



ENHANCING PHOTOCATALYTIC ACTIVITY OF BISMUTH FERRITE BY DOPING WITH COBALT AND ITS USE FOR DEGRADATION OF EVANS BLUE

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An attempt has been made to enhance the photocatalytic activity of bismuth ferrite by doping it with cobalt, to prepare a catalyst to use in wide pH range for the photodegradation of Evans blue dye. The progress of the reaction has been monitored spectrophotometrically by measuring the absorbance of the reaction mixture at definite time intervals. Different parameters such as pH, the concentration of dye, amount of semiconductor and light intensity were varied to achieve the optimum rate of photodegradation. The results show that doping of bismuth ferrite by cobalt increases the rate of photocatalytic degradation due to narrowing of the band gap. Undoped bismuth ferrite has the highest catalytic activity in basic while the Co-doped catalyst in acidic medium. A tentative mechanism for the reaction has been proposed.

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Introduction

Natural water resources are becoming polluted as a result of human activities, including industries causing water pollution. Polluted water may have adverse effects on animals, plant life and humans. One of the sources of polluted water is textile industries, where waste water is colored due to dye components. Azo dyes are the largest and most important class of synthetic organic dyes. It has been observed that azo dyes are used more than 50 % of all dyes because of their chemical stability and versatility.¹ Azo dyes are not biodegradable by aerobic treatment processes,² and under anaerobic condition, they give potentially carcinogenic aromatic amines, which cause long-term health concerns.³ Evans Blue or T-1824 is an azo dye, which has a very high affinity for serum albumin.

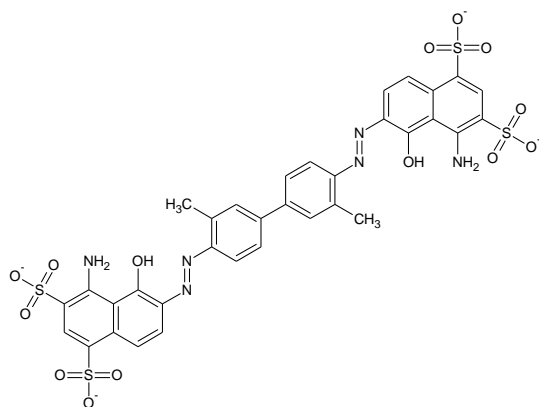


Figure 1. Structure of Evans blue

The synthetic dyes used in a wide-range of technologies,⁴ but their toxic nature generate demand for removal of dyes from wastewater. The most common methods used for the treatment of effluents from dyeing industries are membrane filtration, coagulation-flocculation, biological treatment, catalytic oxidation, sorption process, ion exchange, etc. These treatment methods for the removal of dyes from the waste water suffer from some or other drawbacks.

To develop an efficient method for converting such dyestuffs into harmless products, advanced oxidation processes (AOPs) have been widely studied in recent years. AOPs are promising methods for the treatment of wastewaters containing organic pollutants and involve two stages— first is the formation of strong oxidants and second is the reaction of these oxidants with organic contaminants in water. The efficiency of the AOP is maximized by the use of an appropriate catalyst and/or ultraviolet light.⁵⁻⁷ Photocatalytic degradation has been found to be a very efficient process for mineralization of organic pollutants. The photocatalyst is a substance, which is activated by absorbing a photon and is capable of accelerating a reaction without being consumed.⁸

Bismuth ferrite (BiFeO₃), is the most attractive and promising photocatalyst given photo-oxidation potential and chemical stability. Degradation of a non-biodegradable Evans blue has been carried out by the heterogeneous photo-Fenton-like processes using copper pyrovanadate (Cu₃V₂(OH)₂O₇·2H₂O) as a photocatalyst.⁹ They also observed photocatalytic degradation of Evans blue by heterogeneous photo-Fenton-like catalysts Cu₂V₂O₇ and Cr₂V₄O₁₃.¹⁰ Electrochemical processes for the degradation of Evans Blue based on Fenton's reaction chemistry.¹¹ The effect of Ag deposition on TiO₂ for the degradation of Evans blue.¹²

Bismuth ferrite (BFO) with different particle sizes and morphologies has been synthesized by various preparation methods such as sol-gel, hydrothermal and microwave hydrothermal and studied the effects of particle size and

presence of dopants on the photocatalytic activity,¹³ e.g. in photocatalytic degradation of tetracycline¹⁴ and methylene blue,^{15,16} malachite green,¹⁷ or methyl orange.^{18,19} The effect of various synthetic techniques and the presence of chelating agents on the properties BiFeO₃ in degradation of various organic contaminants such as Bisphenol A or Rhodamin B have also been studied.²⁰⁻²⁴ Now, we have studied the effect of Co-doping on the photocatalytic activity of BiFeO₃ in the degradation of Evans Blue dye.

