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Effective Degradation of Rh-B over Metal Free Graphitic Carbon Nitride/Amide Composite Photocatalyst

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Abstract

Amide (Urea) doped g-C_3N_4 (CNU) composite sample was synthesized by standard impregnation method. The effect of addition of urea as substrate was investigated systematically to get the desired phase of Urea doped g-C_3N_4 material. The effect of CN composite on structure, particle size and morphology of composite sample was investigated. The prepared sample was characterized by XRD, FT-IR and SEM – EDS techniques. The photocatalytic activity of the novel photocatalyst was evaluated using Rhodamine B (Rh-B) as a target pollutant. The CNU composite sample exhibit enhanced photocatalytic performance under visible light irradiation than pure g-C_3N_4.

Keywords: Activated carbon, Carbon nitride, Composite photocatalyst, Rhodamine B

I. INTRODUCTION

In recent years, composite materials have received considerable attention because of their structural, electronic, optical properties and their potential applications [1]. The conducting polymer/inorganic hybrid materials have been extensively studied because of their synergetic effects and potential applications in Chemistry, Physics and Biotechnology [2]. Metal oxide semiconductors are proven to be dynamic photocatalysts [3]. Most of the semiconductor photocatalysts have band gap in the UV region ie; equivalent to or larger than 3,2 eV. The large band gap absorbing only UV light is a major drawback in its potential application [4]. Number of methods have been investigated and found to shorten the band gap is to doping of nonmetals and co-doping with polymer materials. The novel photocatalyst exhibits activity for the removal of organic pollutants under visible light irradiation [5], clearly demonstrating that the metal-free g-C3N4 photocatalyst possess an interesting electronic property as well as high thermal and chemical stability, therefore making them valuable materials for photocatalysis applications. However, to date the photocatalytic efficiency of bare g-C3N4 is still limited due to

the higher recombination rate of photo generated electron-hole pairs. Many methods have been used to extend the photocatalytic performance such as doping with metals or non-metal elementals [6] and coupling with other semiconductors [7]. These methods are effective because the high surface area and small particle size it enhances e--h+ pairs separation [8].

In this work, for the first time Urea / g-C3N4 (CNU) composite was synthesized by impregnation method. The composite should increase the visible light harvesting efficiency by increasing the surface area and to evaluate the photo degradation of Rh-B under visible-light irradiation

II. MATERIALS AND METHOD

2.1 Synthesis of Photocatalysts

The metal free graphitic carbon nitride (g-C3N4) powder was synthesized by thermal treatment of precursor melamine and it was dried with ambient pressure in air. After dried the precursor was put in a Muffle furnace and heated to 550 0C with a heating rate of 10 0C min-1. The resultant yellow product was collected and ground into a powder for further use.

2.1.1 Synthesis of CNU Composite Photocatalyst

Urea doped g-C3N4 composite photocatalyst was prepared by an impregnation method. Synthesis involved mixing calculated quantities of the above prepared CN powder and Urea was dispersed in 1 M HCl and deionized water. The dispersion was magnetically stirred. After that the product was collected by centrifugation and washed with ethanol and deionized water. Finally, the sample was dried in an oven.

2.2 Characterization Techniques

X-ray diffraction (XRD) analysis was carried out at room temperature with a Bruker D8 advance diffract meter. UV-Visible spectral data were collected over a spectral range 200-800 nm with Shimadzu UV-3101 PC spectrophotometer. FT-IR spectra in transmittance mode were recorded for a solid mixture of sample and KBr in the form of pellets on a SHIMADZU FTIR spectrometer. Scanning electron microscope (SEM) analysis was performed on platinum coated samples using a JOEL apparatus model JSM-5610 LV. Elemental analysis was performed by energy dispersive X-ray micro analysis (EDAX) using BRUKER-10498 model instrument.

