Synthesis, Characterization and Photocatalytic Activity of Amino Acid Doped Metal Free g-C$_3$N$_4$ Composite Photocatalyst

M. Jeba Jeeva Rani, G. Allen Gnana Raj

Abstract: The g-C$_3$N$_4$-Amino acid (CNA-g-C$_3$N$_4$) composite photocatalyst was synthesized by simple co-polymerization process. The photocatalyst was characterized by X-ray diffraction (XRD), Scanning election microscopy (SEM) with EDAX and FT-IR analysis. Rhodamine-B (Rh-B) dye solution under visible light irradiation was used to determine the photocatalytic activity. The photocatalytic activity of CNA-g-C$_3$N$_4$ composite posses long term stability and visible light activity than bare g-C$_3$N$_4$.

Keywords: Amino acid, composite, metal free, g-C$_3$N$_4$, melamine.

I. INTRODUCTION

The photocatalytic strategy has received considerable and persistent attention for the removal of contamination because solar energy is an inexhaustible, low-cost, environmentally friendly energy resource. Photocatalysis is a catalytic process occurring on the surface of semiconductor materials under the irradiation of photons[1]. Despite the great advances made in this field, the main issue has been focused on the efficiency of the photocatalyst for large scale industrial applications. To date, a large number of semiconductor materials like metal oxides and sulfides have been identified as active photocatalysts for photodegradation of organic pollutants[2].

Among them TiO$_2$ and ZnO$_2$ shows high efficiency for photodegradation of some dyes in polluted water[3]. Unfortunately, most metal-based photocatalysts are active only in the ultraviolet region and have moderate performance. Accordingly, some scientific research is now devoted to achieving high photocatalytic efficiency with these materials especially working under visible light.

Recently, *Wang et al*[4] reported the first novel metal free polymeric photocatalyst, graphitic carbon nitride (g-C$_3$N$_4$), which exhibits an excellent photocatalytic performance for the splitting of water into hydrogen gas using solar energy. The novel photocatalyst also exhibits activity for the removal of organic pollutants under visible light irradiation[5], clearly demonstrating that the metal free g-C$_3$N$_4$ photocatalyst possess interesting electronic properties as well as high thermal and chemical stability. However, to date the photocatalytic efficiency of bare g-C$_3$N$_4$ is still limited due to high recombination rate of photogenerated electron hole pairs. Several routs have been developed to improve the photocatalytic performance of g-C$_3$N$_4$. For example, loading some co-catalysts onto the surface of a catalyst can evidently promote the separation efficiency of photogenerated electron-hole pairs[6]. Another feasible strategy is to form a composite photocatalyst by designing an appropriate textural porosity[7], doping[8] or combining g-C$_3$N$_4$ with transition metals to improve its conductivity and catalytic performance[9]. But the biologically important molecule such as amino acids[10] have been assembled in very low yield by semiconductor mediated photolysis of simpler organic and inorganic compound.

In this study, one-step route to the synthesis of CNA-g-C$_3$N$_4$ composite material by co-polymerization of g-C$_3$N$_4$ and amino acid (glutamic acid).The photodegradation activity of CNA-g-C$_3$N$_4$ for Rhodamine-B(Rh-B) was greatly enhanced under visible light irradiation as compared to bare g-C$_3$N$_4$, which is due to improvement of separation efficiency of photogenerated electron-hole pairs in CNA-g-C$_3$N$_4$ compsite photocatalyst.

II. EXPERIMENTAL

Melamine and glutamic acid were purchased from Sigma–Aldrich. All other reagents were of analytical grade and were used as without further purification.

2.1. Synthesis of photocatalyst

The metal free bare g-C$_3$N$_4$ powder was synthesized by thermal treatment of melamine in a crucible with a cover under ambient pressure in air. After dried at 80° C for 24 h the precursor was put in a Muffle furnace and heated to 550° C for 3 h to complete the reaction. The product was collected and ground into a powder.

