Cobalt Oxide-Graphitic Carbon Nitride Nanocomposite as an Efficient Photocatalyst for Degradation of Azure B Dye

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Abstract

A user friendly one step calcination method was used for synthesis of cobalt oxide-graphitic carbon nitride nanocomposite for the present study. The precursor used here for graphitic carbon nitride is abundantly available urea. The synthesised samples were characterised by X-ray diffraction (XRD), Field emission scanning electron microscope (FESEM) and Energy dispersive X-ray (EDX). The presence of cobalt oxide was confirmed by EDX. The flower like morphology was observed in FESEM. The XRD confirmed the crystalline nature of the nanocomposite.

The photocatalytic degradation of Azure B was observed under visible light using synthesized nanocomposite as photocatalyst. The various parameters like pH, concentration of dye, amount of composite and intensity of light were also observed. The present investigation showed the increased photocatalytic activity of nanocomposite as compared to g-C_3N_4 and cobalt oxide alone.

Keywords: Photocatalyst, Nanocomposite, Cobalt oxide, g-C_3N_4, Degradation, Azure B.

Introduction

Water is core of life which is significant for human life as well as other living organisms on the earth. Due to change in living standards, modernisation and industrialisation, fresh water supplies are becoming inadequate. There are around ten thousand dyes used in textile, paper, leather and carpet industry. Textile industries are responsible for major contamination of harmful dyes to water though seepage due to high solubility of these compounds in water. Agrochemical and pharma industries waste water is also contaminated with harmful chemicals and active compounds. This contaminated water creates high risk of cancer and other deadly diseases, also impacting on aquatic life.

The recent studies proved that photocatalysis can improve the condition of this water and can help to decontaminate it from wastes like dyes, agrochemicals and API[1,7,8,14]. Das et al[3] studied the effect of cobalt doping into graphitic carbon nitride on photo induced removal of dye from water. g-C_3N_4 with its 2D layered sheet like structure is considered to be the most stable allotrope of carbon nitride at ambient conditions[12]. Having a band gap of ~ 2.7 eV, it exhibits some interesting optical properties and thus acts as an organic and metal free semiconductor. It has potential applications as photoelectric nanodevices, chemical sensors, photovoltaic solar cells and also in energy storage. The material is a prospective candidate for display purposes, especially in bio-labelling and lighting[20]. But the photocatalytic activity of pure g-C_3N_4 gets hampered due to the fast recombination rate of photogenerated electron-hole pairs[11].

To overcome its problem of fast recombination of electron-hole pairs, scientists are making efforts which mainly include doping of heteroatoms and metals, assembling of the mesoporous structure, copolymerization with organic compounds and coupling with other semiconductors[5,9,10,13,15].

Zang et al[18] reported comparison of visible light driven hydrogen peroxide and peroxymonosulfate degradation of norfloxacin CoO-g-C_3N_4. Transition metals with abundant reserves, moderate price and excellent stability commonly serve as a dopant[2,6,19]. Zhou et al[21] worked on cobalt doped graphitic carbon nitride as an effective catalyst for peracetic acid to degrade sulfamethoxazole. Yu et al[16] studied cobalt doping of porous graphitic carbon nitride with Co-N bonds promotes electrocatalytic N_2 fixation under ambient conditions[16]. Incorporation of cobalt on g-C_3N_4 as a bifunctional catalyst for electrochemical water-splitting reactions in acidic media is reported[4]. Recent study was performed on hydrogen and oxygen evolution using cobalt-nanoparticles-supported on g-C_3N_4[17].

Material and Methods

Preparation of Cobalt oxide g-C_3N_4: A mixture of 5 g of $Co(NO_3)_2 \cdot 6H_2O$ and 12 g of urea was mixed homogeneously using mortar and pestle and loaded into a clean alumina crucible. The crucible was sealed using its cover so that the amount of gas loss is minimised, which was then pyrolyzed in a furnace at 400°C for 2 h. Crucible was taken out and naturally cooled down to room temperature.

