect on the efficiency of photocatalytic degradation of Congo red using graphene-BiFeO₃ nanocomposites and need to be optimized to ensure maximum performance is achieved. (Kudo et al., 2000)

7.1 pH of Solution

The pH of the reaction medium is very critical in the establishment of the surface charge of the photocatalyst, and the ionization of the dye molecules. Acidic conditions generally increase the rate of degradation since they facilitate the generation of hydroxyl radical (•OH) which is a very reactive oxidizing agent. Also, positive electrostatic forces between catalyst surface and dye molecules enhance adsorption, thus enhancing the degradation process.

7.2 Catalyst Dosage

The concentration of the photocatalyst has a direct proportionality to the amount of active sites of the reaction. As the concentration of catalyst increases, the degradation efficiency tends to increase because of the presence of a larger number of active surface sites and an increased number of reactive species generated. Nevertheless, the overloading of catalysts may cause particle agglomeration and a decrease of light penetration into the catalysts through scattering effects, which eventually diminishes the photocatalytic activity.

7.3 Initial Dye Concentration

The first addition of Congo red has a substantial influence on the degradation rate. At increased concentrations of the dye, the efficiency declines, mainly because of the light shielding effect, whereby the dye molecules absorb much of the incident light, reducing the amount of photon to activate catalysts. Additionally, an increased concentration will demand a greater amount of reactive species to be fully degraded, which might not be produced in adequate amounts under fixed conditions.

7.4 Light Intensity and Source

The intensity of light and wavelength play a very important role in the initiation of the photocatalytic process. As the BiFeO₃ is a visible light-responsive photocatalyst, the visible light is favourable in order to be effectively activated. An increase in light intensity usually results in a faster rate of electron

generator-hole pairing generation, but an overly high intensity can cause recombination losses or thermal effects. (Irfan et al., 2017) (Irfan et al., 2019)

8. Synthesis Protocol Of Pure And Composite Version Of BiFeO₃

Sigma Aldrich's 99.9% pure raw materials will be used in their entirety. To make the material, stoichiometric volumes of bismuth nitrate penta were dissolved in distilled water while being agitated and heated to 80 °C. Bi loss during synthesis was accounted for by employing a modest amount of bismuth nitrate. After 10 minutes, stoichiometric quantities of iron nitrate nanohydrate were added to the aforementioned solution. A few drops of HNO₃ solution were added. The solution was heated while being continually agitated until a gel formed then dried in an air oven. After that, the powder was annealed for two hours at 550 degrees Celsius. To prepare the composite material optimized amount of BFO powder and graphene powder was ultrasonicated at frequency 20 KHz in solution containing ethanol and DMF.

9. Performance & Comparative Analysis

Fig 6 shows the XRD patterns of BFO. Fig 1 reveals the XRD profile pure BFO which confirms the formation BFO material. The XRD peaks of BFO could be indexed with rhombohedral lattice with R3c space group. Besides of pure phase some impurity phase also has appeared. The small intensity peak near two theta at 27 belongs to oxygen rich impurity Bi₂₅FeO₄₀