CNA-g- C$_3$N$_4$ composite photocatalyst was prepared as follows:

1.0g g-C$_3$N$_4$ was dissolved in 30 ml deionised water, then glutamic acid powder (0.1g) and ammonium persulphate (0.034 g) was added. After dispersing g-C$_3$N$_4$ and glutamic acid solution under vigorous stirring for 2 h, the resultant yellow CNA-g-C$_3$N$_4$ composite powder was filtered and washed with ethanol and deionized water. The composite mixture was dried at 80° C for 3 h in vacuum environment.

2.2. Characterization Techniques

X-ray diffraction (XRD) analysis was carried out at room temperature with a Bruker D8 advance diffractometer. The patterns were run with Cu Kα radiation at a scan rate of 20-80°. UV-vis spectra measured in air at room temperature from 200-800 nm with SHIMADZU UV-3101 PC spectrometer. FTIR spectra in transmittance modes were recorded for a solid mixture of sample and KBr in the form of pellets on a SHIMADZU FTIR-4500 spectrometer with a spectral resolution of 16 (1 cm^{-1}) and an accumulation of 70 scans at room temperature. The morphology of the samples were examined by scanning electron microscopy (SEM JOEL-5610 LV) chemical composition of the samples were analysed using EDAX (BRUKER-10498).

2.3. Reactivity Studies

The Rhodamine-B (Rh-B) was chosen as a model pollutant to test the photocatalytic activities of the prepared photocatalysts. In a typical photocatalytic experiment, 0.1 g of the catalyst was dispersed in 50 ml Rh-B solution (1 x 10^{-5}M). The photocatalytic activities of bare g-C$_3$N$_4$ and CNA-g-C$_3$N$_4$ composite photocatalysts were evaluated by the photodegradation of Rh-B under visible light irradiation. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 min to achieve saturated Rh-B absorption on to the catalyst. The solution was irradiated using solar light. At irradiation time intervals of 0.5 h, the suspensions were collected and centrifuged, to remove the photocatalyst particles through millipore filter paper.

The concentrations of Rh-B organic dye was analysed using UV-visible spectrophotometer. The degradation efficiency of the dye is calculated by the following equation[11].

$$\text{Degradation (\%)} = \frac{C_o - C}{C_o} \times 100$$

Where C_o is the initial concentration of dye before irradiation and C is the concentration of dye after a certain irradiation time.

III. RESULTS AND DISCUSSION

3.1. Characterization of CNA–g–C$_3$N$_4$ Composite Sample

The X-ray diffraction pattern of bare g-C$_3$N$_4$ is shown in Fig.1. It has two distinct diffraction peaks at 27.42° and 13.1°, which can be indexed for graphitic materials as the (002) and (100). These two diffraction peaks are in good agreement with the g-C$_3$N$_4$ reported in the literature[12]. Fig. 2 illustrated the XRD pattern of the CNA-g-C$_3$N$_4$ composite sample. It exhibit the small peaks at 6.16°, 10.99° and 12.28° suggest that the prepared composite sample is crystalline.
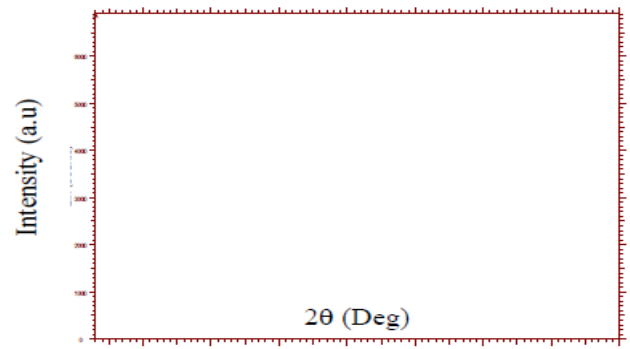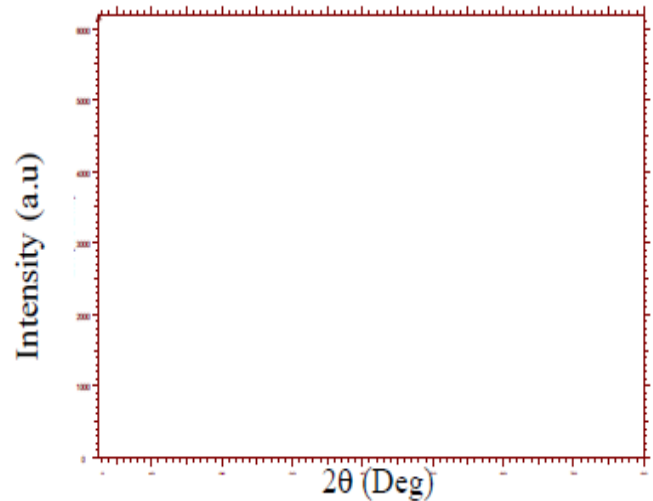

