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

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ABSTRACT

A simple one step pyrolysis 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 observed in FESEM. The XRD confirmed the crystalline nature of the nanocomposite. The photocatalytic degradation of Azure A 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 was also observed. The present investigation showed the increased photocatalytic activity of nanocomposite as compared to $g\text{-C}_3\text{N}_4$ and cobalt oxide alone.

Key words: Photocatalyst, Nanocomposite, Cobalt oxide, $g\text{-C}_3\text{N}_4$, Degradation, Azure A.

Introduction

Textile industry is responsible for pollution problems around the globe due to the discharge of polluted wastewater into the waterways. Researchers have made tremendous efforts to investigate the degradation of organic and toxic pollutants of waste water using different photocatalysts. The photo decolorization of dyes is a hopeful technology for this problem. This technique having ability of its environment friendly method, cheap cost, and does not generate any secondary pollution.

So far, there have been many reports on effective photocatalysts for water splitting, amidst which TiO_2 is widely researched semiconductor owing to its certain superior qualities like, photochemical stability, superhydrophilicity, strong oxidation ability (Chen *et al.*, 2017). However, some remarkable pit-

falls of TiO_2 led to the research of other unconventional visible light-active photocatalysts, Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) to be the most favourable among them because of its abundance, high thermal and chemical stability along with its distinctive electrical and optical properties with medium band gap 2.7eV. But the photocatalytic activity of pure $g\text{-C}_3\text{N}_4$ gets hampered due to the fast recombination rate of photogenerated electron-hole pairs (Thomas *et al.*, 2008, Sridharan *et al.*, 2014). As an allotrope of graphite, $g\text{-C}_3\text{N}_4$ has obey 2D structure and belong to the most stable allotrope of carbon under ambient conditions (Wang *et al.*, 2015). It comprises of carbon and nitrogen, which are the most abundant elements on earth, and so environment friendly. Also synthesized via a simple one-step polymerization of nitrogen-rich precursors with cheap cost (Zang *et al.*, 2012). To overcome its problem of fast recombina-

tion of electron-hole pairs scientists make efforts which mainly include doping of heteroatoms and metals, assembling of the mesoporous structure, copolymerization with organic compounds, and coupling with other semiconductors (Wu *et al.*, 2018, Zhao *et al.*, 2014). The distinctive structural and electronic properties of g-C₃N₄ can be featured to the heptazine rings with pyridinic nitrogen groups in g-C₃N₄ in which the six nitrogen lone pairs can serve as electron donors (Oh *et al.*, 2017). Hence, g-C₃N₄ has a majestic ability to capture metal ions through metal-N interaction. g-C₃N₄ can furnish a flexible platform to immobilize metal catalysts in its structure, which can hinder the leaching of metal ion and enhance its internal charge transfer (Wang *et al.*, 2009).

As a result, cobalt doped g-C₃N₄ has been designed to serve as a catalyst in photocatalytic degradations. Xie *et al.* (2015) reported degradation of monochlorophenols by activation of peroxymonosulfate using Co-g-C₃N₄ (Xie *et al.*, 2019). Yang *et al.* synthesised Co-g-C₃N₄ nanosheet which accelerating charge transfer for degradation of methylene blue, which obtained an excellent treatment efficiency (Yang *et al.*, 2021). Zhou *et al.* worked on cobalt doped graphitic carbon nitride as an effective catalyst for peracetic acid to degrade sulfamethoxazole (Zhou *et al.*, 2022). Ceconet and co-workers reviewed on g-C₃N₄ as a sustainable photocatalyst material for pollutants removal. State-of-the-art, preliminary tests and application perspectives (Ceconet *et al.*, 2021).

Materials and Methods

Preparation of Cobalt oxide g-C₃N₄

A mixture of 5 g of Co(NO₃)₂·6H₂O and 12 g of urea was mixed homogeneously using mortar and pestle and loaded into a clean alumina crucible, as shown in Scheme 1. The crucible is sealed using its cover so that the amount of gas loss is minimises, which was then pyrolyzed in a furnace at 400°C for 2 h. The furnace was cool down naturally after which the crucible was taken out. The obtained reddish-brown powder then finely grounded using an agate mortar and pestle. The sample was named as CoO-g-C₃N₄. 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-C₃N₄. (Sridharan *et al.*, 2014).

