

Photocatalytic activity of $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ for degradation of methyl orange under UV irradiation

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Abstract

BiFeO_3 (bismuth ferrite) nanoparticles are highly significant in the removal or degradation of medical pollutants and industrial wastewater due to their structural and photocatalytic properties. In this study, cobalt doped BiFeO_3 nanoparticles, $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ ($X=0.0, 0.01, 0.03, 0.05$) were synthesized using the sol-gel method, and the effects of cobalt substitution on their physical properties were investigated. X-ray diffraction (XRD) spectroscopy was used for the identification and analysis of these materials, while FT-IR spectroscopy confirmed the integrity of the synthesized samples. The catalytic efficiency of $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ nanoparticles for the photocatalytic degradation of methyl orange, one of the primary polluting dyes in industrial wastewater, was measured using UV/Vis spectroscopy. Various parameters, including dye concentration, pH, irradiation time, and nanoparticle amount, were studied, and optimal conditions were reported. The methyl orange degradation results for a prepared 350 ml dye solution with 0.1 g catalyst and 0.5 ml hydrogen peroxide at pH = 2 over 120 minutes for $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ ($X=0.0, 0.01, 0.03, 0.05$) nanoparticles were 60.48%, 20.67%, 48.55%, and 50.42%, respectively.

Keywords: bismuth ferrite – photocatalyst – industrial wastewater – methyl orange – sol-gel

1. Introduction

Water is the most essential and fundamental resource for the human population worldwide. People need water for drinking, cooking, washing, agricultural irrigation, and various socio-economic activities. However, only about 1% of water is suitable for human consumption[1]. Each year, more than 3.5 million people lose their lives due to waterborne diseases. Treating contaminated water can help alleviate these concerns, making clean and accessible water available[2]. Lately, the discharge of industrial organic dye molecules has emerged as one of the major environmental pollutants among thousands of wastewater contaminants[3]. Industries such as textiles, paper, and rubber produce significant volumes of these pollutants, which are characterized by toxicity, low biodegradability, and harmful effects on human health and environmental sustainability. These pollutants have been identified as carcinogenic agents, intensifying their hazardous nature[4]. Given the rising environmental concerns, research groups are increasingly focused on exploring methods to remove and reduce the presence of vibrant dyes in wastewater[5, 6]. Methyl orange is an anionic dye with an azo structure that is easily absorbed

by the skin and accumulates in the body, as shown in Figure 1. The azo group ($\text{N}=\text{N}$) can cause allergic

reactions upon skin contact, toxicity through inhalation and ingestion, low degradability, and harmful effects on aquatic life. Therefore, the development of new materials for the removal of such dyes has gained attention over the past decade.

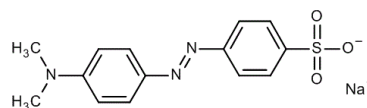


Fig. 1. Chemical structure of methyl orange

Advancements in science and technology have paved the way for the use of photocatalytic degradation as a viable mechanism for removing dye molecules from contaminated water sources[7]. Bismuth ferrite (BiFeO_3), with its rhombohedral perovskite structure, is an important and versatile material due to its diverse properties and applications. BiFeO_3 exhibits various

interesting properties, such as multiferroic nature due to its magnetic and ferroelectric behavior at room temperature, thermodynamic stability, superconducting and redox behavior, excellent chemical stability, and more[8, 9]. Photocatalysis is an advanced oxidation process that is widely used for the degradation of various pollutants. Bismuth ferrite (BiFeO_3) is extensively utilized for the degradation of organic pollutants under UV/Vis light[10, 11]. The unique properties of BiFeO_3 make it an effective photocatalyst for the degradation of organic pollutants. Extensive research efforts have been devoted to leveraging the diverse capabilities of BiFeO_3 for efficient and sustainable photocatalysis[12, 13]. In the removal of pollutants, photocatalysis finds its application in the degradation of contaminants in industrial wastewater and can serve as a cost-effective treatment process[14]. Due to its exceptional efficiency, minimal byproduct production, relatively economical nature, and simple operational methods, it is widely recognized as a highly sustainable approach[6, 15]. Among various ferrite materials, cobalt ferrite has garnered significant interest. Cobalt ferrite is preferred over other ferrites due to its high chemical stability, soft magnetic behavior, superior electromagnetic performance, and hardness[16, 17]. In this study a series of cobalt doped bismuth ferrite (BiFeO_3) nanostructures were synthesized via the sol-gel method to evaluate their photocatalytic efficiency for degrading hazardous dyes under UV/Vis light irradiation. Photocatalytic experiments demonstrated that methyl orange (MO) was effectively degraded within 120 minutes. This finding highlights the potential of BiFeO_3 as a promising candidate for the degradation of various organic pollutants. Bismuth ferrite (BiFeO_3) is considered one of the most attractive and promising photocatalysts due to its high oxidative potential and excellent chemical stability[4, 18]. By incorporating cobalt into its structure, the material was investigated through UV/Vis spectroscopy for the removal of methyl orange dye from industrial wastewater. The effects of various operational parameters, including irradiation time, dye concentration, pH, catalyst dosage, and hydrogen peroxide (H_2O_2) concentration, were systematically studied, and the optimal conditions for efficient photocatalysis were determined.