Fig. 1 XRD pattern of bare g– C$_3$N$_4$.

Fig. 2 XRD pattern of g–C$_3$N$_4$ composite sample.

3.2. FTIR Analysis

FTIR analysis were carried out to confirm the presence of amino acid in the composite organic photocatalyst. Fig. 3 shows the FT-IR spectrum of bare g-C$_3$N$_4$ and fig. 4 shows the CNA-g-C$_3$N$_4$ composite sample.

The main characteristic peaks of bare g-C$_3$N$_4$ as follows. The bands at 1242, 1327, 1411 and 1566 cm^{-1} which can be attributed to the typical stretching modes of C-N heterocycles[13]. Moreover, the characteristic breathing modes of triazine units at 810 and 887cm^{-1}. The band at 3170 cm^{-1} can be attributed to hydrogen bonded N-H bond between amine and imine sites. The band at 1905 cm^{-1} is due to strong C=N stretching vibration. For the CNA-g-C$_3$N$_4$ composite sample also similar to those of bands of bare g–C$_3$N$_4$, but an additional band appears at 1780 cm^{-1} is due to strong C=O stretching vibration mode of acid group. The band at 458 cm^{-1} is due to OH in-plane bending mode of acid group. The results indicate that there is a stronger interaction has been formed between amino acid and g–C$_3$N$_4$.
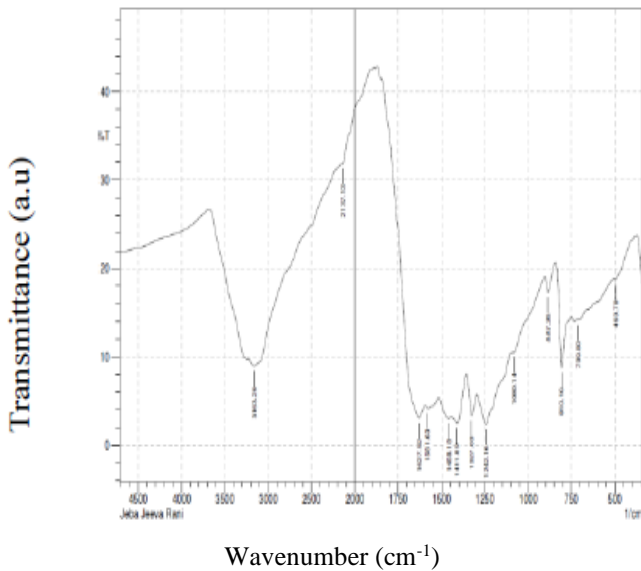
Wavenumber (cm^{-1})

Fig. 3 FT-IR spectrum of bare g-C$_3$N$_4$.

