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Photocatalytic degradation of disperse azo dye coralene dark red 2B by CeFeO_3

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ABSTRACT

In present work efficiency of CeFeO_3 as photocatalyst for degradation of Coralene Dark red 2B (Disperse red 167) was studied. Photocatalytic bleaching of Coralene Dark red 2B was observed spectrophotometrically. The influence of variation of different reaction parameters such as concentration of dye, pH, and amount of photocatalyst were observed. The optimum conditions for photocatalytic degradation have been established. The kinetics of degradation of the dye follows first order kinetics. A tentative mechanism for degradation of dye by CeFeO_3 has been proposed. The presence of hydroxyl radical as an active oxidising species has been confirmed.

Key words: Coralene Dark Red 2B, Photocatalyst, Photocatalytic bleaching.

INTRODUCTION

Textile dyes are abundant source of coloured organic compounds. During dye production and textile manufacturing process a large quantity of waste water containing tons of organic dyes are being discharged into water bodies every year. Bhilwara is known as textile city of Rajasthan. There are nearly twenty major textile processing units which use million litre of water every day and generate huge quantity of effluent containing dyes.

The discharge of dyes in industrial effluents has become a major concern. These dyes are significant source of environmental pollution. [1] Waste water from textile industries is generally high in colour and organic content. More than 10,000 different dyes have been used in textile industry. [2] Azo dyes accounts for the majority of dyes produced and are extensively used in textile industry [3] because their synthesis is simple and cost effective. These dyes have greatest variety of colours. Azo dyes are characterized by one or more azo group. This azo group convert into toxic amines on degradation. Hence these dyes are toxic, mutagenic and carcinogenic. [4] As these dyes are designed to resist oxidative degradation, they pass through most stages of effluent treatment and ultimately released into environment. [5] Many treatment methods have been reported for dye degradation such as flocculation, coagulation [6], ultrafiltration [7], reverse osmosis [8], biodegradation [9] etc. These methods have their own limitation in terms of high cost, specificity for certain group, disposal of sludge formed, and excessive use of chemicals. All these result in secondary pollution. Conventional methods cannot effectively remove dyes from effluent hence study of alternative treatment technologies is necessary. Photocatalytic degradation provides an alternative method for waste water treatment in low cost, less time and easy operative method. Photocatalytic degradation being eco friendly and cost effective is a preferred method. [10] A lot of work has been performed on various photocatalyst materials such as TiO_2 [11], ZnO [12], NiO [13], etc. Recently studies dealing with ternary oxide of rare earth element and transition element as photocatalyst have been reported [14]. Ternary oxides have been used as effective photocatalyst for carrying out a number of chemical reactions. CeFeO_3 has been used for degradation of Brilliant Blue G [15], gentian violet [16] and few other dyes. CeFeO_3 has been prepared by coprecipitation [16] and microwave process [17]. Coralene dark red 2B (Disperse Red 167) has been widely used as

a disperse azo dye in textile industry. In present investigation the degradation of coralene dark red 2B (Disperse Red 167) dye solution was studied in presence of CeFeO₃ as photocatalyst.

MATERIALS AND METHODS

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 and used as photocatalyst for degradation of an azo dye coralene dark red 2B (Disperse red 167). Metal nitrates of Cerium and iron were used for synthesis of photocatalyst because Nitrate group act as oxidising agent and have high solubility in water.

The commercially available monoazo dye was procured from Sulzer processors private limited Bhilwara (Raj). The chemicals Ce(NO₃)₃.6H₂O, Fe(NO₃)₃.9H₂O, sodium hydroxide were obtained from Merck.

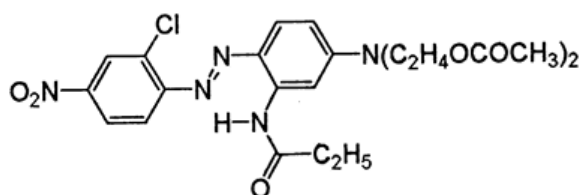


Fig 1: Chemical Structure of (Coralene Dark Red 2B) Disperse red 167
Molecular formula C₂₃H₂₆ClN₅O₇, Molecular weight 519.93

METHOD

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 XRD 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 Coralene Dark Red 2B 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 0.519 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 0.617 was recorded at 478 nm (λ_{max}). The reaction mixture was prepared by taking 3 ml of dye solution (1×10^{-3} M), 0.05 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 3×10^{-5} M. To carry out the photobleaching, the reaction mixture was irradiated under light source (2 x 200 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 478 nm. The rate of decrease of colour with time was continuously monitored. After complete mineralization, the presence of NO₂⁻, NO₃⁻ ions and evolution of CO₂ were tested by standard procedures. The pH of the reaction was adjusted by adding 0.1 M NaOH and 0.1M HCl solutions.

