PHOTOCATALYTIC DEGRADATION OF AZURE B UNDER VISIBLE LIGHT IRRADIATION BY REDUCED GRAPHENE OXIDE–NiS COMPOSITE

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A composite of reduced graphene oxide (RGO) and nickel sulfide (NiS) was prepared via mechanochemical method and further characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and energy dispersive analysis of X-rays (EDAX). NiS was prepared via precipitation method, and RGO was prepared via reduction of graphene oxide. The photocatalytic performances of as prepared RGO/NiS composite, RGO and NiS were evaluated using azure B model system. The composite exhibited good photocatalytic activity as compared to NiS as well as RGO. The optimum conditions obtained for the photocatalytic degradation of azure B were the following: pH = 8.0, [Azure B] = 2.0 × 10⁻⁵ M, amount of composite = 0.10 g, and light intensity = 50.0 mW·cm⁻². The rate of degradation of azure B with the composite was found to be 1.79 × 10⁻⁴ s⁻¹.

Keywords: reduced graphene oxide; nickel sulfide; azure B; photocatalytic degradation

1. INTRODUCTION

Water pollution is currently a common problem. Water pollution involves the mixing of one or more substance that is harmful to humans and animals into water. Water pollution can be caused by many sources, but industrial waste water is a salient issue. Effluents from textile dyes present a substantial problem because they can cause many dangerous diseases and lead to death.

There are many available techniques for waste water treatment, such as precipitation, flocculation, adsorption, thermal dehydration, air stripping, etc.; however, photocatalysis plays an important role in water purification, and numerous studies are being conducted for this purpose. In the last few years, the use of graphene oxide and reduced graphene oxide for waste water treatment has attracted the attention of researchers. Apart from this use, composites of reduced grapheneox-
ide have found applications as counter electrodes in dye-sensitized solar cells [1, 2], in reversible lithium storage [3], in hydrogen evolution reactions [4], as supercapacitors [5], etc.

Vadivel et al. [6] prepared a graphene oxide-BiOBr composite material and used it as a highly efficient photocatalyst for the degradation of methylene blue and rhodamine-B dyes, and Wang et al. [7] prepared a graphene-oxide/Ag2PO4 composite and used it for the photocatalytic degradation of bisphenol A under visible light irradiation. RGO is known to be well-suited for optical, biosensor, medical and supercapacitor applications, but RGO may also play an important role in photocatalysis. Wang et al. [8] used solvothermal method to synthesize reduced graphene oxide/cadmium sulfide (RGO/CdS). CdS nanoparticles were homogeneously distributed on reduced graphene oxide. This composite showed enhanced photocatalytic properties for methylene blue. Moreover, Chakraborty et al. [9] used a RGO/CdS composite to degrade 4-nitrophenol under simulated solar light illumination. In this process, the reduction of graphene oxide (GO) and the attachment of CdS particles onto RGO sheets were performed simultaneously. These authors reported photoinduced electron transfers from CdS nanorods to RGO sheets, and this process reduced the recombination probability of photogenerated electron-holes in the CdS. Their study established that the RGO-CdS composite is a potential photocatalyst for degradation.

A facile microwave method has been used to synthesize a zinc oxide/reduced graphene oxide (ZnO-RGO) nanocomposite in the presence of diethylenetriamine [10]. ZnO nanorods were successfully deposited on RGO sheets. This composite showed excellent performance via enhanced adsorption-photocatalysis under the irradiation of sunlight. This photoactivity was due to the ZnO nanorods, and the RGO acted as a photosensitizer. Shen et al. [11] reported a one-pot ionic-liquid-assisted hydrothermal process, in which ZnCdS nanoparticles were decorated on RGO. The synthesis of RGO and preparation of the ZnCdS/RGO composite were achieved simultaneously. The composite exhibited excellent photodegradation properties for organic dyes. Yan et al. [12] synthesized a Cu2O/PA/RGO composite and used it for photocatalytic dye degradation. Cu2O nanoparticles were successfully synthesized on n-propylamine intercalated graphene oxide, and hydrazine hydrate reduction was subsequently applied to synthesize the desired composite. This composite exhibited significant improvements in both photocatalytic activity and adsorption capacity.

