

## Copper oxide supported on graphene for photodegradation of Rhodamine B

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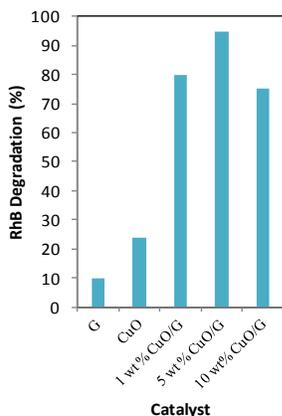
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### GRAPHICAL ABSTRACT



### ABSTRACT

In recent years, dyes are one of the major sources of the water contamination that lead to environmental problems. For instance, Rhodamine B (RhB) which was extensively used as a colorant in textile industries is toxic and carcinogenic. Among many techniques, photocatalytic degradation become the promising one to remove those dyes from industrial wastewater. Recently, graphene has shown outstanding performance in this application due to its intrinsic electron delocalisation which promotes electron transport between composite photocatalyst and pollutant molecules. While, copper oxide (CuO) is well-known has a lower bandgap energies compared to other semiconductors. Therefore, in this study, copper oxide supported on graphene (CuO/G) was prepared and its photocatalytic activity was tested on degradation of RhB. The catalysts were characterized by X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) Spectroscopy. The results showed that the interaction between copper and graphene support could enhance the photocatalytic activity. The 5 wt% CuO/G was found to give the highest degradation (95%) of 10 mg L<sup>-1</sup> of RhB solution at pH 7 using 1 g L<sup>-1</sup> catalyst after 4 hours under visible light irradiation. The photodegradation followed the pseudo first-order Langmuir-Hinshelwood kinetic model. This study demonstrated that the CuO/G has a potential to be used in photocatalytic degradation of various organic pollutants.

**Keywords:** copper oxide, graphene, photodegradation, rhodamine B

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## 1. INTRODUCTION

Dyes widely used in the textile, paper, cosmetics and plastics industries led to severe environmental contamination due to emission of toxic and colored wastewater into water bodies [1]. The discharge of dye was increased about 10,000 tons per year due to many large scale-productions [2]. Rhodamine B (RhB) is a well-known synthetic dye that has been used extensively in textile and printing industries which can contribute to water pollution because of its high solubility in water [3, 4]. In addition, it was toxic and carcinogenic to the humans and other living things when used as a colorant [5].

In a view of the rising awareness toward water quality preservation and improvement, the development of a clean and efficient water purification technology has become the focus for researcher in the last few decades. Various techniques have been developed to remove dyes which include Fenton reagent, ozonation, and electrochemical destruction, adsorption, membrane filtration and

ion exchange [6]. However, these techniques suffer from high operational cost and possibility for the generation of secondary pollutant. Among those techniques, heterogeneous photocatalysis has emerged as one of the most powerful methods for water decontamination because of its potential to transform recalcitrant organic contaminants into mineral salts and harmless species such as CO<sub>2</sub> and H<sub>2</sub>O [7]. This method involves the utilization of a semiconductor catalyst (such as TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, CdS, GaP or ZnS) irradiated with light of appropriate wavelength, to generate highly reactive species (i.e., •OH, •O<sup>2-</sup>, •HO<sub>2</sub>) for mineralization of organic impurities. Unfortunately, the insufficient quantum efficiency, narrow excitation wavelength, high recombination rate of the electron-hole pairs, and poor adsorption capacity are the limitation for the practical application of this technique [8]. In order to overcome these problems, a variety of approaches have been attempted including metal particle loading, co-catalysts, dye sensitization, metallic and non-metallic doping.

Recently, rapid advancements in nanoscience and nanotechnology gained attention toward harnessing the outstanding physicochemical properties of graphene/semiconductors nanocomposites (GSN) for designing new photocatalyst systems. Graphene, as a new material with zero band gap semimetal has the potential to enhance the photocatalytic activity of semiconductors [9]. It can absorb light over a broad range of wavelengths and thus facilitate the visible light catalysis. In addition, the excellent charge trapping ability of graphene nanosheets can be utilized to retard the electron-hole pairs recombination [10]. Moreover, owing to its infinitely large surface-to-volume ratio, graphene has a tendency to adsorb a wide range of synthetic organic compounds as well as inorganic substances [11]. In view of these attractive attributes, photocatalytic performance of copper oxide supported on graphene was investigated. The properties of the catalysts were characterized by XRD and FTIR.

