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# Photocatalytic Degradation of Evan's Blue in Aqueous Solution using Graphitic Carbon Nitride

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**ABSTRACT**

The photocatalytic degradation of Evan's blue was carried out using graphitic carbon nitride (g-$C_3N_4$) as a photocatalyst. The effect of various parameters such as amount of catalyst, pH, light intensity and concentration of the dye has been studied on the rate of reaction. It was observed that this photocatalytic process followed pseudo-first order kinetics. The optimum conditions for degradation of Evans blue were achieved as: pH 9.5, [Evans blue] $1.00 \times 10^{4}$ M, g-$C_3N_4$ 0.10 g and light intensity 60.0 mW $cm^2$

***Key words:*** *Photocatalytic degradation, Evan's blue, Graphitic carbon nitride, Advanced oxidation, Visible light.*

## Introduction

Water is very important component to all kinds of living beings. Industrial waste or organic pollutants like dyes, pesticides, drugs, medicinal waste, etc. are major threat to water resources. The different wastewater pollutants such as dyes, antibiotics, phenols etc. are released into the water, soil, lakes and rivers, which show an adverse effect on human health and ecosystem. It is all due to rapid industrialization that environmental pollution has become one of the major problems for human society. Photocatalysis can be applied to solve such environmental problem by using everlasting solar energy (Qiu *et al.,* 2021).

The photodegradation of three reactive azo dyes (Reactive black 5, Reactive yellow 84 and Reactive red 120) in aqueous solution was investigated by using low pressure mercury lamp (Neamtu *et al*., 2002). They used six different doses of hydrogen peroxide at constant concentration of dye (100 mg $l^{1}$). They observed effectiveness of the UV/$H_2O_2$ system based on degree of mineralization of total organic carbon (TOC). The advanced Fenton process (AFP) can be used as an efficient technique to degrade azo dye in the aqueous medium using zero valent metallic iron (ZVMI). It was observed that degradation rate was found to decrease at higher iron dosages as well as higher oxidant concentrations. The rate constant for Fe (0)/UV and Fe (0)/APS/UV processes was almost double as compared to dark. It was revealed that degradation of methyl orange (MO) was faster at pH 3. The efficiency of different processes for the decolorization of MO followed the order:

Fe (0)/$H_2O_2$/UV > Fe (0)/$H_2O_2$/dark > Fe (0)/APS/UV > Fe (0)/UV > Fe (0)/APS/dark > $H_2O_2$/UV approximately Fe (0)/dark > APS/UV (Devi *et al.,* 2009).

The degradation of two azo reactive dyes; Reactive yellow 84 (RY84) and Reactive red 120 (RR120) by photo-Fenton and Fenton-like routes was reported (Yediler *et al.,* 2003). The optimal conditions were found at pH 3 and hydrogen peroxide-to-iron molar ratio = 20:1 under UV or solar irradiation. It was indicated that color removal of RY84 after 15 min followed the decreasing order:

Solar/Fe (II)/ $H_2O_2$ > UV/Fe (II)/ $H_2O_2$ >UV/Cu (II)/Fe (III)/ $H_2O_2$ > UV/Fe (III)oxalate/ $H_2O_2$ >

UV/Fe (III)/ $H_2O_2$ > dark/Fe (II)/ $H_2O_2$ > solar/Fe (III)oxalate/ $H_2O_2$ > UV/ $H_2O_2$ > UV/Fe (II) = UV.

During the same reaction period, the relative order for RR120 removal rate was slightly different:

Solar/Fe (II)/$H_2O_2$ > UV/Fe (II)/$H_2O_2$ > UV/Fe (III)/$H_2O_2$ = UV/Cu (II)/Fe (III)/ $H_2O_2$ > UV/Fe (III)oxalate/ $H_2O_2$ = UV/ $H_2O_2$ > UV.

The Evans blue (0.245) could be degraded using $Fe^{2+}$ (0.50 mM) at pH 3.0. (Antonin *et al.*, 2015). The degradation of Evans blue obeyed a pseudo-first-order kinetic model. The graphitic carbon nitride (g-$C_3N_4$), can be used as a non-metallic photocatalyst. This as-prepared photocatalyst can effectively remove 99.3% of rhodamine B within 15 min, which was 16.8 times higher than that of bulk g-$C_3N_4$ under visible light irradiation (Guo *et al.*, 2023).

