Photocatalytic degradation of methylene blue and crystal violet by sulfur/reduced graphene oxide composite

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Abstract
In this paper, graphene oxide sheets were prepared and reduced to graphene via green chemistry method. Sulfur/reduced graphene oxide (S/RGO) composite has been synthesized using a facile and low cost method with thiosulfate and graphene oxide (GO) as precursors. The photocatalyst powders were characterized FT-IR, DRS, XRD and SEM images. Photocatalytic activity of S/RGO composite was evaluated by photodegradation of methylene blue and crystal violet. Compared to pure sulfur and pure graphene, the as-prepared S/RGO composite showed much enhanced photocatalytic activity for the degradation of methylene blue and crystal violet under visible LED light irradiation.

Keywords: Photocatalytic degradation, Sulfur/reduced graphene oxide composite, Methylene blue, Crystal violet.

1. Introduction
Graphene in recent years was rising as a phenomenon in world science. Graphene oxide (GO) is of great interested due to its facile access with low cost material and using in many branch of science such as electronic, chemistry, biochemistry and mechanical. Graphene orbital hybridization is sp² and very thin atomic thickness and the structure of graphene in a hexagonal lattice [1]. Utilizing renewable photo degradation to clean environmental pollution in water is a significant problem. Graphene oxide (GO) constitutes a versatile surface photochemistry compatible with a broad range of technologically Significant support materials. Recently graphene has been used in photocatalyst for degradation some pollutes. However graphene has been increasing used as a support for metal or metal oxides in the fabrication with excellent activity [2]. Ionic sulfur is widely used in sulfide photocatalysts or as a dopant in oxide
photocatalysts [3,4]. Sulfur has good properties such as low cost, high accessibility and low toxicity. However, the use of sulfur/reduced graphene as a photocatalyst for degradation of MB and CV have never been explored, to the best of our knowledge. Elemental sulfur has more than 30 allotropes [5,6]. In this study, we investigated effect of photocatalyst in destruction of methylene blue and crystal violet with sulfur coated graphene.

2. Experimental process

2.1. The Materials and methods section

All materials were of analytic grade used without further purification. graphite flakes (60 meshes 98% pure), potassium permanganate (KMnO₄), sodium nitrate (NaNO₃), sulfuric acid (H₂SO₄ 98%), sodium thiosulfate (Na₂S₂O₃) and ascorbic acid were purchased from Merck company. The particle morphologies of S/GR powder by an AIS2100 (Seron Technology) scanning electron microscopy (SEM). The FT-IR analyses were carried out on a Shimadzu FTIR-8400S spectrophotometer using a KBr pellet for sample preparation. DRS spectra were prepared via a Shimadzu (MPC-2200) spectrophotometer.

2.2. Preparation of graphene oxide

Graphene oxide was prepared by Hummer’s method [7]. In summary, graphite (0.5 g) was mixed with NaNO₃ (0.5 g) in 25 ml of concentrated H₂SO₄ 98% and KMnO₄ (3 g) at 0°C was added slowly in to the system. The mixture was then stirred at 300°C for 12 hours. After has been stirred the mixture was diluted by adding 100 ml water at 500°C. The mixture was further treated with H₂O₂ (20%) 10 ml. suddenly color of solution was change to bright yellow. After this event the mixture was diluted by adding 40 ml water. Finally graphene oxide was formed then graphene oxide was filtered and washed with DI water.

2.3. Preparation of graphene/sulfur composite

Briefly sodium thiosulfate (6.2 g) was added into 25 ml of GO solution. The PH value of the solution was adjusted to 2 by adding of H₂SO₄ 30%. Subsequently Ascorbic acid (0.5 g) was added. The PH was adjusted to 11 by addition of NaOH (5% wt). The mixture was heated to 900°C for 4 hours. The composite formed and was washed with DI water and dried in an oven at 80°C.
2.4. Photocatalysis procedure

Photo decomposition of methylene blue was complete in a photo-reactor for typical process for methylene blue 20 mg of photocatalyst was first dispersed in 20 ml of methylene blue to an initial concentration of 20 mg/l. Before exposure to light the solution was stirred in the dark to allow adsorption of methylene blue. Irradiation was carried out using 5w LED lamp. The distance between photo reactor and light source was 15cm. The degradation was showed by measuring the absorbance amount using a double beam UV–vis spectrophotometer (Shimadzu UV-1700) at 664 nm wavelength.

