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Reduced Graphene Oxide/CuS Nanocomposite: An Efficient Photocatalyst for Degradation of Crystal Violet

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ABSTRACT

Scarcity of both quality and quantity of water has become a burning problem all over the world. Pollution by dyes constitutes a major portion. Advanced oxidation processes have been developed as green chemical technology to combat against water pollution. Graphene oxide is a 'miracle material' with 2D honeycomb structure, which is also known for enhancement of photocatalytic activity of different semiconductors. In this paper, reduced graphene oxide with a combination of copper sulphide (rGO-CuS composite) is used to remove crystal violet photocalatytically from waste water. The photocatalytic performance of rGO/CuS composite and CuS was evaluated by using a model system of crystal violet. Optimum conditions obtained for photocatalytic degradation of crystal violet are: pH = 5.0, [Crystal Violet] = 3.40×10^{-5} M, amount of composite = 0.12 g and light intensity = 50.0 $mWcm^{-2}$. It was observed that composite showed good photocatalytic activity as compared to individual CuS (48.1% increase) and rGO (32.8% increase).

1. Introduction

Wastewaters from food colouring, cosmetics, paper and textile industries are polluted by dyes. When these coloured effluents enter rivers or any other surface water system, they upset the biological activity. Ground-water systems are also affected by these pollutants because of leaching from the soil. Dyes are frequently used in various industries. During its production and application in dyeing, a huge amount of effluent water containing high concentration of organic dyes is generated. Due to high solubility of dyes in water, it is quite difficult to remove these from waste water. Many dyes may cause allergy, skin irritation, and various health issues like nausea, vomiting, profuse sweating or some time mutation in humans, even some of them are carcinogenic. The conventional methods for treating dye-containing wastewaters are: electrochemical reduction method [1], adsorption [2-3], coagulation and flocculation [4-6], nanofiltration or reverse osmosis [7-9] etc. These are widely used for removal of organic pollutants.

Recently, advanced oxidation processes (AOPs) have been focused for degradation of dye in waste water due to their advantages such as eco-friendly, economically viable and capability to degrade many dyes or organic pollutants present in water. Photocatalysis is one of the advance oxidation processes and it is mainly carried out under irradiation of light and presence of suitable photocatalytic materials. The photocatalytic activity of the photocatalytic materials mainly depends on the band gap, surface area, and generation of electron–hole pair. It has been observed that the surface area plays a major role in photocatalytic degradation of dyes, which leads to the higher adsorption of dye molecule on the surface of photocatalyst and enhancement of photocatalytic activity [10]. Several photocatalysts like TiO_2, SiO_2, ZnO, BiOI/BiOBr, SnO_2, Ag_3VO_4, etc. are used to degrade various pollutants. These photocatalysts are used as individual or after making composites with some natural, synthetic or carbon-based adsorbents [11-23]. In the present work, reduced graphene oxide and copper sulphide (rGO-CuS) composite was used for the removal of crystal violet.

2. Experimental Methods

2.1 Preparation of Composite

The composite of rGO and CuS was fabricated by mechanochemical method following a top-down approach. Equal amounts of rGO and CuS were ground with agar mortar-pestle. This synthesised composite was characterised by several techniques like XRD, FESEM and EDX and used in experiment.

2.2 Characterisation

XRD of rGO and rGO-CuS were recorded with the help of X-ray diffractometer (XPERT-PRO model) in the range 20° to 80°. A characteristic peak of rGO was present around 25°. The crystal size of rGO-CuS was calculated using Debye – Scherrer equation. Its average particle size was found to be about 43.95 nm. FESEM was recorded on XFlash 6130 (Bruker) (Fig. 1). FESEM image of rGO-CuS is in the favour of CuS attached to rGO, which provides more surface area for better photocatalytic activity. It is also easy to transfer photogenerated electrons in the composite permitting electron-hole recombination. The composition of composite was also determined with the help of EDAX. The results are given in Fig. 2 and Table 1.

2.3 Photodegradation Process

Stock solution of 1.0×10^{-3} M concentration was prepared by dissolving 0.0408 g of crystal violet dye in 100.0 mL of doubly distilled water. Further working solutions were prepared from this stock solution as and when required. The absorbance of experimental solution was determined by spectrophotometer at λmax = 540 nm. Experimental solutions were irradiated with a 200 W tungsten lamp. Control experiments were performed, which indicates that the degradation required both; light and composite. The desired pH of the reaction mixture was adjusted by addition of standard 0.1 N sulfuric acid and 0.1 N sodium hydroxide solutions. A decrease in absorbance of crystal violet dye solution was observed with increasing time of exposure. A plot of 1 + log A against time was found to be linear, which indicates that the photocatalytic degradation of crystal violet follows pseudo–first order kinetics.

