

## Reduced graphene oxide/CuS nanocomposite as an efficient photocatalyst for degradation of azure A

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Water pollution is a serious issue all over the world because water is contaminated by various pollutants, out of which dyes are most common and hazardous because of their complex structures making them stable, non-degradable and hazardous. Azure A is such a dye. Composite of rGO/CuS was prepared by mechanochemical method and further characterized by XRD, FTIR and EDAX techniques. This composite was used to degrade azure A photocatalytically. This composite showed better photocatalytic property as compared to pure CuS. Optimum conditions for maximum dye degradation were observed as: pH = 6.5, [Azure A] =  $3.4 \times 10^{-5}$  M, amount of composite = 0.06 g and light intensity =  $50.0 \text{ mW cm}^{-2}$ .

Keywords: Copper sulfide, reduced graphene oxide, azure A, photocatalytic degradation.

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### Introduction

Water pollution is becoming a burning issue all over the globe because of rapid industrialization, transportation, construction, etc. Photocatalysis has emerged as an advanced oxidation technologies for the treatment of waste water containing organic pollutants particularly dyes. ZnO nanorods-reduced graphene oxide composite was synthesized by Lu *et al.*<sup>1</sup> and used to degrade methyl orange under UV-Vis light illumination. Dye almost degraded in 120 min that means this composite has a good photocatalytic activity while Zhou *et al.*<sup>2</sup> prepared rGO/BiVO<sub>4</sub>/SiO<sub>2</sub> composite via one step solvothermal process at 180°C for 4 h. The composite was used to photodegrade reactive blue 19 under visible light irradiation. This composite showed higher photocatalytic activity as compared to BiVO<sub>4</sub> and BiVO<sub>4</sub>/SiO<sub>2</sub>. Reduced graphene oxide and zinc selenide (rGO/ZnSe) nanocomposite was prepared successfully and characterized by Chakraborty *et al.*<sup>3</sup>. Rhodamine B was degraded by this composite, which indicates that the composite is catalytically active. Here, rGO plays an important role in photoinduced charge separation and hindering the electron-hole recombination. An ice templating method was used by Chen *et al.*<sup>4</sup> to fabricate TiO<sub>2</sub>/Chitosan/rGO composite, which has

highly aligned macroporous structure. They degraded methyl orange by this composite. A facile ultrasonic method was reported by Lin *et al.*<sup>5</sup> to prepare CdS/rGO composite. They used graphene in different weight ratio at room temperature and ammonia was used as reducing agent for GO and complexing agent for Cd<sup>2+</sup>. This composite showed improved photocatalytic activity towards degradation of methylene blue under visible light irradiation. p-BiOI/n-rGO composite was prepared via solvothermal reaction. In this process, nitrogen doped rGO flakes were self assembled on the BiOI nanoplates. This composite also showed improved photocatalytic activity for degradation of rhodamine B<sup>6</sup>.

A novel calcined ZnFe layered double hydroxides/reduced graphene oxide (ZnFe-CLDH/rGO) composite was prepared by Zhu *et al.*<sup>7</sup> via hydrothermal-calcination method. This composite showed improved photocatalytic activity to degrade paracetamol. Recently, an efficient photocatalyst was synthesized by Li *et al.*<sup>8</sup> depositing CuS nanoparticles on surface of Co-doped ZnO nanowires. They observed that Co-doped ZnO nanowires modified with CuS nano-particles have three times more photocatalytic efficiency than ZnO nanowires alone. Photocatalytic degradation of methyl orange was observed in its presence. Flower like CuS



easier, which leads to an efficient separation of photogenerated carriers in the coupled rGO/CuS system. Thus, such composite can have enhanced photocatalytic activity.

#### FTIR analysis:

The Fourier-transform infrared spectroscopy (FTIR) spectrum of synthesized rGO was recorded with a Perkin-Elmer spectrum RXI spectrometer in the range from  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  at a scanning rate of  $1\text{ cm}^{-1}/\text{min}$ . FTIR studies were carried out to confirm the presence of functional group. The FTIR of as-prepared rGO is shown in Fig. 4.