Nickel sulfide nanoparticles have been synthesized in the presence of thioacetamide or thiourea to act as a sulfur source with variations in temperature and capping agents. Molla et al. [13] reported that this catalyst has the ability to generate reactive oxygen species in both the absence and presence of light. This property is responsible for dye decomposition. This catalyst was tested on crystal violet, rhodamine B, methylene blue, Nile blue and Eriochrome black T. Pourretdal and Memenakedeh [14] used a controlled precipitation method to synthesize Ni3S2, NiS, NiO, NiO0.5S0.5 and NiS0.15S1.5. These catalysts were then calcined at 700°C, and their photocatalytic dye degradation efficiencies were compared using a methylene blue model dye system. These authors observed the following trend:

$$\text{NiO}_1\text{S}1.5 > \text{NiO}_0\text{S}0.5 > \text{NiS} > \text{NiO} > \text{Ni}_2\text{O}_3 > \text{Ni}_2\text{S}_3$$

Rusu et al. [15] performed photocatalytic degradations of the azo dyes amaranth, sunset yellow and tartrazine using TiO2-Pt nanoparticles, TiO2-Pt/graphene oxide and TiO2-Pt/reduced graphene oxide composites in the presence of UV and natural sunlight irradiation, and Fan et al. [16] reported the use of zinc oxide (ZnO)/reduced graphene oxide (rGO) hybrids for the degradation of methylene blue, methylene orange, and rhodamine 6G upon ultraviolet light irradiation. Ucar et al. [17] prepared a silicotungstic acid (SiW)-decorated reduced graphene oxide (rGO) nanocomposite (rGO-SiW) and evaluated it as a heterogeneous nanocatalyst for the degradation reactions of methylene blue and rhodamine B. Mittal et al. [18] independently evaluated the photocatalytic degradation of azure B using manganese dioxide as a photocatalyst. While studying the rate-affecting parameters, these authors observed that the photocatalytic degradation of azure B followed first-order kinetics. Ameta et al. [19] studied the effects of operating parameters on the photocatalytic degradation of azure B dye using calcium oxide as a photocatalyst. Upadhyay et al. [20] examined the photodegradation of azure B under visible irradiation in the presence of copper hexacyanoferrate(II) as a photocatalyst. After studying the rate-affecting parameters, these authors concluded that, after exposure to light and the photocatalyst for 2 hours, 86% of the azure B dye was degraded following the addition of 0.05 g / 50 ml copper hexacyanoferrate (II) to a $1 \times 10^{-5}$ M solution of azure B. Aarthi et al. [21] investigated the photocatalytic degradations of azure A, azure B and Sudan dyes (III and IV) by combustion-synthesized TiO2 and Degussa
The photodegradation rate was found to be higher in solvents with higher polarities, and metal ions reduced the photocatalysis rates. Keeping the hazardous effect of azure B dye in focus, in the present work, a RGO/NiS composite was produced and used in presence of light to degrade the dye. The RGO/NiS composite was found to be a good photocatalyst for degradation of azure B. Because this composite is insoluble in water, it is easy to remove from treated water.

2. MATERIALS AND METHODS

2.1. Chemicals

Graphite was purchased from Merck, and NiSO₄ and ascorbic acid were purchased from Himedia.

2.2. Preparation of RGO, NiS and the composite

The RGO was synthesized from graphite by a new green chemical route, and NiS was produced by a precipitation method. The RGO was synthesized from graphite in a process involving the oxidation of graphite in the first step followed by the reduction of the obtained graphene oxide into reduced graphene oxide. The oxidation of graphite was performed with singlet oxygen, and the reduction was achieved with ascorbic acid. Singlet oxygen and ascorbic acid are eco-friendly chemicals. The composite of RGO and NiS was prepared with a mechanochemical method following a top-down approach. Equal amounts of RGO and NiS were ground with an agate mortar pestle.

