

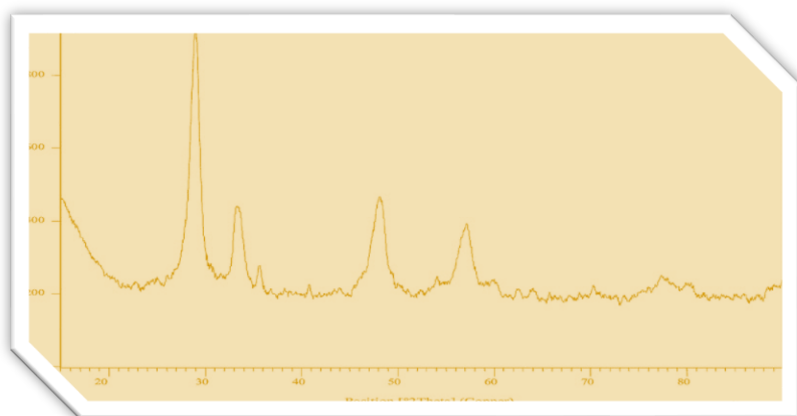
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Cerium-Iron Oxide: An Efficient Photocatalyst for the Degradation of Methylene Blue Dye

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This study investigates the photocatalytic degradation of methylene blue using cerium-iron oxide (Ce-FeO) nanoparticles as efficient photocatalysts. The Ce-FeO nanoparticles were synthesized and characterized using X-ray diffraction (XRD) technique and their photocatalytic activity was evaluated for the degradation of methylene blue dye by monitoring the degradation of Methylene Blue under visible light irradiation. Furthermore, the effects of various parameters such as the pH of the dye solution, dye concentration, amount of photocatalyst and light intensity on the dye degradation efficiency were investigated. The progress of dye degradation was monitored spectrophotometrically by observing the optical density of the dye solution at regular intervals. Maximum dye degradation was observed with a dye solution of 2.25×10^{-5} M concentration at 11.5 pH and 700 Wm^{-2} light intensity using 0.04g cerium-iron oxide nanoparticles per 50 ml of dye solution. It was observed that Ce-FeO nanoparticles serve as an effective and environmentally friendly photocatalyst for dye degradation under visible light.

Graphical abstract



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1. Introduction

Clean, safe and adequate water is vital for the survival of all living organisms and for the smooth functioning of ecosystem. But the quality of water is increasingly endangered as human population grow and industrial and agricultural activities expand. Poor water quality poses a threat to human health as well as to the ecosystem as the availability of safe water for drinking is reducing [1-3].

There are many industries which generate wastewater [4-6]. Among this, textile dyeing industries contribute to a major share. Dyes are a class of organic compounds, widely used in textiles, printing and food industry. Dye effluents have a considerable negative influence on the environment, and most of them are highly toxic and nonbiodegradable [7-8]. Contaminants with dyes in industrial wastewater were of great

concern because of their high visibility, toxicity, and difficulty in degradation [9]. Thus, removing color from the wastewater is essential in preventing water contamination. Common dye pollutants in wastewater were Rhodamine Bue, Methylene Blue, Methyl Orange, Congo Red, etc. This harmful wastewater is either dumped into open - oceans or rivers or released into the ground.

Therefore, there is an urgent need for both the public and private sector of the global community to work together to take on the task of protecting and improving the quality of water. The conventional methods for treating wastewater include adsorption, coagulation, ozonation and biological treatments [10-13], but they are suffering from one or other drawbacks. Several traditional methods have been used for the treatment of wastewater, for example, adsorption, membrane filtration, and coagulation, while these are time-consuming, limited efficiency, and induce secondary pollution and incomplete removal [14]. Most of these methods require further treatment since they convert the dyes from the liquid to the solid phase [15].

