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# Photocatalytic Degradation of Azure B by Reduced Graphene Oxide-Copper Sulphide Composite (rGO-CuS): A Green Approach Towards Environmental Remediation

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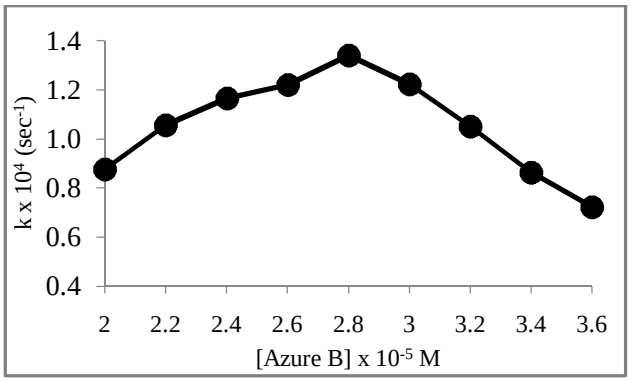
## ABSTRACT

*Nanotechnology is an emerging field that covers a wide range of technologies which are presently under development in nanoscale. It plays a major role in the development of innovative methods to produce new products, to substitute or reformulate new nanomaterials and chemicals with improved performance to reduced harm to the environment as well as environmental remediation. Graphene, an atomically thin two-dimensional hexagonal array of carbon atoms, and its analogues have been visualized as ultimate materials for the separation of pollutants from water. In this paper, photocatalytic performance of rGO/CuS composite, rGO and CuS was evaluated by using a model system of azure B. Optimum conditions obtained for photocatalytic degradation of azure B are: pH = 8.5, [Azure B] = 2.80 × $10^{-5}$ M, amount of composite = 0.10 g and light intensity = 50.0 mW $cm^{-2}$. It was concluded that composite showed good photocatalytic activity as compared to individual CuS and rGO.*

## Graphical Abstract




Effect of concentration of Azure B.

**Keywords:** Photocatalysis, wastewater, reduced graphene oxide (rGO), copper sulfide, Azure B.

## INTRODUCTION

Polluted waste water plays a significant role in environmental pollution. Industrial effluents contain different chemicals especially synthetic dyes, which are carcinogenic in nature also. Some dyes decompose aerobically and anaerobically resulting in the formation of carcinogenic compounds. Classical techniques, which are still in use to decontaminate polluted water include adsorption [**1-3**], chlorination [**4, 5**], coagulation [**6, 7**], ion flotation [**8**], membrane process [**9, 10**], sedimentation [**11**] and solvent extraction [**12, 13**]. The end products of these techniques need to be processed further for complete purification. There are newer advanced oxidation processes, which can be used to degrade dyes into harmless products like carbon dioxide and water [**14**]. These include biodegradation [**15, 16**], Fenton/photo-Fenton degradation [**17-20**], UV/Visible light driven photocatalytic degradation process [**21**] etc. These advanced oxidation processes are better than chemical ones. Photocatalysis is the field, where nanomaterials can play an important role. Different nanostructures of $TiO_2$, ZnO, $CeO_2$, $SnO_2$, $SnS_2$, CdS, $BiFeO_3$, etc. are used as individual or in the form of composites as photocatalysts for the degradation of several organic pollutants like phenols, drugs, hydrocarbons, dyes, etc.[**22-28**]. These organic pollutants are transformed in relatively harmless molecules such as $CO_2$, $N_2$, $H_2O$, some inorganic anions, etc. after degradation. The latest addition to the nanocarbon family, graphene, an atomically thin two-dimensional hexagonal arrays of carbon atoms, has been proclaimed to be the material of the century. Due to their tuneable property, it is applicable in diverse fields including catalysis. The high surface area and volume ratio make graphene oxide (GO) or reduced graphene oxide (rGO), an interesting candidate in the field of environmental remediation.

## MATERIALS AND METHODS

**Preparation of rGO, CuS and composite:** The rGO was synthesized from graphite by a new green chemical route and CuS by precipitation method. The composite of rGO with CuS was prepared by mechanochemical method following top-down approach. As-synthesized composite was characterized by FTIR, FESEM, EDX and further used for photocatalytic degradation [**29**].