It was also suggested that the outstanding structural property and stronger oxidizability of holes ($h^+$ in valence-band) are responsible for its higher photocatalytic activity. The graphene was chemically bonded to $TiO_2$ film (G- $TiO_2$) (Kumar *et al.*, 2020). It was observed that activity of G- $TiO_2$ catalyst was increased for photochemical degradation of Evans blue under solar light irradiation. Solution of dye almost becomes colorless in 60 min of irradiation with sun light. It was also revealed that significant catalytic activity could be retained even after recycling it for five times. The g-$C_3N_4$/$TiO_2$ hybrid photocatalyst was synthesized through a modified sol–gel technique (Li *et al.*, 2016).

It was indicated that a heterojunction is formed between $TiO_2$ and g-$C_3N_4$. The $TiO_2$ nanoparticles are well dispersed on graphitic carbon nitride sheets. It was reported that g-$C_3N_4$/$TiO_2$-80% sample exhibited highest photocatalytic activity under visible light irradiation for degradation of methylene blue, which was around 3.5 times higher as compared to g-$C_3N_4$. It was also revealed that g-$C_3N_4$/$TiO_2$ hybrid photocatalysts exhibited good photocatalytic performance as only a little loss in activity was observed even after five cycles. The heterogeneous palladium nanoparticles decorated on functionalized graphitic carbon nitride (g–CN–$SiNH_2$Pd)was prepared as a catalyst (Antony., *et al* 2023).

It was observed that as-prepared g–CN–$SiNH_2$Pd nanocatalyst exhibited an excellent activity for degradation of dyes such as Evans blue (99.50%), methylene blue (99.63%), Congo red (99.54%) and Chrysoidine Y (99.97%) with $NaBH_4$ as the reducing agent. It was also indicated that nanocatalyst can be reused up to five cycles. ZnO-layered double hydroxide graphitic carbon nitride composite (ZnO-LDH$C_3N_4$) was synthesized via co-precipitation and solvothermal treatment (Zhang *et al.*, 2016).

It was reported that this composite can be used for photocatalytic degradation of orange II sodium salt and methylene blue. It was also revealed that ZnO-LDH$C_3N_4$ composite exhibited excellent performance in both; adsorption as well as photocatalytic degradation of these dyes as compared to ZnO-LDH and g-$C_3N_4$. Use of Water-dispersible g-$C_3N_4$ photocatalystHYPERLINK "https://www.sciencedirect.com/topics/materials-science/photocatalysts" was in photocatalytic degradation of methylene blue (Anh Nguyen *et al.*, 2021). It was observed that exfoliation of bulk g-$C_3N_4$ by chemical oxidation is responsible for its higher activity because of increased band gap, high surface area, thin-layered morphology, and reduced recombination of photogenerated electron-hole pairs.

**Experimental**

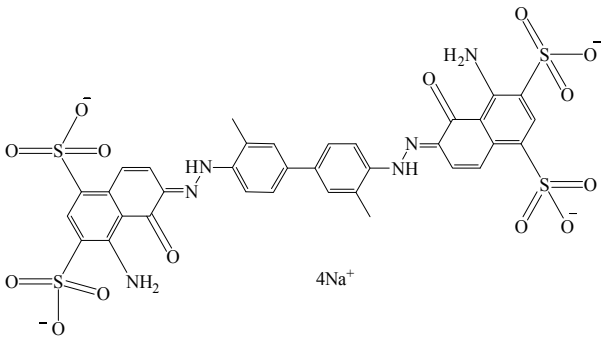


**Fig. 1.** Structure of Evan's blue

## Materials and Methods

Evan's blue is an azo dye. Solution of Evan's blue (0.096 g Evan's blue in 100.0 mL water; $1.0 \times 10^{4}$ M) was prepared in volumetric flask with distilled water and stored as a stock solution. The absorbance (A) of Evan's blue dye solution was determined with the help of a spectrophotometer at max = 608 nm. The dye solution was placed in equal amounts in four beakers.

