

NITROGEN-DEFECTIVE gC₃N₄ SYNTHESIS PHOTOCATALYTIC ACTIVITY FOR MB DYE DEGRADATION.**Dilaver YAŞAR**

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ORCID ID: 0000-0001-8747-0635**ABSTRACT**

Environmental and energy management have become increasingly important over the years as a result of the world's ongoing industrialization. Because refractory organic compounds are widely used in consumer products, pesticides, dyes, and other industrial chemicals, rising environmental concerns are endangering human health and hindering our civilization from progressing sustainably. Due to its excellent stability, cheap cost, abundance, and responsiveness to visible light, graphitic carbon nitride (gC₃N₄) has been regarded as one of the most useful materials in photocatalytic degradation of pollutants and photocatalytic water splitting. The study involves the fabrication and analysis of nitrogen-defective gC₃N₄ using a urea thermal polymerization method with KOH as an alkali additive. XRD analysis confirms the (002) plane of gC₃N₄ at 27.6°, consistent with previous research. FTIR analysis reveals N-H and cyano group vibrations, C-N stretch modes, and a unique triazine unit respiratory mode. UV-vis spectroscopy indicates the gC₃N₄ sample's absorption spectrum, and subsequent photodegradation of methylene blue (MB) solution under a Xenon lamp is demonstrated. The degradation rate reaches 94.53% , showcasing efficient photocatalytic capability. ln(C₀/C_t) vs time analysis yields a k value of 0.08134 min⁻¹, indicating high pseudo-first-order rate constant for the gC₃N₄ sample. This research demonstrates successful nitrogen-defect induction in gC₃N₄ through KOH-doped urea thermal polymerization, leading to potent photocatalytic activity, particularly evident in MB degradation.

Keywords: gC₃N₄ , MB, photocatalytic activity.

1. INTRODUCTION

The recent discovery of graphitic carbon nitride (gC_3N_4) as a non-metallic photocatalyst holds remarkable promise for tackling pressing energy and environmental concerns. gC_3N_4 exhibits distinctive properties, including impressive thermal conductivity, remarkable stability across an expansive pH spectrum, and an optimally tuned band gap energy (ranging from 2.7 to 2.8 eV), allowing for effective utilization under both ultraviolet and visible light wavelengths [1, 2].

Presently, the paramount focus for developing nations lies in the swift advancement and intensive acceleration of industrial production. However, this growth is accompanied by a concerning surge in pollution, primarily attributed to unregulated emissions and the dissemination of contaminants into the environment. Notably, the textile industry has gained notoriety for its contribution to detrimental waterway pollution through the discharge of chemical reagents, surfactants, and organic dyes [3, 4].

Since the pioneering efforts of Honda and Fujishima, along with the experiments conducted by Schrauzer and Guth in the 1970s, numerous researchers have delved into the realm of semiconductor photocatalysis. Their primary objective has often revolved around the creation of photocatalysts capable of efficiently harnessing light for the conversion of chemical energy. Notably, there has been a pronounced emphasis on metal oxide-mediated photocatalytic processes for the elimination of organic contaminants from both industrial and domestic wastewater. This field has garnered substantial attention in recent years due to its remarkable pollutant degradation capabilities, broad applicability, and inherent environmental friendliness [5–8].

In this study, we employed a straightforward thermal polymerization process to fabricate nitrogen-defective gC_3N_4 . The resulting sample's structural and optical properties were comprehensively characterized using various analytical techniques. Furthermore, we explored the degradation potential of methylene blue dye. This research underscores a novel and uncomplicated approach to synthesizing nitrogen-defective gC_3N_4 , showcasing its efficacy in degradation applications.

2. MATERIAL and METHOD

Here is the production steps for gC_3N_4 photocatalysts synthesized: In aqueous KOH solutions (KOH 1.0 g in 30 mL of ultra-pure water), 15 g of urea was dissolved with stirring, and the

resultant solution was then dried overnight in an oven at 75 °C. The solid mixes of urea and KOH were then calcined at 550 °C for 4 hours in a muffle furnace at a heating rate of 3 °C min⁻¹.