The furnace was cool down naturally after which the crucible was taken out. The obtained reddish-brown powder was then finely ground using an agate mortar and pestle. The sample was named as CoO-g-C_3N_4. Conversely, a pale-yellow colour powder was obtained when 10 g of urea was thermally treated under the same conditions, which was named as g-C_3N_4[11].

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Results and Discussion

EDX Spectrum: The presence of cobalt oxide, carbon and nitrogen element was confirmed by an energy–dispersive X-ray spectroscopy. EDX spectrum of CoO-g-C_3N_4 nanocomposite is given in fig. 1.

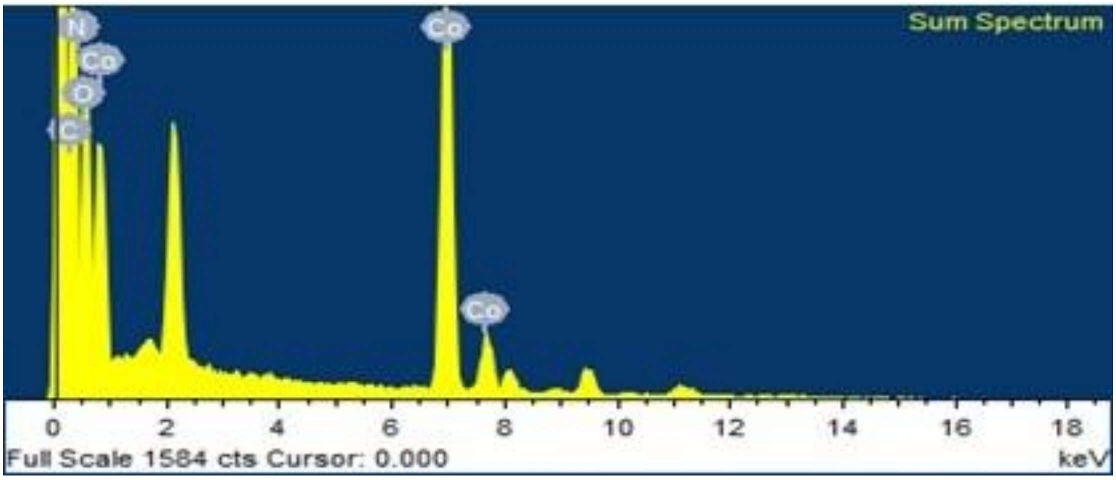

Fig. 1: EDX spectrum

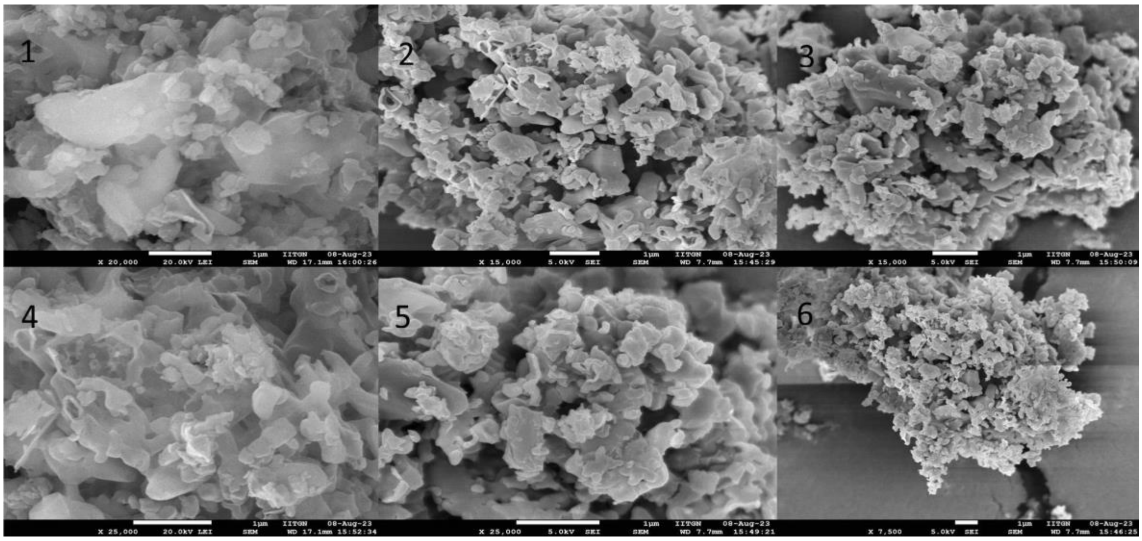