(a)

Wavenumber (cm^{-1})
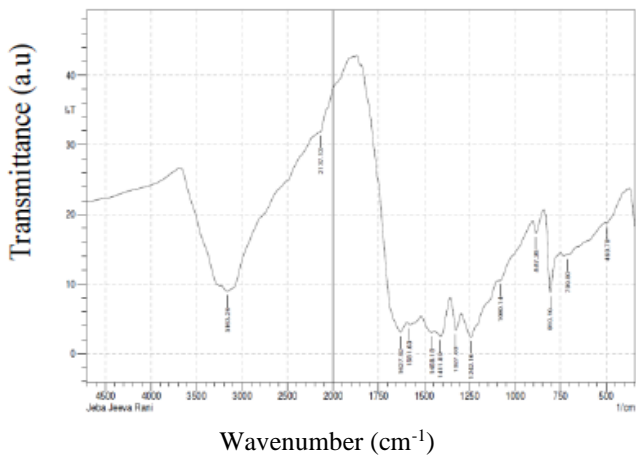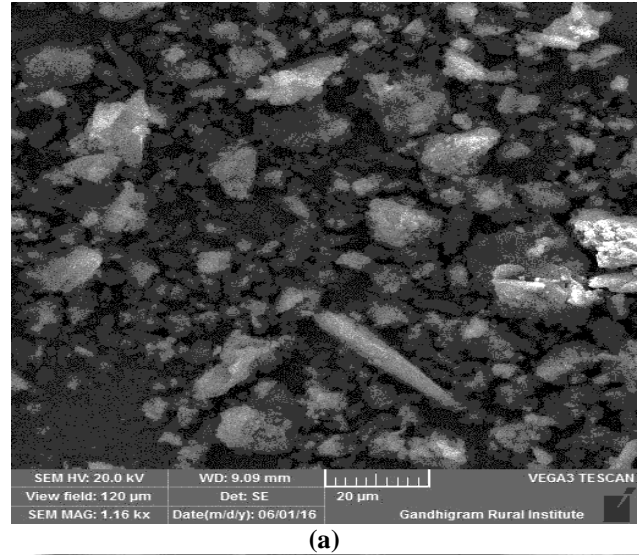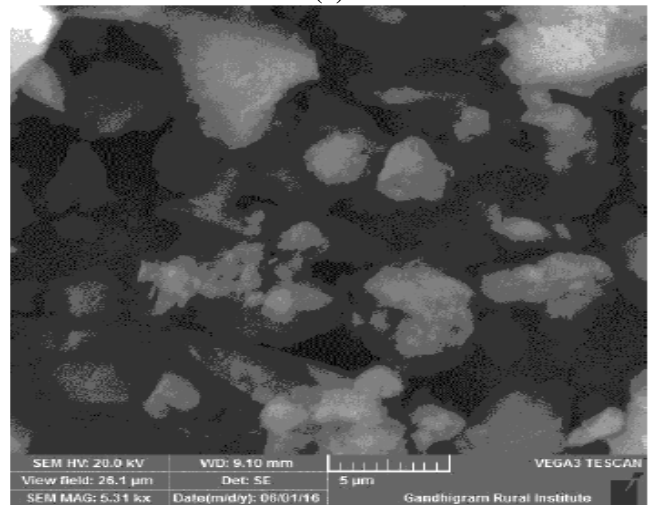**Fig. 4 FT-IR spectrum of CNA-g-C$_3$N$_4$.**

(b)

Fig .5 a,b SEM images of bare g-C$_3$N$_4$.

