

Photocatalytic Degradation of Commercial Textile Azo Dye Reactive Blue 160 by Heterogeneous Photocatalysis

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ABSTRACT

The photocatalytic bleaching of textile azo dye Reactive Blue 160 has been carried out in the presence of semiconductor photocatalyst $CeFeO_3$ and the progress of reaction was observed spectrophotometrically. The effect of various operating parameters like pH, concentration of the dye, amount of photocatalyst on the efficiency of the reaction has been studied. Kinetic analysis of photodegradation reveals that the degradation follows pseudo first order kinetics according to the Langmuir- Hinshelwood model. The optimum conditions for the degradation of Reactive Blue 160 dye have been found as dye concentration $3 \times 10^{-5} M$, pH= 8 and amount of catalyst 0.06 g/100 ml.

Key words: Textile azo dye, Semiconductor, Photocatalyst

INTRODUCTION

Due to shortage and pollution of water resources, it is vital to prevent contamination of these valuable resources. Different contaminations are released into water bodies with the rapid industrialization. Dye effluent from textile industry is one of the most important sources of environmental pollution. Approximately 10,000 different dyes and pigments are utilized by textile industry with annual production of almost 7×10^5 tons [1]. It is estimated that fifteen percent of the total dye production is lost during textile manufacturing process and it is released in textile effluents [2]. Azo dyes are most versatile class of textile dyes because of their simple synthesis and greatest variety of colour. Azo dyes are characterized by one or more azo group (-N=N-) as chromophore and makes up to 60-70% of all synthetic dyestuff produced [3]. Textile wastewater contains a considerable amount of unfixed azo dyes. Dyes are able to colour water even in very small concentration as 1ppm. Textile waste water contains much higher amount of dye which is about 200 ppm [4]. These dyes absorb the sunlight and reduce the photosynthetic capability of aquatic plants and microorganism. Many of these are dyes are carcinogenic, mutagenic and genotoxic [5]. Azo dyes are largely non-biodegradable under aerobic conditions and persist into environment for very long time [6, 7]. In anaerobic condition, azo dyes can be degraded but in these conditions potentially hazardous and carcinogenic amines are produced [8, 9].

Treatment of waste water by physical and chemical methods has been applied in many studies [10, 11]. These methods have some drawback of high operational cost and complicated operational methods [12]. Simultaneously these methods are unable to completely remove the recalcitrant dye molecules and significant amount of sludge is formed which cause secondary pollution [13, 14].

In recent years Advance Oxidation Processes (AOPs) have been effectively used to completely mineralize recalcitrant dyes present in textile waste water [15, 16]. These processes imply generation of hydroxyl radical which is the most powerful oxidizing agent after fluorine [17]. Among AOPs heterogeneous photocatalysis have proven to yields very good results either for complete mineralization of dyes or their transformation into less complex and easily biodegradable structure [18].

The main objective of the present work is to study the degradation kinetics of azo dye Reactive Blue 160 (RB160) by heterogeneous photocatalysis using semiconductor CeFeO₃. Cerium iron oxide in mixed oxide state can be a potent material to remove contamination from textile waste water. Coupling of semiconductors can significantly improve the photocatalytic activity and charge separation properties [19]. This mixed oxide possesses the combination of properties that neither individual possesses. The suitable band gap of mixed oxide allows absorption in visible region which covers the most of the part of solar light. The mixed oxide of Cerium and iron would be an effective photocatalyst. Thus this mixed oxide is selected for degradation of RB 160. Ternary oxides have been used as effective photocatalyst for carrying out a number of chemical reactions [20, 21]. CeFeO₃ has been used for degradation of Brilliant Blue G [22], gentian violet [23] and few other dyes. CeFeO₃ has been prepared by coprecipitation [24] and microwave process [25]. The effect of operational parameters such as pH, photocatalyst amount and dye concentration was examined in present study.

MATERIALS AND METHODS

Materials

For the present photocatalytic degradation studies Reactive blue 160 (Fig: 1) was used. Reactive Blue 160 (RB160) is diazo dye containing sulphonate groups. The commercially available azo dye was procured from Sulzer processors private limited Bhilwara (Raj). All reagents of analytic grade were used as received without further purification. The CeFeO₃ nanoparticles were synthesized by co-precipitation followed by calcinations. The synthesized particles were characterized by power X-Ray Diffraction and used as photocatalyst for degradation of RB 160. The chemicals Ce(NO₃)₃.6H₂O, Fe(NO₃)₃.9H₂O, sodium hydroxide, hydrochloric acid were obtained from Merck. All laboratory reagents were of analytical grade.

