PROJECT - II
PRESENTATION

Photo-Fenton Degradation of Eosin Yellow dye using Co-doped Bismuth Ferrite

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Introduction

- Water pollution has become a major global issue due to increased industrial and urban water consumption which leads to increased effluent and sewage discharge.
- Physical and chemical water treatment methods are slow and not very effective in treating organic pollutants and volatile organic compounds (VOC's).
- Due to these shortcomings Photo-Fenton based wastewater treatment processes have begun to become more popular in research.

Eosin Yellow Dye

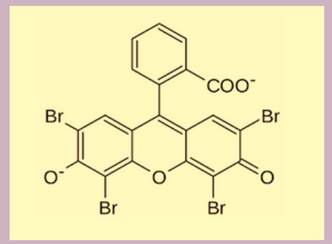


Fig.1: Structure of Eosin Yellow Dye
(CAS No.17372-87-1)

- Eosin Yellow Dye is a member of triaryl methane dye family.
- It is widely used in the field of pathology, for staining the cells before their study under a microscope.
- It is highly soluble in water, therefore physical treatment processes for its removal are ineffective.

$BiFeO_3$ as a Photocatalyst

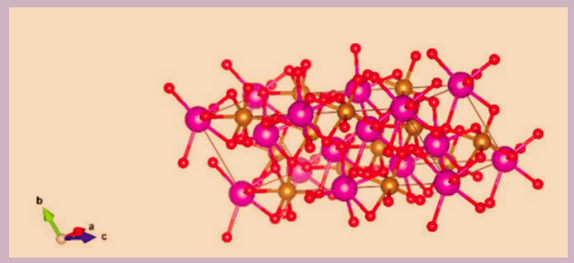


Fig.2: Structure of $BiFeO_3$ (ball and stick model)
(Crystallography Open Database, Moreau et. al.,1971)

- Bismuth ferrite has a perovskite structure with a general formula of ABO3.
- $BiFeO_3$ is a semiconductor due to which it has a narrow band gap which enhances its catalytic activity.
- $BiFeO_3$ is thermally stable up to about 1000°C, and it can demonstrate its electrical, magnetic and multiferroic properties well up to its melting point.

Literature Survey

Sn. No.	Reference	Key Findings
1.	Paliwal et al. (2018)	Co-doped $BiFeO_3$ was synthesised via the polyol method, and its photocatalytic activity was tested by degradation of Evans blue dye.
2.	Li et al. (2019)	Co-doped $BiFeO_3$ was prepared from pre-synthesised metal oxide frameworks (MOFs) followed by acid leaching and calcination. Catalyst was used to degrade methylene orange.
3.	Khajonrit et al. (2018)	Co-doped $BiFeO_3$ was synthesised via the sol-gel route followed via calcination to oxidise the gel obtained. Ferromagnetic properties of the catalyst was noticed as increasing with increased Co-doping.
4.	Khalek et al. (2018)	Degradation efficiency of 20% under high power visible light irradiation, Ag doping increased efficiency to 80+%. Starting concentration was 10 ppm solution.
5.	Liu et al. (2012)	BiOCl and TiO_2 alone only managed to give degradation of 2% and 53% respectively of 50 ppm EY solution.
6.	Sunkara & Botsa (2019)	Tin oxide and ferric oxide nanocomposite catalyst gave 31% degradation efficiency for 10 ppm dye solution with visible light irradiation.

Sn. No.	Reference	Key Findings
7.	Zheng et al. (2007)	$FeSO_4$ catalyst gave maximum 50% degradation under 450 W UV light irradiation of 20 ppm EY solution.
8.	Rani Rosaline et al. (2020)	Nickel-tungsten based nanocomposite catalyst gave maximum 30% degradation efficiency of 1 ppm EY solution.
9.	Ojha & Thareja (2020)	Graphene oxide-TiO_2 nanocomposite gave maximum 50% degradation under visible light irradiation for 6 hours of 10 ppm EY solution.
10.	Sharma et al. (2017)	ZnO nanoparticles annealed at different temperatures were used as photocatalyst. Catalyst annealed at 300°C showed a degradation efficiency of 40%, while that annealed at 700°C showed a degradation efficiency of nearly a 100%.
11.	Raja et al. (2018)	Zn_2SnO_4 and V_2O_5 photocatalysts were used in nanocomposite form as well as separately to degrade 20 ppm EY solution. Zn_2SnO_4 and V_2O_5 gave 40% and 30% degradation after 3 hours respectively. Nanocomposite catalyst gave a maximum degradation of 90% after 3 hours.
12.	Oppong et al. (2018)	Pure ZnO, GO-ZnO nanocomposite, and La-doped GO-ZnO nanocomposite catalyst were used to degrade EY solution. Degradation efficiencies of 15%, 40% and 90% were obtained respectively under 4 hours for these three photocatalysts.

Research Gap

Insufficient study of exact composition of $BiFeO_3$ catalytic nanoparticles and lack of use of characterization techniques like EDX.

Many researchers have guessed the composition of $BiFeO_3$ nanoparticles sample on stoichiometric basis which leaves the exact composition of catalyst undetermined.

