

# Photocatalytic Degradation of Phenol using Copper-Doped Graphitic Carbon Nitride under Fluorescent and Sunlight Irradiation

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Phenol is one of the toxic chemicals that can cause water pollution in Malaysia. It can be degraded using a photocatalyst such as graphitic carbon nitride, g-C<sub>3</sub>N<sub>4</sub>, which has an appropriate band gap for low-energy activation. Nonetheless, g-C<sub>3</sub>N<sub>4</sub> has low photocatalytic activity due to the fast charge carrier recombination and low surface area. However, g-C<sub>3</sub>N<sub>4</sub> can be doped with metal such as copper to increase the photocatalytic performance in degrading phenol. Therefore, this research aims to evaluate the photocatalytic efficiency of synthesized pure g-C<sub>3</sub>N<sub>4</sub> and copper-doped g-C<sub>3</sub>N<sub>4</sub> (Cu/g-C<sub>3</sub>N<sub>4</sub>) for the degradation of phenol under fluorescent and sunlight irradiation. Pure g-C<sub>3</sub>N<sub>4</sub> and Cu/g-C<sub>3</sub>N<sub>4</sub> were synthesized using the thermal decomposition of melamine and the liquid exfoliation method and characterized using FTIR, XRD, FESEM and EDX. The FTIR confirmed the presence of all vibration peaks of g-C<sub>3</sub>N<sub>4</sub>. The XRD patterns show that the copper-doped has no significant influence on the structure of pure g-C<sub>3</sub>N<sub>4</sub>, while the EDX analysis shows the presence of copper in g-C<sub>3</sub>N<sub>4</sub>. The phenol was treated under fluorescent and sunlight irradiation in the presence of a synthesized photocatalyst. The degradation efficiencies of phenol using 0.5Cu/g-C<sub>3</sub>N<sub>4</sub> under the fluorescent light irradiation was 50.76%, while under sunlight irradiation, the degradation efficiency was 55.38% for 120 minutes. The results show the potential of Cu/g-C<sub>3</sub>N<sub>4</sub> as a photocatalyst for phenol degradation under visible light irradiation. This study can contribute to the solution of how to address pollution and protect the water ecosystem.

**Keywords:** Copper doped; graphitic carbon nitride; photocatalytic activity; degradation of phenol

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Industries and factories, in general, are frequently linked to environmental problems. Environmental systems can easily be harmed by chemical pollution and cause secondary pollutants to arise as a result of reactions with other reagents and may also produce volatile gases. Other than benzene, alcohol, and other compounds, phenol is one of the substances that can be categorized as harmful chemical pollutants [1]. Phenol is one of the chemical or organic compounds often used in many industries, such as oil refining, plastics manufacturing, petrochemicals, and others, that can result in water pollution. Phenol is high in toxicity and is volatile. A small amount of it can affect the smell and taste of water, which can have a negative effect on human health [2]. In their research, Mei et al. [3] stated that phenol can impact pregnant women,

resulting in low-birth-weight kids to preterm delivery. This is because phenol could disrupt the placenta and decrease the baby's development during pregnancy. According to Ismanto et al. [4], phenol is labelled as an anthropogenic Endocrine Disrupting Chemical (EDC). Anthropogenic EDCs are a combination of materials that could affect human health, especially the function of the endocrine system. Disruption to the human endocrine system can increase the possibility of diabetes, thyroid illness, obesity, and other severe diseases.

To tackle this issue, phenol must be degraded to reduce pollution, especially in wastewater. However, the degradation of phenol is limited because the process is complex and require high energy consumption. It

also requires a lot of maintenance, although there are several types of degradation techniques that can be applied [5]. Nevertheless, the ideal approach for phenol degradation is photocatalysis. According to Ameta et al. [6], photocatalysis is a chemical reaction that takes place by a semiconductor and utilizes lights. Oxidation and reduction processes are also reactions that help in the degradation of phenol. In the photocatalysis process, light and photons are involved in the catalyst interaction, creating electron holes. For an efficient photocatalysis process, a semiconductor must have a suitable band gap, good photochemical stability, and high sunlight absorption coefficients [7-10]. One of the most excellent and unique photocatalysts is graphitic carbon nitride, g-C<sub>3</sub>N<sub>4</sub> [11].

Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is composed of triazine and heptazine or tri-s-triazine and has a suitable band gap for low-energy activation. It is also very stable, inexpensive, and non-toxic to the environment. However, g-C<sub>3</sub>N<sub>4</sub> has its drawbacks, especially in photocatalytic activity reactions where it has a high recombination of charge carriers and a low specific surface area [12].

There are many ways to overcome the drawbacks of g-C<sub>3</sub>N<sub>4</sub>, including doping any metal elements towards it. Metal doping with g-C<sub>3</sub>N<sub>4</sub> can improve photocatalytic activity by inhibiting and delaying the recombination of the photogenerated electron-hole pairs in the semiconductors [13]. In addition, the electron entrapment in the center of the metallic dope helps in the production of a highly oxidized hole. Furthermore, a lower band gap of doped g-C<sub>3</sub>N<sub>4</sub> can also increase the longevity and mobility of the charge carriers [14]. Based on research by Zhao et al. [15], transition metals such as cobalt, copper, and iron can coordinate with the nitrogen pockets of some nitrogen-rich compounds, other than being a component of the catalyst. Doping metals like copper with g-C<sub>3</sub>N<sub>4</sub> can help reduce the phenol since Cu/g-C<sub>3</sub>N<sub>4</sub> has excellent electrocatalytic activity for oxygen reduction in the basic medium [16]. Other than that, copper is also affordable. It is one of the plentiful metals with an outstanding activation performance on the breakdown of contaminants over a wide pH range. Doping copper with g-C<sub>3</sub>N<sub>4</sub> can increase the photocatalytic activity by increasing the g-C<sub>3</sub>N<sub>4</sub>'s electron-hole separation efficiency [17]. Furthermore, doping g-C<sub>3</sub>N<sub>4</sub> with copper can prevent the recombination of the photogenerated carrier by enhancing the copper's metal surface's electrons and increasing the formation of the active sites in the nitrogen-rich matrix [18]. The band gap can also be reduced by improving UV light absorption by increasing the amount of copper doped with g-C<sub>3</sub>N<sub>4</sub> [19].

Therefore, this study focuses on copper-doped graphitic carbon nitride as a photocatalyst to degrade

phenols under fluorescent and sunlight irradiation. This study utilized fluorescent and sunlight since sunlight is the most efficient and readily available renewable energy on earth. In contrast, UV light irradiation is a small part of the solar radiation, providing only 3-5% of the total.

## METHODOLOGY

### Synthesis

The chemicals used were melamine (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>, 99%, Sigma-Aldrich), copper (II) nitrate (99%, CuNO<sub>3</sub>, R&M Chemicals), phenol (99%, C<sub>6</sub>H<sub>5</sub>OH, R&M Chemicals), and deionized water. The pure g-C<sub>3</sub>N<sub>4</sub> was prepared by the thermal decomposition of melamine and continued with the liquid exfoliation method according to a previous study with minor modifications [20]. The 20 g of melamine was placed in an alumina crucible and covered with a lid, and then heated at 3°C per minute with a heating rate of 2 hours in a muffle furnace. After switching off the heat, it was maintained at a temperature of 600°C for 2 hours. After cooling to room temperature, the pure g-C<sub>3</sub>N<sub>4</sub> was dispersed in 100 mL of deionized water before being sonicated for about 5 hours. The product was centrifuged for 5 minutes at 3000 rpm before it was dried overnight and ground into fine powder. In addition, a series of g-C<sub>3</sub>N<sub>4</sub> doping with copper was prepared by changing the mass of copper (II) nitrate. The weighed copper (II) nitrate was mixed with 30 mL of deionized water, and stirred until dissolved. Then, the dissolved copper (II) nitrate was added into 20 g of melamine powder and placed in an alumina crucible. The synthesis of copper-doped g-C<sub>3</sub>N<sub>4</sub>, (Cu/g-C<sub>3</sub>N<sub>4</sub>) was prepared using the same conditions as pure g-C<sub>3</sub>N<sub>4</sub>, except that the mass of the copper (II) nitrate was changed to 0.1 g, 0.2 g, 0.3 g, 0.4 g, and 0.5 g.

### Characterization

The synthesized sample was characterized using Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Field-emission scanning electron microscopy (FESEM), and energy dispersive X-ray (EDX) analysis.

FTIR was utilized to study the functional group of the samples. For this analysis, the solid sample was mixed with potassium bromide, KBr at 1:100 ratio, and ground using a pestle and mortar. The mixture was then put in a mini-press to compress the KBr and photocatalyst mixture to form a thin and semi-transparent disk. FTIR spectra were recorded on a Perkin Elmer 100 FTIR Spectrometer using the Attenuated Total Reflectance (ATR) method in a range of 4000-500 cm<sup>-1</sup>.

XRD was used to identify the crystalline of the pure g-C<sub>3</sub>N<sub>4</sub> and Cu/g-C<sub>3</sub>N<sub>4</sub>. XRD patterns of the

samples were obtained via an X-Ray diffractometer, Bruker/ D8 advanced, XRD operating at 40 kV, 30 mA and Cu K $\alpha$  radiation ( $\lambda = 1.5406$  nm) at  $2\theta = 10^\circ$ – $90^\circ$ .

The surface morphology of pure g-C<sub>3</sub>N<sub>4</sub> and Cu/g-C<sub>3</sub>N<sub>4</sub> was investigated by FESEM (Crossbeam 340 Zeiss FESEM). Meanwhile, the elements weight percentage of the sample surface was investigated via the energy dispersive X-ray (EDX) analysis. Each sample was scanned using the following parameters: 15.0 kV accelerating voltage, 2.56160 nA probe current, and a 0-20 keV energy range.

### Photocatalytic Activity

The photocatalytic activity of pure g-C<sub>3</sub>N<sub>4</sub> and Cu/g-C<sub>3</sub>N<sub>4</sub> was evaluated by the degradation of phenol under visible light (fluorescent) and sunlight irradiation, and analyzed by UV-Vis Spectrophotometer. The photocatalytic process under fluorescent irradiation was carried out in the photoreactor equipped with four quartz tube reactors. Fluorescent light source was 300 W Xe lamp with a cut-off filter of less than 400 nm.

The 10 mg of catalyst was added into 20 mL of 10 ppm phenol solution. Then, the suspensions were magnetically stirred for 30 minutes in the dark for phenol adsorption. After that, the suspension was irradiated under fluorescent or sunlight irradiations. The temperature was maintained at 20°C with a circulating air system in the photoreactor.

After the irradiation, the suspensions were then collected, centrifuged, and analyzed by UV-Vis spectrophotometer, where the wavelength was detected at 275 nm. The degradation efficiency ( $E_t$ ) of phenol was evaluated using the following equation [21]:

$$E_t = (1 - C_t/C_0) \times 100\% \quad (1)$$

where  $C_0$  denotes the phenol concentration at the time  $t=0$  and  $C_t$  denoting the concentration of phenol at the time,  $t$ .

The kinetics reaction of phenol degradation was analyzed by the pseudo-first-order kinetics using the following equation [21]:

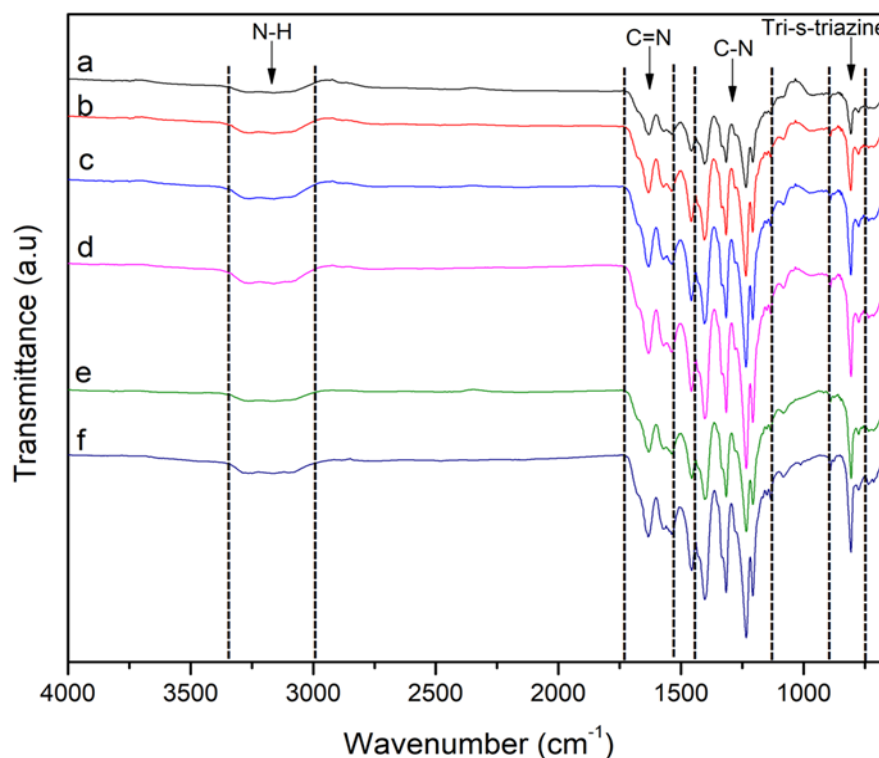
$$\ln(1 - C_t/C_0) = -kt \quad (2)$$

Where  $C_0$  and  $C_t$  denote phenol concentration at the time,  $t=0$ ,  $t$  and  $k$  denoting the rate constant.

## RESULTS AND DISCUSSION

### Characterization

The pure graphitic carbon nitride g-C<sub>3</sub>N<sub>4</sub> and copper doped g-C<sub>3</sub>N<sub>4</sub> were synthesized using the hydrothermal of melamine and copper (II) nitrate. The synthesized sample was characterized by using FTIR, XRD, FESEM, and EDX.



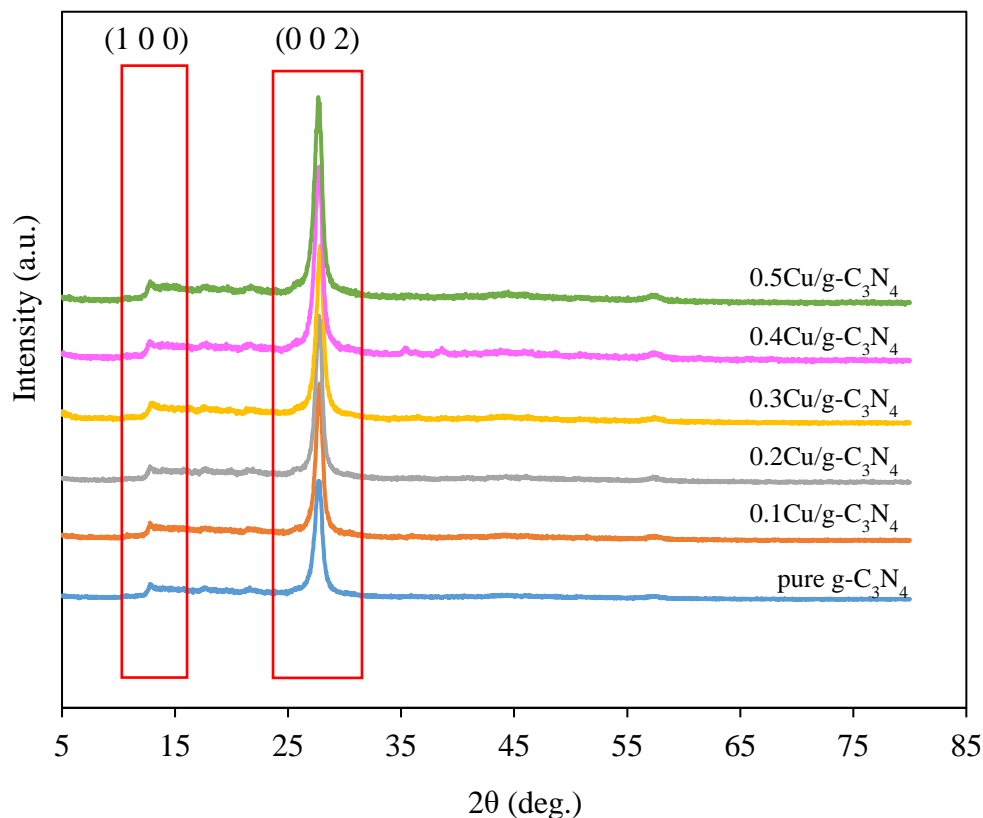
**Figure 1.** FTIR for (a) g-C<sub>3</sub>N<sub>4</sub>, (b) 0.1Cu/g-C<sub>3</sub>N<sub>4</sub>, (c) 0.2Cu/g-C<sub>3</sub>N<sub>4</sub>, (d) 0.3Cu/g-C<sub>3</sub>N<sub>4</sub>, (e) 0.4Cu/g-C<sub>3</sub>N<sub>4</sub>, (f) 0.5Cu/g-C<sub>3</sub>N<sub>4</sub>

**Table 1.** The summaries of significant peak of g-C<sub>3</sub>N<sub>4</sub>

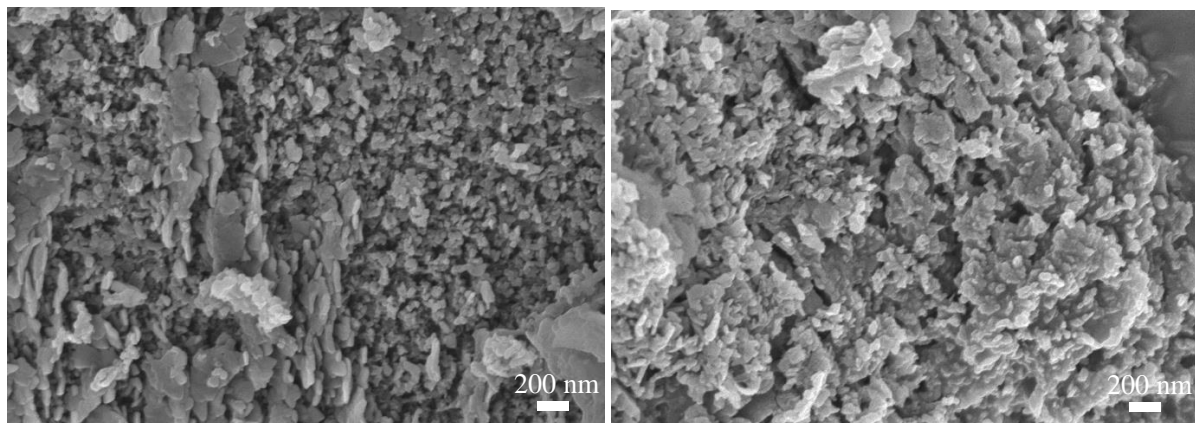
Vibration	Wavenumber (cm <sup>-1</sup> )	Wavenumber (cm <sup>-1</sup> ) from references	References
N-H	3249.26	3000-3400	[17, 22, 23]
C-N Stretching	1403.45	1411	
	1456.11	1461	
	1315.19	1311	
	1233.80	1234	
C=N heterocycles	1622.74	1627	
	1538.31	1539	
Tri-s- triazine structure	807.09	806	

Figure 1 shows the IR spectrum for pure g-C<sub>3</sub>N<sub>4</sub> and Cu/g-C<sub>3</sub>N<sub>4</sub>, with different masses of copper doped with g-C<sub>3</sub>N<sub>4</sub>. Based on the IR spectrum g-C<sub>3</sub>N<sub>4</sub>, the broadband at 3249.26 cm<sup>-1</sup> indicates the N-H stretching with the interaction of the O-H absorbed H<sub>2</sub>O [17, 22]. In addition, the absorption peaks at 1633.74, 1538.31, 1403.45, 1315.19, and 1223.80 cm<sup>-1</sup> indicate the heterocycles of the carbon nitride [17, 22, 23]. The sharp absorption peak at 807.09 cm<sup>-1</sup>

indicates the absorption of the tri-s-triazine ring structure [17, 22]. Hence, it can be concluded that the g-C<sub>3</sub>N<sub>4</sub> was successfully synthesized, as reported previously [17, 22, 23]. Moreover, the IR spectrum also shows their similarity in the absorption features, which also indicates that the doping of g-C<sub>3</sub>N<sub>4</sub> with different amounts of copper has a basic structure which is the same as pure g-C<sub>3</sub>N<sub>4</sub> and successfully synthesized [17].



**Figure 2.** XRD patterns of pure g-C<sub>3</sub>N<sub>4</sub>, 0.1Cu/g-C<sub>3</sub>N<sub>4</sub>, 0.2Cu/g-C<sub>3</sub>N<sub>4</sub>, 0.3Cu/g-C<sub>3</sub>N<sub>4</sub>, 0.4Cu/g-C<sub>3</sub>N<sub>4</sub>, and 0.5Cu/g-C<sub>3</sub>N<sub>4</sub>



**Figure 3.** a) FESEM results for pure g-C<sub>3</sub>N<sub>4</sub>, and (b) FESEM results for 0.5Cu/g-C<sub>3</sub>N<sub>4</sub>

**Tabel 2.** Elemental analysis of synthesized samples by EDX.

Sample	N	w (%)	
		C	Cu
Pure g-C <sub>3</sub> N <sub>4</sub>	51.9	48.1	0
0.5Cu/g-C <sub>3</sub> N <sub>4</sub>	54.2	44.6	1.3

The XRD patterns of pure g-C<sub>3</sub>N<sub>4</sub> and Cu/g-C<sub>3</sub>N<sub>4</sub> with different masses of copper are shown in Figure 2. The XRD patterns show a weak diffraction peak at 12.8° and a stronger one at 28.4°. The diffraction peak at 12.8° was attributed to the (100) peak of the in-plane structural pattern of tri-s-triazine units [24]. The peak at 28.4° was attributed to the interlayer stacking of the conjugated aromatic ring, identified as the (002) peak of g-C<sub>3</sub>N<sub>4</sub> [24]. The peak of Cu/g-C<sub>3</sub>N<sub>4</sub> with different masses of copper has a pattern that matches the pure g-C<sub>3</sub>N<sub>4</sub>, with a slight decrease in the intensity of diffraction at the weak peaks. The XRD pattern also shows that the structure of g-C<sub>3</sub>N<sub>4</sub> does not change even when doped with copper, and that all of them have similar structures [25].

Figure 3 shows the surface morphologies of the pure g-C<sub>3</sub>N<sub>4</sub> and 0.5Cu/g-C<sub>3</sub>N<sub>4</sub>, which were captured by FESEM. It shows that the size particles of 0.5Cu/g-C<sub>3</sub>N<sub>4</sub> become more aggregated compared to the pure g-C<sub>3</sub>N<sub>4</sub> after copper was introduced on the surface of the g-C<sub>3</sub>N<sub>4</sub> [17].

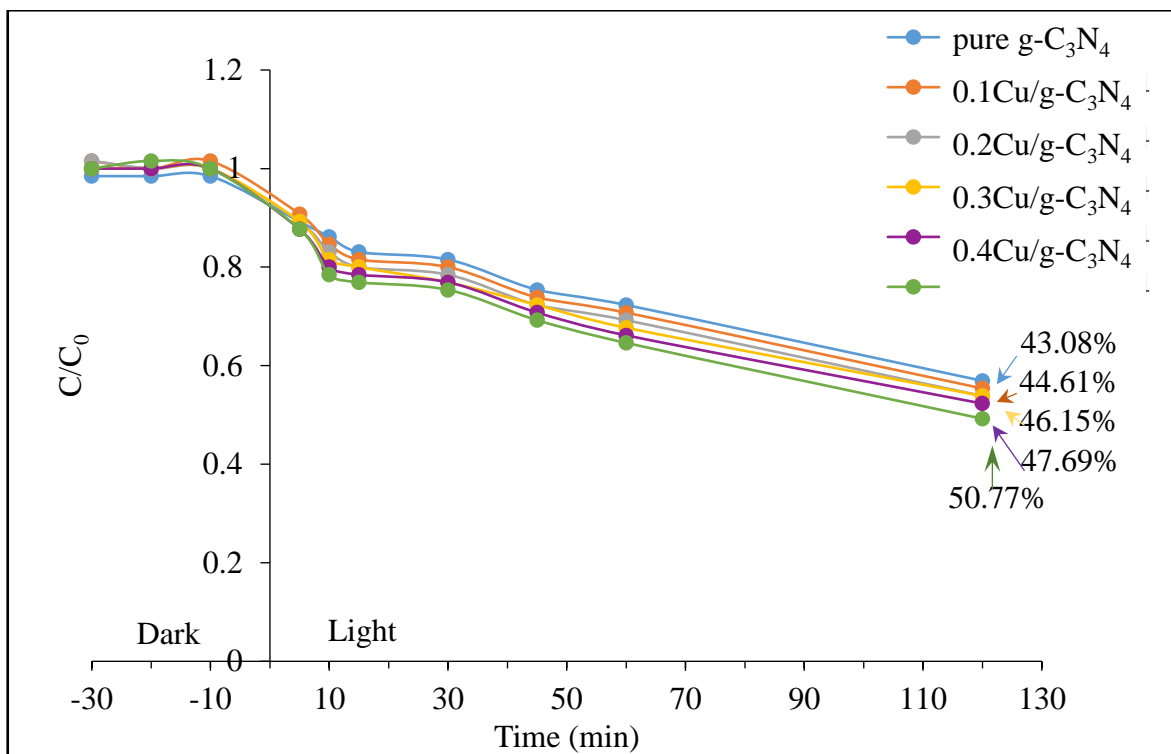
Table 2 shows the elemental analysis by EDX analysis, which proves that the elements present were N, C, and Cu. Based on the EDX findings, there was 1.3% Cu in 0.5Cu/g-C<sub>3</sub>N<sub>4</sub>, which concludes that Cu was successfully doped into the g-C<sub>3</sub>N<sub>4</sub> structure compared to the pure g-C<sub>3</sub>N<sub>4</sub>.

### Photocatalytic Degradation Studies

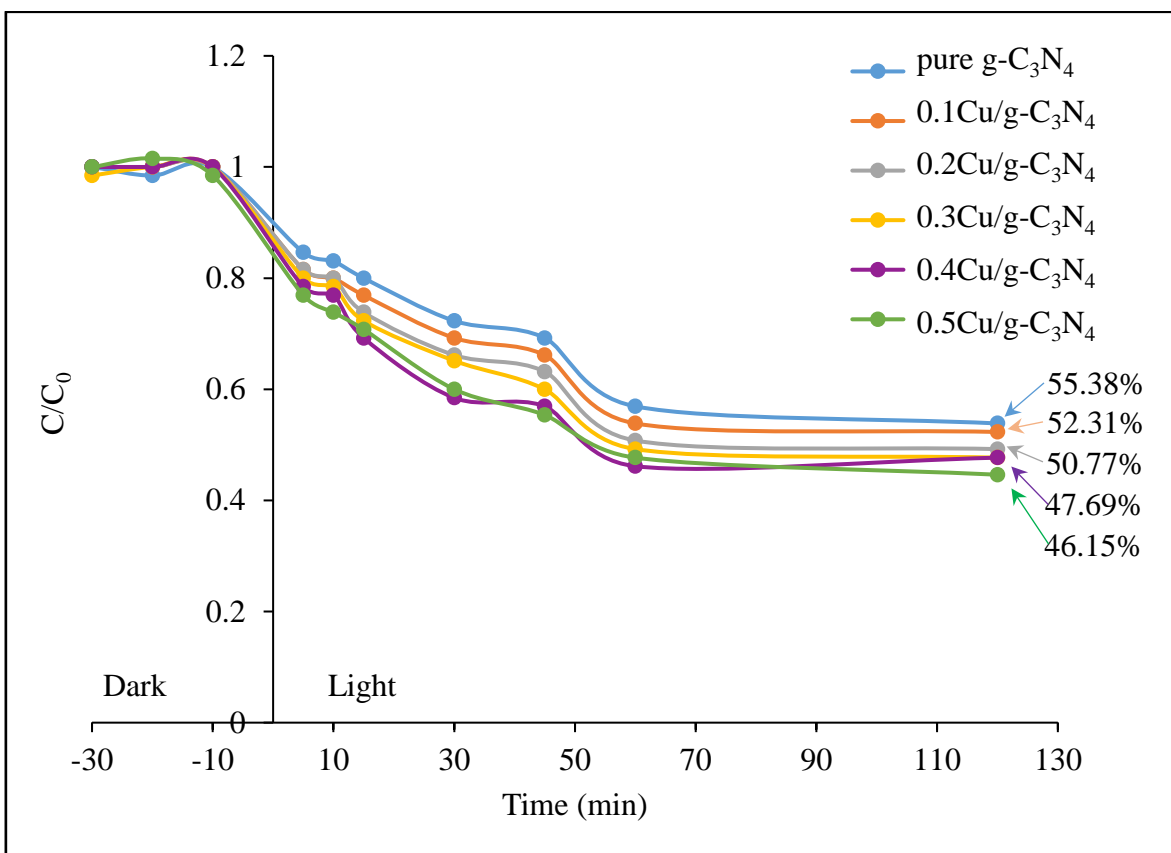
The photocatalytic degradation of phenol solution was studied with pure g-C<sub>3</sub>N<sub>4</sub>, and the different amounts

of copper doped with g-C<sub>3</sub>N<sub>4</sub> ranged from 0.1g to 0.5g in their mass. Three conditions were tested namely dark, fluorescent irradiation, and under sunlight for 5 to 120 minutes. The residual was analyzed using UV-Vis Spectroscopy with 275 nm as the maximum absorption wavelength for phenol.

Figure 4 shows the degradation efficiency of pure g-C<sub>3</sub>N<sub>4</sub>, 0.1Cu/g-C<sub>3</sub>N<sub>4</sub>, 0.2Cu/g-C<sub>3</sub>N<sub>4</sub>, 0.3Cu/g-C<sub>3</sub>N<sub>4</sub>, 0.4Cu/g-C<sub>3</sub>N<sub>4</sub>, and 0.5Cu/g-C<sub>3</sub>N<sub>4</sub> for phenol degradation under fluorescent irradiation. The higher the C/C<sub>0</sub> values, the lower the efficiency of degradation. From the figure, it can be seen that all the photocatalysts have poor degradation efficiency under dark conditions, as their C/C<sub>0</sub> value is high. Moreover, there was also a fluctuating trend indicating the occurrence of adsorption/desorption during the darkness. Meanwhile, Cu/g-C<sub>3</sub>N<sub>4</sub> shows the highest photocatalytic efficiency compared to pure g-C<sub>3</sub>N<sub>4</sub> under fluorescent irradiation. The degradation efficiency of the 0.5Cu/g-C<sub>3</sub>N<sub>4</sub> towards phenol at 120 minutes was 50.77%. Meanwhile the pure g-C<sub>3</sub>N<sub>4</sub> shows the lowest degradation efficiency of 43.08%. This shows that phenol degradation is highly dependent on the degree of the copper doping with the g-C<sub>3</sub>N<sub>4</sub>, as the degradation efficiency increased with increasing copper doping from 0.1 g to 0.5 g under fluorescent light irradiation. A similar observation was made by Oliveros et al. [20], where the degradation efficiency increased with the amount of copper-doped with g-C<sub>3</sub>N<sub>4</sub>, implying that an increase in copper mass could provide more catalytic areas for the phenol degradation.



**Figure 4.** Photocatalytic degradation efficiency of pure  $g-C_3N_4$ , 0.1Cu/ $g-C_3N_4$ , 0.2Cu/ $g-C_3N_4$ , 0.3Cu/ $g-C_3N_4$ , 0.4Cu/ $g-C_3N_4$ , and 0.5Cu/ $g-C_3N_4$  under fluorescent irradiation.