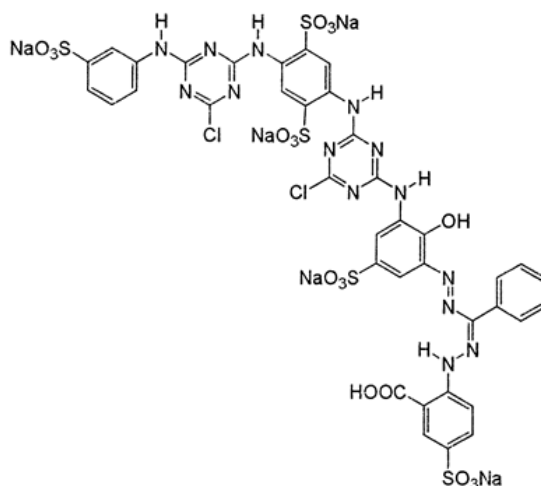


Fig - 1: Structure of Reactive Blue 160

Molecular formula C₃₈H₂₃Cl₂N₁₄Na₅O₁₈S₅, Molecular weight 1309.86

Methods

Preparation of photocatalyst: The cerium iron oxide particles were synthesized by precipitation of metal nitrates of cerium and iron. The Ce(NO₃)₃.6H₂O and Fe(NO₃)₃.9H₂O were respectively dissolved in distilled water at room temperature to produce 0.1 M aqueous solution. The ternary oxide CeFeO₃ was prepared by adding 1M NaOH drop wise to the solution of Ce(NO₃)₃.6H₂O and Fe(NO₃)₃.9H₂O with continuous stirring. The pH of solution was monitored and complete precipitation was obtained at pH 9. The precipitate was filtered and washed. This precipitate was kept in oven at 120°C for drying. After drying it was grounded in mortar and pestle. Subsequently, calcinations were performed. The powder was calcined at 600°C for 5 hours.

Characterization: - Power X-Ray diffraction was performed with Rigaku Micromax-007 HF instrument using Cu K α ($\lambda=1.54\text{\AA}$) radiation. The stoichiometry of The CeFeO₃ has been established with the help of published diffraction data file JCPDS. All peaks can be indexed to the typical perovskite structure. (JCPDS card 22-0166).

Experimental Procedure: - The degradation of RB 160 was studied in presence of photocatalyst CeFeO₃ at different pH level, catalyst loading and dye concentration. 1×10^{-3} M dye solution was prepared by dissolving 1.309 g of dye in 1000 ml of distilled water. The initial absorbance of dye solution was observed with the help of UV-VIS spectrophotometer (Shimadzu, UV- 1700, Pharmaspec). The maximum absorbance value 0.652 was recorded at 560 nm (λ_{max}). The reaction mixture was prepared by taking 3 ml of dye solution (1×10^{-3} M), 0.06 g of Cerium iron oxide in a round bottom flask. The total volume of the reaction mixture was made 100 ml by adding double distilled

water. The concentration of dye in the reaction mixture was $3 \times 10^{-5} \text{M}$. To carry out the photobleaching, the reaction mixture was irradiated under light source ($2 \times 200 \text{ W}$ Tungsten lamps). Water filters were used to cut off thermal radiation. The pH of the solution was measured by pH meter (Systronics, 106). The progress of the reaction was observed at definite time intervals by measuring absorbance using spectrophotometer at 560 nm (λ_{max}). The rate of decrease of color with time was continuously monitored. After complete mineralization, the presence of NO_2^- , NO_3^- , SO_4^{2-} ions and evolution of CO_2 were tested by standard procedure.

RESULTS AND DISCUSSION

The synthesized CeFeO_3 was analyzed for its composition and crystal structure by powder XRD. The XRD pattern of CeFeO_3 is shown in figure 2. The graph has been plotted between intensity and 2θ value (in degrees). All peaks can be indexed to typical perovskite structure (JCPDS Card 22-0166). Any peak of impurity was not observed. The sharp and narrow peaks indicate high crystallization of prepared CeFeO_3 .