**Photocatalytic degradation process:** Stock solution of $1.0 \times 10^{-3}$ M concentration was prepared by dissolving 0.0306 g of Azure B in100.0 mL of doubly distilled water. It was used as a stock solution. This stock solution was used to prepare working solutions during the whole experiment.

The dye solution was placed in equal amounts in four beakers.

- The first beaker containing Azure B solution was kept in dark.
- The second beaker containing Azure B solution was exposed to light.
- The third beaker containing Azure B solution and 0.1 g composite was kept in dark.
- The fourth beaker containing Azure B solution and 0.1 g composite was exposed to light.

After exposing these beakers for 3 h, absorbance of solution of each beaker was measured with the help of a spectrophotometer. The absorbance of the solution of first three beakers was found almost constant, but the solution of the fourth beaker showed a decrease as compared to initial value of its absorbance. It is clear from all these observations that the degradation required light and rGO, CuS or composite. The desired pH of the solution was adjusted by the addition of standard 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. About 3 mL aliquot was taken out after fixed time interval to measure absorbance with the help of spectrophotometer (Systronics Model 106) at $\lambda_{max}$ = 650 nm. A water filter was used to cut off thermal radiations. The intensity of light was varied by changing the distance between the light source and reaction mixture, and it was measured by Suryamapi (CEL model SM 201). It was observed that the absorbance of the solution decreases with increasing the time of exposure.

## RESULTS AND DISCUSSION

Typical runs of rGO-CuS (composite), CuS and rGO are graphically represented in figure 1. The rate constant for degradation was calculated with the help of equation:

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

The rate constant was found to be 1.34 x $10^{-4}$ $s^{-1}$ as compared to individual rGO (1.06 x $10^{-4}$ $s^{-1}$) and CuS (9.51 x $10^{-5}s^{-1}$),at optimum values of operational parameters; pH = 8.5, rGO, CuS orrGO-CuS composite = 0.10 g, [Azure B] = 2.80 x $10^{-5}$ M, Light intensity = 50.0 mW $cm^{-2}$.

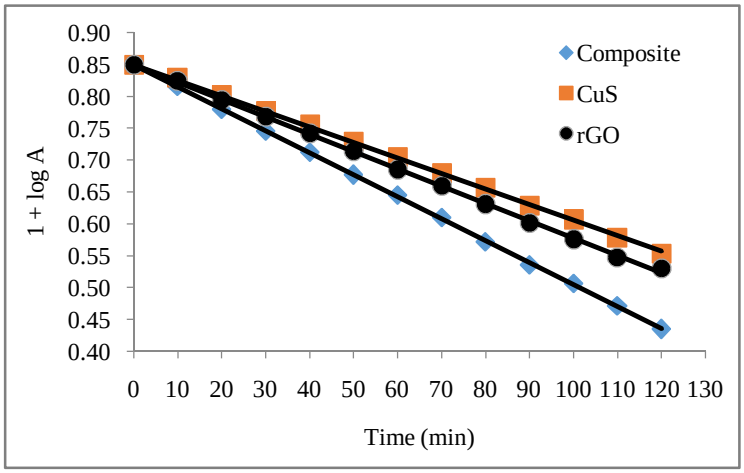



**Figure 1.** Typical runs.

Different rate affecting parameters were studied to obtain the optimum values for the maximum rate of reaction for photocatalytic degradation of crystal Azure B.

**Effect of pH:** The pH of the solution may affect the degradation of Azure B. The effect of pH on the rate of degradation of Azure B was investigated in the pH range 5.0–9.5. The results are graphically reported in figure 2. It was observed that the rate of photocatalytic degradation increased with increase in pH up to 8.5, but rate of the reaction gradually goes declined on increasing pH above 8.5.

