Photodegradation of aqueous eosin yellow dye by carbon-doped TiO$_2$ photocatalyst

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Abstract. In this study, a novel photocatalyst, carbon-doped TiO$_2$ was prepared via a sol-gel technique with titanium (III) chloride as a precursor. The characterization of C-doped TiO$_2$ was obtained by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), and BET surface area analyses. The prepared catalyst's photocatalytic activity was investigated using UV irradiation for the photo-oxidation of eosin yellow (EY) dye. The photocatalysis of EY dye was performed under various experimental parameters such as solution pH and oxidant dosage (H$_2$O$_2$). The prepared photocatalyst dosages were also taken separately to optimize process efficiency. About 77.43% of EY decolorization was obtained at an optimum pH of 3, and the performance was also observed by varying the oxidant concentration ranging from 5-10 mM. The % decolorization was higher for C-doped TiO$_2$-200 photocatalyst (81.88%) compared to carbon-doped TiO$_2$-400 photocatalyst (75.55%). It can be concluded that the carbon-doped TiO$_2$, calcined at 200°C, can effectively decolorize EY dye in an aqueous medium.

Keywords: Photocatalyst, carbon-doped TiO$_2$, dye degradation, eosin yellow dye, textile industry wastewater treatment.

1. Introduction
The removal of toxic compounds from water bodies is a major ecological concern in controlling water pollution. Water pollution by industrial effluents containing dyes and phenolic compounds is a grim issue for human beings and aquatic life [1]. Even small traces of colors are noticeable and detrimental because of their higher amount of toxicity and carcinogenicity. Thus, the remediation of dyes from the...
industrial effluents is of utmost importance. About 100,000 commercial dyes are accessible, with 70,000 tons of annual production, and 15% of total dye production is used in the dyeing process [2]. Dye containing wastewater is not easy to treat since the refractory dye compounds are highly resistant to the bio-degradation and show stability to the heat energy, light, and various oxidizing species [3]. It has been observed that neither the secondary wastewater treatment such as biological processes nor chemical treatment gives a significant amount of percentage decolorization and the reduction in the chemical oxygen demand (COD) [4]. The advanced oxidation processes (AOPs) are supposed to be promising technologies, treat the recalcitrant compounds found in industrial wastewater. AOPs are completely based on hydroxyl (●OH) radical species’ production during treatment [5]. In conjunction with some new dye effluent treatment processes, the various advanced oxidation technologies have been widely studied elsewhere [5]–[9]. Semiconductor materials such as titanium dioxide (TiO$_2$) and ZnO are generally used in the photocatalytic processes to remove organic and inorganic pollutants [10]. The photocatalyst, TiO$_2$ with the large bandgap 3.2 eV, can only be activated in the presence of UV light, which is a major limitation. Therefore, doping has been modified, enabling to work under visible light range [11], [12]. The doping of TiO$_2$ notably improves the visible-light response of titanium dioxide. The doping of TiO$_2$ with p-block elements such as nitrogen, carbon, sulphur, boron, and fluorine is a famous method for preparing visible-light catalysts [13]. The doped photocatalysts have different band gap electronic structure than undoped photocatalysts. The non-metallic elements like carbon (C) and nitrogen (N) may occupy the cationic and anionic sites in the lattice of titanium dioxide. The dopants like carbon (C) and nitrogen (N) can reduce the band-gap during the addition and combination of electrons (e$^-$) in higher energy levels than valence band or the addition of energy-orbitals below the energy of the conduction band [14]. The carbon doping has gained intense research interest since carbon can be immobilized in the lattice in diverse ways: as an anion by replacing the oxygen atom; as a cation by inhabiting interstitial sites or even substituting titanium atoms [15]. The doping of photocatalyst is carried out for the effective use of the UV-irradiation, either in the form of any mercury lamps or solar energy) [16]. In the present study, C-doped catalyst was prepared via a sol-gel technique by using titanium (III) chloride as precursor. Further, the synthesized photocatalysts was characterized for the SEM/EDX and BET surface area analysis. Prepared catalyst was also calcined at different temperatures (200°C and 400°C) to enhance its effectiveness for the final application. The photocatalytic activity of modified photocatalysts were reported with the decolorization of eosin yellow dye using low pressure mercury vapour lamp of 125 W intensity. Photocatalysis of EY dye was carried out under various operating conditions such as pH and oxidant dosage (H$_2$O$_2$). The photocatalyst dosages for the photocatalysis of EY dye were taken individually to optimize the process efficiency. Table 1 shows the physico-chemical properties of eosin yellow dye.