- The first beaker containing dye solution was kept in dark,
- The second beaker containing dye solution was exposed to 200 W tungsten lamp,
- The third beaker containing dye solution with 0.10 g photocatalyst graphitic carbon nitride was kept in dark, and

- The fourth beaker contain dye solution and 0.10 g photocatalyst graphitic carbon nitride was exposed to 200 W tungsten lamp.

The absorbance of dye solution was measured with the help of a spectrophotometer. It was observed that the absorbance of first beaker remained almost same after 3-4 h while the second beaker had a decrease in initial value of its absorbance. The initial absorbance value of the third beaker showed a slight difference. The initial absorbance value of the fourth beaker experienced a significant reduction. This observation confirmed that the reaction between Evan's blue and photocatalyst is a photocatalytic reaction.

## Results and Discussion

The data of typical run are graphically presented in Table 1 and Fig. 2. The photodegradation of Evan's blue was monitored by taking absorbance of samples of dye solution containing 0.10 g photocatalyst (g-$C_3N_4$) and exposed to 200 W tungsten lamp (60.0 mW $cm^2$). The absorbance of Evan's blue was found to decrease with increasing time of exposure. A plot of 1 + log A versus time was found to be linear. The rate constant of reaction was calculated with the following expression k = 2.303 x slope.

[Evan's blue] = 1.00 × $10^3$ M, pH = 9.5, g-$C_3N_4$ = 0.10 g, Light Intensity = 60.0 mW $cm^2$

**Table 1.** A typical run

| Time (min) | Absorbance (A) | 1+ log A |
|---|---|---|
| 0 | 0.407 | 0.60 |
| 10 | 0.381 | 0.58 |
| 20 | 0.359 | 0.55 |
| 30 | 0.310 | 0.49 |
| 40 | 0.295 | 0.47 |
| 50 | 0.282 | 0.45 |
| 60 | 0.270 | 0.42 |
| 70 | 0.260 | 0.41 |
| 80 | 0.240 | 0.38 |
| 90 | 0.226 | 0.35 |
| 100 | 0.216 | 0.33 |

Rate constant (k) = 1.05 x $10^{-4}$ $sec^{-1}$

### Effect of pH

The effect of pH on photocatalytic degradation was observed in the range of 6.0 to 10.5. The results are given in Table 2 and Fig. 3.

[Evan's blue] = 1.00 × $10^4$ M, Light Intensity = 60.0 mW $cm^{-2}$, g-$C_3N_4$ = 0.10 g,

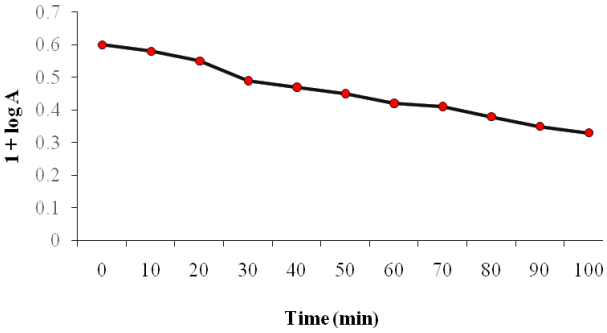


**Fig. 2.** A typical run

**Table 2.** Effect of pH

| pH | Rate constant (k x$10^4s^{-1}$) |
|---|---|
| 6.0 | 0.51 |
| 6.5 | 0.72 |
| 7.0 | 0.94 |
| 7.5 | 1.10 |
| 8.0 | 1.24 |
| 8.5 | 1.40 |
| 9.0 | 1.48 |
| 9.5 | 1.50 |
| 10.0 | 1.40 |
| 10.5 | 1.30 |

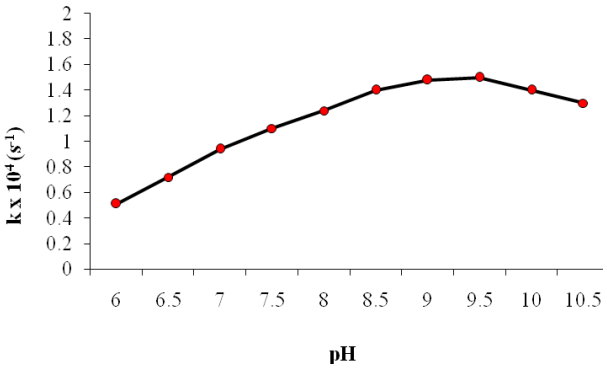


**Fig. 3.** Effect of pH

It was noticed that the degradation rate of Evan's blue increases with increasing pH of solution up till 9.5 but above this value of pH, the rate of reaction of photodegradation of Evan's blue started decreasing. It may be explained on the basis that at lower pH, the anionic dye will be available in it neutral form and it faces no attraction or repulsion for positively charged surface of photocatalyst. whereas at higher pH values, a negatively charged surface will be formed due to adsorption of OH ions and anionic

dye will be repelled. As a result, photodegradation of Evan's blue started decreasing.

