PREPARATION OF C-TiO₂ NANOPHOTOCATALYST AND ITS USED FOR DEGRADATION OF EVANS BLUE

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ABSTRACT

The present work incorporates the study of efficiency of carbon doped TiO₂ for photocatalytic degradation of Evans blue dye. Effect of some factors such as catalyst dose, concentration of dye, intensity of light, pH etc., on degradation of the dye was examined. The reaction followed pseudo first order kinetics. Participation of ˙OH free radical was confirmed by scavenger studies. Optimum conditions were determined by variation of operational parameters. A tentative mechanism for photocatalytic degradation of Evans Blue has been proposed.

Key words: Carbon doped TiO₂, Photocatalytic degradation, Evans blue dye.

INTRODUCTION

Water pollution is increasing day by day, which attracted the attention of many resercheres on this subject. Out of various technique used for the removal of toxic substance, photocatalytic method has emerged as most effective and promising technique. Photcatalytic degradation of basic blue –24 and orange-G over ZnO powder in the presence of surfactant was been reported by Ameta et al.[1] Rao et al.[2] observed the photocatalytic degradation of crystal violet in aqueous suspension of zinc oxide. Papadam et al.[3] worked on photocatalytic converstion of acid orange 20 and Cr (VI) in aqueous TiO₂. Photocatalytic bleaching of dye pollutants under visible irradiation on Al (III) modified TiO₂ was reported by Zhao et al.[4] Cheng et al.[5] used visible light in degradation of dye pollutants over Fe (III) loaded resin in the presence of H₂O₂ at neutral pH values. Byrappa et al.[6] reported sunlight mediated photocatalytic degradation of rhodamine B dye. Arslan et al.[7] reported heterogeneous photocatalytic treatment of simulated dye house effluent using novel TiO₂ catalyst. Photocatalytic degradation of azo dyes in water using ZnO as photocatalyst was studied by Daneshwar et al.[8] De Silva and Faria[9] investigated about photochemical and photocatalytic degradation of an azo dye in aqueous solution by UV irradiation. Dunlop et al.[10] analysed the disinfection of drinking water. Chem et al.[11] reported visible light assisted photodegradation of dye pollutants catalyzed by porous K₃PW₁₂O₄₀. Mahmoodi et al.[12] made use of immobilized titanium dioxide nanoparticle for degradation and

reduction in toxicity of textile wastewater. Sleiman et al.[13] investigated photocatalytic degradation of an azo dye metanil yellow while photodegradation of squarylium cyanine dye under visible light irradiation was studied by Wu et al.[14]

EXPERIMENTAL

IUPAC Name: Tetrasodium (6E,6'E)-6,6-[(3,3'-dimethylbiphenyl-4,4'-diyl)di(1E)hydrazin-2-yl-1-ylidene]bis(4-amino-5-oxo-5,6-dihydronaphthalene-1,3-disulfonate)

Molecular formula: $C_{34}H_{24}N_6Na_4O_{14}S_4$

Molar mass: 960.809

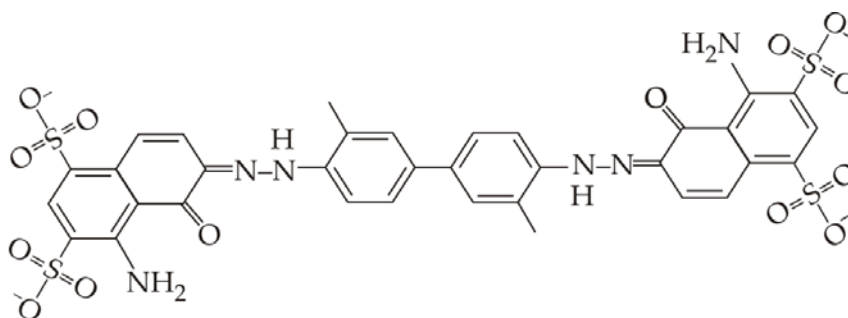Solubility: Water soluble

λ_{max}: 620 nm

Fig. 1: Structure of Evans blue

A stock solution of Evans blue (1.0×10^{-3} M) was prepared by taking 0.9601 g of Evans blue in 100.0 mL of doubly distilled water so that the concentration of dye solution was 1.0×10^{-3} M. The stock solution was further diluted as and when required. The absorbance of the solution was measured with the help of spectrophotometer at $\lambda_{max} = 620$ nm. The 50 mL dye solution was placed in four beakers.