Characterization of Composite

EDX Spectrum

The presence of cobalt oxide, carbon and nitrogen element was confirmed through an energy-dispersive X-ray spectroscopy. EDX spectrum of CoO-g-C₃N₄ nanocomposite is given in Fig. 1.

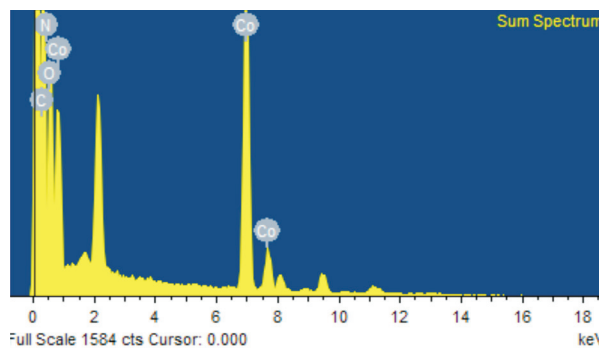


Fig. 1. EDX spectrum

FESEM Images

The field emission scanning electron microscopy (FESEM) was performed. FESEM images of different resolutions are given in Fig. 2. It shows porous nanoparticles with flower shape morphology.

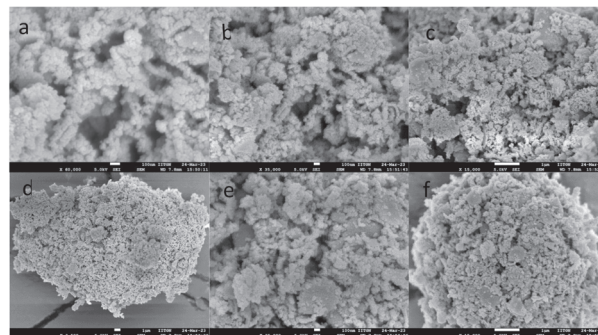


Fig. 2. FESEM images of CoO-g-C₃N₄

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 A dye was prepared in

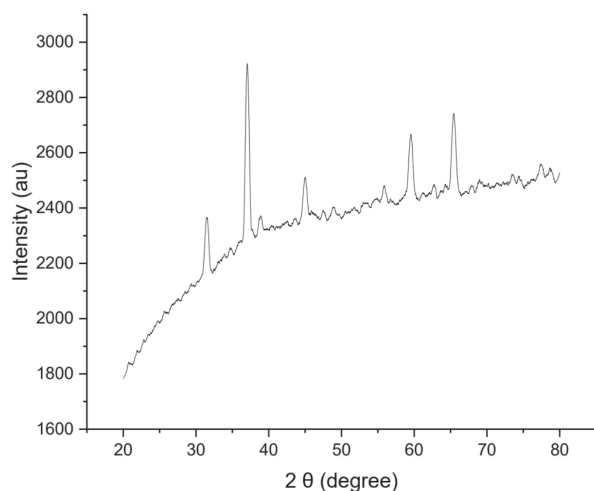


Fig. 3. XRD Spectra

double distilled water (1.0×10^{-3} M). Working solution of solution of azure A dye was arranged (3.0×10^{-5} M) by diluting the stock solution and 0.08 g synthesized CoO-g- C_3N_4 nanocomposite of was added to it. The pH of reaction mixture was kept 9.0 and then this solution was exposed to a 200 W tungsten lamp. The absorbance of azure A solution was determined by using a spectrophotometer at $\lambda_{\text{max}} = 630$ 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 show decomposition of azure A dye with time. And observed rate constant for first order reaction $3.53 \times 10^2 \text{ S}^{-1}$.