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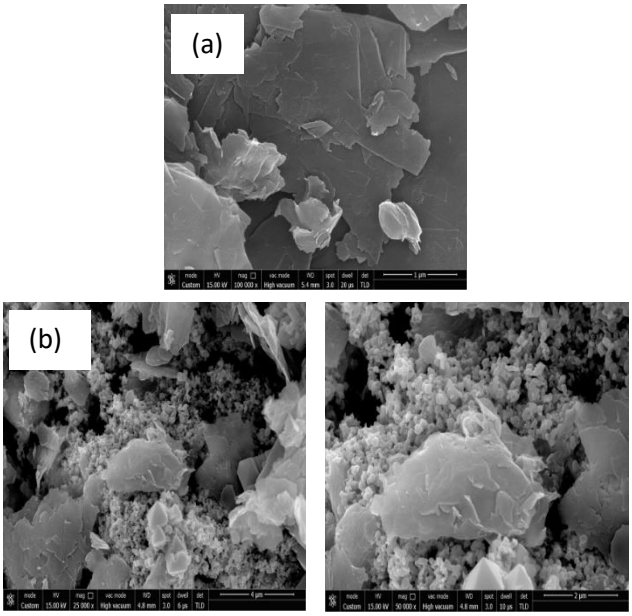

Fig. 1 FESEM image of a) rGO and b) CuS-rGO

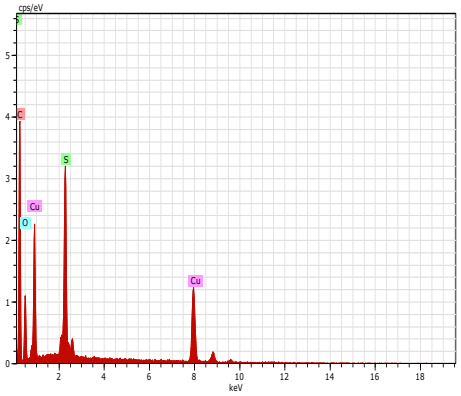

Fig. 2 EDAX image of rGO-CuS

Table 1 EDAX results of rGO-CuS

Element	Weight (%)
Carbon	56.16
Oxygen	15.81
Copper	19.39
Sulphur	8.64

3. Results and Discussion

The rate constant for degradation was measured with the help of equation, k = 2.303 × slope, Typical runs of rGO, CuS and rGO-CuS composite is graphically represented in Fig. 3. The rate constant was found to be 1.54 x 10^{-4} s^{-1} as compared to individual rGO (1.16 x 10^{-4} s^{-1}) and CuS (1.04 x10^{-4} s^{-1}), at optimum values of pH = 5.0, crystal violet concentration = 3.40 x 10^{-5} M, amount of rGO, CuS, composite = 0.12 g and light intensity =50.0 $mWcm^{-2}$. Different rate affecting parameters were varied to obtain the maximum rate of degradation for photocatalytic degradation of crystal violet.

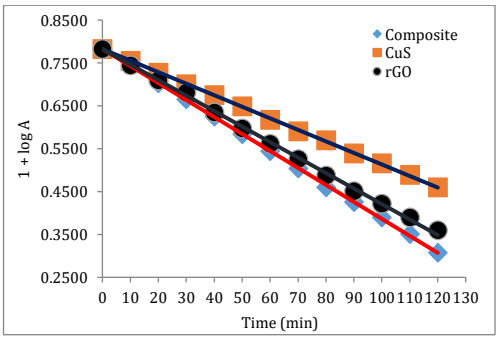

Fig. 3 Typical runs of rGO, CuS and rGO-CuS composite

3.1 Effect of pH

The pH of the solution may affect the degradation of crystal violet. The effect of pH on the rate of degradation of crystal violet was investigated in the pH range 4.0–8.5 and is shown in Fig. 4. It was observed that the rate of photocatalytic degradation increased with increase in pH up to pH 5.0 but on increasing pH above this limit, rate of the reaction gradually declined. Maximum degradation was found in acidic medium. As pH was decreased, acidic nature will increase and adsorption of H^+ ions will be more on composite. A decrease in reaction rate may be due to force of repulsion between cationic dye molecules and + ve charged surface of the composite.

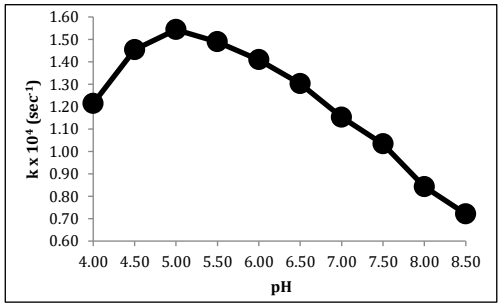

Fig. 4 Effect of pH

3.2 Effect of Dye Concentration

The effect of dye concentration was observed by taking different concentrations of Crystal violet. The results are graphically represented in Fig. 5. It was observed that the rate of photocatalytic degradation increases with an increase in dye concentration and attained optimum rate at 3.40 × 10^{-5} M. It may be explained that as the concentration of dye was increased, a large number of dye molecules were available for excitation and energy transfer and as a result, the rate of photocatalytic degradation increased appreciably. It was found that the rate of photocatalytic degradation decreased with an increase in the concentration of dye further.

