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Photocatalytic Degradation of Commercially Important Azo Dye Reactive Orange 16 by Heterogeneous Photocatalysis

Vinod Kumar Mehta And B.V.Kabra
Department of Chemistry, M.L.V. Govt. College, Bhilwara (Raj.)India
Corresponding Author: Vinod Kumar Mehta

Abstract
The photocatalytic bleaching of textile azo dye Reactive Orange 16 has been carried out in the presence of photo catalyst $CeFeO_3$ and the progress of reaction 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 photo catalytic 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: Reactive Orange 16, Photocatalyst, Photocatalytic bleaching.

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I. Introduction

Azo dyes are versatile class of colored organic compounds, which are characterized by the presence of one or more azo bonds (-N=N-). These are widely used in number of industries such as textile dying, food, leather, additive, cosmetic, paper, pharmaceutical industries etc.[1-2].During dye production and textile manufacturing processes, a large quantity of waste water containing dyestuffs with intensive color and toxicity are introduced into the aquatic systems [3].These dyes do not decompose rapidly through natural processes and are resistant to aerobic degradation. The azo linkage is reduced to aromatic amines under anaerobic conditions that can be toxic and potentially carcinogenic [4-6].It is necessary to find an effective method of wastewater treatment in order to remove color from effluents. A number of physical and chemical techniques has been reported for the removal of dye compounds such as adsorption on activated carbon [7], biodegradation [8], ozonation [9] and advanced oxidation processes (AOPs) such as Fenton and photo-Fenton catalytic reactions [10,11]and H_2O_2/UV processes [12]. 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. [13] A lot of work has been performed on various photocatalyst materials such as TiO_2; [14], ZnO[15], NiO [16], etc. Recently studies dealing with ternary oxide of rare earth element and transition element as photocatalyst have been reported [17]. 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 [18], gentian violet [19] and few other dyes. $CeFeO_3$; has been prepared by coprecipitation [20] and microwave process [21]. Reactive Orange 16 has been widely used as a reactive azo dye in textile industry. In present investigation the degradation of Reactive Orange 16 dye solution was studied in presence of $CeFeO_3$ as photocatalyst.

II. Matareial And Methodes

All reagents of analytic grade ware used as received without further purification. The $CeFeO_3$ nanoparticles were synthesized by co-precipitation followed by calcinations. The synthesized particles were characterized and used as photocatalyst for degradation of an azo dye Reactive Orange 16 Metal nitrates of Cerium and iron were used for synthesis of photocatalyst because Nitrate group act as oxidizing agent and have high solubility in water.

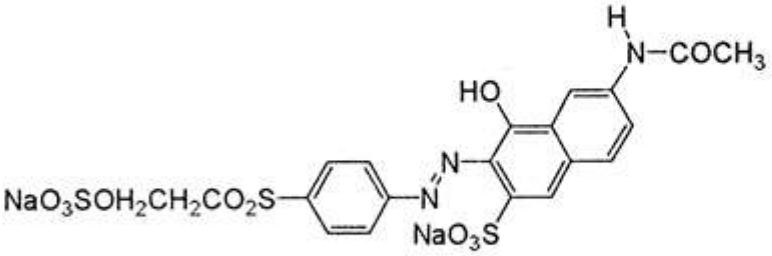


Fig I Chemical Structure of Reactive Orange 16
[Molecular formula-$C_{20}H_{17}N_3Na_2S_3O_{11}$,Molecular Weight-617.54]

III. Method

The cerium iron oxide particles were synthesized by precipitation of metal nitrates of cerium and iron. The $Ce(N0_3)_3.6H_20$ and $Fe(N0_3).9H_20$ were respectively dissolved in distilled water at room temperature to produce 0.1 M aqueous solution. The ternary oxide $CeFeO_3$ was prepared by adding l M NaOH drop wise to the solution of $Ce(N0_3)_3.6H_20$ and $Fe(N0_3).9H_20$ with continuous stirring. The pH of solution was monitored and complete precipitation was obtain 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 pastle. Subsequently, calcinations were performed. The powder was calcined at 600° C for 5 hours.

Characterization:

Power XRD was performed with Rigaku Micromax-OO7 HF instrument using Cu Ka (ʎ=l.54A°) 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 perovskii structure. (JCPDS card 22-0166).

Experimental Procedure:

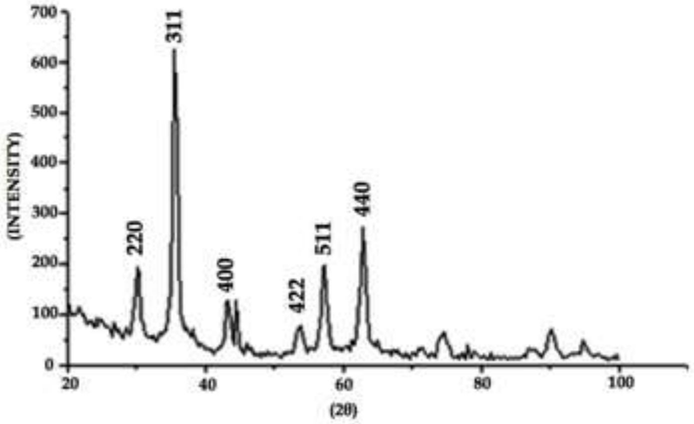
The degradation of Reactive Orange 16 was studied in presence of photocatalyst $CeFeO_3$ at different pH level, catalyst loading and dye concentration. $1X\ 10^{-3}$ M dye solution was prepared by dissolving 0.617 g of dye in 1000 ml of distilled water. The initial absorbance of dye solution was observed with the help of UV-VIS spectrophotometer(Shimadzu, UV-700, Pharmaspec). The maximum absorbance Value 0.457 was recorded at 490 nm ($ʎ_{max}$). The reaction mixture was prepared by taking 3 ml of dye solution ($1x10^{-3}$ 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 $3.0x10^{-5}$ 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 490 nm. The rate of decrease of colour with time was continuously monitored. After complete mineralization, the presence of $N0_2^-$, $N0_3^-$ ions and evolution of CO_2 were tested by standard procedures. The pH of the reaction was adjusted by adding 0.1 M NaOH and 0.1M HCl solutions.