No research exists as of yet that has studied the behavior of the Eosin Yellow Dye and its degradation in the presence of $BiFeO_3$, especially Co-doped $BiFeO_3$.

Eosin Yellow is a very recalcitrant dye, where the removal rates of the dye are very low, usually below 50%, even after prolonged irradiation by powerful light sources for long periods of time.

Objectives

- **Objective 1**

  To synthesize $BiFeO_3$ photocatalyst nanoparticles doped with cobalt in two separate molar ratios (1:1 and 2:1) via sol-gel route.

- **Objective 2**

  To characterize Co-Doped $BiFeO_3$ nanoparticles by analytical techniques like EDX, SEM and XRD.

- **Objective 3**

  To carry out Photo-Fenton degradation of Eosin Yellow Dye in a batch reactor under different reaction conditions.

- **Objective 4**

  To carry out kinetic study (determination of rate constant) of degradation reaction and study of its reaction mechanism.

Overview

1. Synthesis of Phocatalyst

Co-doped $BiFeO_3$ was synthesized via the sol-gel route for two different molar ratios. Doping was done to enhance the photocatalytic properties of $BiFeO_3$ nanoparticles.

2. Characterization

The catalyst was characterized via the analytical techniques of SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-ray Spectroscopy), and XRD (X-Ray Diffraction).

3. Degradation Reactions

Reaction runs were carried out under varying reaction conditions and the concentration vs. time data was collected.

4. Kinetic Study

The concentration vs. time data were analyzed to conduct a kinetic study and determine rate constant of the degradation reactions under varying reaction conditions.

Methodology: Synthesis of Co-doped $BiFeO_3$

Preparation of Ethylene Glycol Solution:
15 ml of ethylene glycol was measured into a beaker and stirring was started.

Addition of Metal Nitrates:
0.01 mol each of the precursors bismuth nitrate, ferric nitrate and cobalt nitrate was added to the solution for 1:1 doped catalyst. For 2:1 doped catalyst, 0.02 mol of cobalt nitrate was used.

Heating and Stirring of Solution:
The solution was stirred and heated at 100°C for 2 hours until a thick paste was obtained.

Transfer of paste to crucible:
The paste obtained was transferred into the crucible.

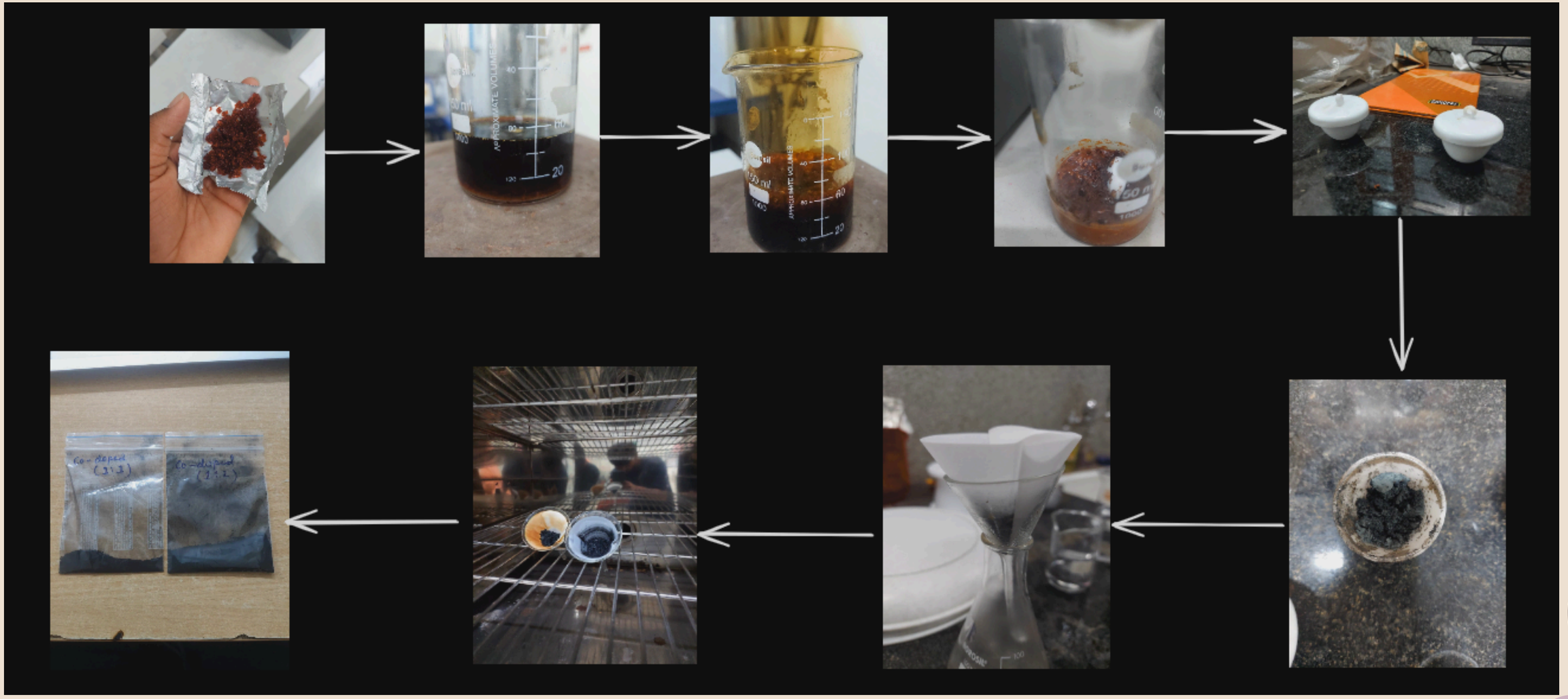
Heating in Muffle Furnace:
The paste was calcined in the muffle furnace at 600°C for 3 hours.