### Effect of dye concentration

The effect of dye concentration on the rate of reaction was also observed using different concentrations of Evan's blue solution. The results are shown in Table 3 and Fig. 4.

pH = 9.5, Light Intensity = 60.0 mW $cm^{-2}$, g-$C_3N_4$ = 0.10 g

**Table 3.** Effect of dye concentration

| [Evans blue] x $10^4$M | Rate constant (k) x $10^4(s^{-1})$ |
|---|---|
| 0.2 | 0.8 |
| 0.4 | 1.0 |
| 0.6 | 1.10 |
| 0.8 | 1.25 |
| 1.0 | 1.50 |
| 1.2 | 1.27 |
| 1.4 | 1.10 |
| 1.6 | 0.85 |
| 1.8 | 0.74 |

It was observed that the rate of photocatalytic degradation increases with increase in the concentration of the dye up to 1.0 × $10^4$ M. It may be due to fact that as the dye was increased, more dye molecules were available for excitation and consecutive degradation. After the 1.0 $10^4$M the dye will start acting as an internal filter and it will not allow the desired light intensity to reach the surface of the semiconductor present at the bottom of the beaker. Due to this rate of photocatalytic degradation was found to decrease with further increase in the concentration of dye.

### Effect of amount of photocatalyst

The effect of amount of photocatalyst on the rate of photocatalytic degradation of Evan's blue was also observed. The results are shown in Table 4 and Fig. 5.

pH = 9.5, Light Intensity = 60.0 mW $cm^2$, [Evans blue] = 1.0 x$10^4$ M

**Table 4.** Effect of amount of photocatalyst

| g-$C_3N_4$(g) | Rate constant (k)x $10^4(s^{-1})$ |
|---|---|
| 0.02 | 1.36 |
| 0.04 | 1.40 |
| 0.06 | 1.45 |
| 0.08 | 1.49 |
| 0.10 | 1.50 |
| 0.12 | 1.48 |
| 0.14 | 1.38 |
| 0.16 | 1.32 |

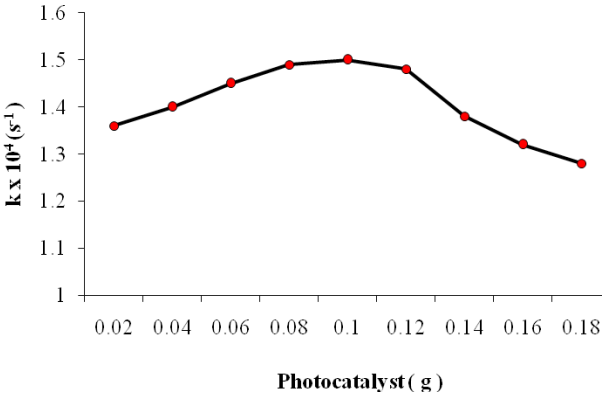


**Fig. 5.** Effect of amount of Photocatalyst

It was noticed that the rate of reaction increases with increase in the amount of photocatalyst up to 0.10 g, but above this value of photocatalyst, the rate of reaction decreased. This may be due to the fact that as the amount of photocatalyst was increased the exposed surface area of the photocatalyst will also increase but after this limiting value (0.10 g), any further increase in the amount of semiconductor will not increase the exposed surface area but only the thickness of the photocatalyst layer.

### Effect of light intensity

The effect of light intensity on the rate of Evan's blue was also observed. The results are reported in Table 5 and Fig. 6.