**Table 1. Characteristics of eosin yellow dye**

| Properties                  | Structural view of eosin yellow dye |
|-----------------------------|------------------------------------|
| Molecular Weight (g/mol)- 647.89 | ![Structural view of eosin yellow dye](image) |
| Formulae- C$_{20}$H$_6$Br$_2$Na$_2$O$_5$ |                                    |
| Maximum wavelength- 517 nm |                                    |
| Colour index No. (C. I.)- 45380 |                                    |
2. Materials and methods

2.1 Materials
Titanium (III) chloride solution, TiCl₃ (assay ≥ 12%) was purchased from Sigma-Aldrich. Starch powder (99.9%), Eosin Yellow dye (Eosin Y, > 99% purity), ammonia solution was procured from Merck chemicals, India. Merck again supplied analytical grade sulphuric acid (H₂SO₄, > 99%), sodium hydroxide (NaOH) pellets, ferrous (II) sulphate and 30% (w/v) H₂O₂. All the chemicals in the preparation of catalyst and experimental runs were used without any cleansing.

2.2 Methods

2.2.1 Catalyst synthesis. The modified carbon-doped TiO₂ catalyst was synthesized using a sol-gel technique. The starch powder was used as a carbon resource in the reaction. 5 ml, 12% titanium (III) chloride solution was added in a beaker having 0.5 L of starch solution (1%) with continuous stirring by magnetic stirrer at 720 rpm. In this aqueous medium, the surplus amount of ammonia (51.7 ml, 0.88 gm/cm³) was added in a dropwise manner with continuous stirring. After 20-25 min of this treatment, titania precipitate of white color was obtained. The titania precipitate was further washed 3 to 4 times with the de-ionized water so that an excessive amount of ammonia was washed off from the titania solution and dried at room temperature. This was a prepared C-doped TiO₂ catalyst [17]. Further, the prepared photocatalyst samples were divided into two parts and calcined for 6 hr at 200 oC (C-TiO₂-200) and 400oC (C-TiO₂-400), individually.

2.2.2 Characterization of the prepared photocatalysts. The study of the modified catalyst's physicochemical properties is challenging, and many analytical techniques were used to characterize the prepared materials. The prepared C-doped photocatalysts were characterized by SEM utilizing the model of ZEISS EVO 18 series to study catalyst morphology. The EDX analysis performed a detailed analysis of elements in the photocatalyst. The prepared photocatalysts (C-doped TiO₂-200 and C-doped TiO₂-400) were also characterized for their surface area/ pore volume and their average diameters using the BET surface area analyzer (Smart instruments, India and single point).

2.2.3 Experimental. Experiments were carried out in a cylindrical shaped photochemical reactor with an effective reactor volume of 300 ml under batch flow condition. The reactor set up consists of inside reflecting surface and UV irradiation source (125 W, low-pressure mercury-vapor lamp) surrounding glass/quartz cylinder, which was placed centrally in the reactor. The feed tank of the photochemical reactor was made up of glass material. 250 mL of 100 mg/L solution of EY dye was prepared and fed to the reactor. The reactor set up was switched on along with its stirrer. The solution was continuously stirred for 10 min at 300-400 rpm.

Further, 1000 mg/L of titanium dioxide (TiO₂) was added, and an appropriate amount of hydrogen peroxide (H₂O₂) was added to start TiO₂ photocatalysis for the oxidation of dye wastewater. The reaction begins immediately after the addition of H₂O₂ in the solution. After every 5 min of a time interval, the samples were taken out from the reactor and tested under a UV-vis spectrophotometer (UV 1800, Shimadzu) for absorbance using a quartz cell of path length 1 cm. The calibration curve equation of an aqueous eosin yellow dye was \( Y_{EY} = 0.117X_{EY} - 0.011 \), \( R² = 0.998 \); where, \( Y_{EY} \) is the absorbance value obtained at maximum wavelength of 517 nm and \( X_{EY} \) is the dye concentration (eosin yellow) in mg/L. The EY dye, percentage decolorization was calculated by Eq. 01.

\[
\text{Percentage decolorization of EY (%) } = \left( \frac{C₀ - Cₜ}{C₀} \right) \times 100
\]  

(1)

Where, \( C₀ \); initial concentration of eosin yellow dye and \( Cₜ \) being the dye concentrations at time \( t \).
3. Results and discussion

The prepared photocatalysts from titanium (III) chloride were initially characterized by different analytical techniques for its suitability in the final application. Further, the trends in the decolorization efficiency of eosin yellow dye using photocatalysis has been reported by varying different experimental parameters on percentage decolorization.