Experimental

Synthesis of undoped and Co-doped bismuth ferrite

Undoped and Co-doped bismuth ferrite were synthesized by hydrothermal, and polyol methods, respectively and these were characterized by SEM-EDS techniques.²⁵ To a solution of Bi(NO₃)₃·5H₂O in ethylene glycol, a stoichiometric amount of Fe(NO₃)₃·9H₂O in distilled water was slowly added under vigorous stirring for 30 min. Aqueous ammonia (approx. 60 mL) was slowly dropped into the homogeneous solution to adjust pH > 10 by constant stirring to give brown colored precipitates. Then it was filtered, washed with water and dried at 80 °C. The resulting solid was calcined for 3 hours at 200 °C.

Co-doped bismuth ferrite was synthesized from Bi(NO₃)₃·5H₂O (4.85 g), Fe(NO₃)₃·9H₂O (4.04 g), and Co(NO₃)₂·6H₂O (0.24 g) taken in a beaker contains 36 mL of ethylene glycol. The solution was heated up to 200 °C for 90 min to remove the ethylene glycol.

Photocatalytic procedure

The photocatalytic activity of the catalyst was evaluated by measuring the rate of degradation of Evans blue. A stock solution of dye (1.0 × 10⁻³ M) was prepared by dissolving (0.0960 g) of dye in 100 mL of doubly distilled water. pH of the dye solution was measured by a digital pH meter (Systronics Model 335), and the desired pH of the solution was adjusted by the addition of standard 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. The reaction mixture containing 0.10 g photocatalyst was exposed to a 200 W tungsten lamp, and about 3 mL aliquot was taken out every 10 min. Absorbance (A) was measured at λ_{max}=620 nm. A water filter was used to cut off thermal radiations. The intensity of light was varied by changing the distance between the light source and reaction mixture, and it was measured by Suryamapi (CEL Model SM 201). The absorbance of the solution at various time intervals was measured with the help of spectrophotometer (Systronics Model 106).

It was observed that the absorbance of the solution decreases with increasing the time of exposure, which indicates that the concentration of Evans blue dye decreases with increasing time. The calculation of degradation efficiency (φ) was made by the relation:

$$\phi = 100 \frac{A - A_0}{A_0} \quad (1)$$

Here A₀ is initial absorbance, and A is absorbance after degradation of dye at time t. A plot of 1 + log A versus time was linear following pseudo-first order kinetics. Typical runs are given in Table 1 and graphically presented in Figure 2.

The rate constant was calculated by using the expression:

$$k = 2.303 \times \text{slope} \quad (2)$$

Table 1. Typical runs for photocatalytic degradation of Evans blue.

Time, min	Undoped BiFeO ₃		Co-doped BiFeO ₃	
	A	1 + log A	A	1 + log A
0.0	0.337	0.5276	0.339	0.5302
5.0	-	-	0.324	0.5105
10.0	0.317	0.5010	0.305	0.4843
15.0	-	-	0.294	0.4683
20.0	0.303	0.4814	0.279	0.4456
25.0	-	-	0.265	0.4232
30.0	0.288	0.4594	0.255	0.4065
35.0	-	-	0.239	0.3784
40.0	0.270	0.4314	0.231	0.3636
45.0	-	-	0.220	0.3424
50.0	0.258	0.4116	0.206	0.3139
60.0	0.245	0.3892	-	-
70.0	0.230	0.3617	-	-
80.0	0.220	0.3424	-	-
k, s ⁻¹	8.95 × 10 ⁻⁵		16.12 × 10 ⁻⁵	
φ, %	34.71		39.23	