It was observed that the rate of degradation was increased on increasing light intensity, because any increase in the light intensity will increase the number of photons striking per unit time per unit area of

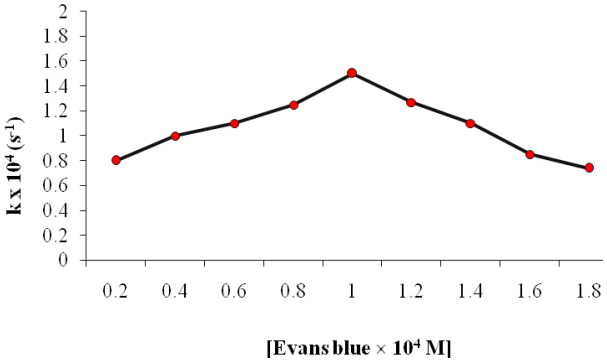


**Fig. 4.** Effect of dye concentration

the photocatalyst powder. Rate of degradation decrease on increasing the intensity above 60.0 mW $cm^2$ and therefore, higher intensities were avoided due to thermal effects.

pH = 9.5, [Evans blue] = 1.0 x$10^4$ M, g-$C_3N_4$ = 0.10 g,

**Table 5.** Effect of light intensity

| Light intensity (mW $cm^{-2}$) | Rate constant (k) x $10^4(s^{-1})$ |
|---|---|
| 30.0 | 0.82 |
| 40.0 | 0.99 |
| 50.0 | 1.05 |
| 60.0 | 1.50 |
| 70.0 | 1.23 |

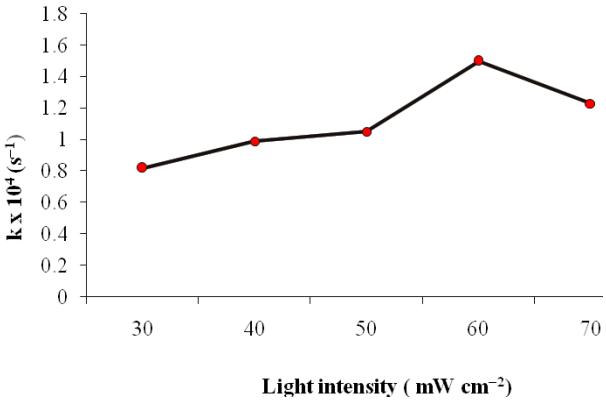


**Fig. 6.** Effect of light intensity

### Mechanism

On the basis of the experimental observations, a tentative mechanism has been proposed for the degradation of Evan's blue in the presence of graphitic carbon nitride.

$^1EB_0 \xrightarrow{hv1} EB_1$ (1)

$^1EB_1 \xrightarrow{ISC3} EB_1$ (2)

g-$C_3N_4 \xrightarrow{hv}$ g-$C_3N_4$ [$h^+$ (VB)+$e^-$ (CB)] (3)

$^-OH$ + g-$C_3N_4 \longrightarrow$ ($h^+$)·5B5; + g-$C_3N_4$ (4)

·OH + $\longrightarrow$ $^3EB_1$ Leuco EB (5)

Leuco $\longrightarrow$ EB Products (6)

When the solution of Evan's blue dye was exposed to light in presence of g-$C_3N_4$, the dye molecules are excited to their first excited singlet state. Then these excited molecules are transferred to the triplet state through intersystem crossing (ISC). On the other hand, the semiconductor g- $C_3N_4$ also absorb photons and as a result electron - hole pair is generated. The $^-$OH will react with hole of the photocatalyst to generate ·OH radicals and then these radicals will convert the dye molecules into its leuco form, which ultimately degrades into products. The participation of ·OH radicals as an active oxidizing species was confirmed by carrying out the reaction in presence of some hydroxyl radical scavengers like isopropyl alcohol, where the rate of degradation was drastically reduced.

## Conclusion

The viability of photocatalytic degradation of Evan's blue dye was tested using graphitic carbon nitride (g-$C_3N_4$) as a photocatalyst. It was indicated that degradation of Evan's blue was affected by pH, concentration of dye, amount of photocatalyst and light intensity. It was assumed that photocatalytic treatment increased the biodegradability of dye containing polluted water. In the present work, graphitic carbon nitride (g-$C_3N_4$) was successfully used as a photocatalyst for degradation of Evan's blue. It may be further explored for removal of other contaminated materials or industrial waste in future.

## Acknowledgements

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### Conflict of Intrest

There is no conflict of interests regarding the publication of this article.

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