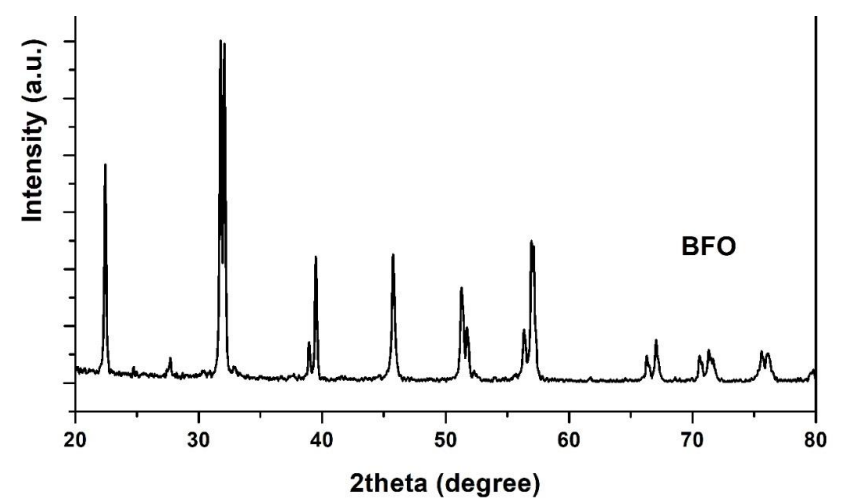


Fig: 6 XRD pattern of BFO

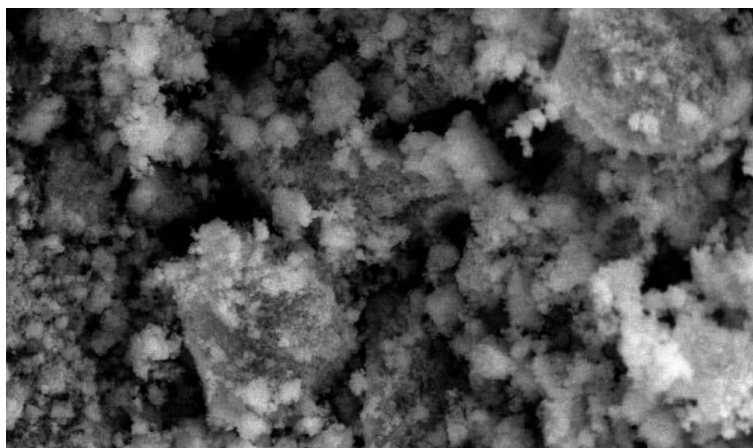


Fig: 7 XRD Scanning electron micrograph of graphene-BFO composite

Microstructure analysis of graphene –BFO composite was done by scanning electron microscopy technique which is shown in Fig: 7. Micrograph clearly shows that the BFO nano particles are well anchored on graphene sheets. The average particle size of graphene was found to be nearly 100nm. Wrinkled shaped graphene sheet could be clearly seen in the micrograph.

In order to investigate the dye degradation

efficiency of the prepared photocatalyst, we have prepared congo red dye solution in distilled water. The concentration of dye was taken is about 0.1g per liter. Very small amount of catalyst was added in the prepared solution of congo red dye and then solution exposed under UV- Vis radiation. We have taken the spectrum of resulting solution prior to exposure and after exposure in definite interval which is shown in Fig 8.

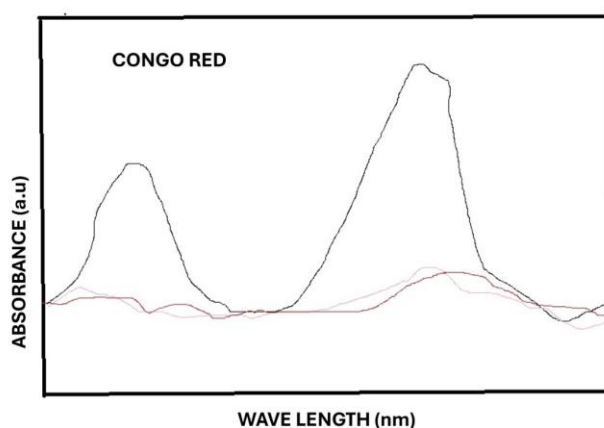
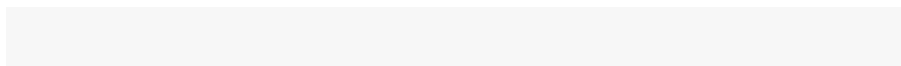


Fig: 8UV-Vis spectrum of of graphene-BFO composite before and after irradiation of light

Fig 8 shows after irradiation of light the absorption decreases significantly which confirms that the degradation of dye occurs. Hence, the prepared material is showing good photocatalytic activity under the visible light irradiation. In order to determine the degradation efficiency, we have measured C_t/C_0 ratio with time of irradiation which is shown in Fig: 9.