2.3 Evaluation of Photocatalytic Activity

The photocatalytic degradation of Rh-B was performed under the natural sunlight in the presence of CNU composite photocatalysts. In the photocatalytic treatment of dye, a known concentration of Rh-B dye solution 1x10-5 M was prepared in deionized water resulting in a solution with pH 7.6 was taken in a beaker. 0.1 g photocatalyst was added to the 50 ml (2 g/l) of dye solution. Before irradiation of the dye solution, the suspension was stirred for 30 min in the dark to realize adsorption-desorption equilibrium in the presence of catalyst. The dye solution was agitated with an electromagnetic stirrer at a constant speed of 790 rpm. The dye solution was directly exposed to sunlight radiation in an open atmosphere. At given intervals of irradiation a known volume of

sample along with the catalyst particles were collected, centrifuged and then filtered through Millipore filter paper. The filtrates were analysed by UV-Visible spectrophotometer. The determination wavelength is 553 nm for Rh-B dye, which is the maximum absorption wavelength.

The degradation efficiency of dye is calculated by the following equation

$$\text{Degradation efficiency (\%)} = \frac{C0 - C}{} \times 100$$

III. RESULTS AND DISCUSSION

3.1Characterization Technique

3.1.1 XRD Analysis

The XRD patterns of non-metal doped g-C_3N_4 composite are examined as follows: Fig. 1 shows the XRD patterns of CNU composite sample. The peaks observed at around 27.4° and 12.2° represent an interplanar staking peaks of aromatic system and the inter layer structural packing pattern [9] which corresponds to the characteristic peaks of g-C_3N_4 composite. Other than this, small additional peaks appear at 2θ = 6.1°, 11°, 18.4°, 21°, 22.9°, 25.5°, 30.9° indicate that there is a strong interaction between carbon and nitrogen present in the urea deposited on the metal free composite sample by impregnation method.

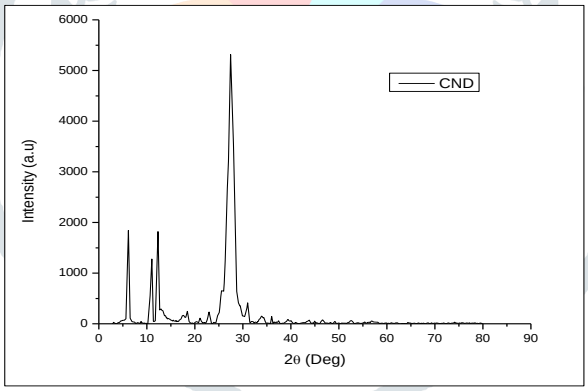

Fig.1 XRD patterns of CNU composite sample

3.1.2 FT-IR Analysis

Fig. 2 shows the FT-IR spectrum of CNU composite photocatalyst. The spectrum shows important bands at 1242, 1327, 1411 and 1473 cm^{-1}, which can be represented as the stretching modes of C-N heterocyclic [10]. Moreover, the excellent breathing modes of tri-azine units are at 802 and 887 cm^{-1}. The bands at 3271 and 3109 cm^{-1} are due to the hydrogen bonded N-H between amine and imine sites. The above-mentioned bands are the main characteristic peaks of g-C_3N_4, but an additional strong band appears at 1720 and 1851 cm^{-1} is due to strong C = O stretching vibration mode of keto group present in diamide. The band at 1905 cm^{-1} originates from the C-N stretching vibration of CN and the C-C vibration of diamide.