Preparation of 20% v/v nitric acid:
20% v/v nitric acid was prepared by adding 0.956 ml of 70% v/v nitric acid to 19 ml of distilled water and making up the volume to 75 ml.

Washing of powder with dilute nitric acid:
The calcined powder obtained was washed with the dilute nitric acid solution prepared above.

Drying and Storage:
The washed black powder was dried in the hot air oven for 12 hours at 100°C. The dried powder was stored for characterisation studies.

Pictorial Presentation of Catalyst Synthesis Procedure



Methodology: Degradation Reaction Procedure

Step 1: 400 ml of 10 ppm or 200 ppm eosin yellow dye solution was measured out into a 1 litre beaker. The beaker was put into a stirring condition.

Step 2: A buffer solution of KOH was prepared by dissolving 0.1285 gms of KOH in 230 ml of distilled water. This solution was added dropwise to the reaction mixture until a pH of 6 was reached.

Step 3: 3 ml of hydrogen peroxide (30% v/v) was added to the reaction mixture and the timer was started.

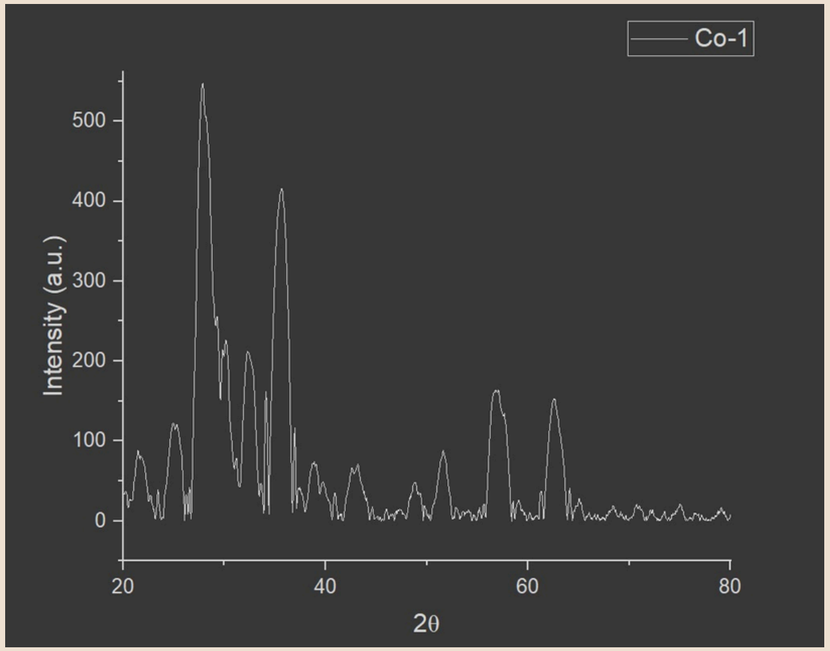
Step 4: Samples were collected at 15 minute intervals for two hours.

Step 5: The collected samples' concentrations were measured by spectrophotometry.

Results: Characterization of Catalyst

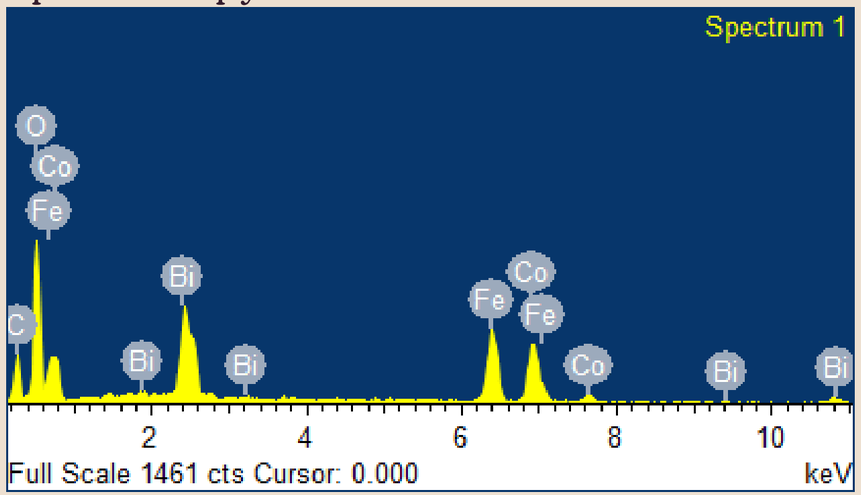
Cobalt doped Bismuth Ferrite nanoparticles were characterized by using following analytical techniques:

