



# Photodegradation of methylene blue using magnetically reduced graphene oxide bismuth oxybromide composite



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## ABSTRACT

A magnetically reduced graphene oxide–bismuth oxybromide (MRGO–BiOBr) composite was successfully synthesized and found to possess magnetic, adsorptive and photocatalytic properties. The synthesized composite has been characterized by Fourier transform infrared spectroscopy (FT-IR), X-Ray Diffraction (X-RD), Scanning electron microscopy (SEM) and UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS). Presence of Fe–O bond stretching vibrations and bromo compounds have been confirmed using FT-IR and the diffraction peaks of the composite obtained from X-RD showed a combination of peaks of both MRGO and BiOBr. SEM images further confirmed the presence of minute flakes of BiOBr scattered onto the surface of MRGO. Reduction in band gap energy from 2.76 eV for pure BiOBr to 1.91 eV for the composite was determined using UV–vis DRS. Photocatalytic degradation of Methylene Blue dye under visible light irradiation (150 W Tungsten filament lamp) was examined using MRGO–BiOBr and around 96.84% of dye of 50 ppm was degraded in 2 h. Kinetic studies were done by splitting the kinetic data into 2 regions at 30 min of irradiation and using the Langmuir–Hinshelwood (L–H) model to determine the rate constants. The composite was found to be easily separable in the presence of a magnet and on regeneration, studies showed no significant decrease in the photocatalytic activity of the composite even after 3 runs.

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## 1. Introduction

Textiles, paper, leather, food and cosmetics industries use large amount of dyes and the effluent from these industries are a major environmental concern. Dyes are well known to influence the quality of water resulting in various undesirable consequences like cancers involving kidney, urinary bladder, liver and allergies such as respiratory disease, skin irritation. Most of the dyes are toxic and carcinogenic [20] and even trace levels of these dyes can cause several problems when they enter the environment. Hence a search for a novel and efficient technique for the degradation of dyes so as to completely remove its toxicity is of primary interest.

The most commonly used methods for waste treatment are flocculation/coagulation, adsorption, bio-treatment, ozonation, photochemical decolorisation. However most of these methods transfer the dye from one medium to another and do not result in the complete degradation of the dye [1,7]. Other techniques such as

bio-treatment and ozonation result in generation of toxic byproducts due to incomplete degradation. Other disadvantages include generation of large volumes of sludge and its disposal problems.

Adsorption on the other hand has proved to be a powerful technique for removal of dye constituents from waste water [13,16]. Numerous adsorbents such as activated carbon, alumina and zeolite are widely used. However they simply cause decolorisation of the waste water thereby leaving the toxicity on the adsorbent. Photocatalysis offers a promising technology for dye containing waste water treatment. Recently photocatalytic degradation has been applied in the treatment of wastewater from industries such as leather, dyes, herbicides and others [14,17]. Nanostructured titanium dioxide an environment friendly photocatalytic material is attracting increased interest but has a wide band gap of 3.2 eV and is excited by ultraviolet (UV) light which accounts for only 4% of the solar energy.

The main objective is to develop photocatalysts which perform efficiently under visible light irradiation. As adsorbents lead to dye removal from the bulk stream and photocatalysts assist in complete degradation of the dye molecule, a combination of the

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two has been proved to show synergistic effects [3]. The emerging trend is to synthesize novel photocatalytic materials which would respond in visible light. Bismuth oxyhalide compounds have recently gained attention because of their excellent photocatalytic activity. Bismuth oxyhalides are V–VI–VII ternary compounds with tetragonal matlockite structure. They are layered structure characterized by  $[\text{Bi}_2\text{O}_2]$  slabs interleaved by double slabs of halogen atoms [35]. This layered structure provides space large enough to polarize the related atoms and orbitals and then the induced dipole can separate the electron hole pair efficiently, which is beneficial to enhance the photocatalytic activity [28]. As a lamellar structured p-type semiconductor with an indirect band gap [34], BiOBr is of great interest owing to its relatively superior photocatalytic activity and stability under visible light irradiation. The photocatalytic performance of BiOBr can also be further improved by integrating it with any carbonaceous material.

Graphene, a monolayer or few layers (<10) of hexagonally arranged  $\text{sp}^2$  bonded carbon atoms has attained great importance due to its physical and chemical properties [36]. Recently graphene hybrids with metal oxides, metals and polymers have been developed for various applications [25], but these nanostructured hybrids suffer from separation problems due to their small size.

The present work aims at developing photocatalysts that can be easily separated from the effluent as well as having relatively low band gap energy for application in visible light region.

## 2. Experimental

### 2.1. Chemicals and materials

Graphite powder of ~300 mesh and 99% purity was obtained from Alfa aaser, Sodium nitrate ( $\text{NaNO}_3$ ), Potassium permanganate ( $\text{KMnO}_4$ ) from Merck, Sulphuric Acid ( $\text{H}_2\text{SO}_4$ ) (98.08%) from Spectrum, Bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ), Ferric Chloride Anhydrous ( $\text{FeCl}_3$ ), Ethylene Glycol (EG) and Potassium bromide (KBr) from SRL, Ammonia solution ( $\text{NH}_4\text{OH}$ ) and Hydrazine hydrate ( $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ ) from RFCL. All chemicals are of analytical grade and all solutions were prepared using distilled water.