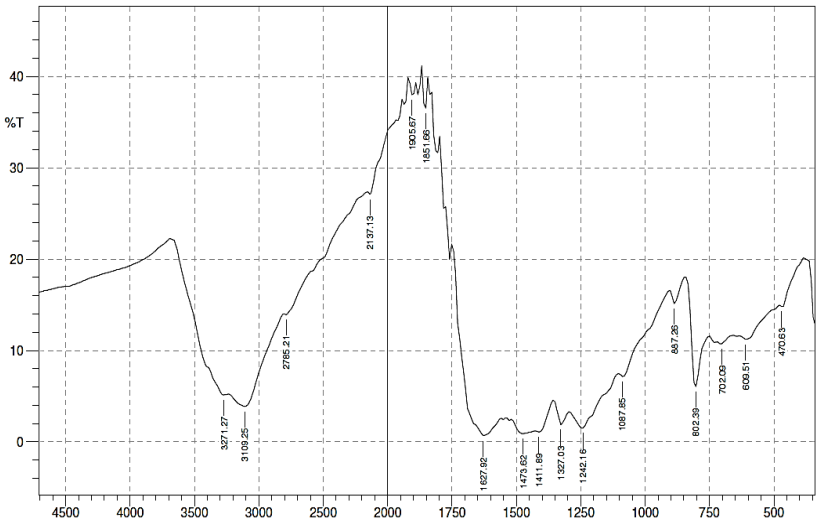

Fig. 2 FT-IR spectrum of CNU composite sample

3.1.3 SEM with EDAX Analysis

The CNU composite sample display micrometer size irregular aggregated morphology as shown in Fig.3 SEM images look like irregular agglomerates because of gases discharged from melamine deposition. There is no substantial changes are seen in the morphologies because very small amount (10:1) of non-metals (C, N and O) are added to the g-C_3N_4 matrix. Fig.4 and Table 1 illustrates the EDAX analysis of the sample.