2- Experimental

2-1- Chemicals

Iron(III) nitrate nonahydrate (99%), bismuth(III) nitrate pentahydrate (99%), methyl orange, and tartaric acid (99%) were obtained from MERCK. Cobalt(II) nitrate (98%) was sourced from FLUKA, nitric acid (65%) was provided by RIEDEL-DEHA, and hydrogen peroxide 37% Neutron was also obtained.

2-2- Instruments

Samples were prepared in the form of solid discs. The vibrational spectrum (FT-IR) of the samples was analyzed and recorded using the spectrophotometer (Avatar 370 FT-IR, Thermo Nicolet) in the range of 400-4000 cm^{-1} . The analysis of crystalline structures and material identification was conducted using X-ray diffraction (XRD) with the Philips Analytical X-Ray B.V. model. The oven (Pars Azma Co) was used for drying samples, while the furnace (SCI FINETECH) was utilized for drying samples at higher temperatures. Solutions were stirred and heated using a magnetic stirrer (Heidolph MR Hei), and pH measurements were performed with a pH meter (MetRoHM). A digital balance (Sartorius) with an accuracy of 0.0001 grams was employed for weighing materials. For analyzing the concentration of methyl orange dye in this study, a UV-Vis spectrophotometer (Varian, Cary Bio50) was used. Additionally, a photochemical device equipped with a 250-watt mercury lamp was utilized for irradiating the samples and monitoring changes in the solution.

2-3- Synthesis of BiFeO_3 and $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$

Compounds by the sol-gel method

2-3-1- Synthesis of BiFeO_3

Bismuth ferrite (BiFeO_3) was synthesized using the sol-gel method, utilizing bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) as the precursor materials. The synthesis procedure consisted of several key steps to form the perovskite structure of BiFeO_3 . Initially, the required amounts of bismuth nitrate and iron(III) nitrate were accurately weighed and dissolved in either ethylene glycol or distilled water. The solution was stirred continuously to ensure homogeneity. Once the precursors were completely dissolved, acetic acid was added dropwise to the solution to adjust the pH. The pH was carefully controlled to facilitate the formation of a gel. Upon successful pH adjustment, the solution was heated to induce gelation. The heating process promoted the transformation of the solution into a gel-like substance. Following gel formation, the material was dried at 100°C to remove the solvent, leaving behind a solid gel precursor. The dried gel was then subjected to calcination at 600°C for 4 hours. This high-temperature treatment allowed the crystallization of BiFeO_3 . After the calcination process, the sample was allowed to cool to room temperature, resulting in the formation of BiFeO_3 .

2-3-2 Synthesis of $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$

$\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ nanoparticles ($x=0.01, 0.03, 0.05$) were synthesized through the sol-gel process, utilizing tartaric acid for the preparation of the photocatalyst nanoparticles. To synthesize the $\text{BiFe}_{1-x}\text{Co}_x\text{O}_3$ compound, 20 milliliters of deionized distilled water was added to a beaker and heated to 60 degrees Celsius. After that, nitric acid was added, and once it dissolved, bismuth nitrate (2.52 grams – $5\text{H}_2\text{O}$), iron(III) nitrate (1.99 grams

– 9H₂O), and cobalt nitrate in amounts of (0.01, 0.05, 0.07) were added. Once the salts were completely dissolved, tartaric acid (1.5 grams) was introduced to form a yellowish-brown homogeneous solution. By adding ammonia, the solution turned lemon-yellow, and the pH reached 3. The solution was placed in an oven at 80 degrees Celsius, with the temperature increased by 20 degrees Celsius every 8 hours until it reached 120 degrees. After that, the temperature was raised by 10 degrees Celsius every 30 minutes and maintained at 200 degrees Celsius for 2 hours. The powdered materials were transferred to a crucible and placed in a furnace at 400 degrees Celsius for 3 hours. The cooled materials were then washed with acid, and the crucible was returned to the furnace at 650 degrees Celsius for 4 hours before being analyzed using X-ray diffraction (XRD).