2.3. Characterization

2.3.1. X-ray diffraction (XRD)

The crystal size of the prepared RGO was determined with an X-ray diffractometer (XRD) (XPERT-PRO model, SAIF, Chandigarh) using CuKα radiation (λ = 0.154060 nm) in the 2θ scanning range from 20° to 80° with a scan rate at 10° min⁻¹. The applied voltage and current were 45 kV and 40 MA, respectively. The powder XRD pattern of a prepared RGO is shown in Figure 1. RGO exhibits an intensity and broadness peak at 2θ = 26.45°, and the average particle size is 26.75 nm. The characteristic peak of the RGO is at 27.6°.

![Fig. 1. XRD pattern of RGO](image)

2.3.2. Fourier-transform infrared spectroscopy (FTIR)

The FTIR spectrum of the synthesized RGO-CuS composite was recorded with a Bruker spectrometer (SAIF, Chandigarh) in the range of 4000 to 400 cm⁻¹ at a scanning rate of 1 cm⁻¹/min.

The FTIR studies were performed to confirm the presence of NiS in the composite. The FTIR of the prepared RGO-NiS composite is shown in Figure 2. The characteristic peak of NiS-C was obtained at 1576 cm⁻¹, and the Cu-S vibration peak was located at 942 cm⁻¹. The presence of these two peaks indicated that the NiS had been incorporated into the RGO in the composite. The peaks at 1393 and 1622 cm⁻¹ may be attributable to the O-H deformations of the C-OH and carboxy OH in the RGO [22–24].
2.3.3. Energy dispersive analysis of X-rays (EDAX)

The elemental composition was determined with an energy dispersive X-ray (EDAX) spectrometer. The results are summarized in Table 1.

| Element  | Weight % |
|----------|----------|
| Carbon   | 99.41    |
| Oxygen   | 0.59     |

2.4. Photocatalytic degradation

Azure B (0.0305 g) was dissolved in 100 ml of doubly distilled water to achieve a concentration of dye solution of 1.0 × 10⁻³ M. This solution was used as a stock solution and was further diluted when required. The absorbance of azure B was determined spectrophotometrically at λ_{max} = 650 nm.

Equal amounts of dye solution were placed in four beakers. The first beaker containing azure B solution was kept in the dark, and the second beaker containing azure B was exposed to light. The third beaker containing azure B solution and 0.10 g of the RGO/NiS composite was kept in the dark, and the fourth beaker containing azure B solution and 0.10 g of the RGO/NiS composite was exposed to light. After 3–4 h, the absorbance of the solution in each beaker was measured with a spectrophotometer (Systronics Model 106). The absorbances of the solutions in the first three beakers remained almost the same. However, in the fourth beaker, the absorbance decreased relative to the initial value. Based on these observations, it was clear that this reaction was photocatalytic in nature because it required the presence of both; light and the RGO/NiS composite.

A solution of 2.0 × 10⁻⁵ M azure B was prepared in doubly distilled water, 0.1 g of RGO/NiS composite was added, and the pH of this solution was adjusted to 8.0. Next, this reaction solution was exposed to a 200 W tungsten lamp at 50.0 mW·cm⁻². A decrease in the absorbance of the dye solution with increasing time of exposure was observed.

3. RESULTS AND DISCUSSION

The plot of 1 + logA against time was found to be linear (Table 2 and Fig. 3). This graph indicates that the photocatalytic degradation of azure B followed pseudo-first order kinetics.

The rate constant (k) was calculated using equation (1).

\[
k = 2.303 \times \text{slope} \tag{1}
\]
Photocatalytic degradation of azure B under visible light irradiation by reduced graphene oxide–NiS composite

Table 2

A typical run

\[ \text{pH} = 8.0, \ [\text{azure B}] = 2.00 \times 10^{-5} \text{ M}, \]
\[ \text{amount of RGO/NiS composite} = 0.10 \text{ g}, \]
\[ \text{light intensity} = 50.0 \text{ mW cm}^{-2} \]