Fig. 3. **XRD:** X-Ray Diffraction



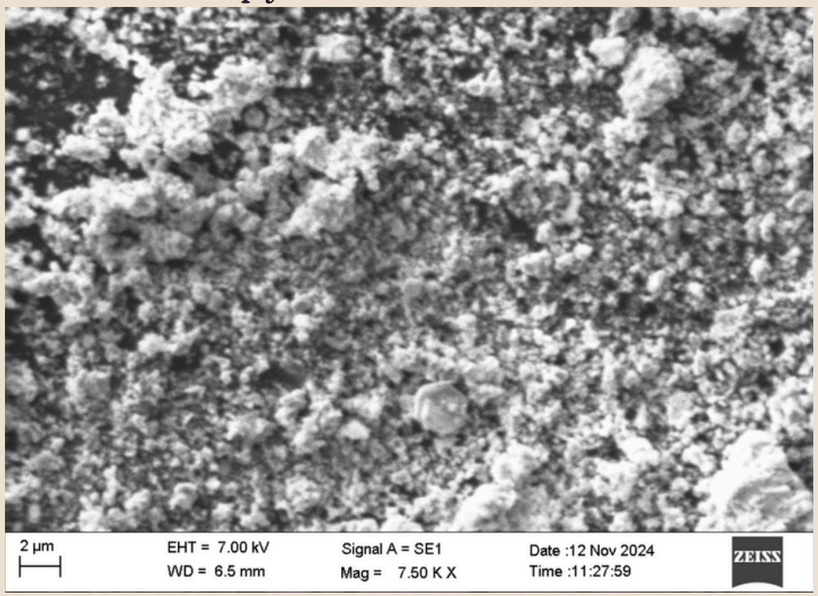
- Reduced intensity due to Co doping observed.
- Crystal defect or microstrain possible due to observed broad peaks.

Fig. 4. **EDX:** Energy Dispersive X-ray Spectroscopy



Element	Weight%	Atomic%	
C K	1.90	5.07	
O K	34.69	69.30	
Fe K	19.93	11.41	
Co K	19.45	10.55	
Bi M	24.03	3.68	
Totals	100.00		

Fig. 5. **SEM:** Scanning Electron Microscopy



- Structured grains was observed.
- Hollowness of particles at the micrometer scale was observed.

Degradation Results: 200 ppm Eosin Y, 1:1 Co-$BiFeO_3$, Room Light

First Run:

- 0.011 grams of catalyst doped with cobalt in 1:1 ratio and 3 ml of H_2O_2 solution was used for this degradation run.
- 400 ml of 200 ppm Eosin Yellow reaction mixture was degraded under room light conditions and constant stirring.

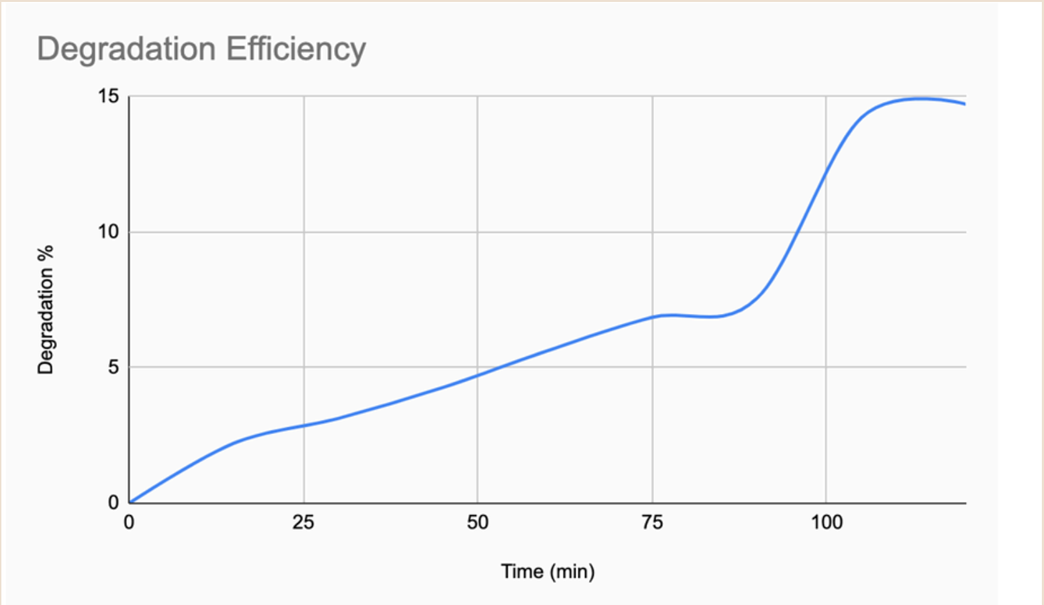


Fig. 6. Degradation Efficiency vs Time (1:1 Catalyst, 200 ppm, room light)