Fig. 2A: FESEM images of graphitic carbon nitride

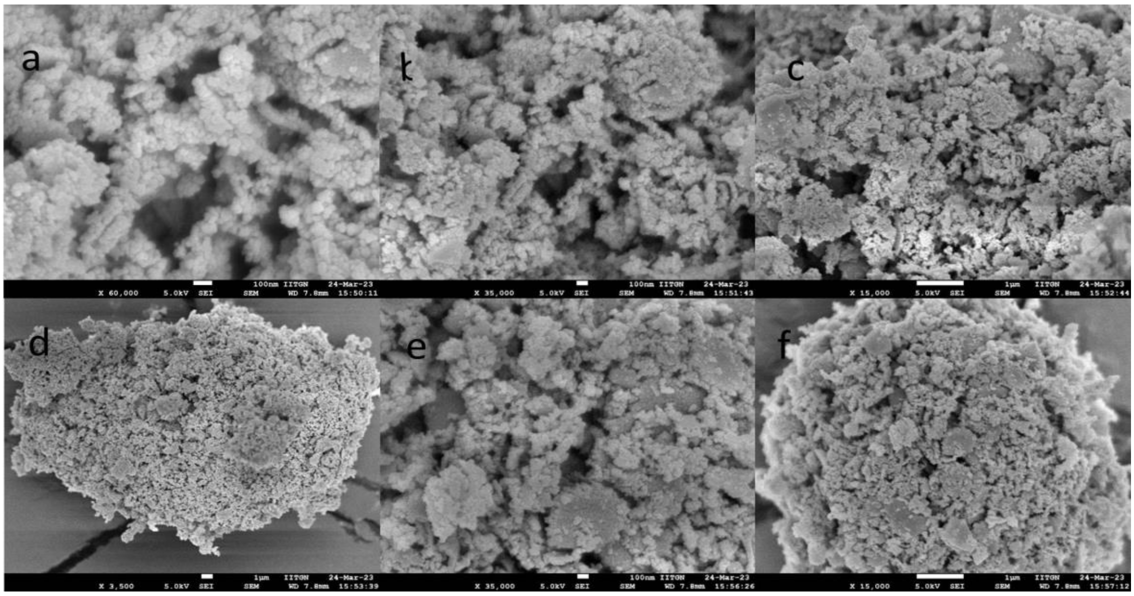

Fig. 2B: FESEM images of CoO-g-C_3N_4

FESEM Images: The field emission scanning electron microscopy analysis (FESEM) was performed for both graphitic carbon nitride and nanocomposite. FESEM images of different resolutions are given in fig. 2A and 2B. It shows porous nanoparticles with flower shape morphology. It is clearly observed that the porosity and active sites improved much more in nanocomposite compared with simple graphitic carbon nitride.

p-XRD: X-ray diffractometer gives sharp peaks at indicating crystalline nature of component. The crystallite size of the nanocomposite was calculated by Debye-Scherrer equation and average crystallite size was found to be 89.14 nm.