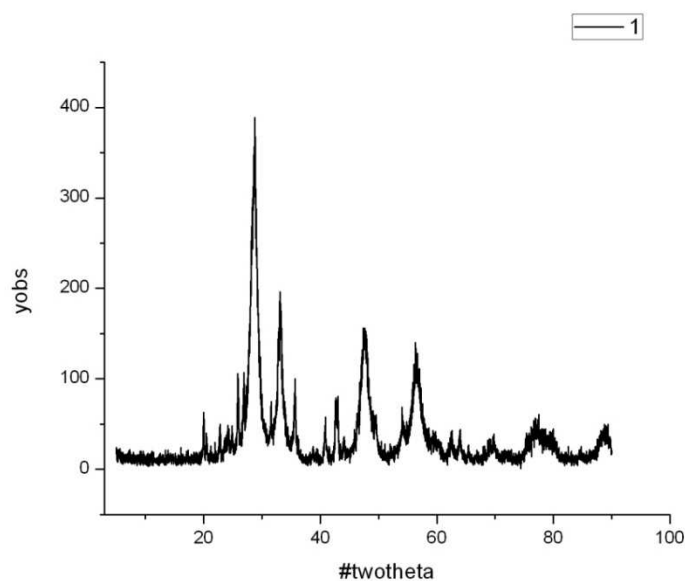


Fig 2 Power XRD of synthesized CeFeO_3

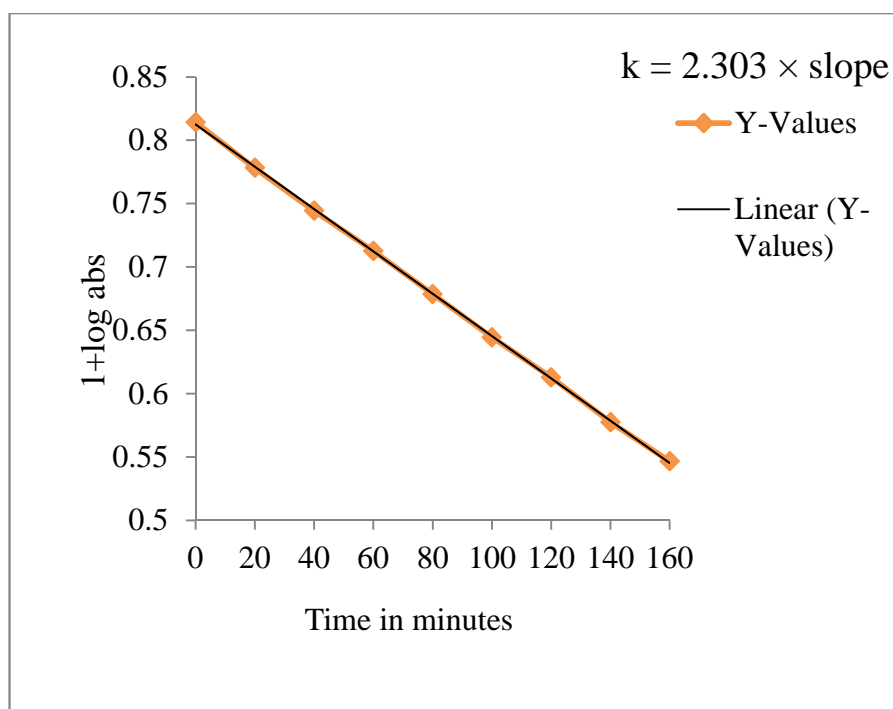


Fig-3: A plot showing a typical run of photobleaching of Reactive Blue 160 by Photocatalyst CeFeO_3 under the optimized conditions

The photocatalytic degradation of RB 160 was observed at 560 nm. The optimum conditions for the photobleaching of dye were $[\text{Dye}] = 3 \times 10^{-5} \text{ M}$, $\text{pH} = 8$, amount of catalyst = 0.06g /100ml dye solution. The result of photocatalytic bleaching of RB 160 is graphically presented in Fig.3

Table 1: A typical run of photocatalytic degradation of Reactive Blue 160

Time (min)	abs	1+log abs
0	0.652	0.8142
20	0.600	0.7782
40	0.555	0.7443
60	0.516	0.7126
80	0.477	0.6785
100	0.441	0.6444
120	0.410	0.6128
140	0.378	0.5775
160	0.352	0.5465

It was observed that absorbance (Abs.) decreases with the increase in time of irradiation indicating that the dye is degraded on irradiation. A graph between $1 + \log \text{abs}$ and time has been plotted. The linearity of the plot indicates that the photocatalytic bleaching of Reactive Blue 160 follows a first order kinetics. The rate constant of this photobleaching process was determined using the expression.

$$\text{Rate (k)} = 2.303 \times \text{Slope} = 6.51 \times 10^{-5} \text{ sec}^{-1}$$

The effects of variation in various reaction parameters has been studied, e.g. pH, concentration of the dye, amount of photocatalyst. Control experiments (in absence of photocatalyst, light) confirm the necessity of photocatalyst for the photobleaching of dye.