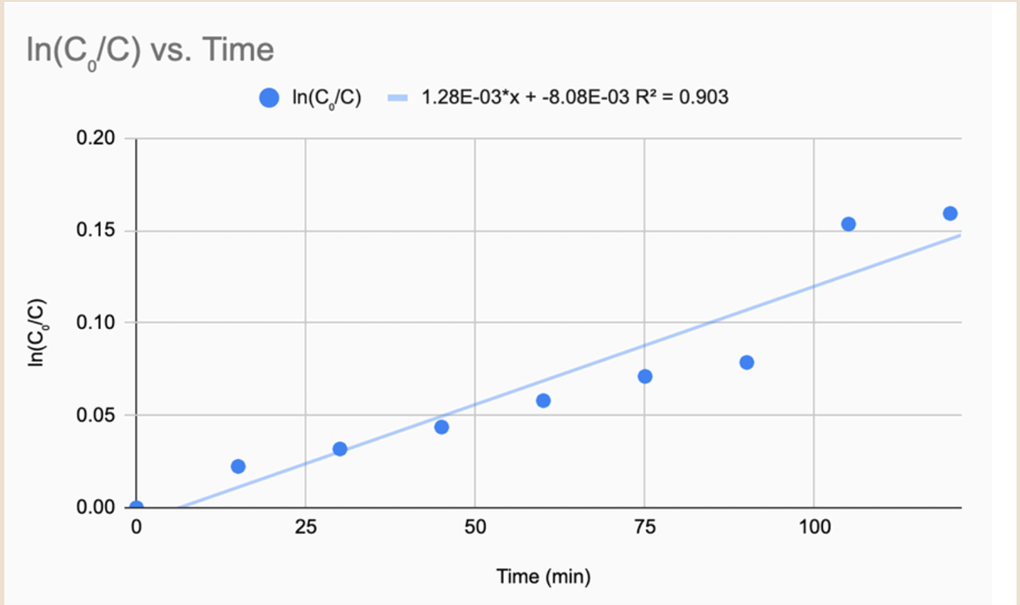


Fig. 7. Linearised Conversion vs Time Data (1:1 Catalyst, 200 ppm, room light)

- A maximum degradation of 14.72% after 2 hours was obtained.
- From the linear equation obtained, we can determine the rate constant as 0.00128 min^{-1}.

Degradation Results: 10 ppm Eosin Y, 1:1 Co-$BiFeO_3$, Room Light

Second Run:

- 0.011 grams of 1:1 Co-doped catalyst and 3 ml of H_2O_2 solution was used for this degradation run.
- 10 ppm of Eosin Yellow reaction mixture was degraded under room light conditions and constant stirring.

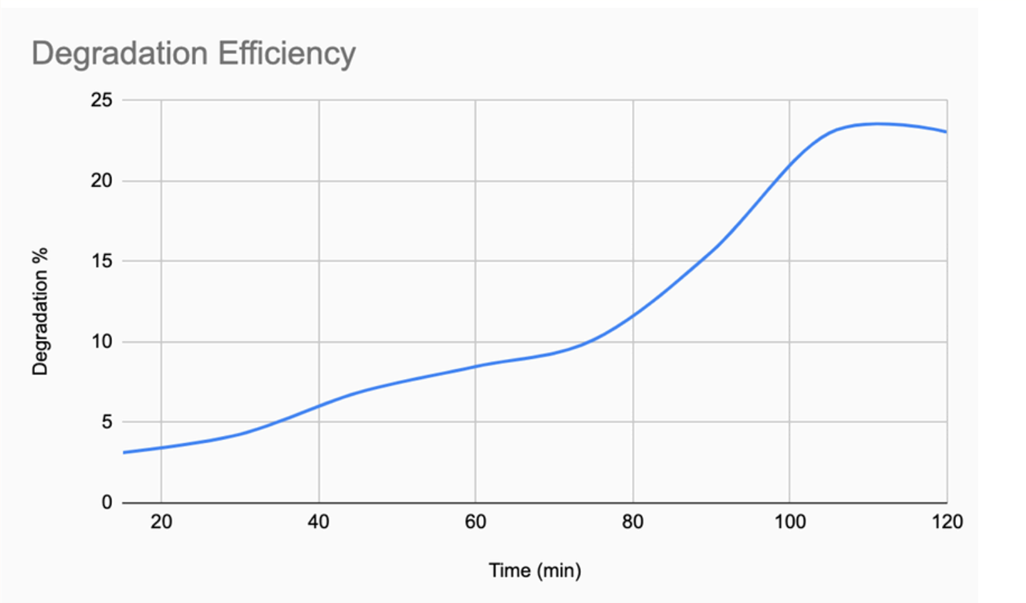


Fig. 8. Degradation Efficiency vs Time (1:1 Catalyst, 10 ppm, room light)