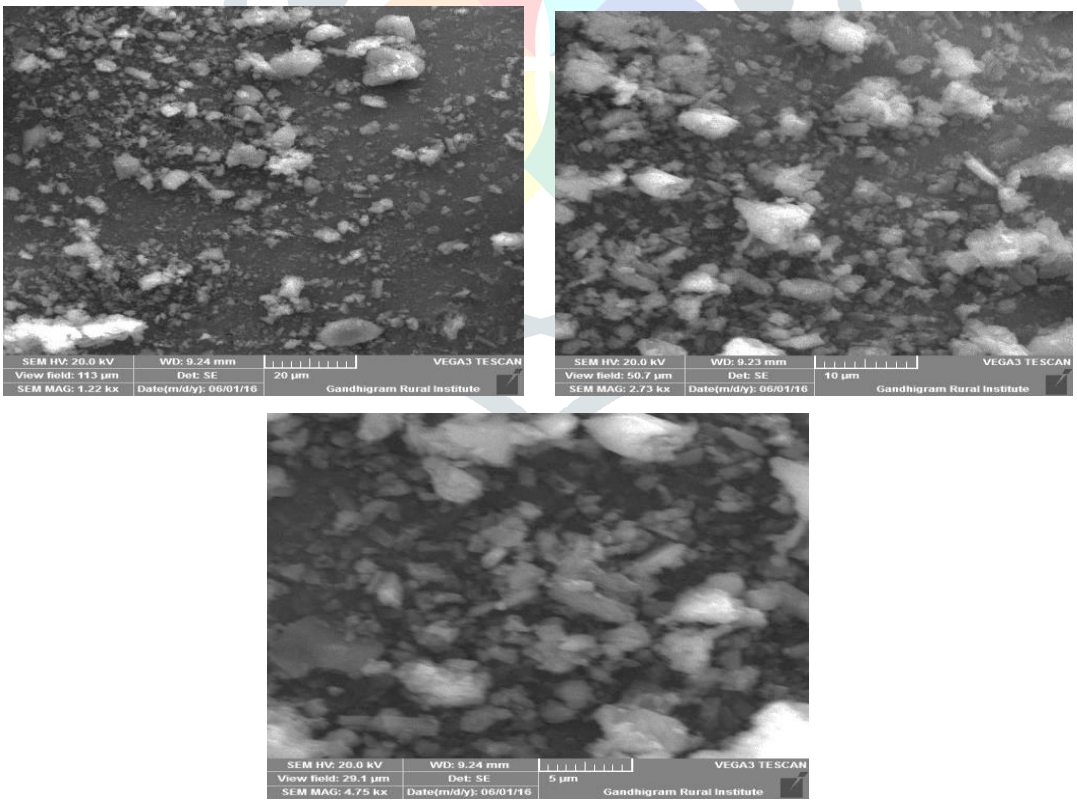

Fig. 3 SEM micrographs of CNU composite sample

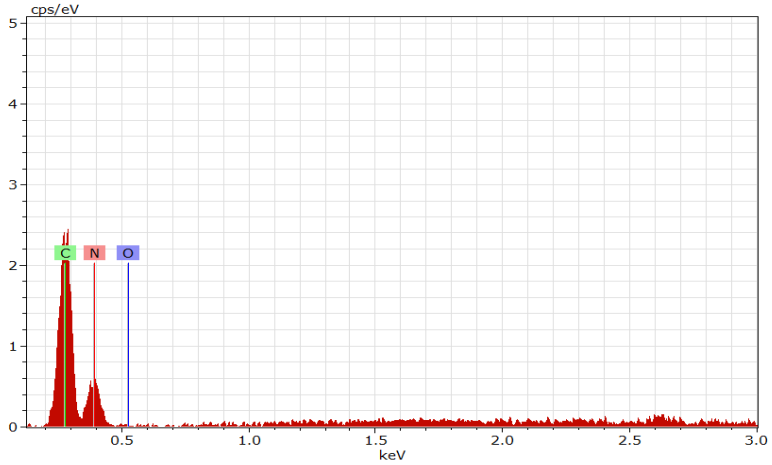

Fig. 4 EDAX spectrum of CNU composite sample

Table 1 Atomic and weight percentage of CNU composite sample

El AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]
N 7	K-series	56.06	56.06	52.45
C 6	K-series	43.41	43.41	47.36
O 8	K-series	0.53	0.53	0.20
	Total	100.00	100.00	100.00

3.1.4 Optical Properties

Inorder to determine the band gap energy (E_g) of the photoatalysts, the technique of UV-Vis diffuse reflectance spectrophotometer is employed. The result of CNU]composite displayed in Fig.5. In CNU composite holds an absorption edge of 404.48 nm, which can be ascribed to an E_g value of ~ 2.87 eV.

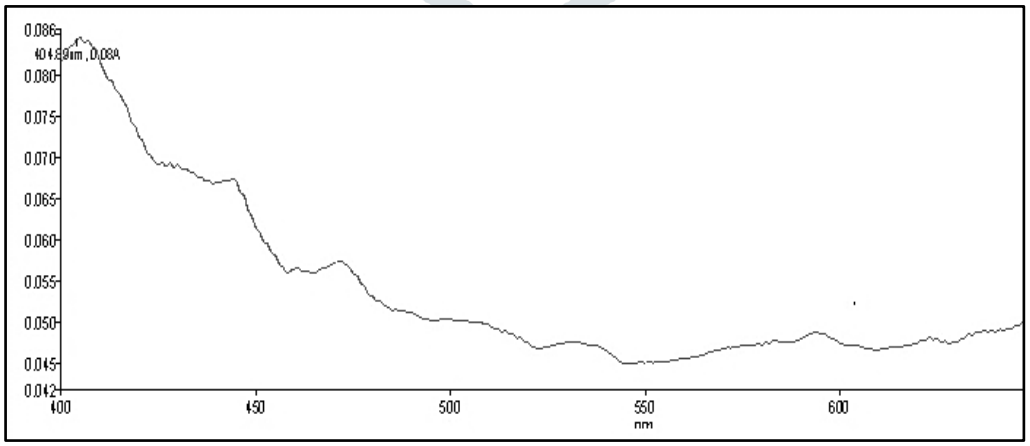

Fig. 5 DRS spectrum of CNU composite sample

3.2 Photocatalytic Activity

3.2.1 Effect of Visible Light on Photodegradation

One of the major factors using Rh-B degradation is sunlight. The result is shown in Fig. 6. The degradation of dye with the photocatalyst CNU in the absence of sunlight is very low which is about 10 %. When experiment is carried out in the presence of catalyst and sunlight; the rate of degradation also increases from 10 to 81 %.