RESULTS AND DISCUSSION

The synthesized CeFeO₃ was analyzed for its composition and crystal structure by powder XRD. The XRD pattern of CeFeO₃ is shown in figure II. 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 CeFeO₃.

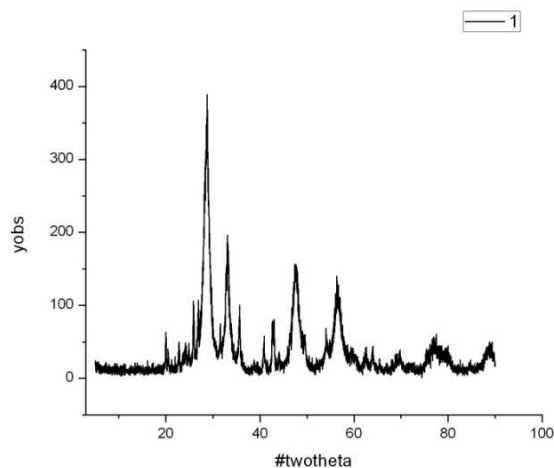


Fig II XRD of synthesized CeFeO₃

The photocatalytic degradation of Disperse red 167 was observed at 478 nm. The optimum conditions for the photobleaching of dye were [Dye] = 3.0×10^{-5} M, amount of catalyst 0.05g/100 ml of dye solution and pH=8.

Table I: A typical run of photodegradation of Coralene dark red 2B

Time (min)	abs	1+log abs
0	0.617	0.7903
10	0.549	0.7396
20	0.488	0.6884
30	0.427	0.6304
40	0.375	0.5704
50	0.332	0.5211
60	0.296	0.4713
70	0.264	0.4216
80	0.227	0.3560
90	0.196	0.2923
100	0.182	0.2601

The result of photocatalytic bleaching of Disperse red 167 is graphically presented in Fig III.

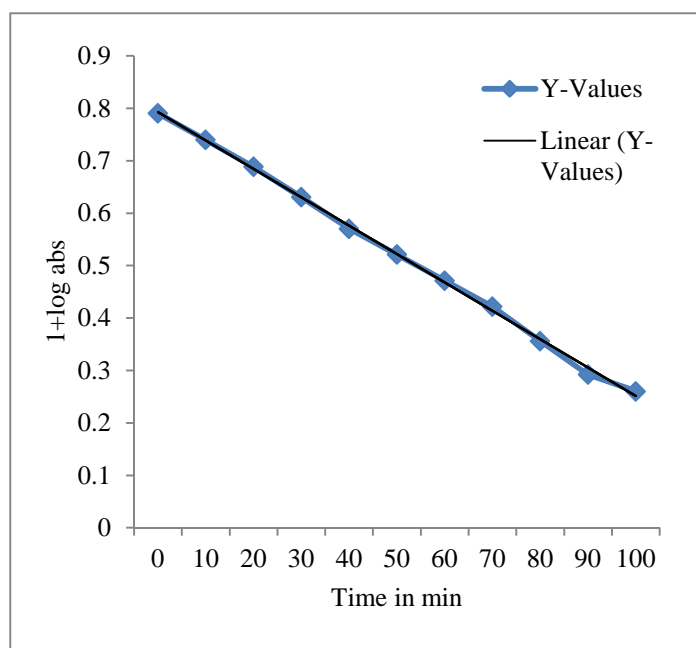


Figure III: Plot of 1 + log abs verses time for a typical run

It was observed that absorbance decreases with the increase in time of irradiation indicating that the dye is degraded on irradiation in presence of photocatalyst CeFeO₃. A graph between $1 + \log \text{abs}$ and time has been plotted. The linearity of the plot indicates that the photocatalytic bleaching of Coralene Dark red 2B follows a first order kinetics. The rate constant of this photobleaching process was determined using the expression.

$$\text{Rate constant (k)} = 2.303 \times \text{Slope} = 2.032 \times 10^{-4} \text{ sec}^{-1}$$

The effect 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 and light for the photobleaching of dye.

Effect of amount of catalyst on the rate of decolorization of the dye

Keeping all other factors identical, the concentration of catalyst was changed and its effect on the rate of photochemical degradation was observed.