2.2. RESULTS

Figure 1 shows the sample's XRD pattern. At 27.6°, the characteristic peak corresponding to the (002) plane of gC₃N₄ is clearly apparent. This XRD obtaining is consistent with numerous previous investigations on the gC₃N₄ structure [9–12].

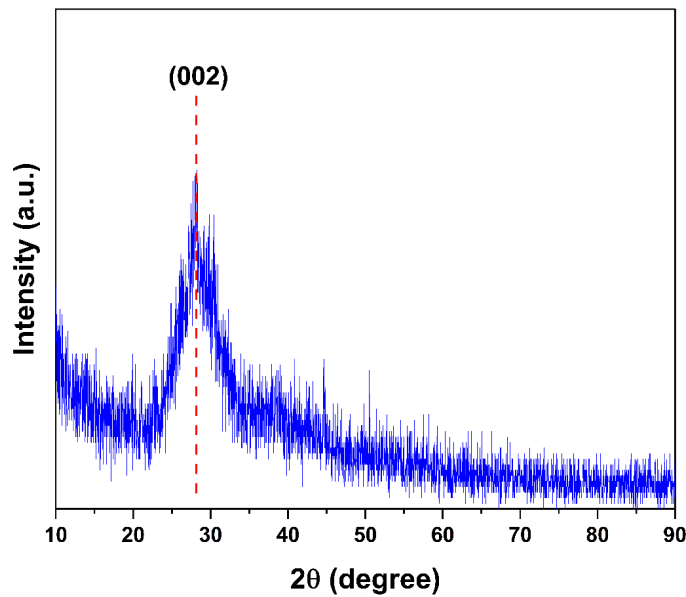


Fig 1. XRD results of the gC₃N₄

The chemical bond structures of the obtained gC₃N₄ sample were examined using FTIR analysis. Figure 2 illustrates the FTIR spectrum that was obtained. Scanning in the 450–4000 cm⁻¹ range was done to produce this spectra. The tensile vibration of the N-H group is responsible for the flat peak at 3350 cm⁻¹. The cyano groups (–C≡N) asymmetric stretching vibration is responsible for the strong peak seen at 2156 cm⁻¹. C-N stretch modes are shown by the peaks in the FTIR spectrum between 1000 and 1750 cm⁻¹. The respiratory mode unique to triazine units is responsible for the pronounced peak at 805 cm⁻¹ [11, 13–15].

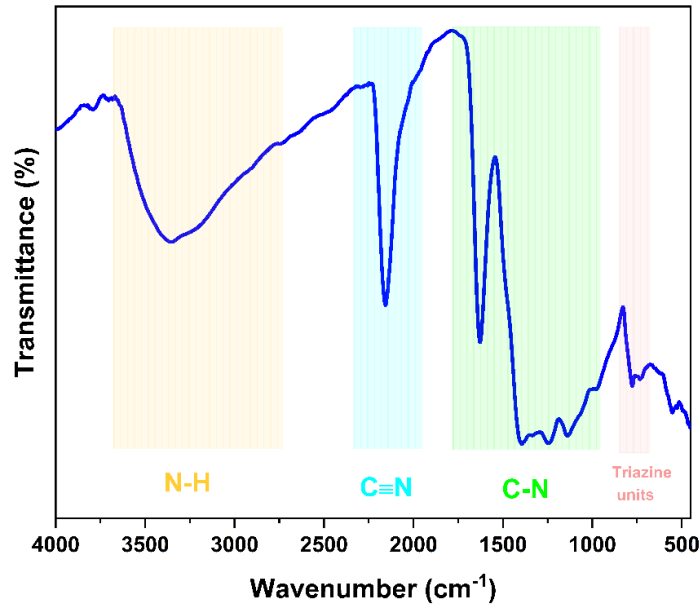


Fig 2. FTIR specturum of the gC_3N_4

UV-Vis spectroscopy measurements have been performed for the absorptions of the obtained gC_3N_4 sample in the wavelength range of 450-750 nm. After the sample had been place to the dye solution and had been left in the dark for 30 minutes, measurements were taken using a UV-Vis spectrophotometer every five minutes for the next 30 minutes. Under a 300 W Xenon lamp, the photocatalytic degradation of gC_3N_4 -catalyzed methylene blue solution with respect to time was studied. The gC_3N_4 sample's absorption curve is shown in Figure 3.

