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Photocatalytic degradation of methylene blue using undoped and Co-doped bismuth ferrite

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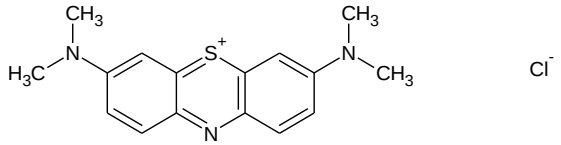
ABSTRACT

This work deals with the degradation of non-biodegradable methylene blue using undoped and Co-doped bismuth ferrite as photocatalyst.The effect of various parameters such as pH, concentration of dye, amount of photocatalyst and light intensity on the reaction rate has been studied. The rate of photodegradation of dye was monitored spectrophotometrically. The results show that doping of bismuth ferrite by cobalt increases the rate of photocatalytic degradation due to narrowing of band gap. Mechanism of the reaction has been tentatively discussed.

Keywords: Methylene blue, Bismuth ferrite, Co-doped bismuth ferrite, Photocatalytic degradation.

INTRODUCTION

The surroundings of a physical system that may interact with the system by exchanging mass, energy, or other properties is called environment. Life is not possible without water in world. In general, water accounts almost 70 to 90% of the weight of living organisms. One cannot imagine life without clean water. Thus, the quality of this valuable resource will directly influence the normal life of human beings. On the other hand, there is no raw material in the world, which is more than water. In general, water pollution refers to the degradation of water quality.



Structure of Methylene blue

Colored solutions containing dyes from industrial effluents may cause harmful effects on human beings, animals and plants, due to photosensitization and photodynamic damage. The color in the wastewater is an obvious indicator of water pollution due to dyes and pigments [1, 2]. Dyes also affect photosynthetic activity in water due to reduced light penetration and may be toxic to some aquatic lives [3]. Increasing

demand and shortage of clean water sources due to the rapid development of industrialization, population growth and long-term droughts have become an issue worldwide.Several methods have been tried from time to time for the treatment of wastewater from dyeing industries, out of which, most common are biological treatment, catalytic oxidation, membrane filtration, coagulation-flocculation, ion exchange, etc. These treatment methods for the removal of dyes from the waste water suffer from some or another drawback.

Chemical oxidation process is an alternative technology that can be successfully applied for the degradation of a broad spectrum of organic compounds [4, 5]. Among these, Advanced Oxidation Processes (AOP's) are innovative environmental remediation technologies that are gaining importance for degradation of most of the organic pollutants [6]. AOPs are promising techniques to efficiently and effectively convert non-biodegradable compounds into biodegradable or less harmful substances. Several types of AOPs have been developed. These processes refer to a set of chemical treatment procedures designed to remove organic and inorganic materials in waste water by oxidation.

Photocatalysis can be generally used to describe a process, in which light is used to activate a substance, the photocatalyst, which modifies the rate of a chemical reaction without being involved itself in the chemical transformation. An important advantage of photocatalytic process is that this may be carried out at low or ambient temperature and usually leads to the complete mineralization of pollutants [7]. The photocatalytic method of effluent treatment involves the exposure of polluted water to light in the presence of photocatalyst. The photocatalytic process not only enhances the rate of degradation, but also provides an oxidising as well as reducing environment to the substances simultaneously. The photocatalyic technique has proved to be faster, economical and environment friendly than the traditional technique of treating industrial effluents. Therefore, photocatalytic methods for wastewater treatment seems to the most promising and ecofriendly process now-a-days.

Semiconductor materials having narrow gap between valence band and conduction band are used as photocatalysts. An activation is achieved with the absorption of photons by the semiconductor particle possessing enough energy to promote an electron (e^-) from its valence band to the conduction band, creating hole (h^+) in the valence band that will act as oxidizing sites [8].

Urea assisted hydrothermal synthesis of pure $BiFeO_3$ at 120°C was carried out by Wei et al. [9]. These BFO microcrystals exhibit efficient photocatalytic activity under visible light irradiation. Wang et al. [10] observed effects of chelating agents on the catalytic degradation of bisphenol A (BPA) in the presence of $BiFeO_3$ nanoparticles as a heterogeneous photocatalyst and H_2O_2 as a green oxidant. Kaur et al. [11] observed that undoped $BiFeO_3$ nanoparticles have less photocatalytic ability but considerably enhanced photocatalytic activity was obtained by adding dopant La^{3+} in $BiFeO_3$ nanoparticles for photocatalytic degradation of azo-dye RB-5.