The exploitation of more efficient wastewater treatment technologies for the removal of organic pollutants is currently a highly discussed and researched field. In contrast to traditional methods, Advanced oxidation processes (AOPs) are a class of oxidation techniques in which organic contaminants are degraded to harmless products. In this process, $\cdot\text{OH}$ radicals are produced which initiate oxidation reactions ending with complete mineralization of CO_2 and H_2O [16-17]. Semiconductor photocatalysis is a promising technique which is considered to be efficient and economical for treating the wastewater containing organic pollutants. Semiconductors are used as activators in AOPs for several reasons, including their low cost and non-toxicity, favorable electronic and optical properties, ability to facilitate multi-electron transfer processes, and recyclability without significant loss of photocatalytic activity [18].

Photocatalytic method has been emerged as a favorable alternative and widely adopted to remediate wastewater containing textile dyes [19-21] due to its cost-effectiveness, mild reaction conditions, and remarkable efficacy in transforming organic pollutants into environmentally friendly products [22, 23].

Methylene blue (MB) is a phenothiazine derivative, used for dyeing textiles, and it is highly toxic and carcinogenic [24]. TiO_2 was the principal photocatalyst in the majority of early research [25-27]. The photodegradation of methylene blue is also well established with TiO_2 . Despite its good chemical stability and low production cost, there are certain limitations of using Titanium dioxide (TiO_2) as a photocatalyst for the degradation of dyes such as large/wide band gap which absorbs ultraviolet light about less than 387 nm in wavelength, thereby limiting photocatalytic activity in the visible-light region, Electron-Hole Recombination and Selective Dye Degradation [26-28].

Thus, it became necessary to develop materials which will absorb in the visible-light regime and prevent electron-hole recombination [29-31] and to overcome this problem, a number of novel photocatalysts impregnated with metal oxide and composite metal oxide semiconductors have been employed recently to address these limitations.

On the other hand, Cerium iron oxide (CeFeO_3) presents significant advantages over titanium dioxide (TiO_2) for photocatalytic degradation of dyes as it exhibits absorption in the visible light spectrum. This property allows CeFeO_3 to utilize a larger portion of the solar spectrum, lower rates of

electron-hole recombination compared to TiO_2 , unique electronic structure and surface properties, chemical Stability more than TiO_2 under various pH conditions and in the presence of certain chemical species, selective reactivity towards specific dye molecules based on their molecular structure and surface interactions. All these properties make CeFeO_3 , a promising alternative photocatalyst for efficient and sustainable degradation of dyes and other organic pollutants in water treatment applications and is generally considered environmentally benign, with low toxicity and minimal environmental impact [32, 33].

In the present study, efforts were made to photocatalytically degrade Methylene blue dye often known as basic blue 9 using cerium iron oxide nanoparticles. For this, cerium-iron oxide nanoparticles were synthesized and the effect of various parameter such as initial dye concentration, pH of dye solution and light intensity were evaluated for optimum conditions for dye degradation.

2. Material and Methods

Synthesis of cerium-iron oxide nanoparticles

The synthesis of mixed cerium-iron oxide was achieved by co-precipitation method. The mixed oxide was prepared by adding aqueous solution of 1M NaOH drop-wise to the aqueous solution of 0.1M of both $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with concurrent vigorous stirring. The pH of the mixed solution was adjusted at different pH in alkaline range but at 10 pH complete precipitation was observed so the pH was maintained at 10. After 4 hours of continuous stirring, the precipitate was filtered and repeatedly washed with deionized water. The residue was dried in an oven at 110°C overnight and then grounded in acetone with mortar and pestle. The powder received was then calcined at 500°C for 4 hours under static air in muffle furnace.

Characterization of the synthesized nanoparticles

X-ray powder diffraction study was performed to establish the phase purity and crystallinity of the prepared bimetal oxide by X-ray diffractometer. The nanoparticles size was determined by the Scherrer equation.

Photocatalytic Degradation of dye

Photocatalytic degradation of methylene blue dye was studied by exposing the dye solution under visible light in the presence of synthesized bimetal oxide nanoparticles.