Effect of variation in hydrogen ion concentration on the rate of decolorization of the dye

Photocatalytic degradation of dye is known as a highly pH dependent process since pH plays an important role in the mechanism of hydroxyl radical production. In this study, photodegradation was performed at different pH from 5.5 to 10 keeping all other reaction parameters constant.

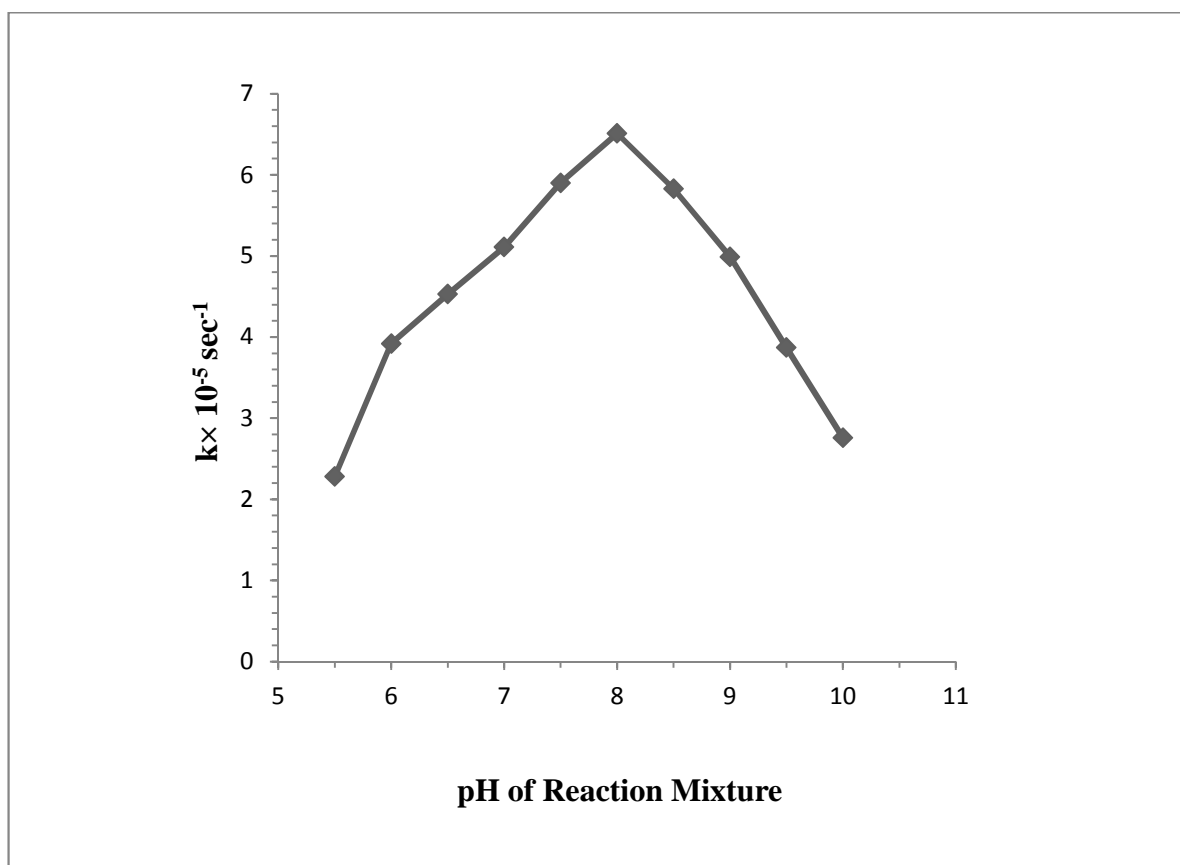


Fig- 4: A plot showing effect of variation in hydrogen ion concentration on the rate of decolorization of the dye by CeFeO_3

Fig 4 proves that pH 8 is the optimal pH for RB 160 decolorization. Hence all subsequent experiments were carried out at pH 8. The dye degradation by semiconductor is mainly attributed to surface charge properties of photocatalyst at different pH. It was found that as pH increases, rate of reaction increases. It attains a maximum value at pH 8. After this, rate of reaction decreases with increase in pH. Increase in pH increases the number of OH⁻ ions which makes the photocatalyst surface negatively charge. This causes repulsion between negatively charged dye and photocatalyst. This results into a decrease in the rate of photocatalytic degradation of dye.