Li et al. [12]have used a wet chemical technique to produce $BiFeO_3$ crystals with a wide range of sizes and morphologies. It was concluded that the variation in particle size and morphology had a substantial effect on its band gap. A change in band gap from 1.80 to 2.19 eV has been observed with a variation in particle size. It has been used for photocatalytic decomposition of Congo red.

Wang et al. [13] studied the photocatalytic activity of the $BiFeO_3$ nanoparticles for the degradation of rhodamin B as a model pollutant in aqueous solution. Dai et al. [14] synthesized $BiFeO_3$ nanoparticles using polyacrylamide gel method. $BiFeO_3$-graphene nanocomposites were prepared by mixing $BiFeO_3$ nanoparticles and graphene into ethanol followed by thermal drying at 60°C. The photocatalytic experiments indicated that the $BiFeO_3$-graphene nanocomposites exhibit higher photocatalytic activity for the degradation of methyl orange under simulated sunlight irradiation than naive $BiFeO_3$ nanoparticles. It is because of the fact that the photogenerated electrons are captured by graphene, leading to an increased

availability of h^+ for the photocatalytic reaction. Zhang et al. [15] investigated the effect of Gd doping on photocatalytic activity of $BiFeO_3$ while Xue et al. [16] observed the photocatalytic degradation of tetracycline with $BiFeO_3$ prepared by a simple hydrothermal method. Patil et al. [17]studiedphotocatalytic degradation of acid violet 19 dye using photocatalyst PANI–Fe_3O_4 whereas Soltani and Entezari[18] reported the degradation of methylene blue by bismuth ferrite nanoparticles under sunlight irradiation.Mohan et al. [19]also reported the degradation of methylene blue under the irradiation of direct sunlight by Ag NPs-decorated BFO particulates. Jain et al. [20] reported photocatalytic degradation of malachite green by Ti^{4+} doped $BiFeO_3$ prepared by low temperature solution combustion method. Xie et al. [21] synthesized single phase of three bismuth ferrites ($BiFeO_3$, $Bi_{25}FeO_{40}$, $Bi_2Fe_4O_9$) and used these for degradation of methyl orange while Liu et al. [22] synthesized high purity $BiFeO_3$ nanoparticles of a rhombohedrally distorted perovskite structure, prepared by chemical coprecipitation method and used these also for the degradation of methyl orange.

MATERIALS AND METHODS

Synthesis of undoped and Co-doped bismuth ferrite: Undoped bismuth ferrite and Co-doped bismuth ferrite were synthesized by hydrothermal method and polyol method respectively and these were characterized by SEM-EDS techniques [23].

Photocatalytic degradation: The photocatalytic activity of photocatalyst was evaluated by measuring the rate of degradation of methylene blue. Stock solution of dye (1.0×10^{-3} M) was prepared by dissolving (0.0373 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 15 min. Absorbance (A) of reaction mixture was measured at λmax 650 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 solution at various time intervals was measured with the help of spectrophotometer (Systronics Model 106).

RESULTS AND DISCUSSION

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

$$Degradation\ \% = \frac{A_0 - A}{A_0} \times 100 \qquad (1)$$

Here A_o 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 Fig.1. The rate constant was calculated by using the expression:

$$k = 2.303 \times slope \qquad (2)$$

Table 1. Typical runs for photocatalytic degradation of methylene blue

Undoped $BiFeO_3$: pH = 7.7, [Methylene blue] = 1.50×10^{-5} M, Semiconductor = 0.10 g, Light intensity = 70.0 $mWcm^{-2}$

Co-doped $BiFeO_3$: pH = 3.5, [Methylene blue] = 2.00×10^{-5} M, Semiconductor = 0.10 g, Light intensity = 40.0 $mWcm^{-2}$

	Undoped $BiFeO_3$		**Co-doped $BiFeO_3$**	
Time(min.)	**Absorbance (A)**	**1 + logA**	**Absorbance (A)**	**1 + logA**
0.0	0.429	0.6325	0.676	0.8299
15.0	0.410	0.6125	0.624	0.7952
30.0	0.390	0.5911	0.596	0.7752
45.0	0.374	0.5729	0.565	0.7520
60.0	0.350	0.5541	0.534	0.7275

75.0	0.335	0.5250	0.514	0.7109
90.0	0.325	0.5119	0.485	0.6857
105.0	0.311	0.4928	0.460	0.6627
120.0	0.286	0.4570	0.439	0.6425
Rate constant (k) sec^{-1}	**5.11×10^{-5}**		**5.75×10^{-5}**	
Degradation efficiency (%)	33.33		35.06	