Typical run: A stock solution of Azure B dye was prepared in double distilled water (1.0×10^{-3} M). Working solution of azure B dye was arranged (3.5×10^{-5} M) by diluting the stock solution. 0.10 g synthesized CoO-g-C_3N_4 nanocomposite were added to it. The pH of reaction mixture was kept 9.5 and then this solution was exposed to a 200 W tungsten lamp. The absorbance of azure B solution was determined by using a spectrophotometer at λmax = 644 nm. A water filter was used to cut off thermal radiations. The intensity of light was studied by changing the distance between the light source and dye solution with nanocomposite. Absorbance of the solution at different time intervals was studied with the help of spectrophotometer.

It was noted that the absorbance of the dye solution declines with raising time of exposure which showed decomposition of azure B dye with time. Rate constant for first order reaction was observed as 3.33×10^{2} S^{-1}.

A typical run is given in table 1 and graphically presented in fig. 4. pH = 9, [Azure A] = 3.5×10^{-5} M, Amount of composite = 0.1 g, Light intensity = 60 mW cm^{-2}.

Effect of pH: The impact of variation of pH was studied in the range 5.0-10.0 and the results are reported in fig. 5. It was perceived that the rate of dye degradation improves up to pH 9.5 as the pH increases from 5 to 10. Beyond pH 9.5, the rate of reaction for degradation of dye declined. The unexpected decline in the degradation rate may be due to chemical reaction of base with dye and possible anion formation of azure A dye. The enhancement in rate of reaction with pH may be illustrated on the basis that the electron from conduction band of the photocatalyst may be engaged by dissolved oxygen to stabilize the hole (h^+) with slowing down recombination of electron and hole.

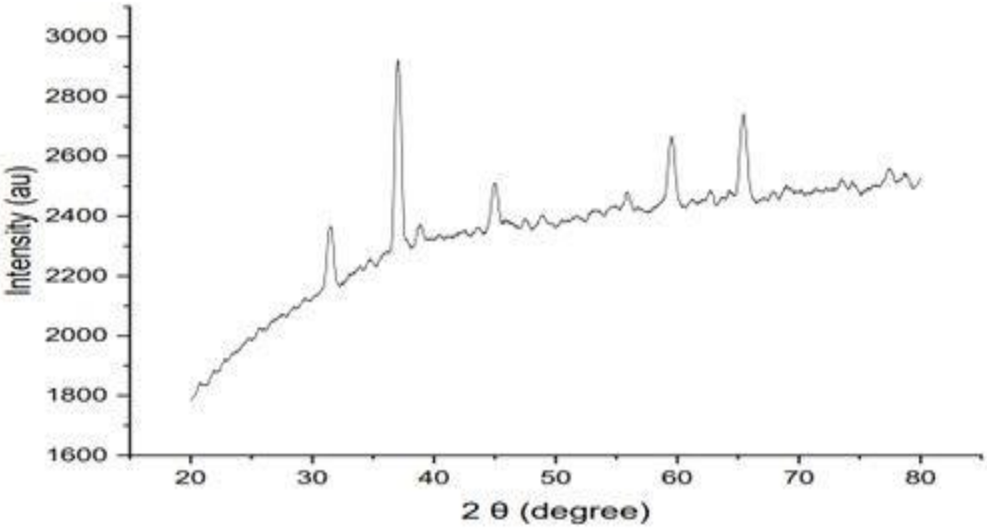

Fig. 3: XRD Spectra

Table 1
A typical run

	With catalyst		With g-C_3N_4	
Time	**Absorbance (A)**	**1+ logA**	**Absorbance (A)**	**1+ logA**
0	0.804	0.9053	0.785	0.8949
10	0.512	0.7093	0.653	0.8149
20	0.335	0.5250	0.521	0.7168
30	0.211	0.3243	0.456	0.6590
40	0.152	0.1818	0.395	0.5966
50	0.132	0.1206	0.312	0.4942
60	0.115	0.0607	0.256	0.4082