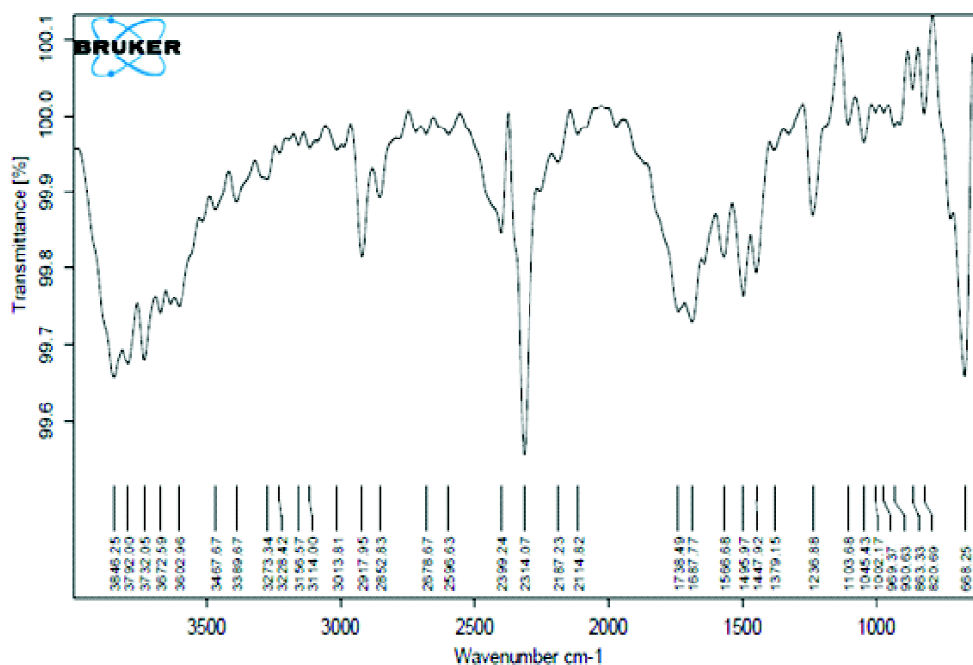


Fig. 4. FTIR of rGO.

Characteristic peak at 1736 (C-O stretching), 1628 (OH stretching in COOH group), 1406 (C-OH stretching and 1089  $\text{cm}^{-1}$  (alkoxy C-O stretching) indicates the formation of rGO.

#### EDAX analysis:

The elemental composition was determined by an energy dispersive X-ray (EDAX) spectrometer. The EDAX result of rGO is given in Table 1.

#### Photocatalytic degradation of azure A:

0.0292 g azure A was dissolved in 100 mL of doubly distilled water, to get a solution with  $1.0 \times 10^{-3}\text{ M}$  dye concentra-

Element	Weight (%)
Carbon	99.41
Oxygen	0.59

tion. This dye solution was used as a stock solution and further diluted as and when required. The pH of the system in the range 5.0 to 9.5 was adjusted by the addition of standardized 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. The temperature of the system was controlled by a thermostat at  $30 \pm 0.1^\circ\text{C}$ . Absorbance of azure A was deter-

mined spectrophotometrically (Systronics Model 106) at  $\lambda_{\text{max}} = 630\text{ nm}$ .

A solution of  $3.40 \times 10^{-5}\text{ M}$  azure A was prepared in doubly distilled water and 0.06 g rGO/CuS composite was added. It was mixed well and allowed to settle. rGO, CuS and rGO/CuS composite are insoluble in the pH range studied. The pH of solution was adjusted at 6.5 and reaction mixture was exposed to a 200 W tungsten lamp at  $50.0\text{ mW cm}^{-2}$ . A water filter was also used to cutoff thermal radiations. Absorbance of this solution was monitored with time. A decrease

was found in absorbance with increasing time of exposure. Experimental set up has been given in Fig. 5.

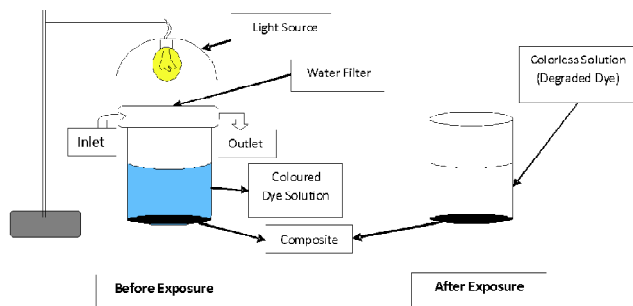


Fig. 5. Experimental set up.

A graph was plotted between  $1 + \log A$  vs time, which was found to be linear (Table 2 and Fig. 6), which indicates that the photocatalytic degradation of azure A followed pseudo-first order kinetics. Rate constant was calculated with the help of eq. (1).

$$k = 2.303 \times \text{slope} \quad (1)$$

Rate constant ( $k$ ) with rGO/CuS =  $1.49 \times 10^{-4} \text{ s}^{-1}$ , rate constant ( $k$ ) with CuS =  $1.03 \times 10^{-4} \text{ s}^{-1}$ , rate constant ( $k$ ) with rGO =  $1.12 \times 10^{-4} \text{ s}^{-1}$ .