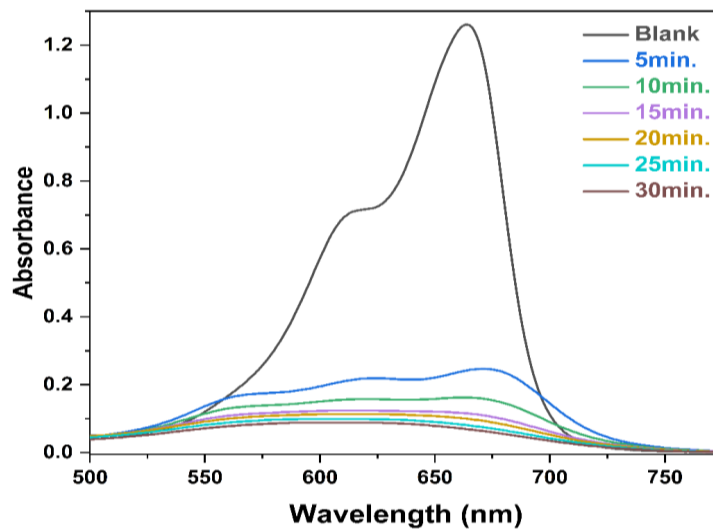


Fig. 3. UV absorption spectra of MB with gC_3N_4

The graph of the degradation rates over time is shown in Figure 4. The degradation rate of the gC_3N_4 sample on the MB was found to be 94.53% in Figure 4.

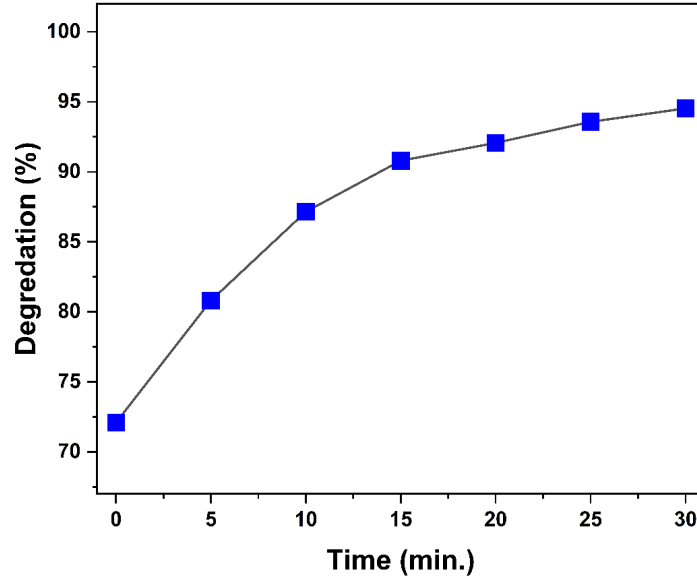


Fig. 4. MB's photocatalytic degradation

The photodegradation of MB aqueous solution was used for evaluating the gC_3N_4 's photocatalytic abilities. In Figure 4, the MB photodegradation (C_0/C_t) by the gC_3N_4 is depicted.