A 1.0×10^{-3} M solution of methylene blue was prepared by dissolving 0.320 g methylene blue in 1000 mL of double distilled water. This solution was used for further dilutions. The absorption maximum of the dye was determined with the help of a UV-VIS spectrophotometer (Systronics Model 106). For irradiation purpose, a 200 W tungsten lamp (Philips) was used. The intensity of light was measured by solar power meter (TENMARS model TM 207). A cutoff water filter was used to avoid thermal radiations and to ensure illumination by visible radiations only. The desired pH was adjusted by the addition of 0.1 N solution of sodium hydroxide and 0.1 N hydrochloric acid solution and measured by a digital pH meter (Systronics Model 324). The progress of photocatalytic degradation of the dye was monitored by withdrawing definite quantity (2.0 mL) of the reaction mixture which contains the dye solution and synthesized bimetal oxide nanoparticles at regular time intervals and measuring the absorbance at

maximum wavelength (λ_{\max} 655 nm). From the decreasing trend of optical density with increasing time, it is clear that the dye degraded during the process.

For this, the dye solution was irradiated with light without adding photocatalyst, and with and without photocatalyst in the absence of light. Optical density was observed at regular time intervals. It was observed that the optical density of solutions kept in dark with or without adding photocatalyst was almost same as before while the solution of beaker kept in light without adding catalyst had a very little decrease in its optical density. But the beaker kept in light with bimetal oxide nanoparticles had a reasonable decrease in absorbance of the solution.

Percentage of dye degradation

The percentage degradation of dye was calculated using the following equation [34]:

$$\text{Dye degradation \%} = \frac{A_0 - A_t}{A_t} \times 100$$

Where A_0 denotes absorbance at zero time; A_t denotes absorbance at t time.

3. Results and Discussion

Characterization of the synthesized bimetal oxide

The XRD pattern for cerium-iron oxide is shown in Fig. 1. Graph has been plotted between intensity (cycles per second) and 2θ values (in degrees). The nanoparticles size was 23.28 nm as determined by Scherrer equation.

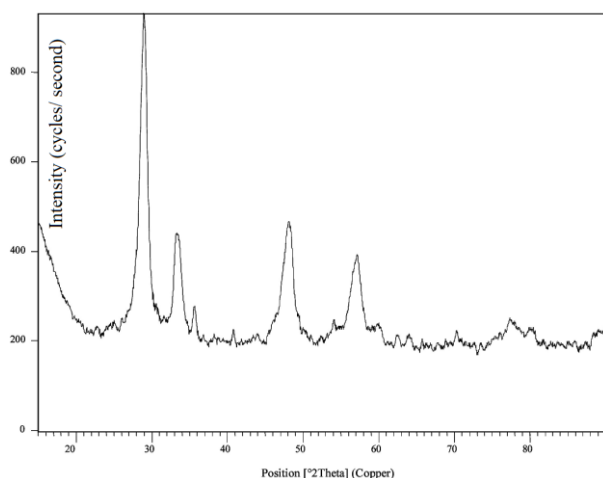


Fig.1. Powder X-ray Diffraction pattern of Cerium-iron oxide.

Photocatalytic degradation of dye

A 2.0 mL of the solution was taken out from the reaction mixture, which contains dye and cerium-iron oxide nano photocatalyst and absorbance was measured against blank reagent. It was observed that the absorbance of the solution decreases with time, showing that the concentration of the dye decreases with increasing time of exposure. A graph of $2 + \log$ O.D. versus time was plotted and it was observed that the degradation followed first order kinetics. The rate constant was calculated by using the expression:

$$k = 2.303 \times \text{slope}$$

The rate constant for the reaction was $3.07 \times 10^{-4} \text{ s}^{-1}$. A typical run for the photocatalytic degradation of methylene blue in the presence of nanosized cerium-iron oxide

photocatalyst is given in Table 1 and graphically represented in Figure 2.

Table 1. A typical run of methylene blue dye using cerium-iron oxide.