Undoped BiFeO₃: pH=7.7, [Evans blue]=1.50×10⁻⁵ M, Semiconductor=0.10 g, Light intensity=70.0 mWcm⁻². **Co-doped BiFeO₃:** pH =3.5, [Evans blue]=2.00×10⁻⁵ M, Semiconductor=0.10 g, Light intensity=60.0 mWcm⁻²

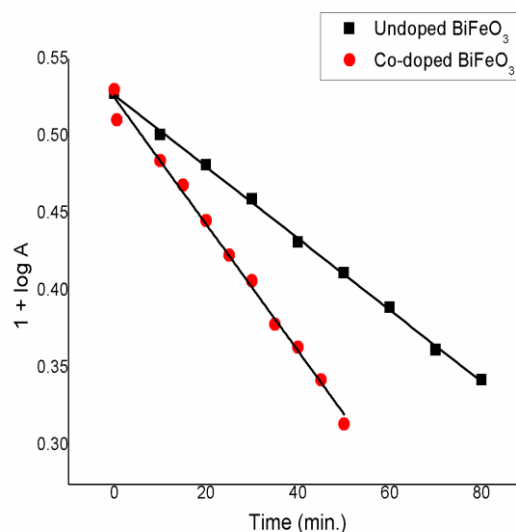


Figure 2. Typical run for photocatalytic degradation of Evans Blue

Results and discussion

Effect of parameters

The rate of degradation has been investigated in pH range 3.0–7.5 and 1.5–3.5 for undoped and Co-doped BiFeO₃, respectively. All other parameters were kept to be identical. The results are summarized in Table 2 and Figure 3. It was observed that with an increase in pH, the rate of reaction increases. After attaining the maximum value at pH 7.0 and pH 2.5 for undoped and Co-doped BiFeO₃, respectively, the rate decreases with a further increase in pH. In this case, the presence of scavenger i.e. 2-propanol does not affect the rate of reaction adversely and hence, it may be concluded that [•]OH radical does not participate in the degradation. It was interesting to observe that undoped BiFeO₃ was active in basic range (3.0–7.5) while Co-doped BiFeO₃ was active in acidic range (1.5–3.5).

Table 2. Effect of pH on photocatalytic degradation of Evans Blue

pH	Rate constant, $k \times 10^5 \text{ s}^{-1}$	
	BiFeO ₃	Co-doped BiFeO ₃
1.5	-	9.64
1.8	-	12.97
2.2	-	15.04
2.5	-	16.12
2.7	-	14.46
3.0	1.51	12.13
3.2	1.86	10.08
3.5	2.32	8.02
4.0	3.80	-
4.5	4.41	-
5.0	5.02	-
5.5	5.72	-
6.0	6.46	-
6.5	7.18	-
7.0	8.95	-
7.5	7.24	-
8.0	6.09	-

Undoped BiFeO₃: [Evans blue]= 1.50×10^{-5} M, semiconductor=0.10 g, Light intensity= 70.0 mWcm^{-2} . Co-doped BiFeO₃: [Evans blue]= 2.00×10^{-5} M, semiconductor=0.10 g, Light intensity= 60.0 mWcm^{-2}

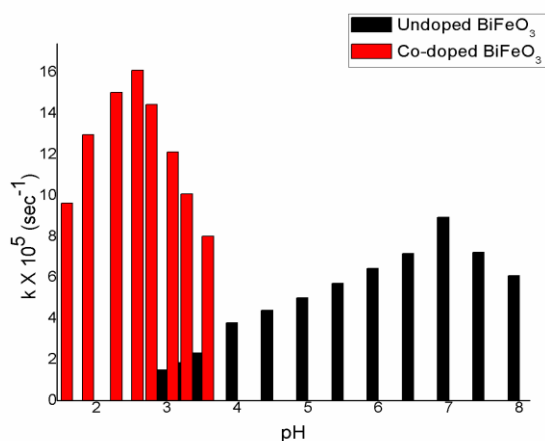


Figure 3. Effect of pH on photocatalytic degradation of Evans Blue

The effect of variation of concentration of Evans blue on its degradation rate has been observed in the range from 0.4×10^{-5} to 1.6×10^{-5} M for both undoped and Co-doped BiFeO₃ keeping all other parameters to be the same. The results are given in Table 3 and Figure 4. It has been observed that the rate of degradation increases with increasing concentration of dye up to 0.6×10^{-5} M for both, undoped and Co-doped BiFeO₃. Further increase in concentration beyond this limit results in a decrease in degradation rate. This may be explained on the basis that on increasing the concentration of dye, the reaction rate increases as more molecules of dyes were available but a further increase in concentration results appearing an internal filter effect which does not permit sufficient amount of light to reach the surface of the photocatalyst thus, decreasing the rate of photocatalytic degradation of Evans blue occurs.