A typical run is given in Table 1 and graphically presented in Fig 4.

pH = 9.0 [Azure A] = 3.0×10^{-5} M
Amount of composite = 0.08 g Light intensity = 60 mW cm^{-2}

Table 1. A typical run

Time (min)	Absorbance (A)	1+Log A
0	0.721	0.8579
10	0.482	0.6830
20	0.272	0.4346
30	0.156	0.1931
40	0.114	0.0569
50	0.102	0.0086
60	0.101	0.0043

Effect of pH

The effect of variation of pH was studied in the

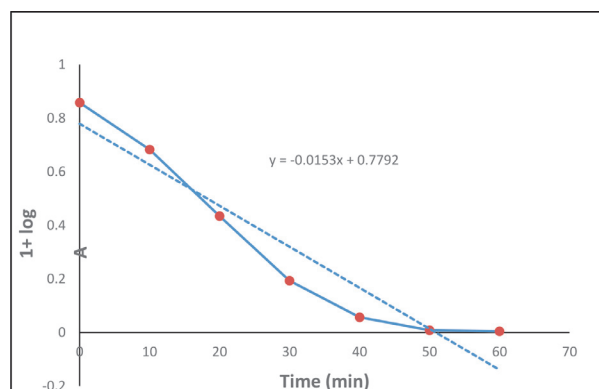


Fig. 4. Typical run

range 5.0-10.0 and the results are reported in Fig. 5.

It was noted that as the pH increases the rate of dye degradation also increases up to the pH 9.0. Further increase in pH resulted into decrease in rate of reaction. The unexpected decrease in the degradation rate may be due to chemical reaction of base with dye and possible anion formation of azure A dye. The increase in rate of reaction with pH may be explained on the basis that the electron from conduction band of the photocatalyst may be taken up by dissolved oxygen to stabilize of the hole (h^+) with slowing down recombination of electron and hole.

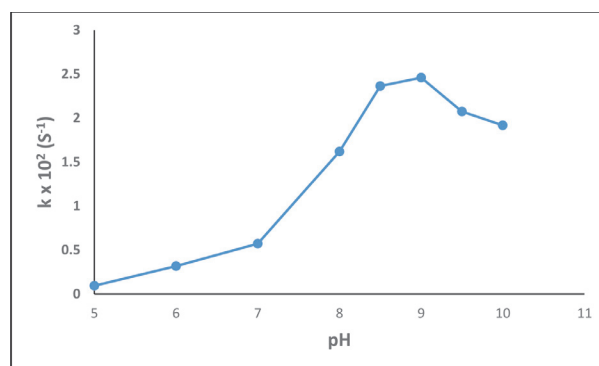


Fig. 5. Effect of pH

Effect of azure A concentration

The effect of azure A dye concentration on the photocatalytic degradation of was studied in the range of 1.5×10^{-5} to 4.0×10^{-5} M and the results are evaluated in Fig. 6.

It was noted that as the concentration of the dye was increased, the dye degradation enhances. But above 3.0×10^{-5} M the rate of dye degradation declines. The enhancement of dye degradation observed due to availability of excess molecules of the

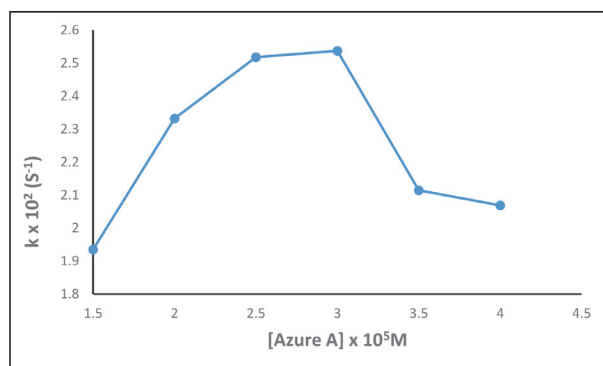


Fig. 6. Effect of dye concentration

dye. And sudden decrease of rate of degradation with concentration above 3.0×10^{-5} may be due to saturation of dye concentration in the solution which hinders the desired light intensity to reach at the surface of the nanocomposite photocatalyst.

Effect of amount of composite

The outcome of variation of the amount of composite on the rate of dye degradation was evaluated in the range from 0.02 to 0.12 g and the results are presented in Fig. 7.