Time (min.)	Optical Density (O.D.)	$2 + \log$ O.D.
0.0	1.235	2.0917
20.0	1.163	1.9343
40.0	0.649	1.8121
60.0	0.443	1.6468
80.0	0.279	1.4452
100.0	0.193	1.2856

$$k = 3.07 \times 10^{-4} \text{ s}^{-1}$$

[Methylene blue] = $2.25 \times 10^{-5} \text{ M}$; Light intensity = 700 Wm^2 ; Amount = 0.04 g; pH = 11.5

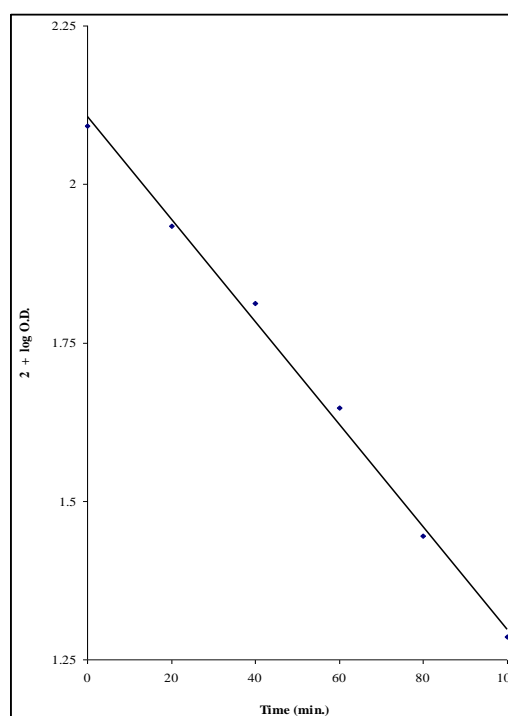


Fig. 2. Plot of $2 + \log$ O.D. versus time for a typical run.

Effect of different variables on photocatalytic degradation of dye

Effect of pH

The effect of pH on the rate of dye degradation has been reported in Table 2.

Table 2. Effect of pH.

Ph	$k \times 10^4 \text{ s}^{-1}$
7.5	0.11
8.0	0.25
8.5	0.37
9.0	0.58
9.5	0.73
10.0	0.96
10.5	1.23
11.0	2.56
11.5	3.07
12.0	2.85

[Methylene blue] = $2.25 \times 10^{-5} \text{ M}$; Light intensity = 700 Wm^2 ; Amount = 0.04 g

The rate of reaction increases with increasing pH of the solution up to pH 11.5. However, a further increase in pH of solution results in a decreased reaction rate. The results of rate of dye degradation have been shown in Figure 3. It was analyzed that photocatalysis process is pH dependent, and the optimum pH value was found to be 11.5.

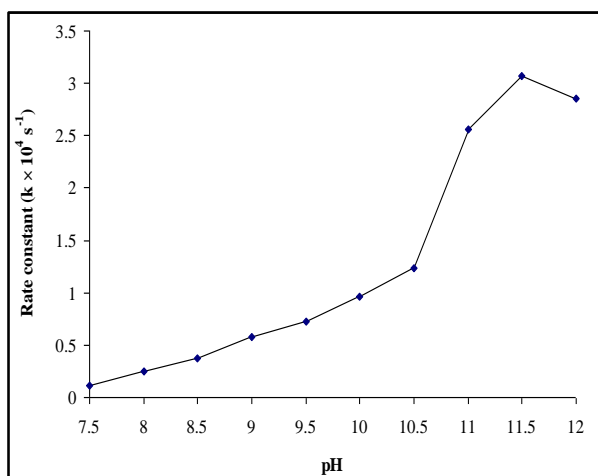


Fig. 3. Effect of pH.

An increase in the rate of photocatalytic degradation of methylene blue with increase in pH may be due to the generation of more hydroxyl radicals, which are produced from the reaction between hydroxyl ions and hole (h^+) of the semiconductor. At low pH values the surface of photocatalysts remains positively charged (due to adsorption of photons) and dye in its cationic form will face a force of repulsion from the positively charged surface of the photocatalyst.