| Time (min.) | Absorbance (A) | 1+ log A |
|-------------|----------------|----------|
| 0.0         | 0.612          | 0.7866   |
| 10.0        | 0.560          | 0.7481   |
| 20.0        | 0.530          | 0.7242   |
| 30.0        | 0.446          | 0.6493   |
| 40.0        | 0.399          | 0.6009   |
| 50.0        | 0.383          | 0.5831   |
| 60.0        | 0.355          | 0.5502   |
| 70.0        | 0.322          | 0.5078   |
| 80.0        | 0.297          | 0.4727   |
| 90.0        | 0.264          | 0.4216   |
| 100.0       | 0.238          | 0.3766   |
| 110.0       | 0.224          | 0.3502   |
| 120.0       | 0.210          | 0.3222   |
| 130.0       | 0.186          | 0.2695   |
| 140.0       | 0.166          | 0.2201   |
| 150.0       | 0.151          | 0.1789   |

\[ k \text{ with RGO/NiS} = 1.79 \times 10^{-4} \text{ s}^{-1}, \]
\[ k \text{ with NiS} = 1.15 \times 10^{-4} \text{ s}^{-1}, \]
\[ k \text{ with RGO} = 1.53 \times 10^{-4} \text{ s}^{-1} \]

Fig. 3. A typical run

Different rate-affecting parameters, such as pH, azure B concentration, amount of RGO/NiS composite and light intensity, were studied to obtain the optimum conditions for the photocatalytic degradation of azure B.

3.1. Effect of pH

The pH of the solution of azure B was varied across the range of 5.0–10.0. The results are shown in Table 3.

The rate of degradation was observed to increase with increasing pH until it reached a maximum at pH 8.0. At pH values below 8.0, a decrease in the rate of the reaction was observed due to the repulsion between the cationic dye molecules and the positively charged surface of the composite due to the adsorption of protons. When the pH was increased towards 8.0, the rate of the reaction was enhanced. This result may be explained by the fact that more OH– ions were available at higher pH values; consequently, more OH radicals were produced, and thus, the reaction rate increased. At pH values above 8.0, the cationic dye molecules converted into the neutral form, which exhibited no attraction toward the negatively charged surface of the composite due to the adsorption of OH– ions; consequently, the rate was retarded.

Table 3

Effect of pH

\[ [\text{azure B}] = 2.00 \times 10^{-5} \text{ M}, \text{ light intensity} = 50.0 \text{ mW cm}^{-2}, \text{ amount of RGO/NiS composite} = 0.10 \text{ g} \]

| pH    | Rate constant \( (k) \times 10^4 \text{ s}^{-1} \) |
|-------|-----------------------------------------------|
| 5.0   | 1.11                                          |
| 5.5   | 1.18                                          |
| 6.0   | 1.25                                          |
| 6.5   | 1.31                                          |
| 7.0   | 1.36                                          |
| 7.5   | 1.52                                          |
| 8.0   | 1.79                                          |
| 8.5   | 1.71                                          |
| 9.0   | 1.43                                          |
| 9.5   | 1.26                                          |
| 10.0  | 1.13                                          |

3.2. Effect of azure B concentration

Different concentrations of azure B (1.40–2.80 \times 10^{-5} \text{ M}) were used to study the effect of the dye concentration on photocatalytic degradation. The results are presented in Table 4.

Table 4

Effect of dye concentration

\[ \text{pH} = 8.0, \text{ light intensity} = 50.0 \text{ mW cm}^{-2}, \]
\[ \text{amount of RGO/NiS composite} = 0.10 \text{ g} \]

| [Azure B] \times 10^{-5} \text{ M} | Rate constant \( (k) \times 10^4 \text{ s}^{-1} \) |
|-----------------------------------|-----------------------------------------------|
| 1.40                              | 0.96                                          |
| 1.60                              | 1.09                                          |
| 1.80                              | 1.42                                          |
| 2.00                              | 1.79                                          |
| 2.20                              | 1.22                                          |
| 2.40                              | 1.15                                          |
| 2.60                              | 1.07                                          |
| 2.80                              | 0.92                                          |

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These observations revealed that the rate constant increased with increasing dye concentration, but after exceeding the dye concentration of $2.00 \times 10^{-5}$ M, the rate decreased. The rate constant increased with the dye concentration because a greater number of dye molecules were available for excitation and energy transfer. The rate constant reached a maximum at a concentration of $2.00 \times 10^{-5}$ M, and it decreased with further increases in the concentration. After reaching a certain concentration, the dye molecules begin to act as a filter of incident light and do not allow the desired light intensity to reach the surface of the photocatalyst.