3.3. Morphological studies

The surface morphology and surface area are very effective parameters in photocatalytic activity of composite photocatalytic activity of composite photocatalysts. Fig. 5 a,b shows the SEM images of bare g-C$_3$N$_4$ and Fig. 6 a,b shows the SEM images of CNA-g-C$_3$N$_4$ composite. As seen in fig .5, the particles are spherical, elliptical, irregularly shaped and it displays micrometer sized. After introducing the aminoacid, the small amino acid particles get deposited on the surface of g-C$_3$N$_4$ and get the composite structure.
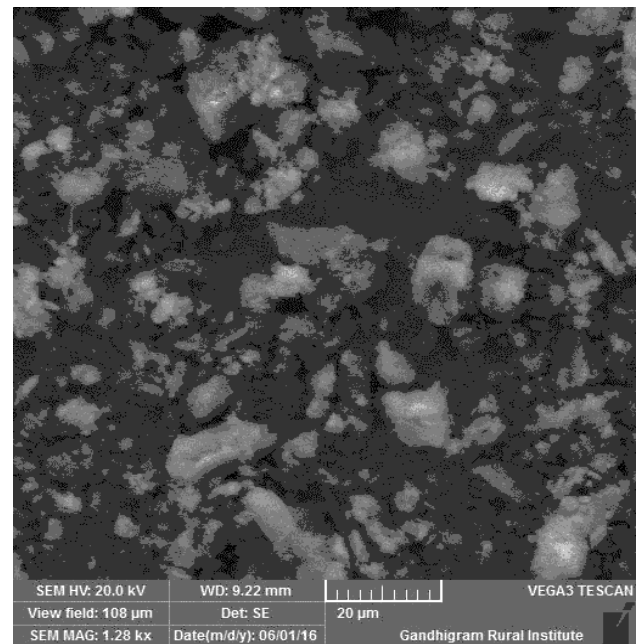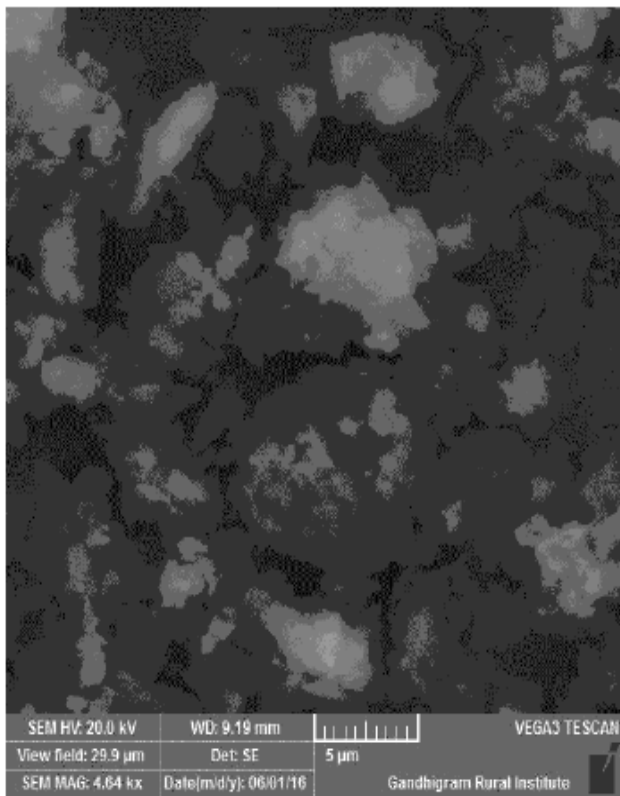

(a)

(b)