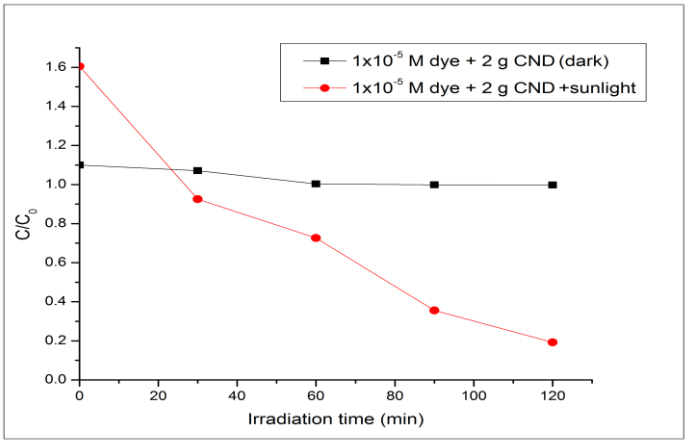

Fig.6 Effect of Visible Light on Photodegradation

3.2.2 Effect of Oxidative Degradation

The redox potential of the photogenerated hole is able to oxidize organic molecules adsorbed on the photocatalyst surface by combination of direct oxidation reactions and production of oxidizing species after reaction with water such as hydroxyl radicals. Recombination of e^--h^+ pairs provides a competitive route for the catalytic process, so that the presence of oxidizing species, commonly dilute oxygen is essential for the removal of the generated electron. Repeated oxidation of the organic intermediates leads to the mineralization of organic compounds.

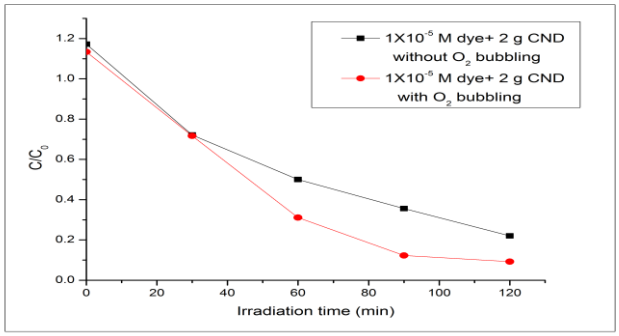

Fig.7 Effect of O_2 bubbling on photodegradation of Rh-B

3.2.3 Degradation of Dye during the Course of the Reaction

As shown in Fig .8 the absorption peaks of Rh-B in the photocatalytic system CNU shift from 553 to ~ 498 nm within 120 minutes irradiation. The degradation degree of Rh-B is estimated to be 81. These results indicate that the degradation of Rh-B molecule especially the cleavage of the conjugated structure of the molecules.

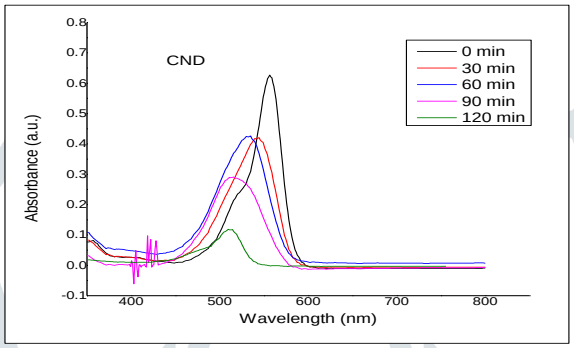

Fig. 8 Absorption peaks of Rh-B in CNU composite sample

3.2.4 Stability of Photocatalysts

Stability test has been performed by executing recycling reactions four times for the photodegradation of Rh-B over CNU sample under visible light irradiation. After each measurement, the photocatalysts are separated by centrifugation and washed with ethanol and distilled water. Fig.9 shows the stability of photocatalyst.

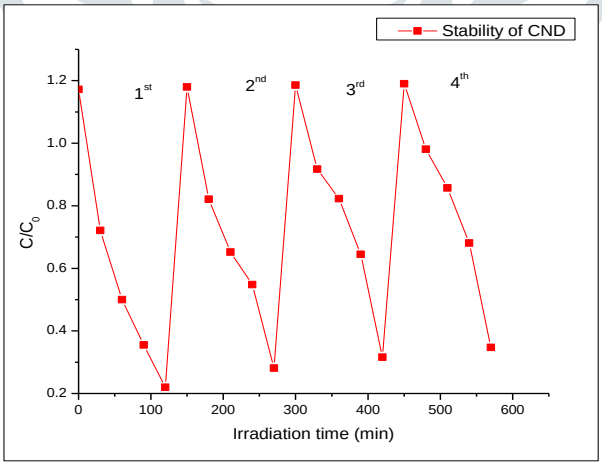

Fig. 9 Recycling runs in the photodegradation of Rh-B using CNU composite

4. GC-MS Analysis

The GC-MS results of the final photodegradation products of Rh-B using sunlight and O_2 over CNU photocatalyst as shown in Fig 10 and summarized in Table 2. The photodegradation product results in the formation of aliphatic compounds such as methyl formate, hydrazine, ethane diol, carbonic dihydrazide etc. These

lower weight aliphatic compounds eventually decompose to give CO_2 and H_2O as reported in literature [11]. In CNU mediated system Rh-B is degraded into 7 different m/z value of molecules ranging from32 to 297.