3.3. Effect of the amount of RGO/NiS composite

The amount of the composite may also affect the degradation of azure B. To observe the effect of the amount of the RGO/NiS composite, this amount was varied from 0.06 to 0.18 g. The results are summarized in Table 5. Here, the rate of the photocatalytic degradation of azure B increased with increasing amounts of the composite. At a certain point, i.e., 0.10 g, maximum degradation of the dye was achieved; thereafter, a decrease in the rate of photocatalytic degradation was observed with further increases in the amount of RGO/NiS composite.

Table 5

| Amount of composite (g) | Rate constant (k) $\times 10^4$ (s$^{-1}$) |
|------------------------|------------------------------------------|
| 0.06                   | 0.97                                     |
| 0.07                   | 1.12                                     |
| 0.08                   | 1.38                                     |
| 0.10                   | 1.79                                     |
| 0.12                   | 1.45                                     |
| 0.14                   | 1.34                                     |
| 0.16                   | 1.18                                     |
| 0.18                   | 0.99                                     |

The rate of degradation of the azure B increased with increasing amounts of the composite, which may have been due to a corresponding increase in its exposed surface area. However, upon increasing the amount of composite above 0.10 g, a decrease in the rate of degradation was observed. This result may have been due to the fact that there was no increase in the exposed surface area above a particular limit; however, in this case, the formation of a multilayer may have occurred and made electron-hole recombination easier. This recombination would act against the photocatalytic degradation of azure B because fewer $'OH$ radicals would be formed, and $'OH$ radicals are the main reactive oxidizing species. This notion was confirmed by stirring the solution, which resulted in a shift of the optimum amount to a higher value.

3.4. Effect of light intensity

The effect of light intensity on the photocatalytic degradation of the dye was observed by changing the distance between the light source and the surface of the composite. The results are presented in Table 6.

Table 6

| Light intensity (mWcm$^{-2}$) | Rate constant (k) $\times 10^4$ (s$^{-1}$) |
|------------------------------|------------------------------------------|
| 20.0                         | 0.96                                     |
| 30.0                         | 1.45                                     |
| 40.0                         | 1.51                                     |
| 50.0                         | 1.79                                     |
| 60.0                         | 1.57                                     |
| 70.0                         | 1.45                                     |

Increasing light intensity was found to increase the rate of the degradation of the dye. The optimum degradation was obtained at 50.0 mW$\cdot$cm$^{-2}$. Thereafter, the rate decreased with further increases in light intensity. This increase in photocatalytic degradation may have resulted from an increase in the number of photons that struck per unit area per unit time and thus increased the light intensity. After this optimum value, a decrease in photocatalytic degradation was observed and may have been due to thermal side reactions; therefore, greater light intensities were avoided.

3.5. Mechanism

Based on these observations, a tentative mechanism for the photocatalytic degradation of azure B (AB) is proposed as follows:
The molecules of azure B absorbed light of a suitable wavelength and were excited to the first excited singlet state, upon which they further underwent intersystem crossing to the triplet state. Semiconducting NiS also absorbs light, and the electrons were excited to their conduction band, which left a hole in their valence band. The electrons from the conduction band may have been abstracted by RGO, which acts as an electron sink. Similarly, the electrons were abstracted from the OH ions by the hole in the valence band of the NiS, which generated ‘OH radicals. ‘OH radicals are an active oxidizing species and oxidized azure B to its leuco form, which was ultimately degraded to smaller and almost harmless products. Isopropanol is a specific hydroxyl radical scavenger. Hence, isopropanol was added to reaction mixture, and the reaction rate was drastically reduced, which confirmed the active participation of the ‘OH radicals as an active oxidizing species.

4. CONCLUSION

Photocatalysis is an emerging field and can be used to degrade various pollutants in an eco-friendly manner. In the present work, azure B dye was successfully degraded in the presence of an RGO/NiS composite and light. After the exposure of an azure B-containing sample to the composite and light for approximately 4 h, 90% of the dye content was found to be degraded. This observation revealed that the RGO/NiS composite exhibited better results than either RGO or NiS. Photocatalysis will prove to be an efficient method for the treatment of waste water that contains different organic contaminants in the future.

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