Effect of variation in dye concentration on the rate of decolorization of the dye

The effect of dye concentration on the degradation of Reactive Blue 160 was studied at different concentrations varying from 1.0×10^{-5} M to 4.5×10^{-5} M keeping all other factors identical. Dye molecules adsorb on catalyst surface and degradation occurs. On increasing the concentration of dye, keeping catalyst dose constant, catalyst surface gets saturated. Simultaneously intense colour of dye does not permit light to reach photocatalyst. As a result rate of degradation decrease.

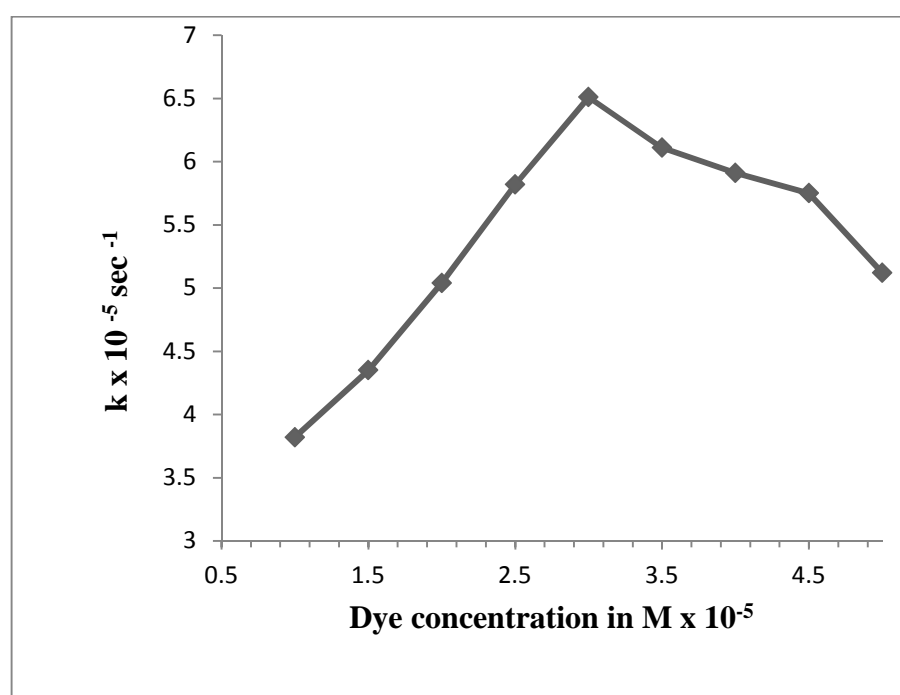


Fig- 5: A plot showing effect of variation in dye concentration on the rate of decolorization of the dye by CeFeO₃

Effect of variation in catalyst concentration on the rate of decolorization of the dye

The effect of amount of photocatalyst on the degradation kinetics of Reactive Blue 160 was investigated employing different amount of the CeFeO₃ varying from .01 to 0.1 g/ 100ml. Keeping all other factors identical, it was observed that the rate of dye decolourization increases with increasing catalyst level up to 0.06 g and beyond this, the rate of reaction becomes almost constant.

The result of Fig-6 reveals that the rate of photobleaching of dye increases with the increase in the amount of catalyst CeFeO₃ up to 0.06 g/100ml dye solution. The increase in amount of photocatalyst in the reaction mixture is accompanied by enhanced generation of •OH radicals, consequently increasing the rate of photodegradation. This may be due to the fact that, initially the increase in the amount of catalyst increases the number of active sites on the catalyst surface that in turn increases the number of hydroxyl radicals. After a certain level of catalyst (0.06g), rate of reaction decrease because substrate dye molecules are not available for adsorption on active sites of semiconductor. The additional catalyst particles therefore are not involved in the catalytic activity. Hence the rate of degradation does not increase.