Table 2

Time	Composite		CuS		rGO	
	Abs.	$1 + \log A$	Abs.	$1 + \log A$	Abs.	$1 + \log A$
0	0.437	0.6405	0.437	0.6405	0.437	0.6405
20	0.362	0.5587	0.387	0.5877	0.376	0.5752
40	0.316	0.4997	0.342	0.5340	0.331	0.5198
60	0.245	0.3892	0.302	0.4800	0.288	0.4594
80	0.216	0.3345	0.267	0.4265	0.255	0.4065
100	0.183	0.2625	0.237	0.3747	0.224	0.3502
120	0.148	0.1703	0.208	0.3181	0.194	0.2878

pH = 6.5, [Azure A] =  $3.40 \times 10^{-5} \text{ M}$ , Amount of rGO/CuS (composite), rGO and CuS = 0.06 g, Light intensity =  $50.0 \text{ mW cm}^{-2}$ .

The experiments were repeated three times and the results were found reproducible within limit  $\pm 0.02$ .

#### Effect of pH:

Variation in pH was carried out from 5.0 to 9.5. The results are presented in Table 3.

It was observed that the rate of dye degradation increases on increasing pH. At a particular pH 6.5, it reaches its maxi-

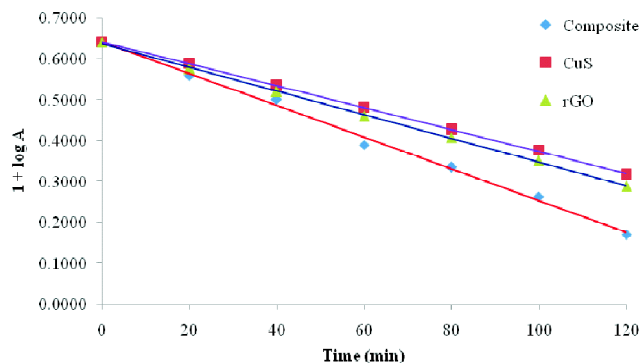


Fig. 6. Typical runs.

Table 3. Effect of pH

pH	Rate constant ( $k$ ) $\times 10^4 \text{ (s}^{-1}\text{)}$
5.0	1.11
5.5	1.25
6.0	1.31
6.5	1.49
7.0	1.30
7.5	1.23
8.0	1.11
8.5	1.09
9.0	0.96
9.5	0.86

[Azure A] =  $3.40 \times 10^{-5} \text{ M}$ , Amount of rGO/CuS composite = 0.06 g, Light intensity =  $50.0 \text{ mW cm}^{-2}$ .

imum, after that a decrease was observed in rate of reaction on increasing pH further. This may be explained on the basis that more OH ions are available in solution with increasing pH, generating more  $\cdot\text{OH}$  radicals; consequently resulting in increase in rate of the reaction. But above pH 6.5, a decrease in reaction rate was observed because cationic molecules are present in their almost neutral forms, so that there will be no interaction between neutral dye molecules and negatively charged surface of the composite. A decrease is also observed below pH 6.5. It may be explained, due to repulsion between cationic dye molecules and positively charged surface of composite.

#### Effect of dye concentration:

Different concentrations of azure A ( $3.00\text{--}5.00 \times 10^{-5} \text{ M}$ ) were used to study the effect of dye concentration on its photocatalytic degradation. The results are shown in Table 4.

It was found that there was an increase in the rate with

**Table 4.** Effect of dye concentration

[Azure A] × 10 <sup>5</sup> M	Rate constant (k) × 10 <sup>4</sup> (s <sup>-1</sup> )
3.00	0.72
3.20	1.15
3.40	1.49
3.60	1.40
3.80	1.27
4.00	1.18
4.20	1.11
4.40	1.02
4.60	0.95
4.80	0.83
5.00	0.78

pH = 6.5, Amount of rGO/CuS composite = 0.06 g, Light intensity = 50.0 mW cm<sup>-2</sup>.

increasing dye concentration but after a certain concentration of dye, 3.40 × 10<sup>-5</sup> M, a decrease in reaction rate was observed. This may be due to the fact that at larger concentrations, dye will start acting like as filter to incident light. This will reduce the light intensity reaching the surface of the composite and as a result, rate of degradation of dye also retarded.