2-4- Photocatalytic Experiment Method

The photocatalytic activity of BiFeO₃ and BiFe_{1-x}Co_xO₃ (X= 0.00, 0.01, 0.03, 0.05) nanoparticles were evaluated in an aqueous solution of methyl orange under mercury lamp irradiation. The first step involved calibration to determine the initial concentration of methyl orange, and a concentration of 3 mg L⁻¹ was selected for the experiments. Next, 300 ml of methyl orange at a concentration of 3 mg L⁻¹ was transferred into a 600 ml beaker. After adding H₂O₂ and the Nano catalyst to the beaker, various pH levels were adjusted using NaOH and HCl. In the next step, the beaker was placed inside the photoreactor (a chemical reactor device that brings photons, the photocatalyst, and reactants into contact). The solution was stirred at 750 rpm under dark conditions for 30 minutes. Every 20 minutes, 3 ml of the solution was drawn with a pipette and transferred to a centrifuge tube. To settle the suspended photocatalyst particles, the mixture was centrifuged at 4000 rpm for 10 minutes, and the absorbance spectrum of the solution was recorded using a UV-Vis spectrophotometer. The mercury lamp in the photochemical reactor was switched on to initiate the photocatalytic process. At predetermined time intervals, the absorbance of the methyl orange solution was measured at its maximum wavelength of 461 nm. The photocatalytic degradation efficiency was calculated using Equation 1, based on the percentage reduction in dye concentration, where C₀ and C_t represent the initial concentration and the concentration at a given irradiation time (0–120 minutes), respectively.

$$\text{Methyl Orange Degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

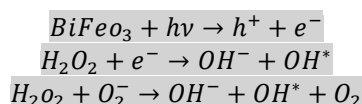
Equation 1 - Percentage Degradation of Methyl Orange

2-5- Preparation of Methyl Orange Solution

A specified amount of methyl orange was diluted to volume in a flask, transferred to a beaker, and a certain amount of BiFeO₃ adsorbent was added. Then, 0.5 ml of

hydrogen peroxide was added, and finally, the solution was tested under various parameters.

The increase in H₂O₂ volume resulted in a higher generation of electron-hole pairs and reactive species. Notably, the photodegradation efficiency of Methyl Orange was significantly enhanced, primarily due to the increased formation of hydroxyl (OH) radicals on the surface of BiFeO₃ or doped BiFeO₃, as described by the following equation 2:



Equation 2 - Photocatalytic mechanism of Methyl Orange degradation via electron-hole pair separation and hydroxyl radical formation on BiFeO₃ catalysts.

This catalytic mechanism efficiently suppresses the recombination of photogenerated electron-hole pairs, thereby enhancing the overall photocatalytic performance in the degradation of Methyl Orange.

3- Results and discussion

3-1-Investigation of Factors Affecting the Photocatalytic Activity of BiFe_{1-x}Co_xO₃ in Methyl Orange Degradation

The degradation of methyl orange dye was measured and tested under the influence of irradiation time, pH, and nanoparticle amount, and then the optimized values were reported.

3-2-Effect of time

A specified amount of the prepared methyl orange solution was poured into a beaker, an appropriate number of nanoparticles was added, and after adding H₂O₂, the pH was adjusted. The prepared solution was transferred to the photochemical apparatus, and the degradation rate was measured at different times and reported in Figure 2.