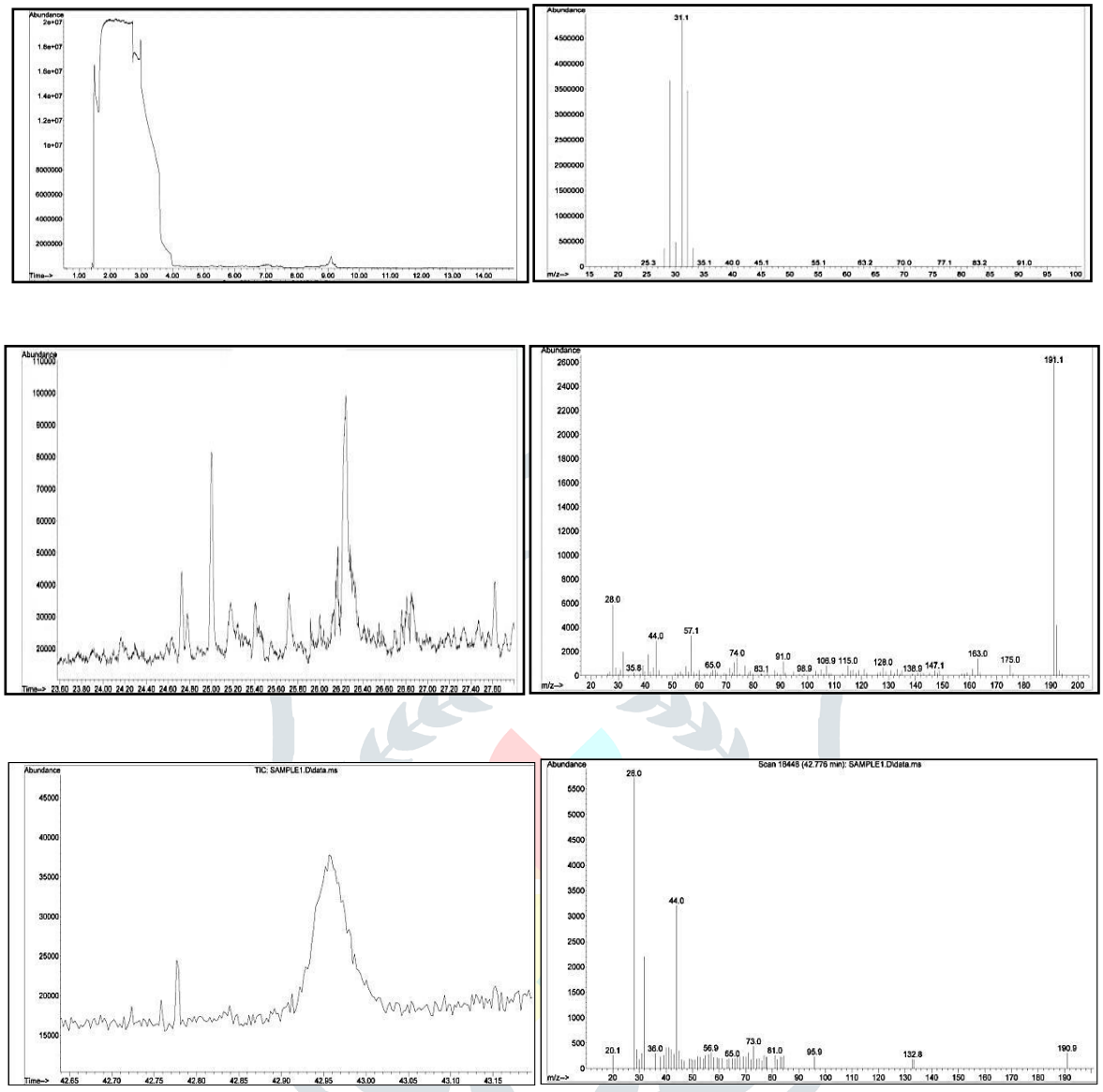

Fig. 10 GC-MS spectra of Rh-B using CNU composite sample

Table 2 Various photoproducts of Rh-B formed in GC-MS analysis over CNU composite sample