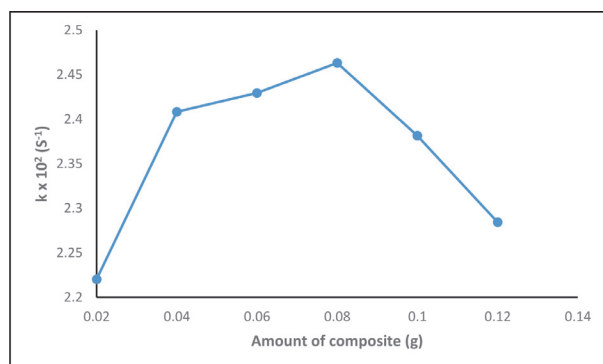


Fig. 7. Effect of amount of composite

It was noticed that increasing the amount of composite improved the photocatalytic activity. The rate of degradation was highest at 0.08 g of the composite. Beyond 0.08 g, the rate declines. 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 0.08 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 length between the light source and exposed surface area of nanocomposite photocatalyst was differing to establish the influence of light strength on the photocatalytic degradation. The light intensity was changed from 20 to 70 mWcm⁻². The results are shown in Fig. 8.

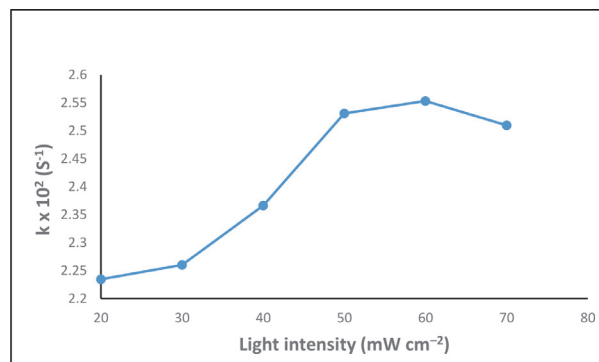
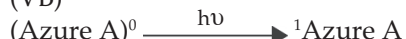
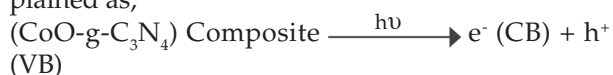


Fig. 8. Effect of light intensity

The degradation of the dye was found to increase with the increase in the light intensity. It may be due to a greater number of photons striking to the surface of the photocatalyst thus forming excitons (electron-hole pairs). At larger 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,



Here the light ($h\nu$) excites e^- from valence band (VB) of the composite to conduction band (CB) creates hole (h^+) at the valence band. And same time dye is also excited to the singlet state and then converted to triplet state (${}^3\text{Azure A}$). The h^+ combines with hydroxyl ions (-OH) on the surface of photocatalyst to produce hydroxyl radical ($\cdot\text{OH}$). Then the $\cdot\text{OH}$ degrade the dye molecules. The reactive species is $\cdot\text{OH}$ 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 for produce the $\cdot OH$.

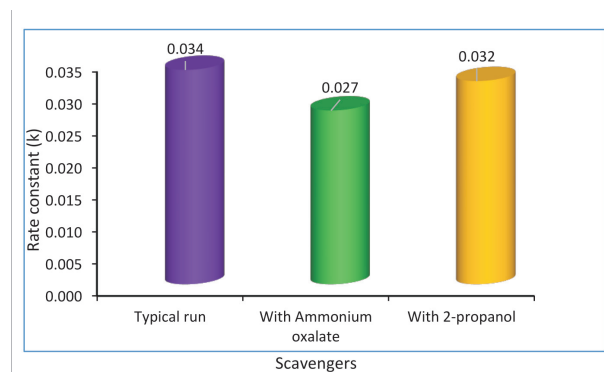


Fig. 9. Scavengers vs Rate constant

Conclusion

The CoO-g-C₃N₄ nanocomposite was synthesized successfully. It was characterised by EDX, FESEM and p-XRD. The synthesized nanocomposite studied successfully for photocatalytic degradation of azure A dye under visible light. Different parameters were studied like pH, concentration of dye, amount of nanocomposite, light intensity. With optimised parameters the azure A dye degraded efficiently. Mechanism investigation clearly indicates that reactive species is $\cdot OH$ which is involved in the degradation of dye. So, CoO-g-C₃N₄ nanocomposite can be used as photocatalyst for degradation of different dyes and organic contaminants in water. It will help to treatments of polluted water and increasing the recyclability of water.

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Conflict of Interest

Authors declares that they have no conflict of interest.

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