## 2. EXPERIMENTS

### 2.1 Catalyst Preparation

The CuO/G was prepared using electrochemical method in accordance with the procedure reported in the literature [12-16]. The process was performed in one-compartment cell equipped with a magnetic stirring bar and two-electrode configuration. A copper plate (2 cm × 2 cm) anode and a platinum plate (2 cm × 2 cm) cathode were carefully cleaned using 1.0 M HCl followed by deionized water before used as electrodes. The electrodes were placed in parallel with a distance of 2.0 cm and were inserted into the solution of 0.1M TEAP, naphthalene mediator and G (1 g). Then electrolysis was conducted at a constant current of 120 mA/cm<sup>2</sup> and 0°C under nitrogen atmosphere. After electrolysis, the mixture was heated at 80°C in an oil bath before being dried overnight at 110°C and calcined at 300 K for 3h. The required copper loading on G support was calculated based on Faraday's law of electrolysis, as follow:

$$n = \left( \frac{It}{F} \right) \left( \frac{1}{z} \right) \quad (1)$$

where  $n$  is the number of moles of Cu,  $I$  is constant current of electrolysis (A),  $t$  is the total time the constant current was applied (s),  $F$  is the Faraday constant (96487 C mol<sup>-1</sup>), and  $z$  is the valency number of ions of the substance (electron transferred per ion). The as-prepared catalyst were obtained and ready to characterize and reaction testing.

### 2.2. Characterization of the catalyst

The study of crystalline structures of the catalysts were carried out using a Bruker Advance D8 X-ray powder

diffractometer (XRD) with CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at  $2\theta$  angle ranging from 20° to 50°. The chemical functional groups present in the catalysts were identified by FTIR spectroscopy (Perkin Elmer Spectrum GX FTIR Spectrometer). IR absorbance data were obtained over a range of wavenumbers 400-4000 cm<sup>-1</sup>.

## 3. RESULTS AND DISCUSSION

Fig. 1A shows wide-angle XRD patterns of the catalysts in order to confirm the purity and crystalline structure of the catalysts. The sharp peaks of CuO at  $2\theta$  of 35.5° and 38.7° is attributed to the (111) and (200) plane, respectively (JCPDS Card No. 05 0661). While the G was clearly identified as the carbonaceous material peaks at  $2\theta$  of 26.1° correspond to (002) plane (JCPDS no. 24-0734) [17]. The XRD pattern of the CuO/G catalyst was similar to those G indicating that the introduction of Cu did not have much effect on the structure of the catalysts. However, the peak intensity of G seemed to decrease with increasing CuO loading. This was most probably due to the good distribution of Cu on the surface of the G [18].

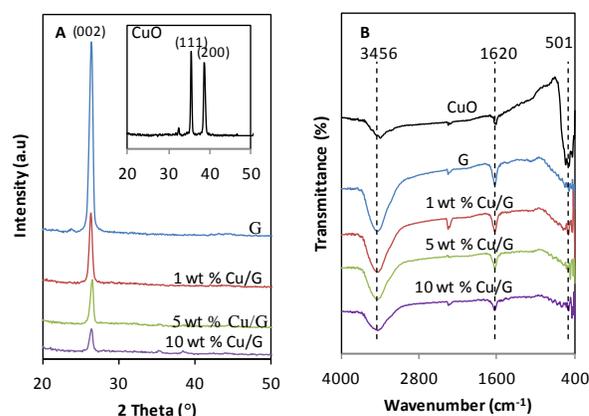


Fig. 1. (A) XRD pattern and, (B) FTIR spectra of the catalysts.