3.1. Characterization of photocatalysts

3.1.1 Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis of photocatalysts. The carbon-doped photocatalysts have been tested under SEM for its morphological study and for the EDX technique to identify the major components in the photocatalysts. Figure 1 displays the SEM images of the prepared photocatalysts and results in the presence of the agglomeration of carbon particles on the titania surface [17]. The particle size cannot be easily resolved with the SEM analysis. The EDX analysis confirmed that the surface of C-doped photocatalysts is fully packed with the carbon element. In contrast, the nanoparticles’ surface becomes apparent with the increment in the calcination temperature from 200°C to 400°C. The exterior of the catalysts was enclosed by the carbon, strongly supported by EDX analysis. The presence of carbon elements on the surface of titania nanoparticles is depicted in Figure 2. The data of EDX analysis reports the presence of 90.16% of elemental carbon, covering the complete surface of the carbon-doped catalyst. Further on calcination at temperatures 200°C and 400°C, there was a severe decrease in surface carbon quantity from around 80.79% to 34.00%.

![Figure 1 SEM images of C-doped photocatalyst.](image-url)
Figure 2 shows that the prepared sample of photocatalyst majorly contains carbon (C), titanium (Ti), and oxygen (O) elements, in addition to a few traces of calcium (Ca), silicon (Si), and phosphorous (P) elements.

![Figure 2 EDX spectrum of C-doped photocatalyst.](image)

### 3.1.2 Analysis of photocatalysts with BET surface area analyzer.
BET, a single-point surface area analyzer, characterized the prepared photocatalysts (C-doped TiO<sub>2</sub>-200 and C-doped TiO<sub>2</sub>-400). Table 2 shows the data for their surface area values, pore-volume, and the modified photocatalysts' average diameters. This analysis's obtained results indicate that the prepared samples' porosity decreases because of the heat treatment from 200°C to 400°C, which ultimately shows the decrease in value of surface area (m<sup>2</sup>/gm) [17].

### Table 2. Data for the values of surface area, pore-volume, and average diameters of C-doped photocatalysts.

| Name of photocatalysts | Surface area (m<sup>2</sup>/gm) | Pore volume (cc/gm) | Average pore diameter (Å) |
|------------------------|-------------------------------|---------------------|------------------------|
| C-doped TiO<sub>2</sub> at 200°C | 48.061 | 0.0298 | 24.8018 |
| C-doped TiO<sub>2</sub> at 400°C | 10.453 | 0.0109 | 41.7105 |

### 3.2. Assessment of photocatalytic activity
The photocatalytic activity of carbon-doped catalysts was assessed for the decolorization studies of eosin yellow dye using a tubular type photochemical reactor.

#### 3.2.1 Effect of initial dye concentration on its percentage decolorization in photolysis.
The photolysis using UV-irradiation is a better way for the generation of free radicals via cleavage of a sigma bond. The produced radicals exist as precursors, which can generate more free radicals [18], [19]. Certain steps are involved in the photochemical reaction of the dye molecules. The dye molecule gets excited with the absorption of one photon. Again, the excited molecules take part in the chemical reaction and result in the dye molecule oxidation in the effluent. In this study, the initial dye concentration was considered in the range of 50-200 mg/L to get the trend of % decolorization for EY dye. Figure 3 reports the percentage decolorization of EY dye at its varying initial concentrations. EY dye was efficiently decolorized to 43.32% for 100 mg/L of its initial concentration in just 60 min of treatment time. At higher concentrations ranging from 150-200 mg/L, the percentage decolorization was decreased to 29.11 and 26.92%, respectively. The percentage decolorization for eosin yellow dye was reduced at higher concentrations (150-200 mg/L) because of the required quantity of free radicals' unavailability in the aqueous medium. The % decolorization of EY dye was found to be maximum at
100 mg/L. So, further consecutive experiments were performed with 100 mg/L for the decolorization of dye with TiO₂ photocatalysis.

Figure. 3 Photolysis of EY dye at its varying initial concentrations (Reaction conditions: 250 mL of 100 mg/L solution of EY dye, 125 W of UV source, and treatment time of 60 min).