Effect of Dye Concentration

It can be seen that rate of dye degradation increased with increasing the dye concentration up to $2.25 \times 10^{-5} \text{ M}$ and after that the rate of degradation decreased with further increase in the dye concentration. The results are reported in Table 3 and graphically represented in Figure 4.

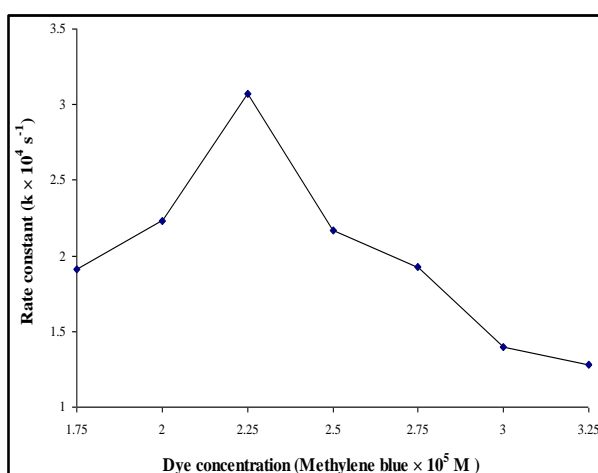


Fig. 4. Effect of dye concentration.

It may be due to the fact that as the concentration of dye was increased, more dye molecules were available for

excitation and energy transfer and, hence an increase in the rate of degradation. But on further increasing dye concentration, dye starts acting as a filter for the incident light and will not permit the light intensity to reach the semiconductor surface and as a result, rate decreases.

Effect of Amount of Catalyst

It was observed that the rate of dye degradation increases rapidly with the increase in the amount of photocatalyst from 0.02 to 0.04 g. On further increase in the amount of photocatalyst from 0.04 to 0.08 g, the rate of dye degradation decreases. The results are reported in Table 4 and graphically represented in Figure 5.

Table 3. Effect of dye concentration

[Methylene blue] $\times 10^5 \text{ M}$	$k \times 10^4 \text{ s}^{-1}$
1.75	1.91
2.0	2.23
2.25	3.07
2.50	2.17
2.75	1.93
3.00	1.40
3.25	1.28

Light intensity = 700 Wm^{-2} ; pH = 11.5; Amount = 0.04 g

Table 4. Effect of amount of catalyst.

Cerium-iron oxide (g)	$k \times 10^4 \text{ s}^{-1}$
0.02	1.31
0.03	2.45
0.04	3.07
0.05	2.35
0.06	1.94
0.07	1.09
0.08	0.88

[Methylene blue] = $2.25 \times 10^{-5} \text{ M}$; Light intensity = 700 Wm^{-2} ; pH = 11.5

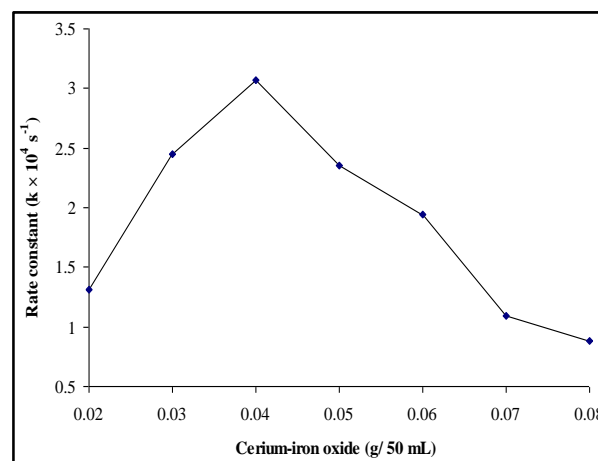


Fig. 5. Effect of amount of cerium-iron oxide.

This can be rationalized in terms of availability of active sites on catalyst surface and light penetration of photo activating substance into the suspension. The decreased percentage degradation at higher catalyst loading may be due to deactivation of activated molecules by collision with ground state molecules.

Effect of Light Intensity

The effect of light intensity on the rate of reaction is

summarized in Table 5 and Figure 6.

Table 5. Effect of light intensity on dye degradation.