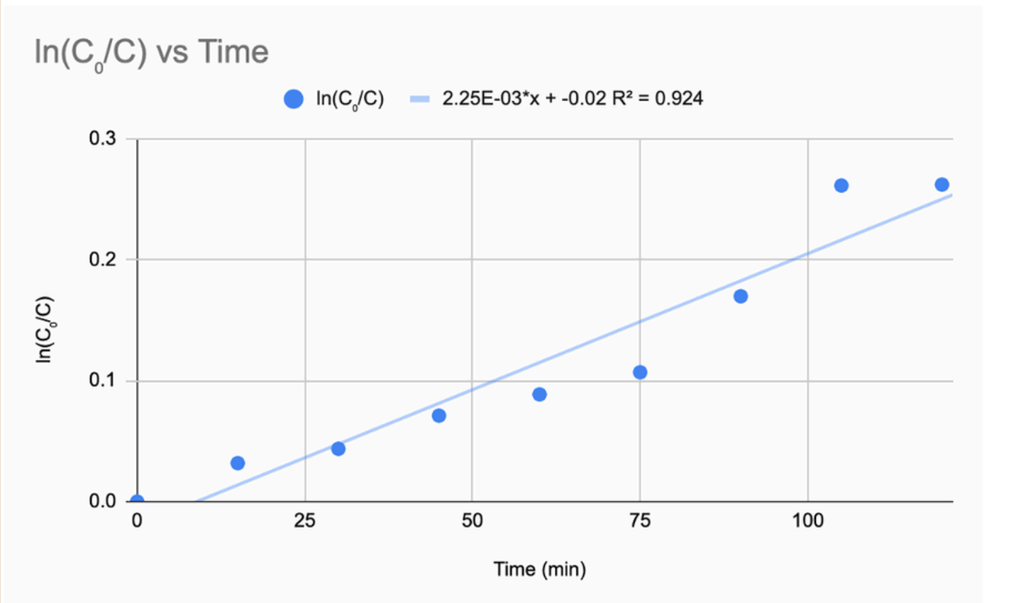


Fig. 9. Linearised Conversion vs Time Data (1:1 Catalyst, 10 ppm, room light)

- A maximum degradation of 23.05% in case of 1:1 doped catalyst.
- The rate constant for 1:1 catalyst under these conditions was determined to be 0.0025 min^{-1}.

Degradation Results: 10 ppm Eosin Y, 2:1 Co-$BiFeO_3$, Room Light

Third Run:

- 0.011 grams of 2:1 Co-doped catalyst and 3 ml of H_2O_2 solution was used for this degradation run.
- 10 ppm of Eosin Yellow reaction mixture was degraded under room light conditions and constant stirring.

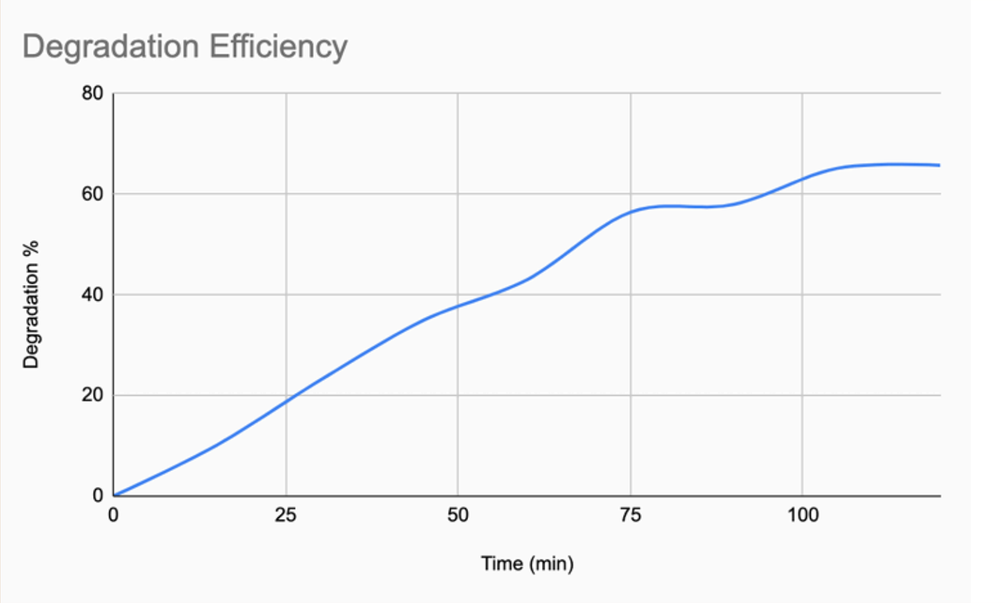


Fig. 10. Degradation Efficiency vs Time (2:1 Catalyst, 10 ppm, room light)