- The first beaker was kept in dark.

- The second beaker was kept in light.

- The third beaker was kept in dark, which contains 0.10 g C-TiO$_2$.

- The fourth beaker was exposed to light, which contains 0.10 g C-TiO$_2$.

The absorbance of the four solution was measured with the help of a spectrophotometer. It was observed that the absorbance of solutions of first three beakers remained almost same, while the solution of fourth beaker show a decrease in absorbance.

The solution of Evans blue with 1.0×10^{-5} M concentration was prepared in doubly distilled water and 0.10 g of carbon doped TiO$_2$ was added to it. The pH of reaction mixture was kept at 8.5 and the solution was exposed to a 200 W tungsten lamp. A decrease in absorbance of dye solution was observed with increasing time of exposure.

The typical run for the photocatalytic degradation of Evans blue in the presence of C-TiO$_2$ semiconductor has been graphically represented in Fig. 1.

The absorbance of Evans blue solution decreases with an increase in the time of exposure indicating the decomposition of Evans blue. The plot of 1 + log A against time was linear, following pseudo-first order kinetics. The rate constant was measured with the expression $k = 2.303 \times slope$ as $k = 5.60 \times 10^{-5} \ sec^{-1}$
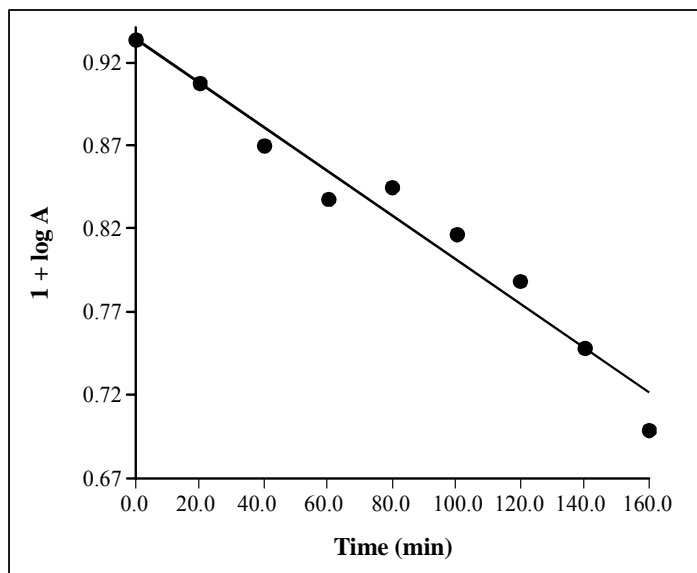

Fig. 1: A typical run

Effect of pH

The effect of pH on the rate of degradation of Evans blue solution was investigated in the pH range 5.0 – 10.0. The results are reported in Table 2.

Table 2: Effect of pH

[Evans blue] = 1.0×10^{-5} M   C-TiO₂ = 0.10 g

Light intensity = 50.0 mWcm⁻²

pH	Rate constant (k) $\times 10^4$ (sec⁻¹)
5.0	2.59
5.5	2.89
6.0	3.00
6.5	3.42
7.0	4.05
7.5	4.70
8.0	4.98
8.5	**5.60**
9.0	3.82
9.5	3.61
10.0	2.95

It is evident from the data that the degradation rate of Evans blue increases with increasing pH of solution upto 8.5 and above pH 8.5, the rate of degradation of Evans blue starts decreasing. This is due to the

fact that at low pH, the anionic dye was attracted by positively charged surface of photocatalyst, but further increase in pH above 8.5, a decrease in the rate of photocatalytic degradation of the dye may be due to the fact that Evans blue feels a force of repulsion between anionic dye and negatively charged surface of the semiconductor due to absorption of $^-$OH ions, and as a result, the rate is retarded.

Effect of evans blue concentration

The effect of Evans blue concentration on its rate of degradation was studied in the range from 0.6×10^{-5} M to 1.2×10^{-5} M keeping all other factors identical. The results are tabulated in Table 3.

Table 3: Effect of evans blue concentration

pH = 8.5   Light intensity = 50.0 mWcm^{-2}
C-TiO$_2$ = 0.10 g

[Evans blue] $\times 10^5$ M	Rate constant (k) $\times 10^5$ (sec^{-1})
0.60	1.13
0.70	2.02
0.80	3.18
0.90	4.26
1.00	**5.60**
1.10	2.80
1.20	1.33

The rate of photocatalytic degradation of dye increases with the increase in concentration of the dye upto 1.0×10^{-5} M. It may be due to fact that as the dye concentration was increased, more dye molecules were available for excitation, resulting in higher rate of degradation. The rate of photocatalytic degradation was found to decrease with further increase in the concentration of dye. This may be attributed to the fact that the dye does not permit the desired light intensity to reach the photocatalyst surface; thus, a decrease in the rate of photocatalytic degradation was observed.