Fig. 6 a,b SEM images of CNA-g-C₃N₄ composite sampl

3.4. Elemental analysis of the sample

Fig.7 shows the EDAX patterns of the bare g-C₃N₄ photocatalyst. EDAX indicated C, N as the major elements in the photocatalyst. Fig.8 shows the EDAX patterns of CNA-g-C₃N₄ composite. It confirms the presence of dopant C, N and O which are indicated by the strong peaks. The g-C₃N₄ and CNA-g-C₃N₄ composite photocatalysts.
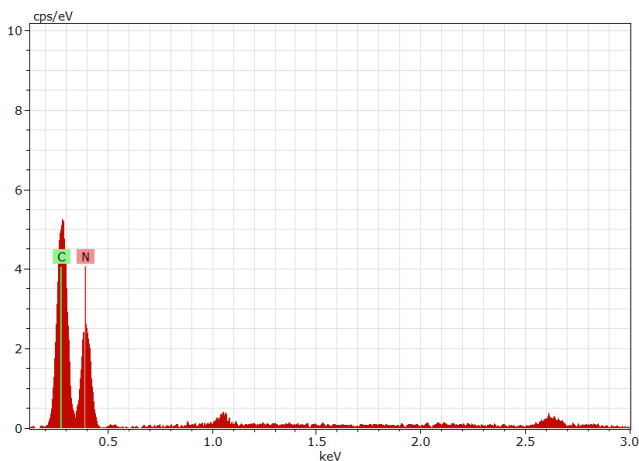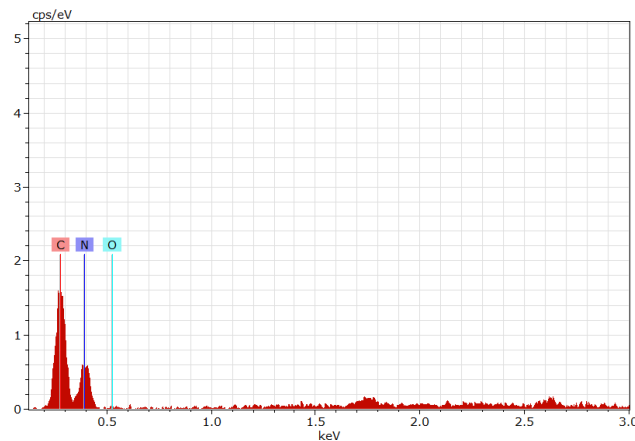

Fig.7 EDAX patterns of bareg-C₃N₄

Fig. 8 EDAX patterns of CNA-g-C₃N₄ Composite Sample.

Table. 1 Atomic and mass percentage of bare g–C₃N₄ and CNA-g-C₃N₄ composite.

Sample	Elements	Mass %	Atom %
bare of g-C₃N₄	N	66.54	63.04
	C	33.46	36.95
	Total	**100.00**	**100.00**
CNA-g-C₃N₄ composite	N	62.82	59.35
	C	36.04	39.71
	O	1.13	0.94
	Total	**100.00**	**100.00**

IV. PHOTOCATALYTIC ACTIVITY

0.1 g of photocatalyst was suspended in 50 ml aqueous Rhodamine-B solution in the reaction vessel. The suspension was kept in the dark to establish adsorption desorption equilibrium. Then the suspension was stirred magnetically and irradiated under visible light. Samples were withdrawn periodically, centrifuged and analysed for the degradation of Rh-B using a UV-visible spectrophotometer. Rh-B has the maximum absorbance at 553.1nm.Fig. 9 shows the UV-visible spectrum of Rh-B dye and fig.10 shows the photocatylatic activities of bare g-C₃N₄ and CNA-g-C₃N₄ composite photcatalysts.
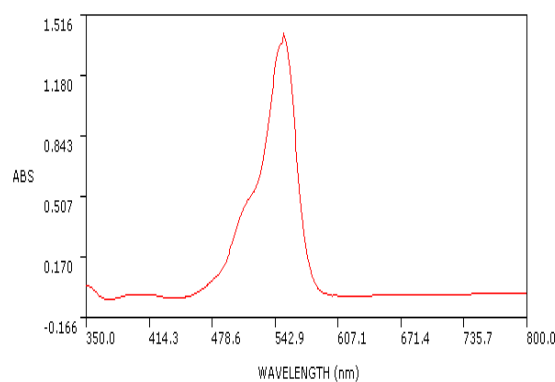