3. Results and discussions

3.1. Morphological study

The morphology of the sulfur/graphene particle was demonstrated from SEM image as shown in figure 1. It is apparent that the presence of abundant oxygen containing groups on the GO surface increased the number of active sites for S precipitation [2].

![SEM image of sulfur/graphene composite](image)

Fig. 1 The SEM images of sulfur/graphene composite

3.2. FT-IR spectroscopy

Fig 2 shows the FTIR spectra of the GO and S/RGO. FTIR was used to analyze the change in functional group during the synthesis complete. The FT-IR spectrum of GO, 1625 cm\(^{-1}\) for COO
group, 1392 cm\(^{-1}\) for OH, 1085 cm\(^{-1}\) for C-O groups. The FT-IR spectrum of S/GR 1220 cm\(^{-1}\) for C=S stretching and 1008 cm\(^{-1}\) for c-s stretching can be identify in the spectrum, resulting that S particle are chemically bonded to the GR sheet [2,8].

![FT-IR spectra of graphene oxide and S/GR](image)

**Fig. 2.** (a) FT-IR spectra of graphene oxide (b) FT-IR spectra of S/GR

### 3.3. XRD pattern

XRD patterns providing information on the sulfur graphene composite of samples were presented in Fig. 3. Typical reflections of carbon sulfur (01-084-2400) were clearly observed for the pure S particles [8,9]. The crystal form of S was not affected by the incorporation of GR at different percentages, thus ensuring the photocatalytic activity of \(\alpha\)-S in the S/GR composites. No characteristic GR diffraction peaks could be clearly identified from the XRD pattern of S/GR,
which might be due to the low amount (≤ 3 wt.%) of GR added and its low diffraction intensity [10].

![Fig. 3. XRD patterns of the samples of GR](image)

### 3.4. DRS spectroscopy

Fig. 4 shows the diffuse reflectance spectra (DRS) of the S/RGO and shows that satisfactory photosensitivity narrow band gap (1.69 eV) resulting that S/RGO composite has good effect under visible light. The optical band-gap of samples was calculated using well-known Tauc method. Generally, the Tauc relation is written as:

\[
(\alpha h\nu)^p = A(h\nu - E_g)
\]

Where \(\alpha\) is the absorption coefficient, \(E_g\) is the optical band gap, \(A\) is a constant related to the effective mass and \(h\nu\) is the photo energy \(p\) is the power depending upon the type of optical transition between the valence and conduction bands which takes the value 2 for direct transition and ½ for indirect transition (Fig. 5).
3.5. Photocatalytic degradation of methylene blue and crystal violet

The photocatalytic activities have evaluated by the degradation of usual of organic dyes (methylene blue and crystal violet) in aqueous solution under LED lamp (7 W). GO with high specific area could be results better effect in photo degradation. S/GR composite were used as a photocatalyst for the decomposition of the MB and CV by the hydroxyl radicals formed at their interface. The absorption of MB and CV at 664 and 580 nm was chosen to monitor the photocatalysts degradation process, respectively. The absorption spectra of the MB solution (initial concentration: 10 mg/l, 20 ml) with S/RGO, pure graphene and pure sulfur (0.005 g) under visible light irradiation was shown in Fig. 5. The removal efficiency of MB by S/RGO, pure graphene and pure sulfur illustrate at Fig. 6. The absorption spectra of the CV solution
(initial concentration: 10 mg/l, 20 ml) with S/RGO, pure graphene and pure sulfur (0.005 g) under visible light irradiation was shown in Fig. 7. The removal efficiency of MB by S/RGO, pure graphene and pure sulfur illustrate at Fig. 8.

**Fig. 5.** The absorption spectra of the MB solution (initial concentration: 10 mg/l, 20 ml) with S/RGO (0.005 g) under visible light irradiation.

**Fig. 6.** The removal efficiency of MB by S/RGO, pure graphene and pure sulfur illustrate
4. Conclusion

In this study we showed that effect of sulfur doped in graphene sheets for degradation of Methylene blue and crystal violet. We demonstrated that S/RGO composite the highest destruction pollutes in comparison with pure sulfur and graphene sheets. However we showed that degradation of MB better than CV, yield for MB is 85% and for CV is 62% .
incorporation of graphene was showed that increases adsorption capacity of sulfur and graphene sheets can function enhanced the oxidation ability of the photo inducted hole and generation of OH radical for degradation of MB and CV. The results indicate that the incorporation of graphene with sulfur results in a more effective environmental photocatalytic applications.

References: