Construction, characterization, and visible light-assisted photocatalytic degradation behaviour of Graphitic carbon nitride (g-C₃N₄) photocatalyst

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Abstract: photocatalysis is a promising process for decomposing organic pollutants in wastewater. Choosing an appropriate photocatalyst that is effective under visible light is essential for environmental applications. In this study, graphite carbon nitride(g-C₃N₄) synthesized by the thermal calcination process, characterization by various characterization analysis techniques such as Field Emission Scanning Electron Microscopy (FE-SEM), X-ray diffraction (XRD), UV–vis diffuse reflection spectroscopy (DRS), and photoluminescence (PL) spectrum, the DRS analysis shows the boundaries of absorbing light by g-C₃N₄ to be lies in the visible light region with aband gap of (2.7ev). Methylene blue (MB) and Rhodamine B (Rh.B) degradation activity in an aqueous solution was investigated over a constructed visible-light-driven g-C₃N₄ photocatalyst. Within 120 min visible light irradiation under condition of PH of 6.7, dyes concentration of 30 ppm, and photocatalyst dose of 0.1 g/l, under constant temperature and pressure was (80.3%) and (81.6%) for MB and Rh.B dyes, respectively. The photocatalytic degradation activity's kinetic reaction of pseudo-first-order has been studied. Also, the mechanism has been investigated in this study.

Keywords: graphitic carbon nitride $(g-C_3N_4)$ Photocatalyst, M.B dye, visible light, organic pollutant degradation

1. Introduction

Due to the development of industries in recent years, many organic pollutants have been produced in the environment[1]. Organic pollutants introduced into the aquatic ecosystem can have detrimental effects due to toxicity. These effects include obstructing sewage treatment facilities, negatively impacting aquatic organisms, and decreasing biochemical oxygen levels[2]. Ultimately, this harms the aquatic ecosystem and its inhabitants [3]. Furthermore, organic pollutants have the potential to negatively impact human health by exhibiting carcinogenic, teratogenic, mutagenic, and endocrine-disrupting properties. Hence, controlling organic contaminants is a significant subject [4]. Photocatalysis, an effective type of advanced oxidation process (AOP), is frequently employed for degrading organic pollutants due to its notable effectiveness, simplicity, reliable reproducibility, and convenient handling[5]. Photocatalysis is a very efficient and cost-effective process for decomposing organic pollutants. Under normal environmental conditions, these pollutants can be converted entirely into non-harmful substances, utilizing only oxygen as the chemical component[6]. Therefore, it eliminates dangerous nontoxic contaminants, does not require significant energy , and is environmentally sustainable. The photocatalysis process depends on the interaction between

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organic contaminants and highly reactive agents (h+ and e-), which oxidize and reduce active sites produced on the surface by UV or visible light [7]. Photocatalysts are the essential components of the photocatalysis process[8]. Therefore, semiconductor photocatalysts have been extensively utilized in photocatalysis[9]. Titanium dioxide (TiO₂) has garnered considerable interest as a photocatalyst under UV irradiation due to its exceptional performance and cost-effectiveness [10].

Nevertheless, numerous studies have demonstrated the presence of certain limitations in semiconductor photocatalysts, including rapid recombination of electron/hole pairs. As a result, the photocatalytic degradation activity will be decreased. The ability to absorb visible light will be limited, which hinders its practical application and utilization, resulting in a reduced degradation rate of organic pollutants [12]. A tris-s-triazine unit forms graphitic carbon nitride and has an N-type nature. It has an adjustable band gap of around 2.7 eV, with the low vacant molecular orbital and the higher employed molecular orbital. This property enables it to enhance the use of renewable solar energy and manage its photoelectronic efficiency [13]. Graphitic carbon nitride is extensively used in photocatalysis due to its nontoxic properties, adjustable band gap, composition, mainly consisting of plentiful carbon and nitrogen atoms, and strong chemical resistance[14]. This study used semiconductor g-C3N4 based photocatalysts for organic pollutants degradation in wastewater. Also, it focuse on enhanced photoactivity and stability of $g-C_3N_4$ for application in the photocatalytic process. Moreover, the mechanism that can transfer organic pollutants to low or nontoxic small molecules (such as CO_2 and H_2O) of the photocatalytic reaction was mainly discussed.

2. Experimental work

a. Chemical materials

Melamine, hydrogen peroxide (30 %), Methylene blue (MB) dye, and Rhodamine.B dye. All chemical components were purchased from Sigma-Aldrich.

b. Synthesis of (g-C₃N₄)

Melamine was the raw material for synthesizing $(g-C_3N_4)$ by direct thermal treatment 6 gm of melamine powder was used in a crucible with cove heated directly at 550 °C using a 6°C/min heating rate for 4h to make pure g-C₃N₄. The obtained g-C₃N₄ was crushed and obtained as a yellow-pale colour in powder form and used for the next stage [15]. Fig 1 shows the steps of preparing the g-C₃N₄ photocatalyst.



(1)

c. Characterization

The synthesized $g-C_3N_4$ sample was characterized by techniques such as X- (XRD), FESEM, UVvisible DRS, N₂ adsorption-desorption, and PL. The XRD was utilized to determine the crystalline structure of the $g-C_3N_4$ utilizing an X-ray diffraction Shimadzu diffractometer XRD-6000. The morphology of the sample's surface was analyzed using FESEM utilizing (Tescan Mira3).DRS analysis was used to obtain the optical characteristics of the photocatalysts by using (Shimadzu-UV-3010). The Barrett-Joyner-Halenda (BET) analytical method measured the sample's surface area, including the N2 adsorption/desorption isotherms. Moreover, the mean pore size and pore volume were calculated. The photoluminescence (PL) spectrum test was utilized to illustrate the efficiencies of $g-C_3N_4$ samples to separate electrons/holes.

d. Photocatalytic degradation activity

The activity of $g-C_3N_4$ to absorb light was studied in the batch photocatalytic reactor, as shown in Figure 2, for the degradation test of MB dye irradiated with a visible light system using two LED lamps of 100 W. The photocatalytic degradation activity of MB started with preparing an aqueous solution of 100 ml volume of MB dye with Conc. Of 30 ppm and PH of 6.7. 0.1 g/l dose of synthesized photocatalysts was added to the dye solution and stirred for 60 min in the dark to reach the absorption-desorption equilibrium state. Moreover, the system was irradiated with a light source and stirred for 120 min. For each 20-minute time interval, 3 mL of a sample of dye solutions were drawn and centrifuged for 20 min at 4000 rpm to measure the concentration of the dye by using UV-visible spectrophotometer absorption at 663 nm wavelength. Furthermore, to investigate the g-C₃N₄ activity in degrading pollutants, another type of organic dye, Rh.B dye, was examined using the same experimental condition except PH of 7, and the wavelength of the UV-visible spectrophotometer for Rh.B was 554nm. The photocatalytic degradation efficiency (n) of two organic dyes has been calculated using equation 1. Moreover, the suggested photocatalytic mechanism and the kinetic reaction were analyzed in this study. $\eta = (C0-C/C0) \times 100\%$

where C0 represents the initial dye concentration, and C is the concentration at reaction time t [16].



3. Result and discussion

3.1 X-ray diffraction examination(XRD)

X-ray diffraction analysis was used to analyze the phase construction of the g-C₃N₄ photocatalysts, as illustrated in Fig. 3. The characteristic diffraction peaks shown at $2\theta = 13^{\circ}$ and 27° , which exist entirely with the g-C₃N₄ (100) and (002) planes, correspondingly, results showing that $g-C_3N_4$ sample was synthesized successfully. The findings were consistent with earlier reports[17].



3.2 FESEM analysis

This investigation was utilized to illustrate the morphology and shape of $g-C_3N_4$ photocatalysts. As shown in Fig.4, a more uniform prominent lamellar structure has been shown in the FESEM images for $g-C_3N_4$. It was the same result for He et al. [18].



Fig. 4. SEM image of g-C3N4 photocatalyst.

3.3. UV-vis DRS analysis

A UV–vis(DRS) analysis was employed to examine the capability of $g-C_3N_4$ photocatalyst to absorb light during the photocatalysis process. Fig.5(a) shows the boundaries of absorbing light by $g-C_3N_4$, which exists in the visible light region. Fig. 5(b) illustrates The Kubelka-Munk equation (Eq. 2) used to find the optical bandgap energy (Eg) of the $g-C_3N_4$ sample. Which was (2.7ev). This explains that the $g-C3N_4$ more sensitivity to visible light provides enough energy for electron-hole separation and a more active site necessary for the degradation process[19]

$$(Ah\nu)2 = A(h\nu - Eg)$$
(2)

Where α is the optical absorption intensity (a.u.), h is the Planck's constant (h = $6.625 \times 10-34$ J s), n is the frequency of the incident radiation (n = c/ λ , where c is the speed of light and λ is the wavelength), n = 2 and A is a proportionality constant.



3.4. N2 adsorbtion desorbtion examine

To determine the specific surface area of the synthesized $g-C_3N_4$ photocatalyst and pore size. The N2 adsorption isotherm was utilized using a BET method. The specific surface area, pore size, and total pore volume of $g-C_3N_4$ were 26.7 m2/g, 11.00377nm, and 0.073468m3/gm, respectively.

3.5. photoluminescence (PL) intensity analysis

photoluminescence spectra (PL) determine the ability to recombine photo-generated charge carriers. It is proportional to the rate at which free carriers recombine in photocatalysts. When the photoluminescence (PL) intensity increases, it refers to a high recombination rate in the photocatalyst. Fig 6 shows the recombination rate of $g-C_3N_4$ photocatalyst in the range of (500-600nm) which means it has a low rate of recombination of electron-hole generated.



3.6. photocatalytic degradation activity

The rate of adsorption and the photocatalytic degradation activity of $g-C_3N_4$ synthesized photocatalysts were examined for degradation of M.B dye under PH of 6.7, M.B dye concentration of 30 ppm, and catalyst dose of 0.1g/l. Fig 7(a) shows that 60 min of dark adsorption was suggested before the photodegradation Process to reach the adsorption-desorption equilibrium. The photodegradation activity of the catalyst after irradiation with visible light Fig.7(b)shows the adsorption efficiencies of M.B. were 50.4%, 67.3%, and 80.3% within 60,90 and 120 min, respectively. However, the Rh.B dye experiment condition was the PH of 7, Rh.B concentration of 30ppm, and a catalyst dose of 0.1g/l. The activity was 61.1%, 73.3%, and 81.5% within 60,90 and 120 min of visible light irradiation, respectively. It was confirmed that g-C₃N₄ was an active catalyst in degrading different organic pollutants. The activity of the g-C₃N₄ photocatalyst increased due to the low bandgap energy, making it more sensitive to visible light and generating a more active site on the surface.



The kinetics study of photocatalytic activity regarding M.B dye was examined to evaluate the enhancement of the photocatalyst's degradation activity. As shown in Fig. 8, the photocatalytic degradation activity kinetics plot against reaction time corresponded to the rate constant (K) found in equation 3 [20]. of pseudo-first-order kinetic energy

$$Ln (CO/Ct) = -Kt$$
(3)

Where:

t: time of reaction (min)

C0: the initial concentration of methylene blue (M.B) dye (mg/L)

C: concentration of methylene blue (M.B) dye (mg/L) at time t (min)



4. proposed Photocatalytic mechanism

When the $g-C_3N_4$ surface is excited by energy which is equal or greater to the band gap energy of the $g-C_3N_4$ photocatalyst, the electron (e⁻) in the valence band will be transferred to the conduction band, leaving a hole (h+) in valence band so a pair of electron-hole will be generated Eq.4. the electron-hole generated will react with O₂ to generate superoxide radical and with H₂O to generate hydroxyl radicals as shown in Eq.5,6.these active radicals oxidized the organic pollutant into CO₂ and H₂O(eq.7), the degradation mechanism shown in Fig.9.

$$g-C_3N_4 + hv \rightarrow g-C_3N_4 (e^- + h^+)$$
 (4)

$$g-C_3N_4(e^-) + O_2 \rightarrow g-C_3N_4(^{\bullet}O_2^-)$$
 (5)

$$g-C_3N_4(h^+) + H_2O \rightarrow \bullet OH \tag{6}$$

$$g-C_3N_4 (\bullet O2^-) + MB \, dye \rightarrow degradation \, products \tag{7}$$



5. Comparison with recent studies

A comparison between the previous and current studies is shown in Table 1. The comparison with photocatalyst dosage, irradiation time, initial concentration, type of organic pollutant, and degradation efficiency was considered. Table 1 shows the activity of $g-C_3N_4$ photocatalyst compared to others in previous studies.

Photocatalyst	Photocatalyst dose	irradiation time(min)	Organic pollutant type	initial concentration (ppm)	Degradation efficiency%	Ref.
N-doped carbon quantum dots (CQDs)/g-C ₃ N ₄	50mg/100ml	180	MB	10	54.6 %	[21]
$Cd_{0.5}Zn_{0.5}S/g-C_3N_4$	50 mg	90	RhB	4.79	90%	[22]
g-C ₃ N ₄	0.01g/100ml	120	M.B	30	80.3%	This study

Table 1. Comparison of photocatalytic degradation activity of methylene blue (M.B) and Rhodamine B (Rh.B) dye using $g-C_3N_4$ photocatalyst with previous studies.

6. Conclusion

The g-C₃N₄-based photocatalysts have the advantages of high efficiency, saving energy, thermal stability, and reusability, making them promising photocatalysts for environmental applications, especially concerning organic pollutant photodegradation. In this study, the g-C3N4 photocatalyst has been synthesized, examined, and applied in the degradation of two types of organic pollutant .it showed high degradation activity in contrast to MB and Rh.B dye of 80.3% and 81.6% within 120 min of light irradiation, respectively. Due to the low band gap of (2.7ev) making it more sensitive to visible light and generates a more active site on the surface. Thus, this work opens an idea for the hybridization of graphitic carbon nitride with another nanoparticle to enhance photoactivity and stability for application in environmental treatment.

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