3.2.2 Influence of pH in TiO₂ photocatalysis. The influence of pH value on the decolorization of EY dye was studied by varying it from 3 to 9. Figure 4 shows that the percentage decolorization of EY dye reduces severely when the solution pH increases from a value of 3 to 7 and further to 9 (acidic to neutral and then to alkaline). The actual amount of solution pH can change the distribution of various protonation stages of the dye molecule in an aqueous medium. The pH value strongly influences the dye adsorption onto the TiO₂ surface [20], [21]. Stronger adsorption of the dye molecules to be oxidized is generally considered as a requisite for effective decolorization of dye molecule in photocatalysis. In this study, the percentage decolorization for EY dye started to decrease continuously, when the solution pH was changed to a value of 7 and 9 from 3, with the decolorization efficiencies of 77.43%, 43.32%, and 33.87%, respectively. The solution pH might also affect the nature of the photogenerated species like hydroxyl radicals and trapped holes.

Figure. 4 Influence of solution pH on percentage decolorization of EY dye in TiO₂ photocatalysis (Reaction conditions: 250 mL of 100 mg/L solution of EY dye, UV source of 125 W intensity, TiO₂-1000 mg/L and oxidant, H₂O₂- 5 mM).
3.2.3 Effect of oxidant (H$_2$O$_2$) in TiO$_2$ photocatalysis. The doses of hydrogen peroxide in TiO$_2$ photocatalysis were varied from 5 mM to 15 mM. 77.43% of dye decolorization was noticed for 5 mM H$_2$O$_2$ dose in photocatalysis by keeping rest of the experimental conditions same. It is a proof for the generation of *OH radicals in the reaction mixture. Further increment in concentration of H$_2$O$_2$ (10 to 15 mM), the percentage decolorization of EY dye gets reduced to 55.36% and 51.79%, respectively. It might have occurred because of the scavenging action of the excessive amount of H$_2$O$_2$ or recombination of the hydroxyl radicals generated in the solution [22]. Figure 5 indicates the effect of oxidant dose on the percentage decolorization of EY dye in TiO$_2$ photocatalysis. The use of a higher amount of H$_2$O$_2$ can reduce the decolorization efficiency usually via i) auto-decomposition of hydrogen peroxide to water and O$_2$ and ii) scavenging action of hydroxyl radicals with H$_2$O$_2$, which generates per-hydroxyl (HO$_2^*$) radicals. These per hydroxyl radicals show less reactivity than hydroxyl radicals, resulting in a decrement of percentage decolorization of EY dye in solution. It means that the excessive amount of H$_2$O$_2$ would trap the hydroxyl (*OH) radicals to produce the weaker oxidant such as per hydroxyl radicals as per reactions (02) and (03) [23].

$$\text{H}_2\text{O}_2 + \text{HO}^* \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \quad (2)$$

$$\text{HO}_2^* + \text{HO}^* \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (3)$$

Figure 5 Effect of H$_2$O$_2$ dosage on the percentage decolorization of EY dye in TiO$_2$ photocatalysis (Reaction conditions: 250 mL of 100 mg/L solution of EY dye, UV lamp of intensity 125 W, TiO$_2$-1000 mg/L and pH 3).

3.2.4 Effect of C-doped photocatalysts on % decolorization of EY dye. Figure 6 shows a comparative photocatalytic behavior of both the photocatalysts, including C-doped TiO$_2$-200 and C-doped TiO$_2$-400. It can be seen that the Eosin Yellow dye was photo-oxidized to 43.32% without adding a single amount of photocatalyst after 60 min of irradiation time (125 W low-pressure mercury lamp). The use of pure anatase TiO$_2$ gave 77.43% of decolorization for EY dye in TiO$_2$ photocatalysis. The carbon-doped TiO$_2$-200 sample shows higher photocatalytic action than the undoped TiO$_2$. Around 81.88% of decolorization efficiency was obtained in the case of C-doped TiO$_2$-200 photocatalyst. This can be ascribed to the accessibility of more surface area for photocatalysis in the case of C-doped TiO$_2$-200 photocatalysis [17].
4. Conclusions

The carbon-doped TiO$_2$ photocatalyst was successfully prepared at the lab scale by using an environmentally friendly method followed by the calcination at 200$^\circ$C and 400$^\circ$C, respectively. The authors used cost-effective and biodegradable material, i.e. starch as a carbon source. The results of the physicochemical analyses, including SEM/EDX and BET surface area of the photocatalysts, confirm the presence of carbon in the crystal lattice of titanium dioxide and higher surface for the oxidation reaction to occur. The carbon-doped TiO$_2$-200 results in a higher percentage of decolorization (81.88%) for aqueous EY dye in just 60 min of treatment time, compared to the effects of undoped TiO$_2$ photocatalysis. It can be concluded that the visible-light photocatalytic behavior of catalysts has been enhanced with the immobilization of carbon into the lattice of titanium dioxide. This method would provide a good option for the invention of nano-materials with a higher amount of visible light activity and its practical applications to treat industrial effluent.

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