*Effect of amount of composite (rGO/CuS):*

Amount of rGO/CuS composite was varied in range of 0.02–0.14 g and results are presented in Table 5. It was found that the rate of degradation of azure A increased with an increase in amount of catalyst but after a particular amount of catalyst (0.06 g), a decrease was observed in reaction rate by further increasing the amount of catalyst.

**Table 5.** Effect of amount of rGO/CuS composite

Amount of composite (g)	Rate constant (k) × 10 <sup>4</sup> (s <sup>-1</sup> )
0.02	1.24
0.04	1.30
0.06	1.49
0.08	1.27
0.10	1.04
0.12	0.98
0.14	0.88

pH = 6.5, [Azure A] = 3.40 × 10<sup>-5</sup> M, Light intensity = 50.0 mW cm<sup>-2</sup>.

An increase in reaction rate of photocatalytic degradation of azure A on increasing the amount of composite may be due to increase in its exposed surface area. But after a

certain amount of catalyst (0.06 g), a decrease in rate of degradation was observed. This decrease in rate may be due to fact that there was no increase in exposed surface area on increasing amount of composite above the limit because of the formation of multilayers, which makes the electron-hole recombination convenient. By recombination of electron-hole, less number of \*OH radicals will form, which is the main reactive oxidizing species.

*Effect of light intensity:*

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

**Table 6.** Effect of light intensity

Light intensity (mW cm <sup>-2</sup> )	Rate constant (k) × 10 <sup>4</sup> (s <sup>-1</sup> )
20.0	0.83
30.0	1.02
40.0	1.13
50.0	1.49
60.0	1.14
70.0	1.12

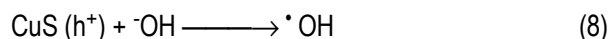
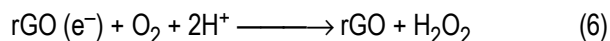
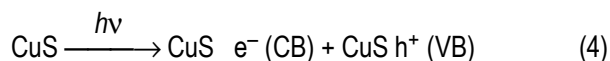
pH = 6.5, [Azure A] = 3.40 × 10<sup>-5</sup> M, Amount of rGO/CuS composite = 0.06 g.

An increase in rate of reaction was found with increasing light intensity. The optimum degradation was achieved at 50.0 mW cm<sup>-2</sup>. After this optimum, a decrease was found in reaction rate by increasing the light intensity further. This increase in photocatalytic degradation can be explained that number of photons, striking per unit area per unit time will increase, when light intensity was increased. But after an optimum value, the decrease in reaction rate was observed, which may be due to thermal side reactions. Therefore, light intensity of the medium order was used.

*Mechanism:*

The photocatalytic degradation of azure A was also carried out in the presence of \*OH scavengers (isopropanol), where reaction rate was reduced a lot, which indicates active participation of \*OH radicals as active oxidizing species. A tentative mechanism for degradation of azure A may be proposed as:





First of all, light of suitable wavelength is absorbed by molecules of azure A (AA). These molecules get excited to their first excited singlet state, which is transferred to triplet state through intersystem crossing. Light is also absorbed by CuS, where an electron is excited from its conduction band leaving behind a hole in its valence band. rGO acts as an electron sink and this electron from conduction band will be abstracted by rGO. rGo ( $e^-$ ) may react with oxygen molecule (dissolved oxygen) and protons to form hydrogen peroxide, which will decompose to generate hydroxyl radicals. Similarly, hole in valence band of CuS abstracts an electron from  $\cdot OH$  ions, generating  $\cdot OH$  radicals. In this photocatalytic dye degradation process, this  $\cdot OH$  radical acts as an active oxidizing species, which will oxidize azure A to its leuco form and finally, this leuco form degrades to almost harmless and smaller products.

## Experimental

### Preparation of rGO, CuS and composite :

Graphite was purchased from Merck and  $CuSO_4$ , ascorbic acid were purchased from Himedia. The rGO was synthesized from graphite by a new green chemical route<sup>18</sup> and CuS by precipitation method. The composite of rGO with CuS was prepared by mechanochemical method following top-down approach. Equal amounts of rGO and CuS (1:1 w/w) were ground with agar mortar pestle. This composite powder was used for further process.

## Conclusion

The results of present investigation revealed that rGO/CuS showed higher efficiency for photocatalytic degradation of azure A as compared to individual component CuS (44.6% increase) and rGO (33.0% increase). Composite of CuS with

rGO showed potential application in the treatment of waste water containing dyes. The present work will open new avenues for further researches on use of rGO-photocatalyst composites for eco-friendly method of waste water treatment in coming decade.

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