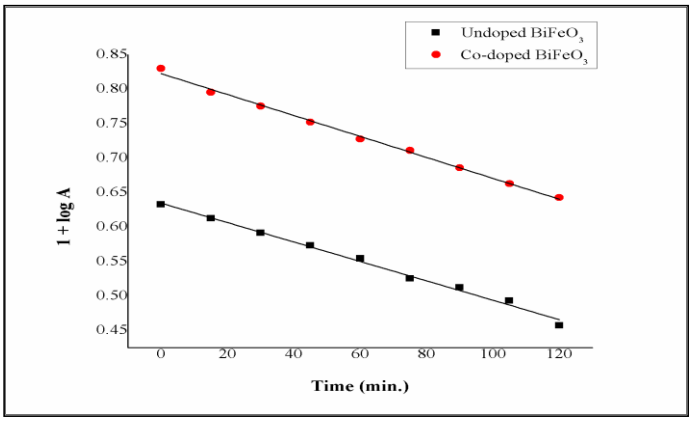


Fig 1. Typical runs

Effect of pH: The effect of pH on the rate of degradation has been investigated in pH range 7.0–8.0 and 2.0-4.5 for undoped and Co-doped $BiFeO_3$, respectively keeping all other parameters identical. The results are summarized in Table 2 and presented in Fig. 2. It was observed that rate of reaction increases with an increase in pH. After attaining the maximum value at pH 7.7 and pH 3.5 for undoped and Co-doped $BiFeO_3$, respectively, 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 $^{\bullet}OH$ radical does not participate in the degradation as an active oxidizing species. It was interesting to observe that undoped $BiFeO_3$ was active in basic range (7.0-8.0) while Co-doped $BiFeO_3$ was active in acidic range (2.0-4.5).

Table 2. Effect of pH

Undoped $BiFeO_3$: [Methylene blue] = 1.50×10^{-5} M, Semiconductor = 0.10 g, Light intensity = 70.0 $mWcm^{-2}$
Co-doped $BiFeO_3$: [Methylene blue] = 2.00×10^{-5} M, Semiconductor = 0.10 g, Light intensity = 40.0 $mWcm^{-2}$

pH	**Rate constant (k) × 10^5 (sec^{-1})**	
	$BiFeO_3$	**Co-doped $BiFeO_3$**
2.0	-	2.23
2.5	-	2.87
3.0	-	5.52
3.5	-	**5.75**
4.0	-	4.15
4.5	-	2.55
7.0	3.25	-
7.2	3.65	-
7.5	4.32	-
7.7	**5.11**	-
8.0	4.35	-

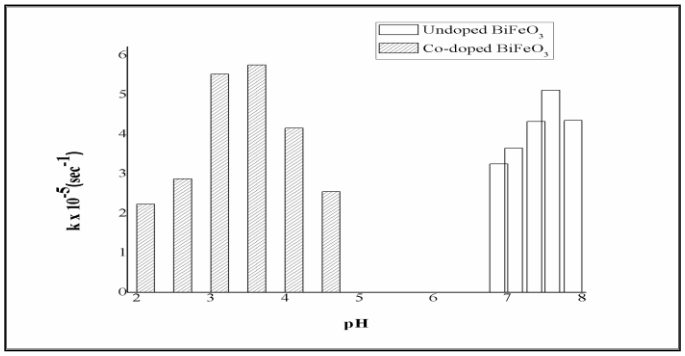


Fig 2. Effect of pH

Effect of concentration of dye: The effect of variation of concentration of methylene blue on its degradation rate has been observed in the range from 1.0×10^{-5} to 3.5×10^{-5} M for both; undoped and Co-doped $BiFeO_3$ keeping all other parameters same. The results are given in Table 3 and diagrammatically presented in Fig. 3. It has been observed that the rate of degradation increases with increasing concentration of dye up to 1.5×10^{-5} and 2.0×10^{-5} M for undoped and Co-doped $BiFeO_3$, respectively. 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 in decreasing the rate of reaction. This may be explained on the basis that after a particular concentration, the dye, it may start acting as an internal filter itself and will not permit the sufficient light intensity to reach the surface of the photocatalyst at the bottom of reaction vessel and thus, decreasing the rate of photocatalytic degradation of methylene blue.