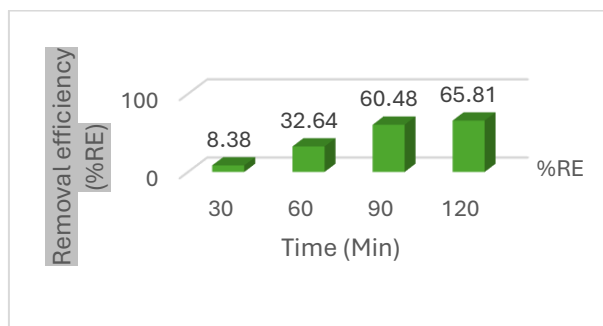
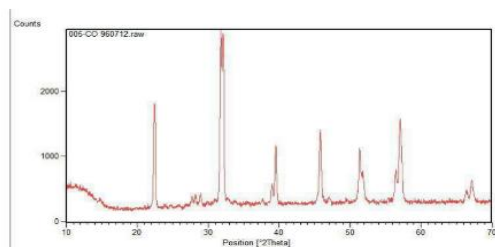


Fig. 2. Effect of different time intervals (30, 60, 90, 120 minutes) on the degradation of methyl orange dye under experimental conditions of 300 ml of methyl orange solution with a concentration of 3 mg L⁻¹, 0.1 g of nanoparticles, and 0.5 ml of hydrogen peroxide at pH = 2.



Catalyst	Source	pH	Time (min)	%RE	Ref
CuO	Sunlight	2	30	98.9	[19]
SiO ₂	UV	7	90	95	[20]
TiO ₂	UV	2	45	98	[21]
Fe ₂ O ₃	Visible	3	120	99	[22]
This Work	UV-A	2	120	60.4	-

Table 1 : Some previous studies

5. Conclusion

In this study, BiFe_{1-x}Co_xO₃ nanoparticles (X = 0.0, 0.01, 0.03, 0.05) were synthesized via the sol-gel method and evaluated as photocatalysts for the degradation of methyl orange dye. The effects of cobalt doping in the BiFeO₃ structure were shown to be rather different for structural characteristics and photocatalytic performance of the nanoparticles. XRD analysis verified the development of a rhombohedral perovskite phase and indicated that increasing cobalt concentration resulted in improved intensity and sharpness of the main peak, together with a decrease in crystal size. Photocatalytic evaluations under optimal conditions (pH = 2, dye concentration of 3 mg/L, 0.1 g of catalyst, and 120 minutes of UV-A irradiation) revealed that the highest degradation efficiency of 60.48% was achieved with the undoped sample. However, cobalt doping at various levels resulted in reduced photocatalytic activity. This reduction may be attributed to increased particle size, alterations in electronic properties, and a decrease in several active surface sites. This study highlights that while cobalt doping reduces the photocatalytic performance, it provides opportunities for fine-tuning the structural and optical properties of nanoparticles. Further optimization of the chemical composition and synthesis parameters could pave the way for the development of advanced photocatalytic materials for environmental applications, particularly in the removal of organic pollutants.

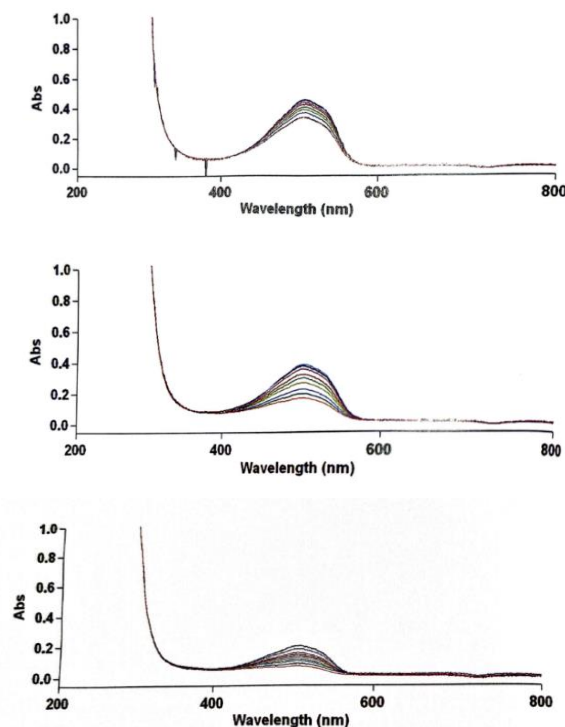


Fig. 9. UV-Vis spectrum at $\lambda_{\text{max}} = 461$ nm showing the effect of time on the removal of methyl orange dye using BiFe_{1-x}Co_xO₃ (X = 0.01, 0.03, 0.05) at pH = 2.

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