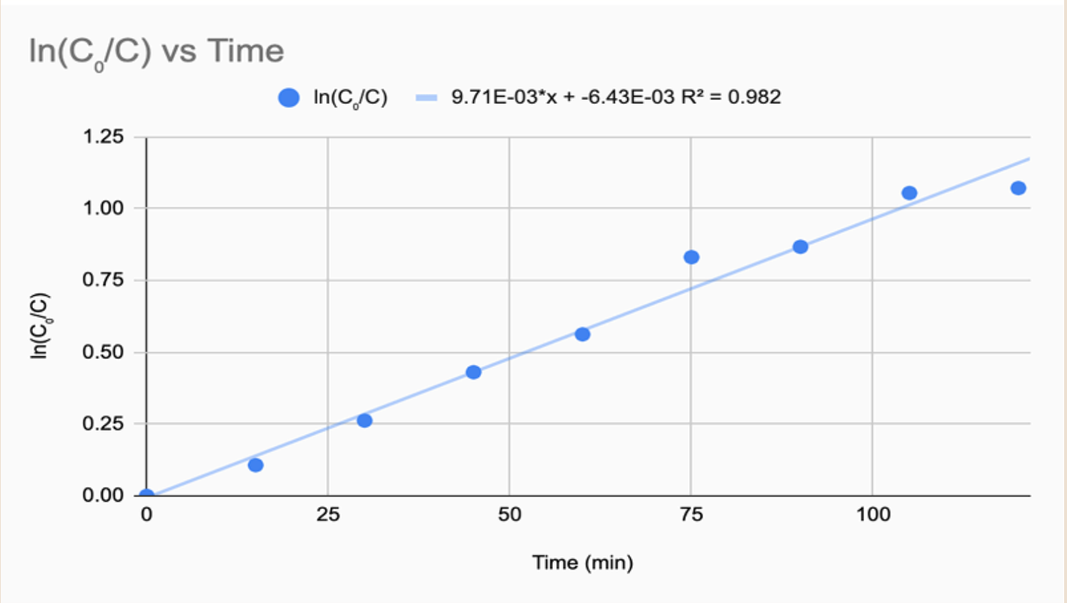


Fig. 11. Linearised Conversion vs Time Data (2:1 Catalyst, 10 ppm, room light)

- A maximum degradation of 65.76% in case of 2:1 doped catalyst.
- The rate constant for 2:1 catalyst under these conditions was determined to be 0.00971 min^{-1}.

Degradation Results: 10 ppm Eosin Y, 1:1 Co-$BiFeO_3$, 50W LED Bulb

Fourth Run:

- 0.011 grams of 1:1 Co-doped catalyst and 3 ml of H_2O_2 solution was used for this degradation run.
- 10 ppm of Eosin Yellow reaction mixture was degraded under a 50W LED bulb irradiation and constant stirring.

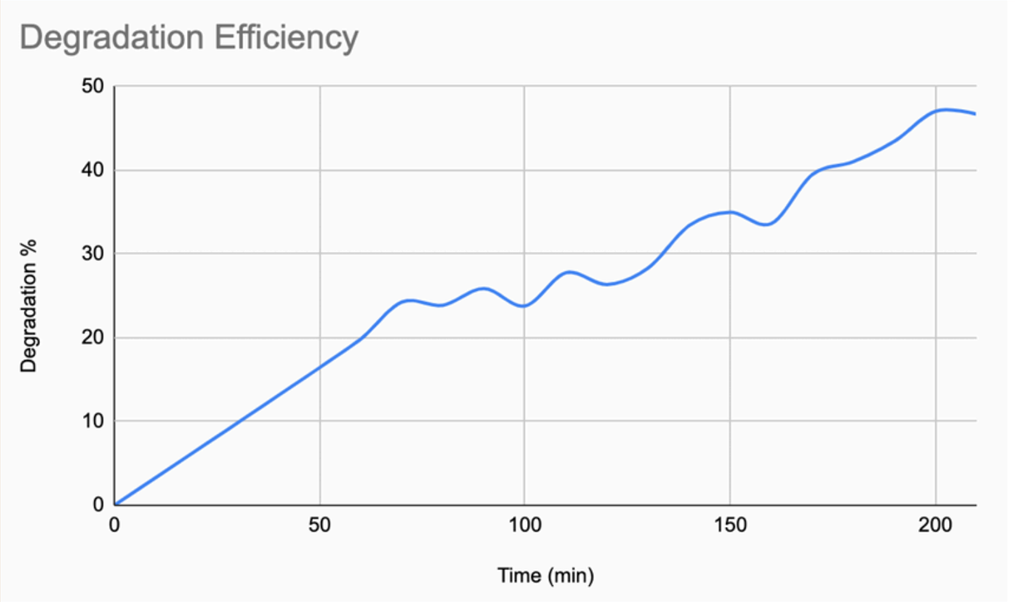


Fig. 12.Degradation Efficiency vs Time (1:1 Catalyst, 10 ppm, LED Bulb)