Table 3. Effect of dye concentration on photocatalytic degradation of Evans Blue

[Evans blue] $\times 10^5$ M	Rate constant, $k \times 10^5, \text{ s}^{-1}$	
	BiFeO ₃	Co-doped BiFeO ₃
0.4	5.26	10.16
0.5	6.71	13.70
0.6	8.95	16.12
0.8	8.02	15.41
1.0	6.43	13.18
1.2	5.10	10.26
1.4	4.07	8.49
1.6	3.24	7.00

Undoped BiFeO₃: pH=7.7, semiconductor=0.10 g, light intensity= 70.0 mWcm^{-2} . Co-doped BiFeO₃: pH=3.5, semiconductor=0.10 g, light intensity= 60.0 mWcm^{-2}

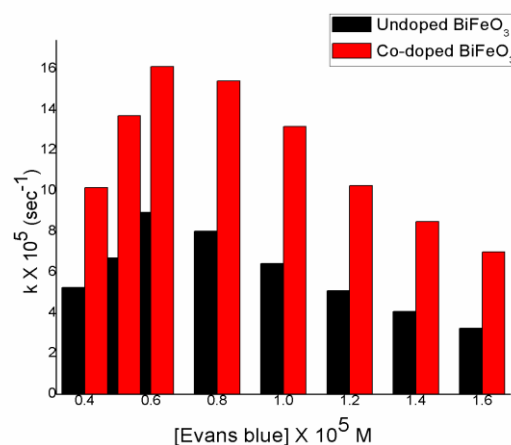


Figure 4. Effect of dye concentration on photocatalytic degradation of Evans Blue

The effect of variation of the amount of catalyst on the rate of dye degradation has been studied in the range from 0.02 to 0.14 g in 50 mL and the results are reported in Table 4 and Figure 5. It has been observed that with an increase in the amount of catalyst, the rate of degradation increases to a certain amount of catalyst i.e. 0.10 g, for both; undoped and Co-doped BiFeO₃. Beyond this point, the rate of reaction becomes virtually constant.

This behavior may be explained by the fact that with an increase in the amount of catalyst, the exposed surface area of catalyst will increase. Hence, the rise in the rate of reaction has been observed, but with further increase in the amount of catalyst beyond a limit, the only thickness of the layer (and not the exposed surface area) will increase at the bottom of the reaction vessel, which was completely covered by the catalyst.

Table 4. Effect of amount of catalyst on photocatalytic degradation of Evans Blue

Photocatalyst g in 50 mL	Rate constant, $k \times 10^5 \text{ s}^{-1}$	
	BiFeO ₃	Co-doped BiFeO ₃
0.02	3.43	5.02
0.04	5.50	7.04
0.06	6.19	8.42
0.08	7.57	13.09
0.10	8.95	16.12
0.12	8.90	16.09
0.14	8.96	16.13

Undoped BiFeO₃: pH = 7.7, [Evans blue] = 1.50×10^{-5} M, Light intensity = 70.0 mWcm^{-2} . Co-doped BiFeO₃: pH = 3.5, [Evans blue] = 2.00×10^{-5} M, Light intensity = 60.0 mWcm^{-2}

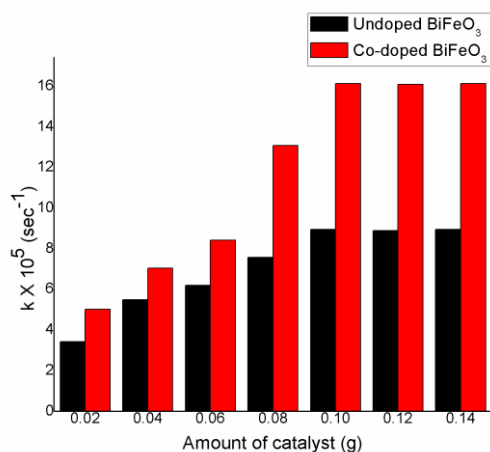


Figure 5. Effect of amount of catalyst on photocatalytic degradation of Evans Blue