S. No	Degraded Product Name	Retention Time (min)	Molecular Formula	Molecular weight
1	Hydrazine	1.47	H_4N_4	32
2	Phenol,2,5-bis(1,1-dimethyl ethyl)-	25.0	$C_{14}H_{22}O$	206
3	Benzemethanol,4-[(1-ethylpropyl)amino]-2-methyl-3,5-dinitro-	26.4	$C_{13}H_{19}N_3O_5$	297
4	N-Formyl-dl-alanine	37.8	$C_4H_7NO_3$	117
5	Formic acid, ethyl ester	38.2	$C_3H_4O_2$	72

6	Cyclohexane carboxylic acid,2-benzyl-5-oxo-	41.2	$C_{14}H_{16}O_3$	232
7	Phenol,4-butoxy-2-[(dimethylamino)methyl]-	42.7	$C_{13}H_{21}NO_2$	223

IV. CONCLUSION

A composite photocatalyst with an improved photocatalytic performance is fabricated between g-C_3N_4 and urea. The results of XRD, FTIR-EDAX confirm the strong interaction between g-C_3N_4 and Urea sample. The greater performance of CNU (C, N and O doped g-C_3N_4) composite photocatalyst in the visible region has been explained on the basis of reduced band gap. The CND composite separates e^- and h^+ pairs through visible light and molecular oxygen. The results demonstrated by studying various parameters indicates the superior degradation efficiency of Rh-B using CNU is about 91 % at basic condition in the presence of oxygen within 120 minutes irradiation. The renewable activity of composite is stable upto four cycles. The complete mineralization of dye can be confirmed by GC-MS analysis. The photocatalytic degradation rate of CNU (0.012644 min^{-1}) is 3 times higher than that of pure g-C_3N_4. This composite presents a promising and green method for addressing environmental pollution.

REFERENCES

1. D.H.X.C. Jiang, T. Herricks, Y.N. Xia, (2002), Nano. Lett., 2,1333.
2. D.P. Wang and H.C. Zeng, (2009), Chem. Mater., 21, 4811.
3. T. Bak, J. Nowotny, M. Rekas, C.C, Sorrell, (2002), Int. J. Hyd. Ene., 27, 1022-27991
4. D.B. Hamal and K. J. Kalabunde, (2011), J. Phys. Che. C., 115, 17359.
5. S.C. Yan, Z.S Li and Z.G Zou, (2009), Photodegradation performance of g-C3N4 fabricated by directly heating melamine, Langmuir, 25: 10397.
6. L. Ge, C.C Han, J. Liu and Y.F Li, (2012), In situ synthesis and enhanced visible light photocatalytic activities of noval PANI-g-C3N4 composite photocatalysts, Journal of Materials Chemistry, 22:11843
7. Q.J. Xiang, J.G Yu and M. Jaroniec, (2011), Preparation and enhanced visible-light photocatalytic H2 -production activity of graphene/C3N4 composites, Journal of Physical Chemistry C, 115: 7355.
8. P.V Kamat,(2008), Quantum dot solar cells, semiconductor nanocrystals as light harvesters, Journal of Physical Chemistry C, 112: 18737-18753

9. J. Qin, S. Wang, H. Ren, Y. Hou & X. Wang, (2015), 'Photocatalytic reduction of CO2 by graphitic carbon nitride polymers derived from urea and barbituric acid', Applied catalysis B: Environmental, vol. 179, pp. 1-8.
10. M. Zhang, J. Xu, R. Zong, & Y. Zhu, (20140, 'Enhancement of visible light photocatalytic activities via porous structure of g-C3N4', Applied Catalysis B: Environmental, vol. 147, pp. 229-235.
11. M. Vautier, C. Guillard & J. M. Herrmann, (2001), 'Photocatalytic degradation of dyes in case study of Indigo and Indigo Caramine', Journal of Catalysis, vol. 201, pp. 46-59.