Light intensity (Wm ⁻²)	k × 10 ⁴ s ⁻¹
200	0.51
300	0.64
400	0.89
500	1.28
600	2.12
700	3.07
800	2.36

[Methylene blue] = 2.25 × 10⁻⁵ M; Light intensity = 700 Wm²; Amount = 0.04 g

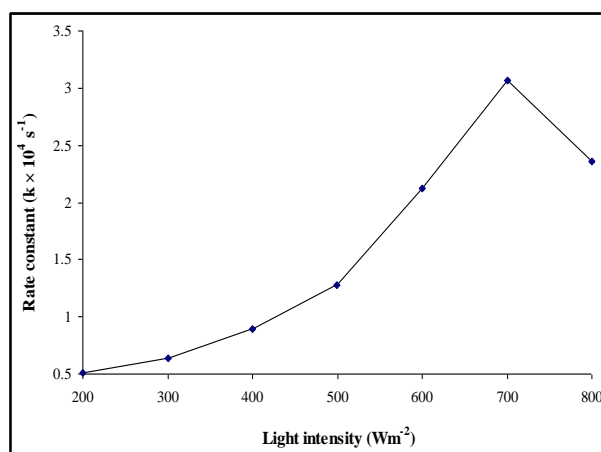


Fig. 6. Effect of light intensity.

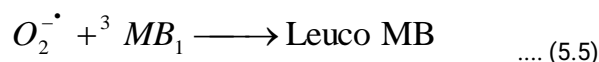
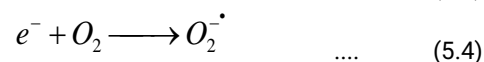
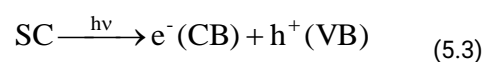
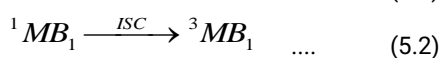
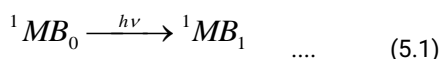
It was observed that the rate of degradation increases on increasing light intensity from 200 to 700 Wm⁻². A small decrease in the rate was observed on further increasing the light intensity. It may be explained on the basis that on increasing the light intensity, large number of photons striking per unit area of the semiconductor powder and hence generation of more electron-hole pair. However, small decrease in the rate of degradation on further increasing light intensity may be due to some thermal or side reactions.

Percentage of dye degradation

The degradation studies were conducted at their maximum absorbance. It was observed that with increase in the time, the percentage of dye degradation rises. Maximum dye Degradation of 85% with synthesized nanoparticle was observed at 100 min under visible light whereas lowest 6 % was observed at 20 min.

Mechanism for Dye Degradation

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



Methylene blue (MG) absorbs radiations of suitable wavelength and gives rise to its first excited singlet state. Then it undergoes the triplet state through intersystem crossing (ISC). On the other hand, the bimetal oxide nanoparticles (SC) also utilize the radiant energy to excite its electron from the valence band to the conduction band. This electron will be abstracted by oxygen molecule (dissolved oxygen) generating superoxide anion radical ($O_2^{\cdot-}$). This anion radical will reduce the methylene blue dye to its leuco form, which may ultimately degrade to products. It was also confirmed that this degradation proceeds through reduction and not oxidation as the rate of degradation was not affected appreciably in the presence of hydroxyl radical scavenger.

4. Conclusions

Experimental results showed that various parameters such as pH of the dye solution, concentration of dye, light intensity and amount of semiconductor had their effect on dye degradation. Both absorption and degradation processes were modeled, and experimental data was fitted to a pseudo-first-order model with sufficient accuracy.

The nanosized cerium-iron oxide showed encouraging results for the degradation of methylene blue dye. The method employed provides an efficient as well as a clean and eco-friendly pathway for combating against ever increasing water pollution. This water may be used for irrigation, washing our food at home and sometimes recycles into drinking water and may be used in industries, which costs tremendous amount of money.

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