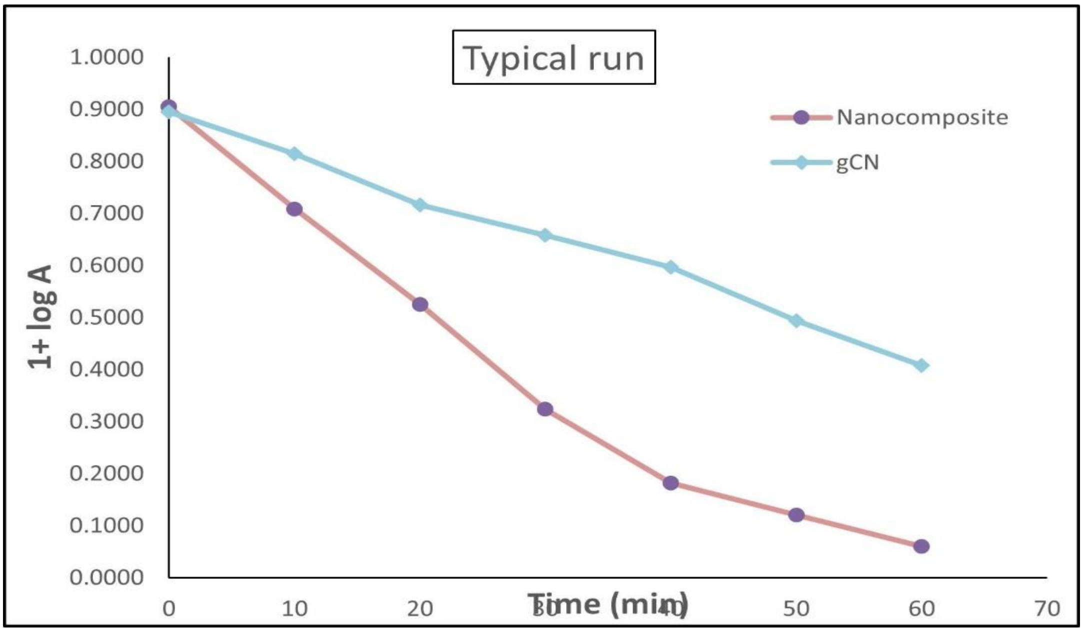

Fig. 4: Typical run

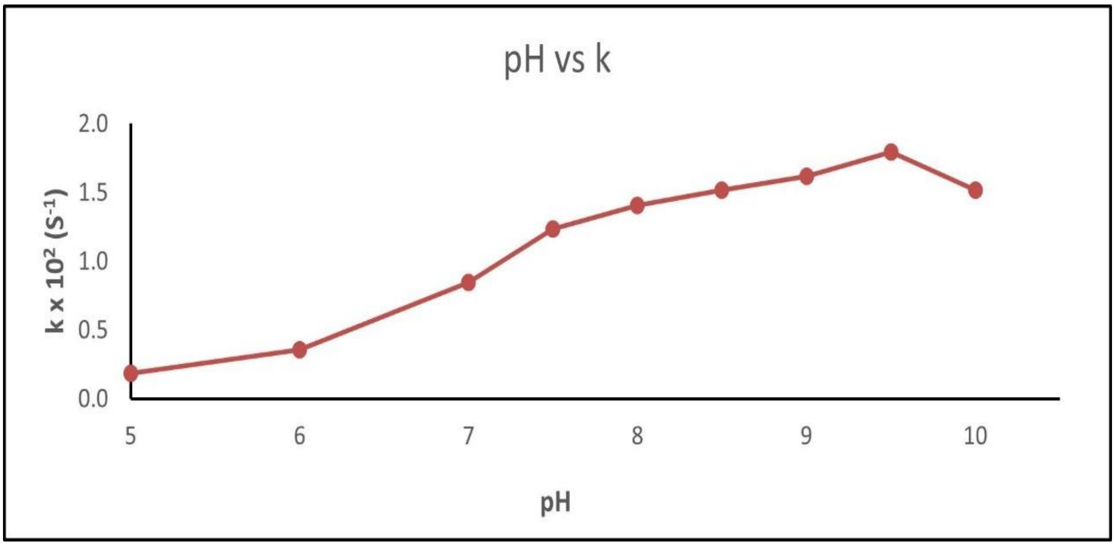

Fig. 5: Effect of pH

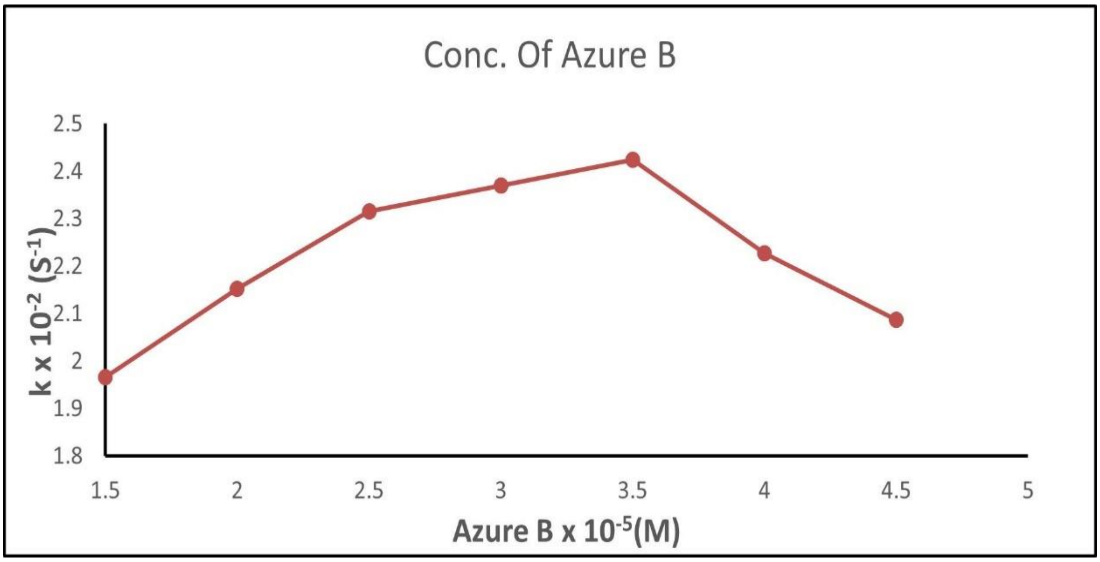

Fig. 6: Effect of dye concentration

Effect of azure B concentration: The effect of azure B dye concentration on the photocatalytic degradation was studied in the range of 1.5×10^{-5} to 4.5×10^{-5} M. It was observed that as the concentration of the dye was increased, the dye degradation enhances. But above 3.5×10^{-5} M, the rate of dye degradation declines. The enhancement of dye degradation was observed due to availability of excess molecules of the dye. Sudden decline of rate of degradation with concentration above 3.5×10^{-5} may be due to saturation of dye concentration in the solution which prohibits the desired light intensity to reach at the surface of the nanocomposite photocatalyst.

Effect of amount of composite: The result of variation of the amount of composite on the rate of dye degradation was studied in the range from 0.02 to 0.12 g and the results are presented in fig. 7.

It was distinguished that increasing the amount of composite enriches the photocatalytic activity. The rate of degradation was highest at 0.1 g of the composite. After 0.1 g, the rate decreases. The increase in the rate of degradation of dye with increase in amount of the photocatalyst is due to increase in exposed surface area of the composite up to 0.1 g. Above this, only thickness of the layer of the photocatalyst is increased with increase in the amount of the composite. This was confirmed by using vessels of the different dimensions.

Effect of light intensity: The distance between the light source and exposed surface area of nanocomposite photocatalyst was changed to establish the influence of light strength on the photocatalytic degradation. The light intensity was changed from 20 to 70 mWcm^{-2}.

The degradation of the dye was found to increase with the increase in the light intensity. It may be due to a higher number of photons striking to the surface of the photocatalyst, thus forming excitons (electron- hole pairs). At higher intensity of light, some thermal reactions may occur, decreasing the rate of degradation of the dye.