IV. 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 20 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 indicates high crystallization of prepared $CeFeO_3$.

Fig II XRD synthesized $CeFeO_3$



The result of photocatalytic bleaching of Reactive Orange 16 are given in table 1 . Table: 1 TYPICAL RUN

[Acid Red 18] = 3 x 10^{-5} M
λ_{max} = 490 nm

Amount of catalyst= 0.05 g/100 ml
pH = 3.0

Time (min)	Absorbance (Abs)	1+log Abs
0	0.457	0.602
10	0.392	0.594
20	0.370	0.531
30	0.267	0.456
40	0.245	0.367
50	0.196	0.356
60	0.188	0.269
70	0.185	0.250

It was observed that absorbence decreases with the increase in time of irradiation indicating that the dye is on degraded irradiation in presence of photocatalyst $CeEe0_3$. A graph between 1 + log abs and time has been plotted. The linearity of the plot indicates that the photocatalytic bleaching of Reactive Orange 16 follows a first order kinetics. The rate constant of this photobleaching process was determined using the expression.

Rate constant (k) = 2.303 x Slope = 2.032x10^{-4} 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 Reactive Orange 16

Catalyst in g/100 ml of dye solution	**Kx10^{-4} sec-1**
0.02	**0.38**
0.03	**0.68**
0.04	**1.95**
0.05	**2.18**
0.06	**1.98**
0.07	**1.94**
0.08	**1.91**

The result reveals that the rate of photobleaching of dye increases with the increase in the amount of catalyst $CeFe0_3$ up to 0.05g/ 100 ml of dye solution and beyond this the rate of reaction becomes almost constant. The increase in amount of catalyst in the reaction mixture is accompanied by enhanced generation of $OH^{\cdot}$ radicals as the surface area of catalyst increase $OH^{\cdot}$ radical is an extremely strong oxidant which degrade the dye molecule. Furthure increase in photocatalyst above 0.05 g 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 1.0 to 6.0. It has been observed that pH 3 is the optimal pH for degradation of Reactive Orange 16. Hence all subsequent experiments were carried out at pH 3. After pH 3 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 increases more 0H 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 $CeFeO_3$ catalyst hence photocatalytic activity.

Table III: Effect of pH on rate of decolorization of Reactive Orange 16

pH	**Kx10^{-4} sec^{-1}**
1.0	**0.64**
1.5	**0.88**
2.0	**1.22**
2.5	**1.42**
3.0	**2.45**
3.5	**1.92**
4.0	**1.89**
4.5	**1.82**
5.0	**1.72**
5.5	**1.65**
6.0	**1.62**

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

The Effect of dye concentration on the degradation of Reactive Orange 16 was studied at different concentrations varying from 1.0x10^{-5} to 7.0x10^{-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 3.0x10^{-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 concentration 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 permits light to reach photocatalyst. As result rate of degradation decrease.

Table IV: Effect of dye concentration on rate of decolorization of Acid orange 8

Dye concentration	Kx10^{-4} sec^{-1}
1.0	1.32
2.0	1.92
3.0	2.88
4.0	1.62

5.0	1.54
6.0	1.45
7.0	1.42

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.

$CeFeO_3 + h\nu \rightarrow CeFeO_3{}^{*}$

$h^+ (vb) + e^- (cb)$

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

$h^+ + OH^- \rightarrow {}^{\bullet}OH$

$h^+ + H_2O \rightarrow OH^{\bullet} + H^+$

$e^- + O_2 (ads) \rightarrow O_2^{-\bullet}$

$O_2^{-\bullet} + H^+ \rightarrow HO_2{}^{\bullet}$

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.

${}^1Dye_0 + h\nu \rightarrow {}^1Dye_1$ (single state)

$${}^1Dye_1 \xrightarrow{ISC} {}^3Dye_1$$ (triple state)

${}^3Dye_0$ + radicals → colourless end products

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.

V. Conclusion

Cerium iron oxide is effectively utilized as photocatalyst for degradation of textile dye Reactive orange 16 in aqueous solution. It is found that degradation is dependent on various reaction parameters web as pH, dye concentration, amount of catalyst. The optimum condition for degradation is at pH 3, 0.05 g $CeFeO_3$/ 100 ml dye solution and $3x10^{-5}$ M dye concentration. Overall findings suggest need to exploit this photocatalyst for wastewater treatment of textile effluent.

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