### 2.2. Synthesis of magnetically reduced graphene oxide (MRGO)

Graphitic Oxide (GO) was synthesized using Modified Hummer's Method [24]. 4 g of graphite and 2 g of sodium nitrate were mixed together followed by the addition of 92 ml of concentrated sulphuric acid under constant stirring. After 1 h, 12 g of  $\text{KMnO}_4$  was added gradually to the above solution while keeping the temperature less than 20 °C to prevent overheating and explosion. The mixture was stirred at 30 °C for 12 h and the resulting solution was diluted by adding 600 ml of water under vigorous stirring. To ensure complete reaction with  $\text{KMnO}_4$ , the suspension was further treated with 30%  $\text{H}_2\text{O}_2$  solution (20 ml). The resulting mixture was washed with 1 M HCl and  $\text{H}_2\text{O}$  for 3 and 7 times respectively, followed by centrifugation at 1400 rpm, filtrated and dried to obtain GO powders. The prepared GO powders were dispersed in water by continuous stirring for 12 h and Graphene Oxide was obtained by exfoliation (EGO). The obtained yellowish-brown colloid was allowed to settle, the water decanted away and the solids dried at 60 °C to obtain EGO powders [21]. 800 ml of EGO colloid of concentration 0.5 mg/ml obtained via mechanical exfoliation was taken in a beaker. To this 5.12 ml of  $\text{NH}_3$  solution and 0.3 ml of hydrazine hydrate was added. The yellowish brown colloidal solution turned black in colour. The black coloured solution was heated at a temperature of 100 °C for a period of 1 h. A black coloured solid precipitated out. The solid were filtered and dried at 110 °C to obtain reduced graphene oxide (RGO) powders

[20]. 50 mg of RGO was dispersed in 30 ml ethylene glycol by sonication. Similarly 50 mg of  $\text{FeCl}_3$  was dispersed in 20 ml ethylene glycol and 0.6 g of  $\text{CH}_3\text{COONa}$  was added to the  $\text{FeCl}_3$  solution and homogenously mixed. Both the solutions were mixed and stirred magnetically for 1 h. The slurry obtained was transferred to an autoclave and maintained at 200 °C for 12 h. The mixture was then cooled, washed with distilled water and ethanol and dried to obtain magnetically reduced graphene oxide (MRGO) powders [8,9].

### 2.3. Synthesis of bismuth oxybromide (BiOBr)

1.94 g of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was dissolved in 6 ml acetic acid and was added slowly to a solution containing 60 ml of distilled water and 0.48 g of KBr. Pale yellow colour precipitates were observed. The solution was stirred in a magnetic stirrer for 30 min to obtain a homogeneous suspension. The suspension was transferred to a Teflon lined autoclave and heated at a temperature of 120 °C for 14 h. The resulting precipitate was washed with distilled water, filtered and dried to obtain pale yellow colored BiOBr powders [10].

### 2.4. Synthesis of MRGO–BiOBr composites

1 g each of MRGO and BiOBr were dispersed in 400 ml distilled water by sonication separately for a time period of 30 min. Both solutions were mixed together and magnetically stirred for a period of 24 h. The obtained composites were extracted from the magnet, centrifuged to remove impurities and dried at 100 °C for a period of 6 h to obtain the final composite.

### 2.5. Photocatalytic experiments

The photocatalytic activity of the as-prepared MRGO–BiOBr composites was determined by evaluating the photodegradation of methylene blue (MB) dye. A known weight of the composite was added to 500 ml of the MB solution of known concentration and was allowed to attain adsorptive equilibrium which required 1 h. The solution was then irradiated for 2 h. Samples were periodically removed for analysis of MB concentration both during the dark adsorption stage as well as during photodegradation. The concentration (C) of the remnant dye was determined by measuring the absorbance of solution at 663 nm (MB) with UV–vis spectroscopy (Hitachi U-2000 Spectrophotometer) [6].

### 2.6. Characterization

The Fourier transform infrared (FT-IR) spectrum was analyzed, using the FT-IR spectrometer PERKIN ELMER RX-1 FT-IR SYSTEM. The samples were prepared in the form of a pellet, by mixing the dry form of materials with KBr (SRL: 99% FT-IR grade). The identification of the purity and phase of the catalysts was done using the X-Ray Diffraction (XRD) Spectrum Xpert-Pro-PAN Analytical Instrument, using the  $\text{CuK}\alpha$  radiation ( $\lambda = 1.540598 \text{ \AA}$ ) with 30 (mA) and 45 (kV). The Scanning Electron Microscopy (SEM) images so as to study the morphology of the catalysts was analyzed by the TESCAN VEGA3 SBU VG8251177IN (Czech Republic). The absorbance of the MB dye samples withdrawn during specific intervals of time during the photocatalytic experiments was analyzed using UV–Vis Spectrophotometer (Shimadzu Model UV-2100S). The optical property of the photocatalyst and its composite was analyzed using UV–vis Diffuse Reflectance Spectroscopy (UV-DRS) from which the band gap energy was determined.

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