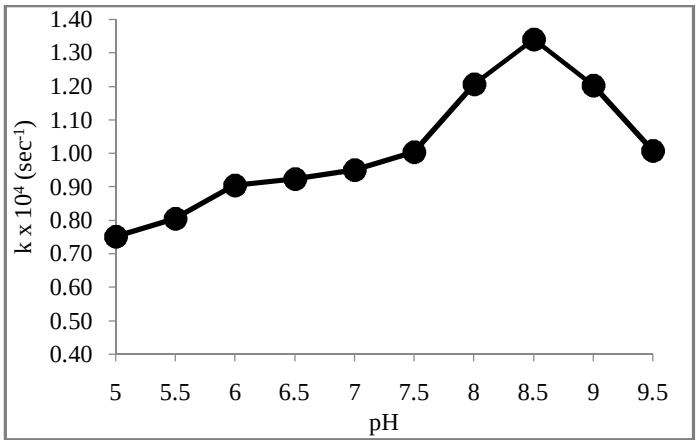



**Figure 2.** Effect of pH.

This increase in rate of reaction may be due to availability of more $OH^-$ ions in solution. After a certain pH, there was a decrease in reaction rate, because cationic molecules are present in their neutral or almost neutral forms, and therefore, there will be no attraction between neutral dye molecules and –ve charged surface of composite.

**Effect of concentration:** The effect of dye concentration was observed by taking different concentrations of Azure B. The results are represented in figure 3.

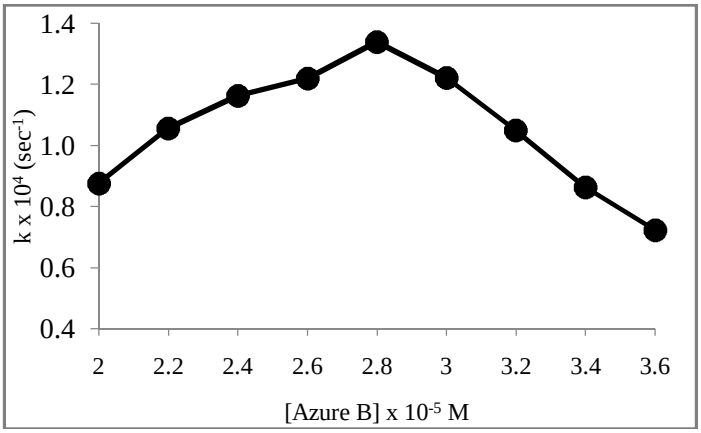



**Figure 3.** Effect of concentration of Azure B**.**

It was observed that the rate of photocatalytic degradation increased with increase in concentration of Azure B up to 2.8 $x10^{-5}$ M, but any increase in concentration above this limit results in a decrease in rate of the reaction. This observation may be explained by the fact that with the increase in concentration of dye; there is an increase in number of dye molecules for excitation and energy transfer. As a result, the rate of photocatalytic degradation increased significantly. A decrease in rate of degradation may be attributed to the fact that after a certain dye concentration, the dye itself starts acting as an internal filter for incident light, and hence, it will not allow the required light intensity to reach the surface of the composite. As a consequence, a decrease in rate of photocatalytic degradation was observed.

**Effect of amount of composite:** The effect of dose of composite on the dye removal was also studied. It was observed that rate of dye removal increases as amount of adsorbent was increased up to a certain amount of composite (0.10 g), after that the rate of reaction decreases. The results of effect of adsorbent dose on the removal of Azure B are given in figure 4. Highest rate of reaction was observed at 0.10 g, and hence, it was taken as optimum value for further studies.

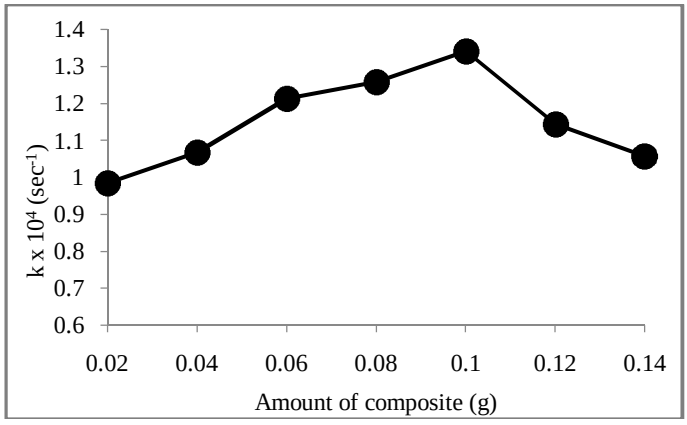



**Figure 4.** Effect of amount of composite.

Such variation may be due to the fact that as the amount of composite was increased, the exposed surface area of the composite increases. An increase in the amount of composite will only increase the thickness of layer of the composite and not its exposed surface area. On increasing the amount of composite above 0.10 g, multilayer is formed making $e^-$- $h^+$ recombination easier. As a result, the rate of degradation decreases slightly.