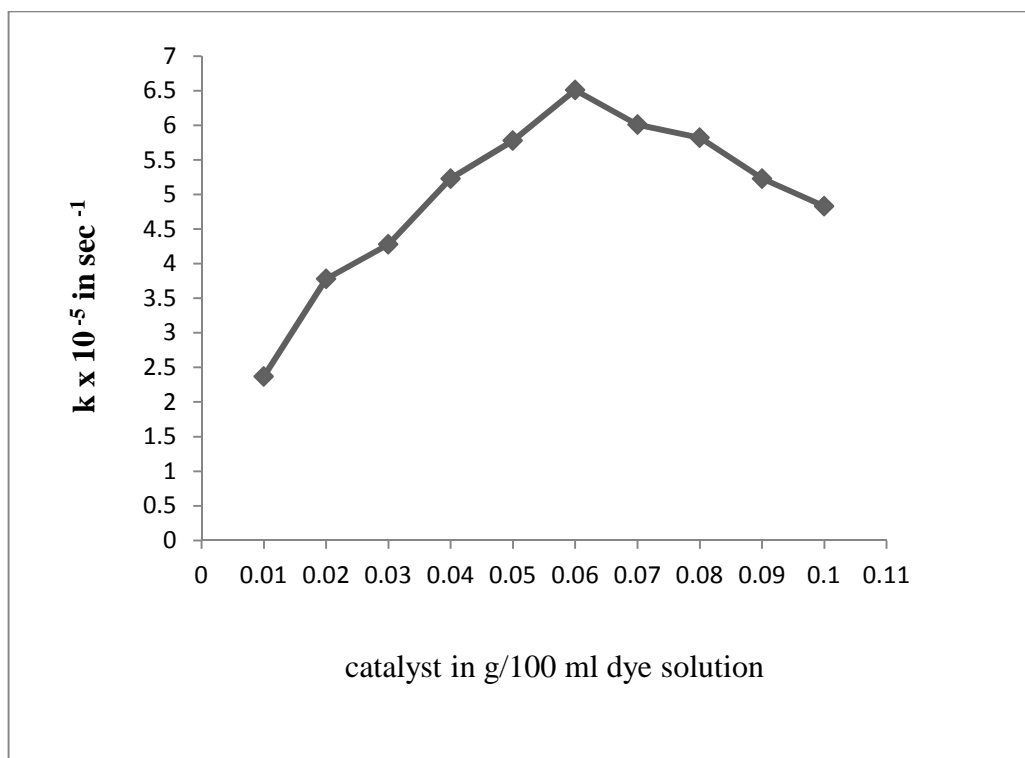
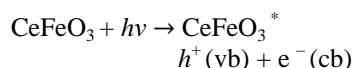


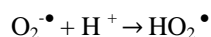
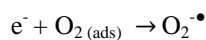
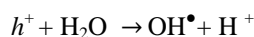
Fig- 6: A plot showing effect of variation in amount catalyst on the rate of decolorization of the dye by CeFeO₃

Mechanism

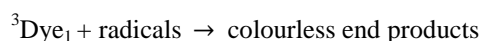
Photocatalysis is initiated by absorption of photon with energy equal or greater than the band gap of semiconductor CeFeO₃. CeFeO₃ absorbs light in visible region. Electrons from valence band shift into conduction band. Thus a hole (h^+) is generated in valence band. The photogenerated hole is strong oxidizing agent and electron in conduction band acts as reducing agent.



These electron hole pairs migrate to catalyst surface where radicals are generated.



OH[•] (hydroxyl radical) O₂^{•-} (superoxide radical) HO₂[•] (peroxide radical) are strong oxidizing species and react with dye molecules to oxidize them. Simultaneously a dye molecule absorb radiation of suitable energy and get excited to its first singlet state followed by intersystem crossing to triplet state.



The participation of OH[•] was confirmed using scavenger 2-propanol. The rate of reaction was drastically reduced in the presence of 2-propanol. The formation of CO₂, NO₃⁻, NO₂⁻ in degraded reaction mixture shows there is a complete mineralization in this process. The end products are harmless to the environment.

CONCLUSION

Cerium iron oxide is effectively utilized as photocatalyst for degradation of textile dye Reactive Blue 160. It is found that degradation is dependent on various reaction parameters such as pH, dye concentration, amount of catalyst. The optimum condition for degradation is at pH 8, 0.06 g CeFeO₃ / 100 ml dye solution and 3×10⁻⁵ M dye concentration. Overall findings suggest need to exploit this photocatalyst for wastewater treatment of textile effluent.

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