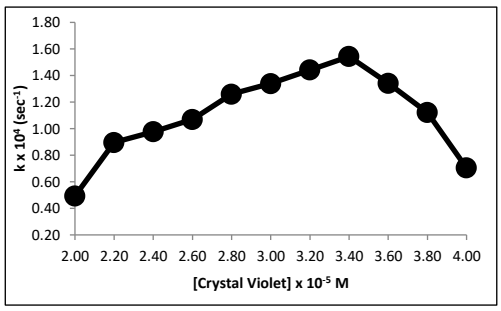

Fig. 5 Effect of crystal violet concentration

This 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 desired light intensity to reach the surface of the composite. As a consequence, decrease in rate of photocatalytic degradation was observed.

3.3 Effect of Amount of Composite

The amount of composite may also affect the degradation of dye and hence, different amounts of rGO-CuS composite were used. Their results are graphically represented in Fig. 6. It was observed that the rate of photocatalytic degradation increased with increase in amount of composite up to a certain value (0.12 g), but on further increasing the amount of composite, the rate of the reaction gradually declined.

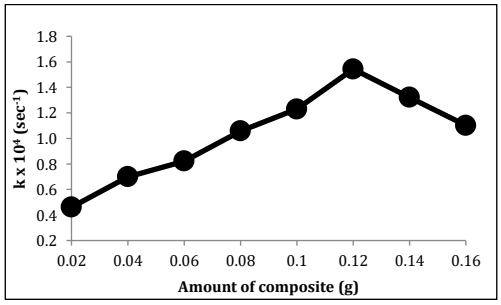

Fig. 6 Effect of amount of composite

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As the amount of composite was increased, the exposed surface area of the composite increases but above 0.12 g, an increase in the amount of composite will only increases the thickness of layer of the composite and not its exposed surface area. As a result, the rate of degradation decreases slightly.

3.4 Effect of Light Intensity

The effect of light intensity on the photocatalytic degradation of crystal violet was also investigated by changing the distance between the light source and the exposed surface area of composite. The variation of results is graphically presented in Fig. 7. It was observed that as the light intensity was increased, the rate of photodegradation increases upto a certain value (50.0 $mWcm^{-2}$). Further increase in light intensity results in decrease in the rate of photodegradation.

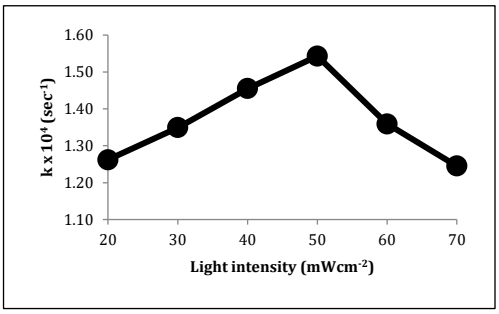

Fig. 7 Effect of light intensity

This observation may 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. Further increase in the light intensity may cause some other thermal side reactions so the rate of the reaction was decreased and therefore, higher light intensities were avoided.

3.5 Mechanism

On the basis of above observations, a tentative mechanism for photocatalytic degradation of crystal violet is proposed as follows:

$$^1\text{Crystal violet}_0 \xrightarrow{h\nu} {}^1\text{Crystal violet}_1 \quad (1)$$

$$^1\text{Crystal violet}_1 \xrightarrow{ISC} {}^3\text{Crystal violet}_1 \quad (2)$$

$$CuS \xrightarrow{h\nu} CuS\{e^- (CB) + h^+(VB)\} \quad (3)$$

$$CuS\ (e^-) + rGO \longrightarrow rGO\ (e^-) \quad (4)$$

$$rGO\ (e^-) + O_2 \longrightarrow O_2^{\bullet -} + rGO \quad (5)$$

$$O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet} \quad (6)$$

$$HO_2^{\bullet} + {}^3\text{Crystal violet}_1 \longrightarrow \text{Leuco Dye} \quad (7)$$

$$\text{Leuco Dye} \longrightarrow \text{Oxidized products} \quad (8)$$

4. Conclusion

People from all around the world are facing the problem of ever-increasing water pollution and as a consequence, there is a scarcity of potable water. Nanocomposite of CuS with rGO show potential application in the treatment of waste water containing dyes. Using this composite, crystal violet was successfully degraded with higher efficiency as compared to individual component CuS (48.1%, increase) or rGO (32.8%, increase). The present work will open new avenues for further researches on use of rGO-photocatalyst composites as an eco-friendly method of waste water treatment in coming decades.

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