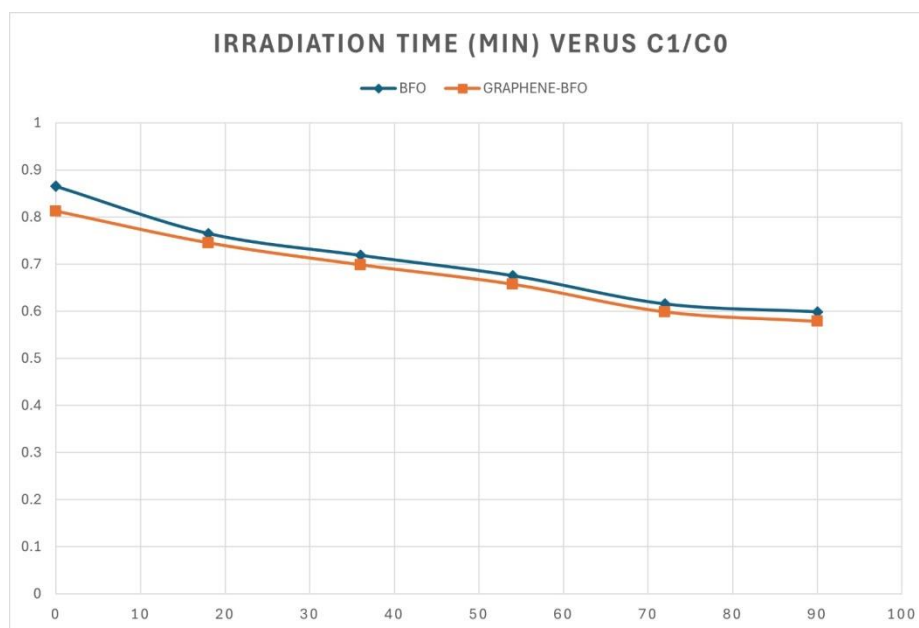


Fig: 9 Dye degradation efficiency of BFO and graphene- BFO composite under the irradiation of light

From Fig: 9, it is confirmed that the pure BFO degraded 40% of dye after 120 min of irradiation whereas Graphene- BFO composite degraded 75% of dye in same time. These results are in favors that Graphene- BFO composite has better photocatlytic activity than pure BFO.

11. Conclusion

This study highlights the effectiveness of graphene-BiFeO₃ nanocomposites as advanced photocatalytic materials for the degradation of Congo red dye under visible light irradiation. The incorporation of graphene into BiFeO₃ significantly enhances photocatalytic performance by improving charge separation, increasing surface area, and facilitating rapid electron transport. These improvements effectively suppress the recombination of photogenerated electron-hole pairs, leading to the enhanced generation of reactive oxygen species responsible for dye degradation. The synthesis of pure BiFeO₃ and its graphene-based composite was successfully achieved using a controlled chemical route followed by thermal treatment. Structural analysis confirmed the formation of the desired rhombohedral phase, while morphological studies revealed uniform dispersion of BiFeO₃ nanoparticles over graphene sheets, which contributes to improved catalytic activity. Photocatalytic experiments demonstrated that the graphene-BiFeO₃ composite exhibits significantly higher degradation efficiency compared to pure BiFeO₃, achieving up to 75% degradation of Congo red dye within 120 minutes. This improvement is attributed to the synergistic

interaction between graphene and BiFeO₃, which enhances light absorption and provides more active sites for the photocatalytic reaction. Despite these promising results, challenges such as large-scale synthesis, cost-effectiveness, and long-term stability remain to be addressed for practical applications. Future research should focus on optimizing synthesis techniques, improving recyclability, and evaluating performance in real wastewater systems. Overall, graphene-BiFeO₃ nanocomposites present a sustainable and efficient solution for wastewater treatment and environmental remediation.

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