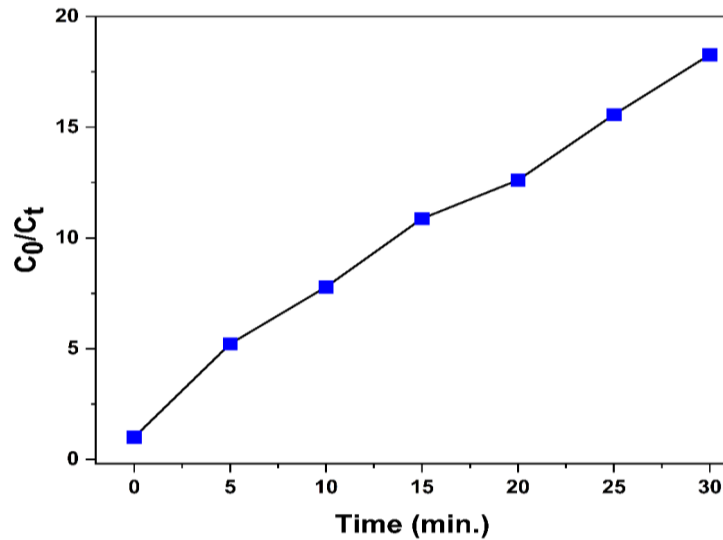


Fig. 5. Graph of the concentration ratio (C_0/C_t)

The synthesized gC_3N_4 sample has shown to be efficient on MB. The graph of $\ln(C_0/C_t)$ vs time is shown in Figure 6. The slope of the graph was used to determine the k (min^{-1}) rate constants (pseudo-first order) [16]. The graph shows that the gC_3N_4 sample with a degradation rate of 94,53% has a k value of $0,08134 \text{ min}^{-1}$.

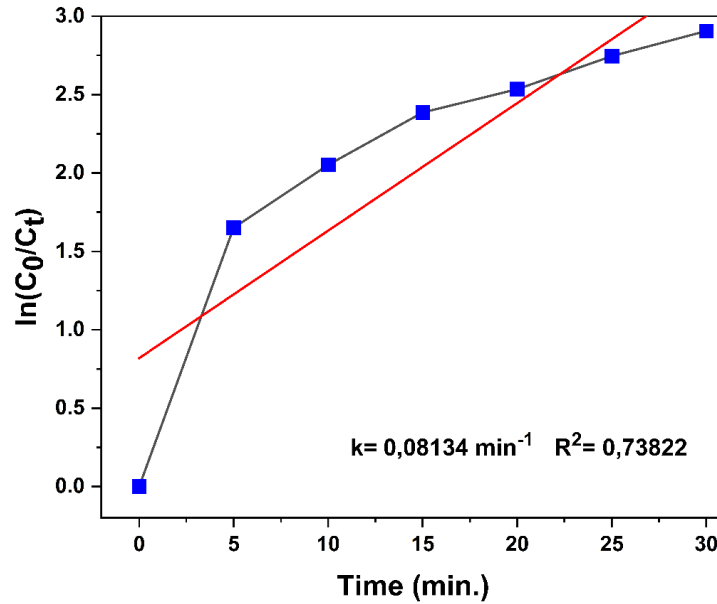


Fig. 6. Graph of the MB degradation $\ln(C_0/C_t)$

In result, urea thermal polymerization was effectively used to induce nitrogen defects into the gC_3N_4 by adding an alkali chemical compound like KOH. Through the degradation of MB, the photocatalytic assessment of produced KOH doped gC_3N_4 sample was examined. High photocatalytic activity has been established for gC_3N_4 .

3. CONCLUSION

The study involves the fabrication and characterization of nitrogen-defective gC_3N_4 through urea thermal polymerization with KOH. The XRD pattern confirms the presence of the (002) plane peak at 27.6° , consistent with previous research. FTIR analysis highlights N-H and cyano group vibrations, as well as C-N stretching and triazine unit respiratory modes. UV-vis spectroscopy shows gC_3N_4 's absorption curve. Photocatalytic degradation of methylene blue (MB) using gC_3N_4 is evaluated over time achieving a degradation rate of 94.53%. MB photodegradation (C_0/C_t) by gC_3N_4 is illustrated in the same figure. The $\ln(C_0/C_t)$ vs time graph determines

pseudo-first order rate constants (k value of 0.08134 min^{-1}) for gC_3N_4 efficient degradation. The study successfully introduces nitrogen defects using KOH and demonstrates high photocatalytic activity for gC_3N_4 through MB degradation.

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