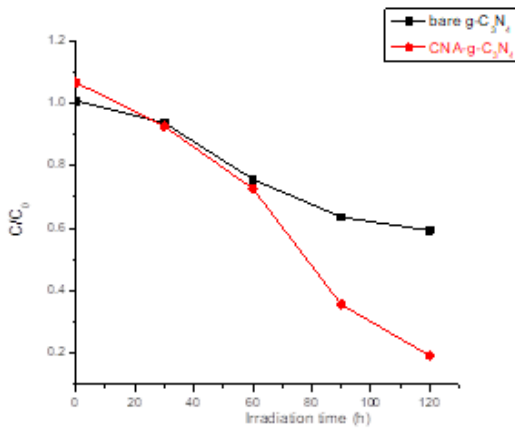**Fig. 9 UV-visible spectrum of the dye Rh–B**

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Fig. 10 Photocatalytic degradation rate of Rh-B under visible light in the presence of bare g-C₃N₄ and CNA-g-C₃N₄ composite samples.

4.1. Effect of pH

The pH of solutions greatly affects the rate of reaction taking place on semiconductor surfaces due to its influences on surface charge properties of the photocatalysts. The effect of pH in the range of 2 -10 on the photocatalytic degradation rate of Rh-B was investigated. The strong effect of 83 % on the photodegradation efficiency of Rh-B was observed at pH of 8.0. Fig. 11 a,b represents the efficiency of pH of photocatalysts.
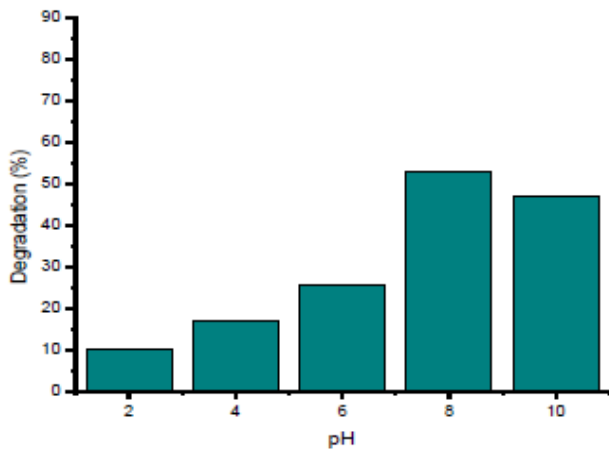
(a)
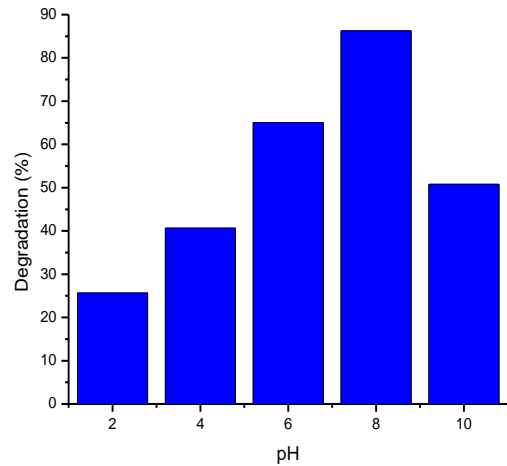
(b)

Fig. 11 Degradation efficiency of Rh-B as function of pH using (a), bare g-C₃N₄ (b) CNA-g-C₃N₄.

4.2. Reaction Kinetics

The experimental datas were fitted by applying a first order model. Inorder to investigate the reaction kinetics of the Rh-B degradation, Fig. 12 shows the first order plots for the degradation of Rh-B over bare g-C₃N₄ and CNA-g-C₃N₄ composite photocatalyst
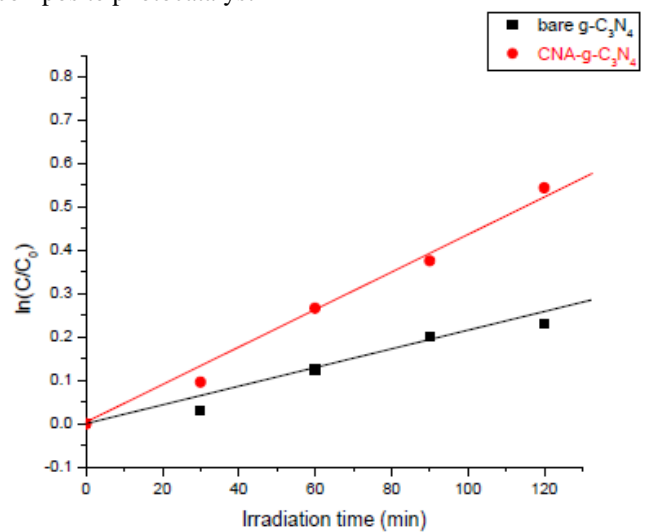