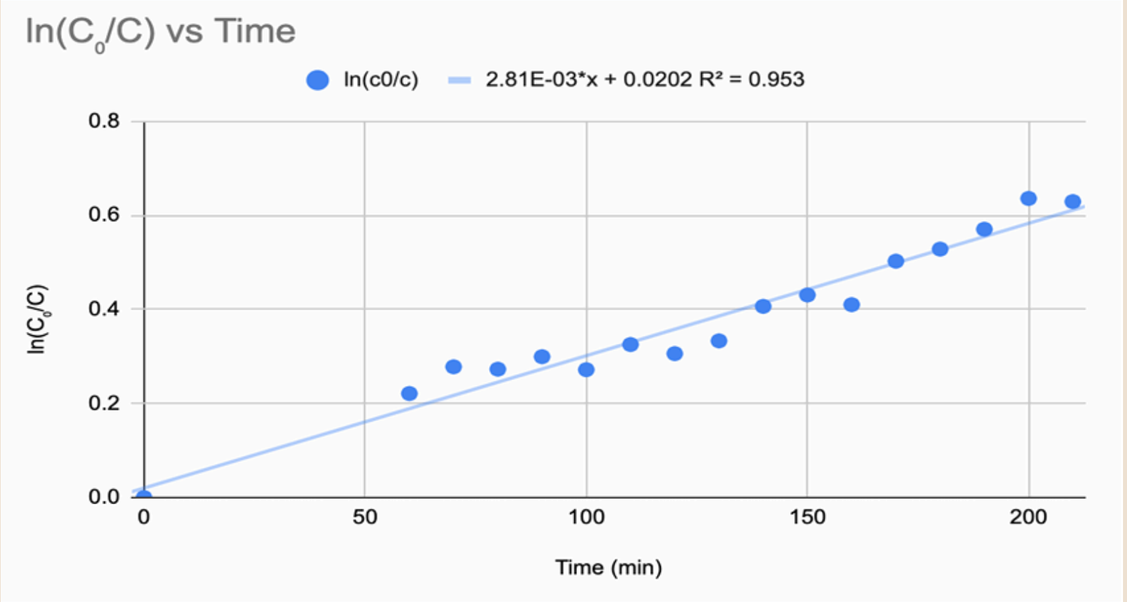


Fig. 13. Linearised Conversion vs Time Data (1:1 Catalyst, 10 ppm, LED Bulb)

- A maximum degradation of 46.7% was observed in this case.
- The rate constant for 1:1 catalyst under these conditions was determined to be 0.00281 min^{-1}.

Reaction Mechanism

Step 1

Light Absorption: When visible light hits the BFO surface with enough energy, it creates energized electrons (e^-) and holes (h^+) by exciting particles across the catalyst's bandgap.

Step 2

Formation of Reactive Species: Electrons (e^-) react with oxygen (O_2) to form superoxide radicals ($O_2^-\bullet$), while holes (h^+) react with water (H_2O) to produce hydroxyl radicals ($\bullet OH$).

Step 3

Degradation of Dye Molecules: Superoxide ($O_2^-\bullet$) and hydroxyl ($\bullet OH$) radicals react with dye molecules, breaking them down into byproducts like CO_2 and H_2O.

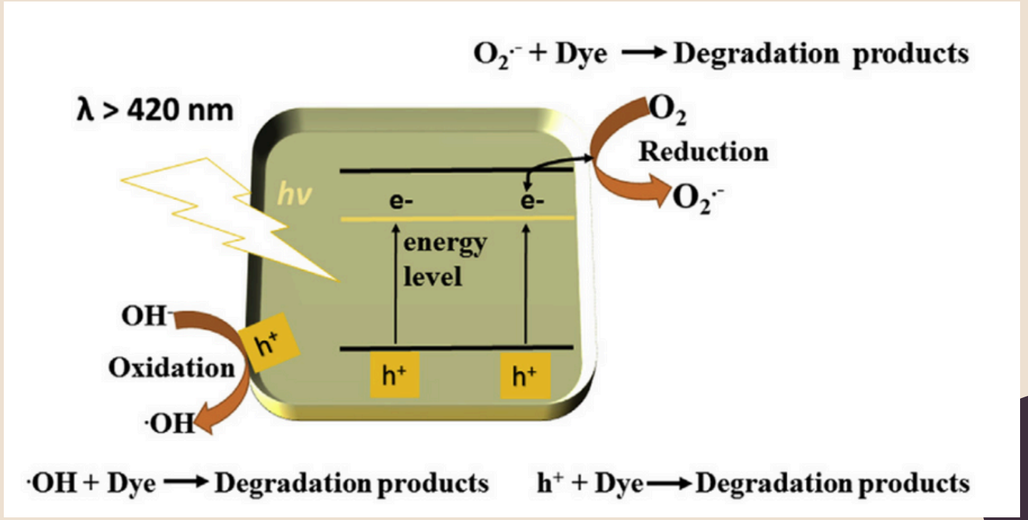


Fig. 14. **Schematic diagram of the mechanism of photocatalytic degradation of dye on doped BFO photocatalyst.**
(Haruna et. al. (2020), Heliyon, 6.)

Conclusion

- The catalysts were synthesised successfully and the characterisation analysis confirmed that the desired compositions in the catalysts were attained. Highly pure and crystalline Co-doped $BiFeO_3$ was obtained via the sol-gel method.

- The catalysts were successfully utilised in carrying out degradation of a very recalcitrant anionic dye, Eosin Yellow, and particularly good results were obtained from the 2:1 Co-doped catalyst, which gave the highest degradation of 65.76% in room light under 2 hours.

- This study has proven the efficacy of the Co-doped $BiFeO_3$ in its ability to degrade Eosin Yellow in a relatively short time frame of 2-3 hours.

Future Scope and Challenges

- The catalyst so synthesized is able to degrade recalcitrant dyes in wastewater, but the final degradation rates achieved, though impressive, are still not sufficient for use on a mass scale.
- Other doping methods on this catalyst with different materials can be investigated, or perhaps co-doping can be undertaken, in order to improve the photocatalyst further and allow its use in an economical manner for industrial effluent treatment.
- The cost associated with synthesis of catalyst is the major challenge in this process of water treatment. The precursors used for the synthesis of the Co-doped $BiFeO_3$ catalyst are more expensive than the standard Photo-Fenton catalyst like ferrous sulphate.
- The significant increase in cost associated with this catalyst precludes its use currently in the industry, therefore advancements can be made to find a procedure for synthesis of bismuth ferrite based catalysts for cheaper.

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