FTIR spectroscopy is analytical technique commonly used to determine the vibrational information about the species of material. Fig. 1B shows the FTIR spectra of CuO, G and various loading of CuO supported on G catalysts in the region between 4000 and 400 cm<sup>-1</sup>. For the CuO sample, a broad band at 501 cm<sup>-1</sup> can be assigned as stretching frequency of Cu-O bond. Two bands at 3456 cm<sup>-1</sup> and 1620 cm<sup>-1</sup> were observed for all samples were assigned to adsorb H<sub>2</sub>O molecules. The results illustrated that the intensity of those peaks were decreased with increasing the CuO loading. This result reveals that higher amount of CuO loaded onto the G, the hydroxyl group adsorbed on the catalyst's surfaces were fewer due to the CuO molecules was immersed on the surface of G during process of electrolysis [19]. Thus, the results demonstrated the combination of catalysts were successful.

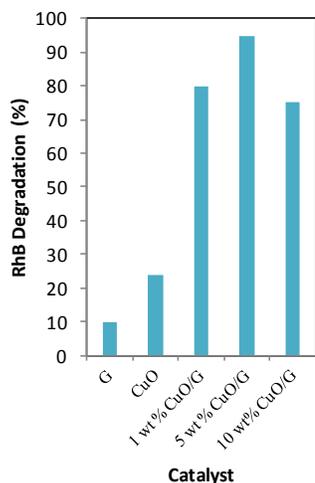


Fig. 2. Catalytic performance of the catalysts ( $[\text{RhB}] = 10 \text{ mg L}^{-1}$ ,  $\text{pH} = 7$ ,  $W = 1 \text{ g L}^{-1}$ ,  $t = 3 \text{ h}$ ,  $30^\circ\text{C}$ ).

The photocatalytic performance of G, CuO, and various loading of CuO supported on G was studied with respect to the degradation of RhB and the results are shown in Fig. 2. Photocatalytic degradation of RhB using 5 wt% CuO/G showed the highest percentage (95%), followed by 1 wt% CuO/G (83%), 10 wt% CuO/G (75%), CuO (25%) and G (10%), signifying the importance of the synergistic effect of Cu and G in the system due to the well dispersion of CuO on the support surface. The degradation of RhB slightly decreased for 10 wt% of CuO loading might be due agglomeration of CuO; thus occurs the pore blockage that reduced surface area and rate of photocatalytic activity as the visible light unable penetrate thoroughly into the catalyst.

The pH of solution is an important controlling parameter in evaluating an aqueous phase for photocatalytic reaction [20]. In this study, the effect of pH on the degradation of RhB using 5 wt% CuO/G was investigated by varying the pH from 3 to 11 as shown in Fig.3A. The results demonstrated that greatest degradation was obtained at pH 7 with 95%, while degradation at pH 3, 5, and 11 were 42%, 47%, 65%, and 50%, respectively. This result could be explained by the amphoteric performance of the catalyst, which is based on its zero point charge ( $\text{pH}_{\text{ZPC}}$ ). The  $\text{pH}_{\text{ZPC}}$  of the catalyst was found to be at pH 5.1 (inset Fig. 3A); thus, above this pH value the catalyst surface would be negatively charged and attracted the positively charged RhB, and vice versa [21].

Fig 3B demonstrates the effect of catalyst dosage of 5 wt% CuO/G at pH 7. It was observed that the degradation was increased by increasing the dosage of the catalyst from 0 to  $1 \text{ g L}^{-1}$ . The highest degradation was achieved when  $1 \text{ g L}^{-1}$  of 5 wt% CuO/G, but a further increasing of catalyst dosage resulted a decreasing in degradation. This is because the higher catalyst dosage contributes to the increasing number of active sites that could absorbed more photons and RhB [22]. However, an excess dosage led to

the turbidity of suspension in the solution, which reduced the light penetration and impeded the photocatalytic process [23].

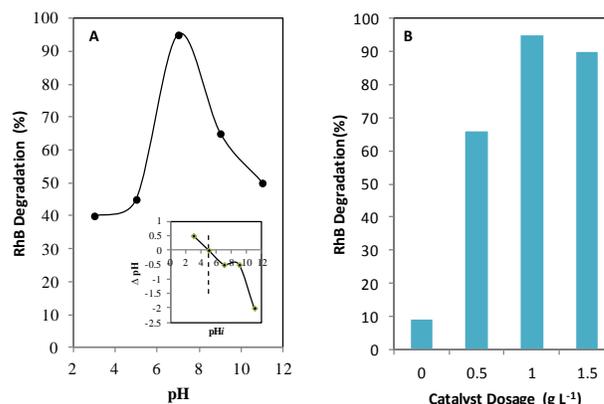


Fig. 3. Effect of (A) pH. Insert figure shows the isoelectric point ( $\text{pH}_{\text{ZPC}}$ ) and (B) catalyst dosage of the catalyst (5 wt% CuO/G,  $[\text{RhB}] = 10 \text{ mg L}^{-1}$ ,  $t = 3 \text{ h}$ ,  $30^\circ\text{C}$ ).