**Effect of light intensity:** The light intensity was varied by changing the distance between the light source and the exposed surface area of composite to study the effect of light intensity on photocatalytic degradation of Azure B. It was observed that the rate of photodegradation increases up to 50.0 mW $cm^{-2}$ and then decreases with further increase in light intensity. The results of observation are graphically presented in figure 5.

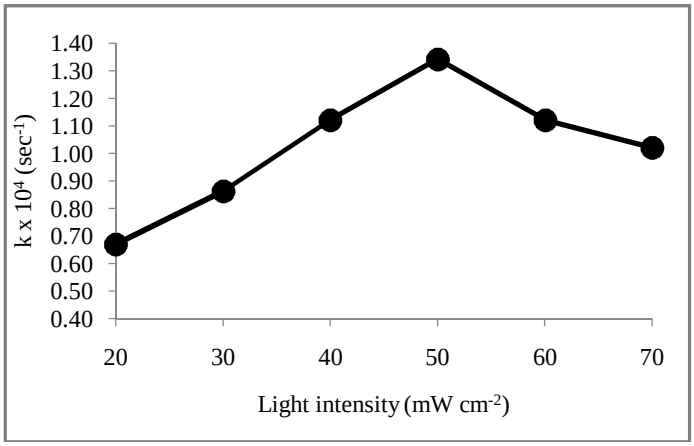



**Figure 5.** Effect of light intensity.

This can be explained on the basis that as the light intensity was increased, number of photons striking per unit area per unit time increases, which leads to higher rate of degradation for dye. Further increase in the light intensity may cause some other thermal side reactions so the rate of the reaction is slightly decreased and therefore, higher light intensities were avoided.

**Mechanism:** A tentative mechanism of photocatalytic degradation of Azure B (AB) in presence of rGO-CuS composite may be proposed as:

$$^1AB_0 \xrightarrow{h\nu} {}^1AB_1 \quad \ldots (2)$$

$$^1AB_1 \xrightarrow{ISC} {}^3AB_1 \quad \ldots (3)$$

$$CuS \xrightarrow{h\nu} CuS\ \{e^-\ (CB) + h^+\ (VB) \quad \ldots (4)$$

$$CuS\ (e^-) + rGO \longrightarrow rGO\ (e^-) \quad \ldots (5)$$

$$CuS\ (h^+) + {}^-OH \longrightarrow {}^{\bullet}OH \quad \ldots (6)$$

$${}^{\bullet}OH + {}^3AB_1 \longrightarrow Leuco\ AB \quad \ldots (7)$$

$$Leuco\ AB \longrightarrow Oxidized\ products \quad \ldots (8)$$

Azure B is excited to its first excited singlet state by absorbing light of suitable wavelength, which undergoes intersystem crossing to its corresponding triplet state. Electrons in CuS are also excited to its conduction band by absorbing light. rGO acts as sink for the photogenerated electrons in the coupled nanocomposite. This minimizes the recombination of the photogenerated electron-hole pairs in CuS and gives sufficient time for these electrons and holes to migrate across the surface of the coupled nanocomposite photocatalyst, where these pairs participate in redox reactions. The holes can react with surface-bond $OH^-$ to produce the hydroxyl radicals. These radicals will oxidize triplet state of Azure B to its leuco form, which will finally degrade to oxidized products.

## APPLICATION

This highly stable photocatalytic material has an improved efficiency to reduce water, when compared to irregularly shaped nanoparticles. This composite may used for the degradation of various organic pollutants and used for environment remediation. One can expect to utilize this new strategy to explore interplay of chemical composition and nanoscale morphology affecting the photocatalytic activity favorably, with the goal of finding new and highly efficient photocatalysts.

## CONCLUSION

The combination of appropriate quantities of rGO with semiconductor CuS made the composite a relatively more efficient photocatalyst; 26.4 and 41.0 % more efficient then rGO and CuS, respectively. Introduction of CuS to the rGO sheet enhances the surface area of CuS-rGO and increases the degradation capacity. It exhibits good removal capacity due to adsorption phenomena of rGO and photocatalytic activity of CuS towards organic pollutants.

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