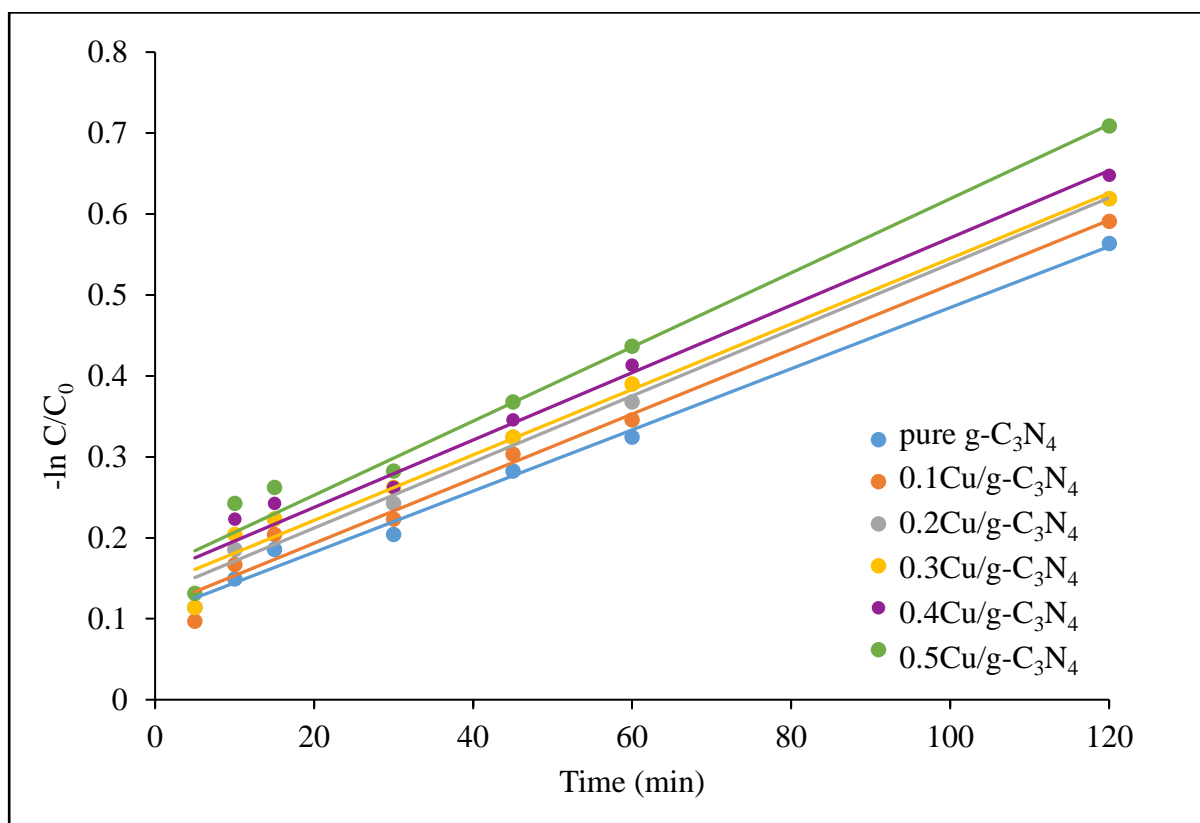
**Figure 5.** Photocatalytic degradation efficiency of pure  $g-C_3N_4$ , 0.1Cu/ $g-C_3N_4$ , 0.2Cu/ $g-C_3N_4$ , 0.3Cu/ $g-C_3N_4$ , 0.4Cu/ $g-C_3N_4$ , and 0.5Cu/ $g-C_3N_4$  under sunlight irradiation.

Next, under sunlight irradiation, the photocatalysts also demonstrated low performance in their degradation under dark conditions since they have higher  $C/C_0$ . Pure  $g\text{-C}_3\text{N}_4$  shows the lowest degradation efficiency (46.15%) towards phenol at 120 minutes compared to  $\text{Cu}/g\text{-C}_3\text{N}_4$  under sunlight irradiation. Moreover, the degradation efficiencies of  $\text{Cu}/g\text{-C}_3\text{N}_4$  increased with an increasing amount of copper, where  $0.5\text{Cu}/g\text{-C}_3\text{N}_4$  has the highest degradation efficiency (55.38%). These results show that the increased amount of copper doped with  $g\text{-C}_3\text{N}_4$  improves photocatalytic performance and increases the production of photogenerated electrons and holes, thus increasing the efficiency of the photocatalysts [21]. In addition, an increase in time will also increase the photocatalysts' efficiency in terms of their percentage towards the degradation of phenol since higher hydroxyl radicals can be formed [22]. Under sunlight irradiation, the percentage of degradation efficiency was slightly higher compared to that under fluorescent irradiation because the sunlight itself efficiently helps the photocatalyst, especially  $\text{Cu}/g\text{-C}_3\text{N}_4$ , to further degrade the phenol as the sunlight power is higher than that of the fluorescent irradiation. According to Vukšić

et al. [22], photocatalyst reaction occurs due to the irradiation of the sunlight right at the surface layer of the  $\text{Cu}/g\text{-C}_3\text{N}_4$ , where their photon energy can be activated.