The effect of light intensity on the rate of dye degradation was also studied by varying the intensity of light from 20.0 to 70.0 mWcm^{-2} . The observations are presented in Table 5 and Figure 6. The data indicate that with increasing light intensity, the rate of reaction increases and maximum rates were found at 70.0 and 60.0 mW cm^{-2} for undoped and Co-doped BiFeO₃, respectively. It may be explained on the basis that as the light intensity was increased, the number of photons striking per unit area also increases, resulting in higher rate of degradation for both. Further increase in the light intensity may start some thermal side reactions.

Mechanism

On the basis of the experimental observations, a tentative mechanism has been proposed for the degradation of Evans blue in the presence of bismuth ferrite (undoped and Co-doped).

Table 5. Effect of light intensity on photocatalytic degradation of Evans Blue

Light intensity, mW cm^{-2}	Rate constant, $k \times 10^5 \text{ s}^{-1}$	
	BiFeO ₃	Co-doped BiFeO ₃
20.0	3.83	10.74
30.0	4.02	11.51
40.0	4.47	13.81
50.0	5.16	14.58
60.0	5.75	16.12
70.0	8.95	15.35

Undoped BiFeO₃: pH = 7.7, [Evans blue] = 1.50×10^{-5} M, Semiconductor = 0.10 g. Co-doped BiFeO₃: pH = 3.5, [Evans blue] = 2.00×10^{-5} M, Semiconductor = 0.10 g

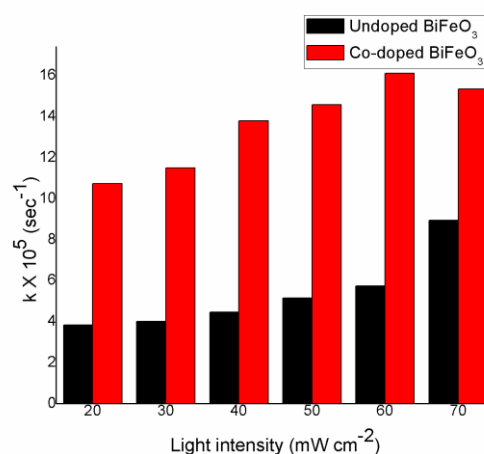
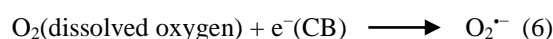
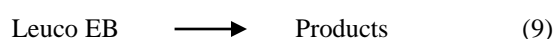
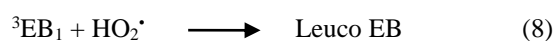
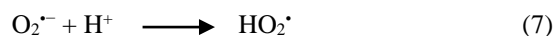


Figure 6. Effect of light intensity on photocatalytic degradation of Evans Blue

Evans blue absorbs radiations of suitable wavelength and transforms to singlet then triplet excited state (intersystem crossing, ISC). The semiconductor also absorbs light to excite an electron from its valence band (VB) to its conduction band (CB), which will be abstracted by dissolved oxygen to generate $\text{O}_2^{\cdot-}$ (in basic media, undoped BiFeO₃) or HO_2^{\cdot} radicals (in acidic medium, Co-doped BiFeO₃). These radicals can oxidize the dye to its leuco form ultimately degrading to products



In acidic medium-



In basic medium-



Carrying out the reaction in the presence of $\cdot\text{OH}$ radical scavenger, 2-propanol, the reaction rates were unaffected. This unambiguously shows that there was no involvement of $\cdot\text{OH}$ radicals in the reactions as an active oxidizing species.

Conclusion

At optimal conditions, the rate of degradation of Evans blue for undoped and the Co-doped BiFeO_3 system was obtained as 8.95×10^{-5} and $16.12 \times 10^{-5} \text{ sec}^{-1}$, respectively. Thus, the doping of BiFeO_3 by cobalt ions enhances the rate of photodegradation of Evans blue almost 1.8 times (80% increase).

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