Mechanism: The mechanism of the dye degradation may be explained as:

$$(\text{CoO-g-}C_3N_4)\ \text{Composite} \xrightarrow{h\upsilon} e^-(\text{CB}) + h^+(\text{VB})$$
$$(\text{Azure B})_0 \xrightarrow{h\upsilon} {}^1\text{Azure B}$$
$${}^1\text{Azure B} \xrightarrow{\text{ICS}} {}^3\text{Azure B}$$
$$h^+ + {}^-OH \longrightarrow {}^\cdot OH$$
$${}^\cdot OH + {}^3\text{Azure B} \longrightarrow \text{Degradation Products}$$

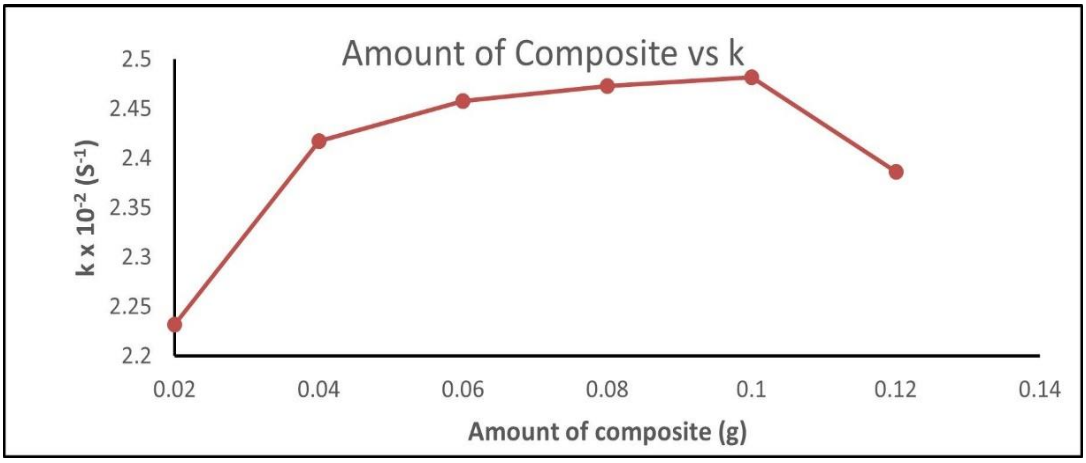

Fig. 7: Effect of amount of composite

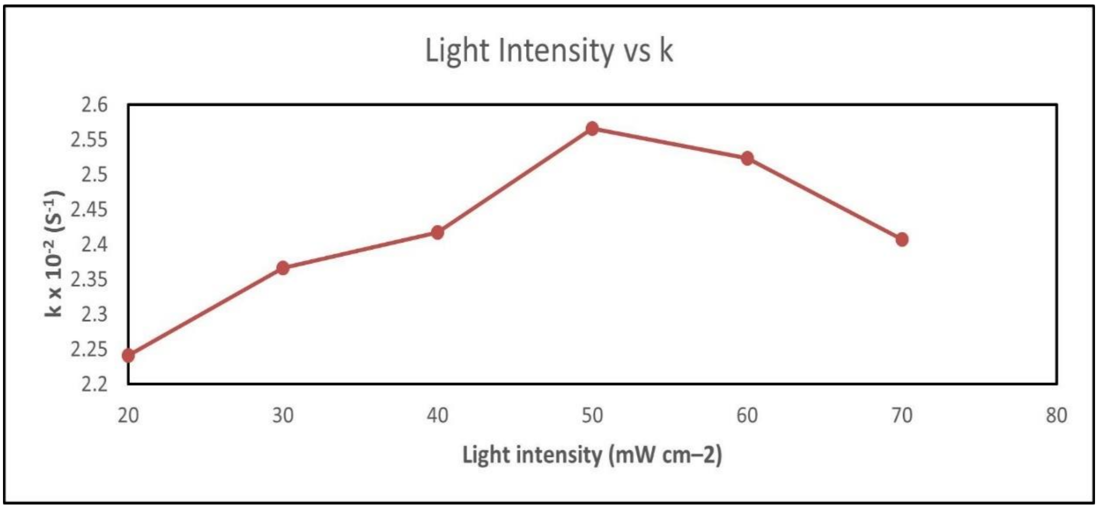

Fig. 8: Effect of light intensity

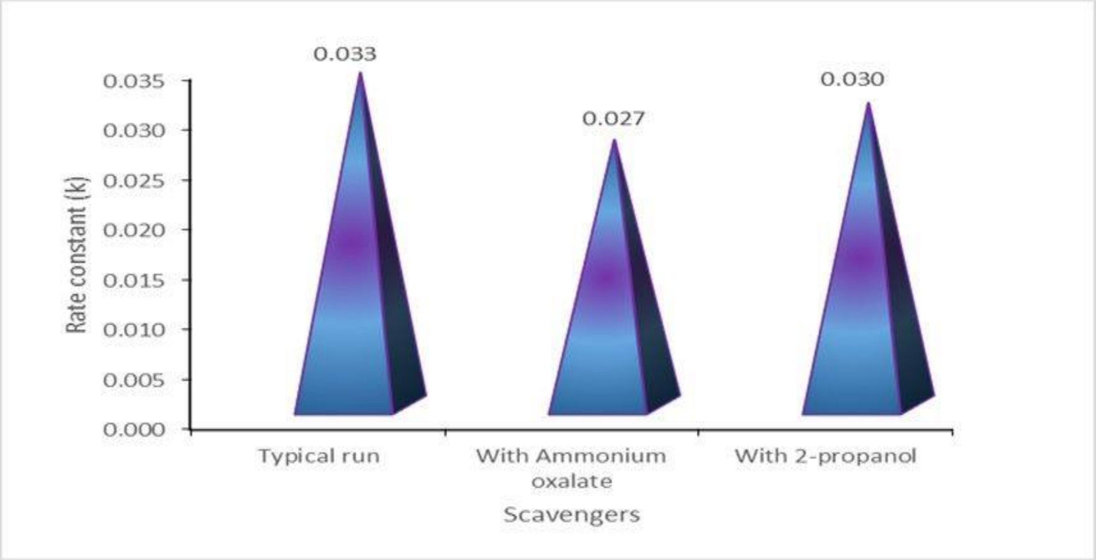

Fig. 9: Scavengers vs Rate constant

Here the light (hυ) excites e^- from valence band (VB) of the composite to conduction band (CB) creating hole (h^+) at the valence band. As the same time dye is also exited to the singlet state and then converted to triplet state (^{3}Azure B). The h^+ combines with hydroxyl ions ($^-$OH) on the surface of photocatalyst to produce hydroxyl radical ($^{\cdot}$OH). Then the $^{\cdot}$OH degrade the dye molecules. The reactive species is $^{\cdot}$OH which was confirmed by observing the reaction in the presence of scavenger 2-propanol where the rate is substantially decreased. Also, the rate remarkably decreases for ammonium oxalate (AO) as h^+ scavenger because h^+ is responsible to produce the $^{\cdot}$OH.

Conclusion

The CoO-g-C_3N_4 nanocomposite and simple graphitic carbon nitride were prepared successfully and were analyzed by EDX, FESEM and p-XRD. The study was successfully performed for photocatalytic degradation of azure B dye under visible light with synthesized nanocomposite. Different parameters were studied like pH, concentration of dye, amount of nanocomposite, light intensity. With optimized parameters, the azure B dye degraded efficiently.

Mechanism investigation clearly indicates that reactive species is $^{\cdot}$OH involved in the degradation of dye. So, CoO-g-C_3N_4 nanocomposite can be used as photocatalyst for degradation of different dyes and organic contaminants in water. Thus, it can be used for decontamination of water and in increasing reusability of water.

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