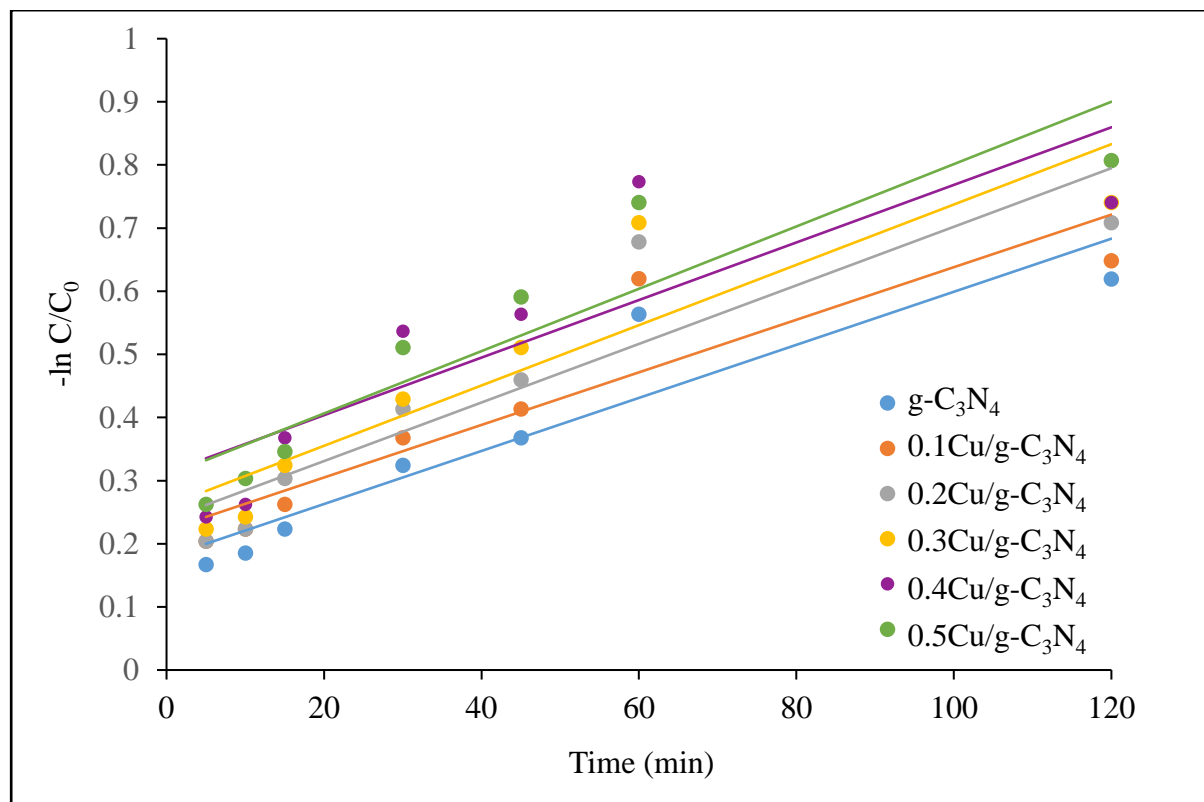
### Kinetic Analysis

In this study, the kinetic behavior of the photodegradation process was tested for each photocatalyst for 0 to 120 minutes under fluorescent irradiation [23]. Figure 6 reveals the plot of  $-\ln(C/C_0)$  vs time. The rate constant,  $k$ , was observed based on the pseudo-first-order rate with  $0.5\text{Cu}/g\text{-C}_3\text{N}_4$  showing the maximum degradation constant ( $0.0046\text{ min}^{-1}$ ). Meanwhile, the pure  $g\text{-C}_3\text{N}_4$  shows the minimum degradation constant for phenol at  $0.0038\text{ min}^{-1}$ . For the rest of the photocatalysts, their degradation rate constant increased with an increasing amount of copper being doped with pure  $g\text{-C}_3\text{N}_4$ , namely  $0.1\text{Cu}/g\text{-C}_3\text{N}_4$  ( $0.0040\text{ min}^{-1}$ ) and  $0.2\text{Cu}/g\text{-C}_3\text{N}_4$  ( $0.0041\text{ min}^{-1}$ ). For  $0.3\text{Cu}/g\text{-C}_3\text{N}_4$  and  $0.4\text{Cu}/g\text{-C}_3\text{N}_4$ , the degradation rate constant was  $0.0040\text{ min}^{-1}$  and  $0.0042\text{ min}^{-1}$ , respectively. Therefore, the rate constant order was  $0.5\text{Cu}/g\text{-C}_3\text{N}_4 > 0.4\text{Cu}/g\text{-C}_3\text{N}_4 > 0.2\text{Cu}/g\text{-C}_3\text{N}_4 > 0.3\text{Cu}/g\text{-C}_3\text{N}_4 > 0.1\text{Cu}/g\text{-C}_3\text{N}_4 > \text{pure } g\text{-C}_3\text{N}_4$ .



**Figure 6.** Pseudo first-order kinetic of pure  $g\text{-C}_3\text{N}_4$ ,  $0.1\text{Cu}/g\text{-C}_3\text{N}_4$ ,  $0.2\text{Cu}/g\text{-C}_3\text{N}_4$ ,  $0.3\text{Cu}/g\text{-C}_3\text{N}_4$ ,  $0.4\text{Cu}/g\text{-C}_3\text{N}_4$ , and  $0.5\text{Cu}/g\text{-C}_3\text{N}_4$  under fluorescent irradiation.





**Figure 7.** Pseudo first-order kinetic of pure g-C<sub>3</sub>N<sub>4</sub>, 0.1Cu/g-C<sub>3</sub>N<sub>4</sub>, 0.2Cu/g-C<sub>3</sub>N<sub>4</sub>, 0.3Cu/g-C<sub>3</sub>N<sub>4</sub>, 0.4Cu/g-C<sub>3</sub>N<sub>4</sub>, and 0.5Cu/g-C<sub>3</sub>N<sub>4</sub> under sunlight irradiation.

The kinetic behavior of the photodegradation process was tested for each photocatalyst for 0 to 120 minutes under sunlight irradiation. Figure 7 shows the plot of  $-\ln(I-C/C_0)$  vs time under sunlight irradiation. This figure shows that 0.5Cu/g-C<sub>3</sub>N<sub>4</sub> has the highest degradation rate constant,  $k$  (0.0049 min<sup>-1</sup>). Meanwhile, pure g-C<sub>3</sub>N<sub>4</sub> shows the minimum degradation constant for phenol at 0.0042 min<sup>-1</sup>. For the rest of the photocatalysts, their degradation rate constant increased with an increasing amount of copper being doped with g-C<sub>3</sub>N<sub>4</sub> namely 0.1Cu/g-C<sub>3</sub>N<sub>4</sub> at 0.0042 min<sup>-1</sup> and 0.2Cu/g-C<sub>3</sub>N<sub>4</sub> at 0.0046 min<sup>-1</sup>. For 0.3Cu/g-C<sub>3</sub>N<sub>4</sub> and 0.4Cu/g-C<sub>3</sub>N<sub>4</sub>, the degradation rate constant was 0.0048 min<sup>-1</sup> and 0.0046 min<sup>-1</sup>, respectively. Therefore, the rate constant order was 0.5Cu/g-C<sub>3</sub>N<sub>4</sub> > 0.3Cu/g-C<sub>3</sub>N<sub>4</sub> > 0.4Cu/g-C<sub>3</sub>N<sub>4</sub> > 0.2Cu/g-C<sub>3</sub>N<sub>4</sub> > 0.1Cu/g-C<sub>3</sub>N<sub>4</sub> > pure g-C<sub>3</sub>N<sub>4</sub>.

Table 3 below shows the detection of the kinetic parameters based on the pseudo-first-order kinetic analysis for the different types of photocatalysts in the degradation of phenol during a contact time of 2 hours at an initial concentration of 10 ppm. Table 3 shows the degradation of phenol under fluorescent light. It can be seen that 0.5Cu/g-C<sub>3</sub>N<sub>4</sub> with a degradation percentage of 50.77% has the highest rate constant,  $k$  (0.0049 min<sup>-1</sup>) and the shortest half-life (2.51 hours) compared to the other photocatalysts. The rate constant,  $k$  of 0.3Cu/g-C<sub>3</sub>N<sub>4</sub> and 0.4Cu/g-C<sub>3</sub>N<sub>4</sub> was lower than the 0.5Cu/g-C<sub>3</sub>N<sub>4</sub> at 0.0040 min<sup>-1</sup> and 0.0042 min<sup>-1</sup>,

respectively, which was lower than 0.5Cu/g-C<sub>3</sub>N<sub>4</sub>. From the value of the rate constant  $k$ , 0.3Cu/g-C<sub>3</sub>N<sub>4</sub> and 0.4Cu/g-C<sub>3</sub>N<sub>4</sub> showed slower reactions compared to the other photocatalysts. The comparison with the degradation of phenol by TiO<sub>2</sub>/AC in previous studies shows that the photocatalyst achieves 93.4% of the percentage degradation with a rate constant of,  $k$  (0.0037 min<sup>-1</sup>) under fluorescent light irradiation.