The degradation efficiency of the catalyst also depends on the initial concentration of the substrate. Table 1 demonstrates that the degradation of RhB was decreased with increasing initial concentration. An increase in initial concentration could inhibited light penetrating to the surface of the catalyst and reduced the formation of the hydroxyl radicals that play important role in degradation of RhB. The kinetic of the catalyst was also being studied using Langmuir-Hinshelwood (L-H) model [24] over 5 wt% CuO/G catalyst and the linear plot of  $\ln(C_0/C_t)$  vs. irradiation time are shown in Fig. 4.

**Table 1:** Percentage degradation at different initial concentrations of RhB and pseudo-first-order apparent constant values for RhB degradation using 5 wt% CuO/G ( $\text{pH} = 7$ ,  $W = 1.0 \text{ g L}^{-1}$ ,  $t = 3 \text{ h}$ ,  $30^\circ\text{C}$ ).

Initial concentration of RhB, $C_0$ ( $\text{mg L}^{-1}$ )	Degradation (%)	Reaction rate, $k_{\text{app}}$ ( $\times 10^{-3} \text{ mg L}^{-1} \text{ min}^{-1}$ )	Initial rate, $r_0$ ( $\times 10^{-3} \text{ mg L}^{-1} \text{ min}^{-1}$ )
10	95	0.84	8.4
30	40	0.44	13.2
50	15	0.27	13.5
70	10	0.21	14.7

All the plots can be roughly fitted to a straight line, indicating the photocatalytic degradation followed pseudo-first-order kinetic model [25]. Table 1 shows that the  $k_{\text{app}}$  decreased with increasing initial concentration, demonstrating the system was favorable at low concentration [26]. The values of  $k_r$  (reaction rate constant)

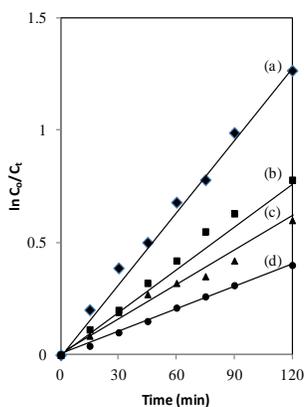


Fig. 4. Photodegradation kinetics of RhB using 5 wt% CuO/G at different initial concentrations (a) 10, (b) 30, (c) 50 and (d) 70 mg L<sup>-1</sup> (pH = 7, W = 1.0 g L<sup>-1</sup>, t = 3 h, 30°C).

and  $K_{LH}$  (adsorption coefficient) were found to be 0.05478 mg L<sup>-1</sup> min<sup>-1</sup> and 0.03776 L mg<sup>-1</sup>, respectively. The value of  $K_{LH}$  was lower compared with  $k_r$  signifying that the adsorption of RhB was the controlling step in the process [27].

#### 4. CONCLUSION

CuO supported on graphene was synthesized using electrochemical method and characterized by XRD and FTIR. The XRD and FTIR results confirmed the presence of CuO on the surface of graphene. The result showed 5 wt% CuO/G gave the highest degradation (95%) of 10 mg L<sup>-1</sup> of RhB solution at pH 7 using 1 g L<sup>-1</sup> catalyst after 4 hours under visible light irradiation. The kinetic studies shows that the degradation of RhB followed pseudo first order Langmuir Hinshelwood kinetic model with  $kr$  and  $K_{LH}$  value were 0.05478 and 0.03776 respectively. The value of  $K_{LH}$  was lower compared with  $k_r$  suggesting the reaction would occur on the surface of the catalyst. Therefore, the synthesis of CuO/G showed the potential of the catalyst in degradation of RhB.

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