Table 3. Effect of dye concentration

Undoped $BiFeO_3$: pH = 7.7, Semiconductor = 0.10 g, Light intensity = 70.0 $mWcm^{-2}$

Co-doped $BiFeO_3$: pH = 3.5, Semiconductor = 0.10 g, Light intensity = 40.0 $mWcm^{-2}$

[Methylene blue] × 10^5 M	**Rate constant (k) × 10^5 (sec^{-1})**	
	$BiFeO_3$	**Co-doped $BiFeO_3$**
1.0	4.55	5.27
1.5	**5.11**	5.43
2.0	3.88	**5.75**
2.5	3.62	5.27
3.0	3.37	4.30
3.5	3.06	4.01

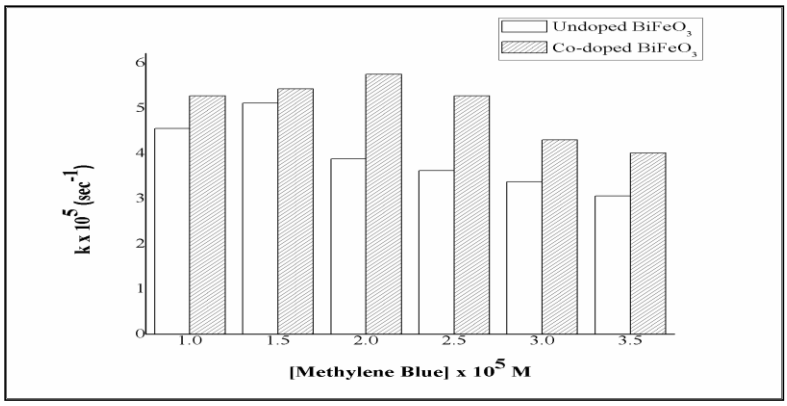


Fig 3. Effect of dye concentration

Effect of amount of photocatalyst: The effect of variation of the amount of photocatalyst on the rate of dye degradation has been observed in the range from 0.02 to 0.14 g and the results are reported in Table 4 and presented in Fig. 4. It has been observed that with an increase in the amount of photocatalyst, the rate of degradation increases to a certain amount of photocatalyst i.e. 0.10 g, for both; undoped and Co-doped $BiFeO_3$. Beyond this point, the rate of reaction becomes almost constant. This behaviour may be explained by the fact that with an increase in the amount of photocatalyst, the exposed surface area of photocatalyst will increase. Hence, the rise in the rate of reaction has been observed, but with further increase in the amount of photocatalyst beyond a limit, only the thickness of the layer (and not the exposed surface area) will increase at the bottom of reaction vessel, which was completely covered by the photocatalyst.

Table 4. Effect of amount of photocatalyst
Undoped $BiFeO_3$: pH = 7.7, [Methylene blue] = 1.50×10^{-5} M, Light intensity = 70.0 $mWcm^{-2}$
Co-doped $BiFeO_3$: pH = 3.5, [Methylene blue] = 2.00×10^{-5} M, Light intensity = 40.0 $mWcm^{-2}$

Photocatalyst (g)	**Rate constant (k) × 10^5 (sec^{-1})**	
	$BiFeO_3$	**Co-doped $BiFeO_3$**
0.02	1.81	4.05
0.04	2.26	4.21
0.06	3.37	4.76
0.08	3.85	5.36
0.10	**5.11**	**5.75**
0.12	5.09	5.72
0.14	5.08	5.74

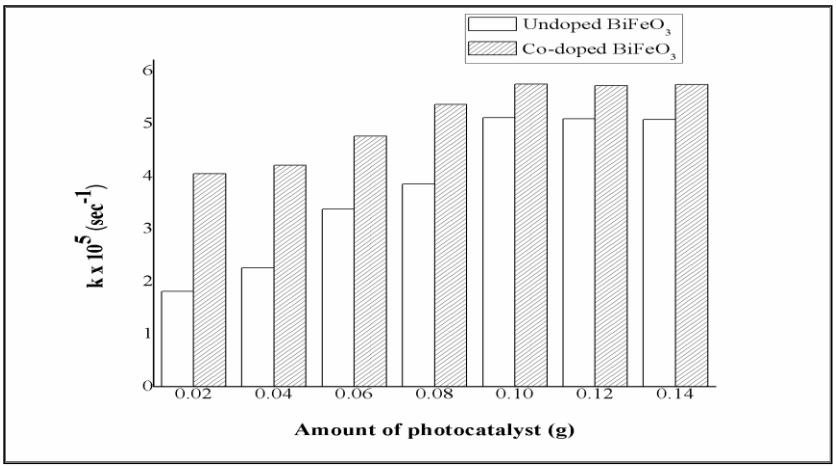


Fig 4. Effect of amount of photocatalyst

Effect of light intensity: The effect of light intensity on the rate of degradation of dye 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 in Fig. 5. The data indicate that with increasing light intensity, the rate of reaction increases and maximum rates were found at 70.0 mW cm^{-2} and 40.0 mW cm^{-2} for undoped and Co-doped $BiFeO_3$, 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 and hence, higher intensities of light have been avoided.