Table 4 below shows the detection of the kinetic parameters based on the pseudo-first-order kinetic analysis for the different types of photocatalysts in the phenol degradation during a contact time of 2 hours at an initial concentration of 10ppm. Table 3 shows the degradation of phenol under sunlight irradiation. Here, it can be seen that 0.5Cu/g-C<sub>3</sub>N<sub>4</sub> with a degradation percentage of 55.38% has the highest rate constant,  $k$  (0.0049 min<sup>-1</sup>) and the shortest half-life (2.36 hours) compared to the other photocatalysts. Meanwhile, compared to another photocatalyst, such as Sn<sub>3</sub>O<sub>4</sub> in the degradation of phenol, the photocatalyst achieved 65% in degradation with a rate constant,  $k$  of (0.0005 min<sup>-1</sup>) under sunlight irradiation. To conclude, the kinetic study is important to determine the dynamics in terms of the adsorption process of the contaminants from the wastewater. These kinetic findings show the potential of the photocatalyst to degrade phenol under both conditions namely fluorescent and sunlight irradiation.



**Table 3.** Kinetic parameters (pseudo-first order) of Cu/g-C<sub>3</sub>N<sub>4</sub> under fluorescent light irradiation in degrading phenol.

Type of Photocatalyst	R <sup>2</sup>	k (min <sup>-1</sup> )	t <sub>1/2</sub> (h)	Degradation (%)	References
Pure g-C <sub>3</sub> N <sub>4</sub>	0.9926	0.0038	3.03	43.08	This study
0.1Cu/g-C <sub>3</sub> N <sub>4</sub>	0.9826	0.0040	2.89	44.61	
0.2Cu/g-C <sub>3</sub> N <sub>4</sub>	0.9828	0.0041	2.83	46.15	
0.3Cu/g-C <sub>3</sub> N <sub>4</sub>	0.9796	0.0040	2.89	44.61	
0.4Cu/g-C <sub>3</sub> N <sub>4</sub>	0.9782	0.0042	2.75	47.69	
0.5Cu/g-C <sub>3</sub> N <sub>4</sub>	0.9742	0.0046	2.51	50.77	
TiO <sub>2</sub> /AC	0.6308	0.0037	Not mention	93.40	[24]

**Table 4.** Kinetic parameters (pseudo-first order) of Cu/g-C<sub>3</sub>N<sub>4</sub> under sunlight irradiation in degrading phenol.

Type of Photocatalyst	R <sup>2</sup>	k(min <sup>-1</sup> )	t <sub>1/2</sub> (h)	Degradation (%)	References
Pure g-C <sub>3</sub> N <sub>4</sub>	0.8736	0.0042	2.75	46.15	This study
0.1Cu/g-C <sub>3</sub> N <sub>4</sub>	0.8422	0.0042	2.75	47.69	
0.2Cu/g-C <sub>3</sub> N <sub>4</sub>	0.8322	0.0046	2.51	50.77	
0.3Cu/g-C <sub>3</sub> N <sub>4</sub>	0.8312	0.0048	2.40	52.31	
0.4Cu/g-C <sub>3</sub> N <sub>4</sub>	0.7232	0.0046	2.51	52.31	
0.5Cu/g-C <sub>3</sub> N <sub>4</sub>	0.8452	0.0049	2.36	55.38	
TiO <sub>2</sub> /AC	0.9841	0.005	Not mention	65.00	[25]

### CONCLUSION

In summary, copper-doped graphitic carbon nitride with different amounts of copper was successfully synthesized and characterized. The pure g-C<sub>3</sub>N<sub>4</sub> and copper-doped g-C<sub>3</sub>N<sub>4</sub> from 0.1Cu/g-C<sub>3</sub>N<sub>4</sub> until 0.5Cu/g-C<sub>3</sub>N<sub>4</sub> were characterized by FTIR, XRD, FESEM, and EDX. The FTIR results show that the pure g-C<sub>3</sub>N<sub>4</sub> and copper-doped g-C<sub>3</sub>N<sub>4</sub> were successfully synthesized since the functional groups of g-C<sub>3</sub>N<sub>4</sub> were present in the IR spectra. The FTIR confirmed the presence of all vibration peaks of g-C<sub>3</sub>N<sub>4</sub>. The XRD patterns show that the copper-doped has no significant influence on the structure of pure g-C<sub>3</sub>N<sub>4</sub>, while the EDX analysis shows the presence of copper in g-C<sub>3</sub>N<sub>4</sub>. Based on the photocatalysts that were synthesized, 0.5Cu/g-C<sub>3</sub>N<sub>4</sub> presented the highest degradation of phenol under visible irradiation for both conditions namely

under fluorescent light and sunlight irradiation. The degradation efficiencies of phenol using 0.5Cu/g-C<sub>3</sub>N<sub>4</sub> under fluorescent light irradiation was 50.76%, while under sunlight light irradiation, it was 55.38% for 120 minutes. The rate constant and half-life of the photocatalyst were determined using the pseudo-first-order rate law with 0.0046min<sup>-1</sup> at 2.51 hours in their half-life under fluorescent light irradiation and 0.0049min<sup>-1</sup> at 2.36 hours in their half-life under sunlight irradiation. This study revealed the potential of Cu/g-C<sub>3</sub>N<sub>4</sub> as one of the highly active photocatalysts that can degrade phenol in the presence of visible light. The result of this study is in line with the Malaysian government's 12<sup>th</sup> Malaysia Plan to provide clean water and sanitization and contribute to achieving the Sustainable Development Goal (SDG6) of improving water quality by reducing pollution by 2030.

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## AUTHOR CONTRIBUTION

Nurul Izzah Norhisan – data curation, writing; Nur Nazzatul Azzin Ahmad Tarmizi data curation, writing; Salman Al Faridzy Akbar – data curation; Siti Hajar Alias – conceptualization, supervision, writing; Siti Nor Atika Baharin – review, editing; Sheikh Ahmad Izaddin Sheikh Mohd Ghazali – review, editing; and Hadi Nur – conceptualization, review, editing.

## CONFLICT OF INTEREST

Authors declare no conflict of interest.

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