Effect of amount of semiconductor

The amount of semiconductor may also affect the rate of degradation of dye. It was observed that the rate of photocatalytic degradation of Evans blue increases on increasing the amount of semiconductor. The results are tabulated in Table 4.

Table 4: Effect of amount of semiconductor

[Evans blue] = 1.00×10^{-5} M   Light intensity = 50.0 mWcm^{-2}
pH = 8.5

C–TiO$_2$ (g)	Rate constant (k) $\times 10^5$ (sec^{-1})
0.02	1.60
0.04	2.28
0.06	3.35
0.08	4.16

C–TiO$_2$ (g)	Rate constant (k) $\times 10^5$ (sec^{-1})
0.10	**5.60**
0.12	3.70
0.14	2.53
0.16	2.04
0.18	1.06

The rate of reaction increases with increase in amount of semiconductor upto 0.10 g and beyond which, the rate of reaction decreases. This may be due to the fact that with increase in the amount of semiconductor, the exposed surface area of the semiconductor also increases. After this limiting value (0.10 g), any increase in the amount of semiconductor will not increase the rate of degradation because the exposed surface area becomes virtually constant.

Effect of light intensity

The effect of light intensity on the photocatalytic bleaching of Evans blue has been investigated keeping all other factors identical. The results are reported in Table 5.

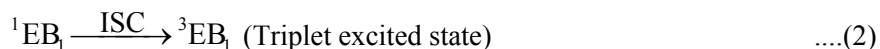**Table 5: Effect of light intensity**

[Evans blue] $= 1.00 \times 10^{-5}$ M   C–TiO$_2$ $= 0.10$ g
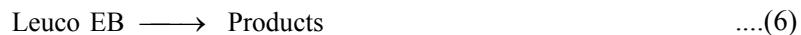
pH $= 8.5$

Light intensity (mWcm^{-2})	Rate Constant (k) $\times 10^5$ (sec^{-1})
20.0	1.97
30.0	2.48
40.0	3.74
50.0	**5.60**
60.0	4.16
70.0	3.18

The rate of photocatalytic degradation of dye increases as the intensity of light was increased, because with increase in the light intensity there is an increase in the number of photons striking per unit area of semiconductor powder per unit time. However, on increasing the intensity above 50.0 mWcm^{-2}, there was a decrease in the rate due to some thermal reactions.

Mechanism

On the basis of these observations, a tentative mechanism for photocatalytic degradation of Evans blue may be proposed as –

$$^1\text{EB}_0 \xrightarrow{\ h\nu\ } {}^1\text{EB}_1 \ \text{(Single excited state)} \quad\quad\quad ....(1)$$

$$^1\text{EB}_1 \xrightarrow{\ \text{ISC}\ } {}^3\text{EB}_1 \ \text{(Triplet excited state)} \quad\quad\quad ....(2)$$

$$\text{SC} \xrightarrow{\ h\nu\ } e^-(\text{CB}) + h^+(\text{VB}) \ \text{or SC*} \quad\quad\quad ....(3)$$

$$h^+ + OH^- \longrightarrow \ ^\bullet OH \qquad\qquad ....(4)$$

$$^\bullet OH + \ ^3EB_1 \longrightarrow Leuco\ EB \qquad\qquad ....(5)$$

$$Leuco\ EB \longrightarrow Products \qquad\qquad ....(6)$$

Evans Blue (EB) absorbs radiations of suitable wavelength and gives rise to its excited singlet state. Then it undergoes intersystem crossing (ISC) to give the triplet state of the dye. On the other hand, the semiconducting carbon doped TiO_2 (SC) also utilizes the radiant energy to excite its electron from valence band to the conduction band; thus, leaving behind a hole. This hole abstracts an electron from OH^- ions to generate $^\bullet OH$ radicals. These radicals will oxidize the dye to its leuco form, which may ultimately degrade to products. The participation of $^\bullet OH$ radicals as an active oxidizing species was confirmed by using hydroxyl radical scavenger isopropanol, where the rate of degradation was drastically reduced.

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