Table 5. Effect of Light Intensity
Undoped $BiFeO_3$: pH = 7.7, [Methylene blue] = 1.50×10^{-5} M, Semiconductor = 0.10 g
Co-doped $BiFeO_3$: pH = 3.5, [Methylene blue] = 2.00×10^{-5} M, Semiconductor = 0.10 g

Light Intensity (mW cm^{-2})	Rate constant (k) × 10^5 (sec^{-1})	
	$BiFeO_3$	Co-doped $BiFeO_3$
20.0	2.87	4.47
30.0	3.19	4.79
40.0	3.51	**5.75**
50.0	4.15	5.43
60.0	4.47	4.79
70.0	**5.11**	4.15

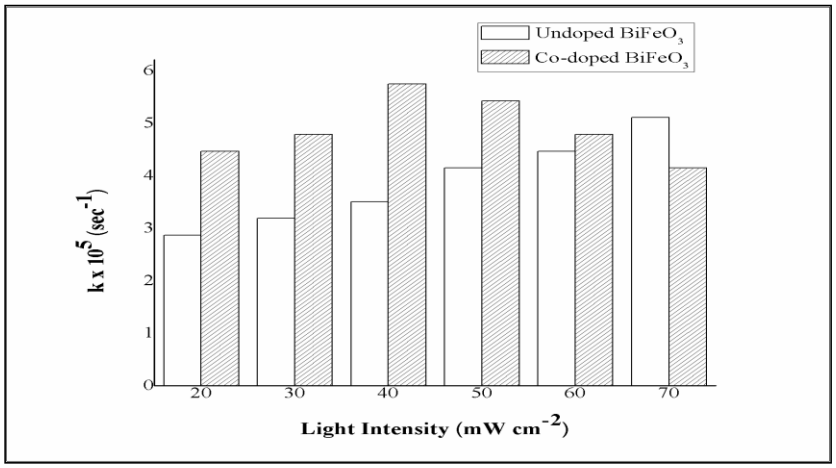


Fig 5. Effect of light intensity

Mechanism: On the basis of the experimental observations, a tentative mechanism has been proposed for the degradation of methylene blue in presence of bismuth ferrite (undoped and doped). Methylene blue absorbs radiations of suitable wavelength and it is excited to its first excited singlet state; which is then converted to its triplet state through inter system crossing (ISC). The semiconductor also absorbs light to excite an electron from its valence band (VB) to its conduction band (CB), leaving behind a hole in the valence band. An electron from the conduction band will be abstracted by dissolved oxygen to generate $O_2^{\bullet-}$ radical, which will oxidize dye to its leuco form ultimately degrading to products in case of undoped $BiFeO_3$. But in case of Co-doped $BiFeO_3$, the optimum pH was 3.5 (acidic) and $O_2^{\bullet-}$radical anion is unstable in acidic medium. It will form $HO_2^{\bullet}$ radical by combing with H^+ ion and this $HO_2^{\bullet}$ radical will oxidize the dye to its leuco form, which ultimately degrades into products.

$$^1MB_0 \xrightarrow{h\nu} {}^1MB_1 \quad (3)$$

$$^1MB_1 \xrightarrow{ISC} {}^3MB_1 \quad (4)$$

$$BiFeO_3 \xrightarrow{h\nu} BiFeO_3\ (h^+\ (VB) + e^-(CB)) \quad (5)$$

$$O_2\ (\text{dissolved oxygen}) + e^-\ (CB) \rightarrow O_2^{\bullet-} \quad (6)$$

In acidic medium-

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet} \quad (7)$$

$$^3MB_1 + HO_2^{\bullet} \rightarrow \text{Leuco MB} \quad (8)$$

Leuco MB→Products (9)

In basic medium-

$^{3}MB_1 + O_2^{\bullet-} \rightarrow$ Leuco MB (10)

Leuco MB →Products (11)

There was no involvement of $^{\bullet}OH$ radicals in the reaction as an active oxidizing species. It was confirmed by carrying out the reaction in the presence of $^{\bullet}OH$ radical scavenger, 2-propanol, where the reaction rates remain almost unaffected.

APPLICATIONS

The doping of $BiFeO_3$ by cobalt ions useful to enhance the rate of photocatalytic activity of bismuth ferrite and in turn degradation of Methylene Blue.

CONCLUSIONS

At optimal conditions, rate of degradation of methylene blue for undoped and Co-doped $BiFeO_3$ system was obtained as $5.11 \times 10^{-5}$and $5.75 \times 10^{-5}sec^{-1}$, respectively. Thus, the doping of $BiFeO_3$ by cobalt ions enhances the rate of photocatalytic activity of bismuth ferrite and in turn degradation of blue.

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