Table II : Effect of amount of catalyst on rate of decolorization of Coralene Dark Red 2B

Catalyst in g/ 100 ml of dye solution	$k \times 10^{-4} \text{ sec}^{-1}$
0.02	0.32
0.03	0.51
0.04	1.43
0.05	2.03
0.06	1.98
0.07	1.94
0.08	1.92

The result reveals that the rate of photobleaching of dye increases with the increase in the amount of catalyst CeFeO₃ up to 0.05g/100 ml of dye solution and beyond this the rate of reaction become almost constant. The increase in amount of catalyst in the reaction mixture is accompanied by enhanced generation of •OH radicals as the surface area of catalyst increase. •OH radical is an extremely strong oxidant ($E^{\circ}=2.80 \text{ V}$) which degrade the dye molecule. Further increase in photocatalyst above 0.05g has negligible effect on dye degradation. The amount of catalyst increase with same concentration of dye, further dye molecules are not available for adsorption. Therefore additional catalyst particles are not involved in catalytic activity and rate of reaction is constant.

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

In this study, photodegradation was performed at different pH from 4.5 to 11.0. It has been observed that pH 8 is the optimal pH for degradation of Disperse red 167. Hence all subsequent experiments were carried out at pH 8. After pH 8 there is an adverse effect on the rate of reaction increasing pH further. The observation can be explained on the basis that as pH of solution increase s more OH⁻ ions are available. These OH⁻ will generate •OH radicals by combining with the hole semiconductor photocatalyst. The pH of reaction mixture has a significant effect on the surface properties of CeFeO₃ catalyst hence photocatalytic activity.

Table III: Effect of pH on rate of decolorization of Coralene Dark Red 2B

pH	$k \times 10^{-4} \text{ sec}^{-1}$
4.5	0.63
5.0	0.87
5.5	1.02
6.0	1.34
6.5	1.55
7.0	1.79
7.5	1.91
8.0	2.03
8.5	1.21
9.0	1.01
9.5	0.72

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

The effect of dye concentration on the degradation of Disperse red 167 was studied at different concentrations varying from 1.0×10^{-5} to 7.0×10^{-5} keeping all other factors identical. The result reveals that initially rate of reaction increase with increase in concentration of dye. The highest rate of reaction was observed for 3.0×10^{-5} M dye solution. Further the rate of photobleaching of dye decreases with the increase in the concentration of the dye. The reason behind it is that the increase in the initial concentration of the dye lies in consistency of the hydroxyl radicals concentrations for all the dye molecules and therefore the rate of decolorization increase. Dye molecules adsorb on

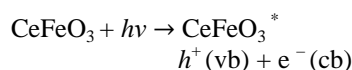
catalyst surface and degradation occurs. On increasing the concentration of dye, keeping catalyst dose constant, catalyst surface gets saturated. Simultaneously intense colour of dye does not permit light to reach photocatalyst. As a result rate of degradation decrease.

Table IV: Effect of dye concentration on rate of decolorization of Coralene Dark Red 2B

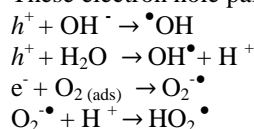
Dye concentration	$k \times 10^{-4} \text{ sec}^{-1}$
1.0	1.01
2.0	1.49
3.0	2.03
4.0	1.62
5.0	1.31
6.0	1.11
7.0	0.82

Mechanism

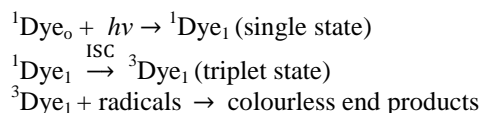
Photocatalysis is initiated by absorption of photon with energy equal or greater than the band gap of semiconductor CeFeO_3 . CeFeO_3 absorbs light in visible region. Electrons from valence band shift into conduction band. Thus a hole (h^+) is generated in valence band. The photogenerated hole is strong oxidizing agent and electron in conduction band acts as reducing agent.



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



$\text{OH}\bullet$ (hydroxyl radical) $\text{O}_2^{\bullet-}$ (superoxide radical) $\text{HO}_2\bullet$ (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 $\text{OH}\bullet$ was confirmed using scavenger 2-propanol. The rate of reaction was drastically reduced in the presence of 2-propanol. The formation of CO_2 , NO_3^- , NO_2^- 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 Coralene dark Red 2B (Disperse Red 167) in aqueous solution. 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, 0.05 g CeFeO_3 / 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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