Fig. 12 First-order plots for the photodegradation of Rh-over bare g-C₃N₄ and CNA-g-C₃N₄ composite photocatalysts.

4.3. Renewable Catalytic Activity

To demonstrate the stability of the composite catalysts, the catalytic activity of the recycled CNA-g-C₃N₄ composite photocatalyst was performed 4 times. The photodegradation rate of the catalyst for two cycles were examined, which is the same as that of the fresh catalyst under experimental conditions. The Rh-B degradation rate slightly decreases for the third and fourth usage, which indicates sufficient stability of the CNA-g-C₃N₄ composite photocatalyst for Rh-B degradation.
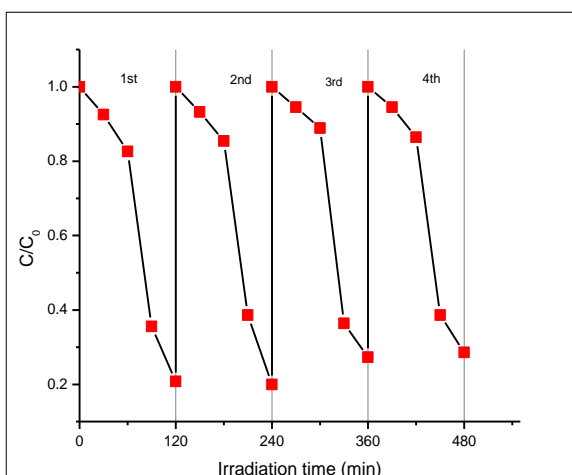
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Fig. 13 Cyclic runs in photocatalytic degradation of Rh-B in the presence of CNA-g-C₃N₄ composite photocatalyst under visible light irradiation.

Mrs. M. Jeba Jeeva Rani, Research Scholar, Scott Christian College, (Autonomous) Nagercoil, Tamil Nadu, India. She obtained her B.Sc from Nesamony Memorial Christian College, Marthandam and received her M.Sc and M.Phil from Scott Christian College, (Autonomous) Nagercoil, Tamil Nadu, India.

V. CONCLUSION

This study explored the synthesis of CNA-g-C₃N₄ composite photocatyst by Co-polymerisation of g-C₃N₄ and glutamic acid. The results of FT-IR and EDAX confirm that strong interaction has been formed between g-C₃N₄ and amino acid composite sample. The superior photocatalytic effect of composite was attributed to the synergistic effect of g-C₃N₄ and glutamic acid, which promotes migration efficiency of the photogenerated carriers on the CNA-g-C₃N₄ interface. The photocatalytic capacity of CNA-g-C₃N₄ composite towards degradation of Rh-B solution also depends on the pH. The optimum pH 8 for maximum degradation of Rh-B dye. The photocatalytic degradation of dye using graphitic carbon nitride-CNA composite presents a promising and green method for addressing environmental pollution.

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Dr. G. Allen Gnana Raj, Associate Professor of Chemistry in Scott Christion College, (Autonomous) Nagercoil, Tamil Nadu, India. He received his B.Sc from Pioneer Kumaraswamy College, Nagercoil, and obtained his master degree from Scott Chris tian College, Nagercoil. He received Ph.D from Madurai Kamaraj University in 1993. He has authored and co-authored over 55 refereed journal publications.