Degradation of an organic pollutant in water using LED light and a photocatalyst

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***Abstract*—This experiment explores the photocatalytic degradation of methylene blue dye under LED light using Fe_3O_4 nanoparticles as a catalyst. We examine dye breakdown kinetics by monitoring absorbance over time and applying Beer-Lambert's law to determine concentration changes. By comparing reactions with and without the photocatalyst, the study evaluates the catalyst's effectiveness in facilitating dye degradation, providing insights into photocatalysis for wastewater treatment.**

I. Introduction

In this experiment, we investigate the photocatalytic breakdown of Methylene Blue (MB), a dye frequently found in industrial wastewater, utilizing iron oxide nanoparticles (Fe_3O_4) as catalysts and LED light as an energy source. Methylene Blue, extensively used in the dye industry, poses significant environmental risks, yet photocatalysis offers a viable approach to degrading such pollutants. This report outlines the experimental setup, including preparation of reaction vials and absorbance spectrum measurements to track the degradation process. Using Beer-Lambert's law to relate absorbance, concentration, and path length, we determine MB concentrations over time. This analysis assesses the photocatalytic efficiency and examines reaction kinetics under varied conditions to gain insight into the degradation process.

II. Theory

Methylene Blue, also called methylthioninium chloride, is a widely-used compound with diverse applications. It is a bright greenish-blue dye in the phenothiazine family, commonly used in textile industries.

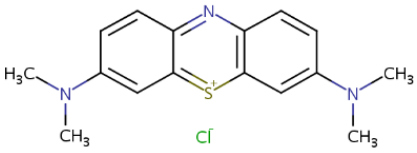

Fig. 1. Structure of Methylene Blue

Photocatalysis is a process in which a catalyst, upon absorbing light, accelerates a chemical reaction. In this experiment, we degrade the organic pollutant Methylene Blue (MB) using iron oxide nanoparticles (Fe_3O_4) as the photocatalyst and LED light as the energy source. The following reactions illustrate the degradation process in photocatalysis:

$$Fe_3O_4 + h\gamma \rightarrow Fe_3O_4\left(e^-(CB) + h^+(VB)\right) \quad (1)$$

$$MB + h^+(VB) \rightarrow \text{Oxidation of MB} \quad (2)$$

$$H_2O + h^+(VB) \rightarrow OH^{\cdot} + H^+ \quad (3)$$

$$MB + OH^{\cdot} \rightarrow CO_2 + H_2O \quad (4)$$

The Beer-Lambert Law, also known as Beer's Law, is a fundamental principle in spectroscopy that relates the attenuation of light to properties of the medium it passes through. This law is frequently used in analytical chemistry to calculate the concentration of solutes in solutions. The law states that the absorbance of a solution is directly proportional to the solute

concentration and the path length of light through the solution. The mathematical expression of Beer-Lambert Law is:

$$A = \epsilon \, l \, C$$

Where:

- A is the absorbance (dimensionless)
- ϵ is the molar attenuation coefficient (L mol^{-1} cm^{-1})
- l is the path length of the sample (cm)
- C is the concentration of the absorbing species (mol L^{-1})

The rate of a chemical reaction is influenced by various factors, including both physical factors (such as pressure, temperature, and light) and chemical factors (such as the catalyst and properties of reactants). Catalysis generally serves to increase the reaction rate.

III. Experimental Procedure

A. Apparatus and Materials Used

- **Test tubes:** Small cylindrical containers used for holding and mixing chemical solutions during experiments.
- **Methylene blue:** The dye used as the target pollutant in this experiment to study degradation.
- **Iron Oxide Nanoparticles (Fe_3O_4):** The photocatalyst used to facilitate the degradation of Methylene Blue.
- **Magnetic bar:** A bar magnet used to stir solutions when placed in a magnetic stirrer.
- **Distilled water:** Purified water used as a solvent to prepare the Methylene Blue solution.
- **Cuvettes:** Small, transparent containers used to hold samples for spectrophotometric analysis.
- **Magnetic stirring bar with LED lights:** Used to provide both mixing and light exposure for photocatalytic reactions.
- **Magnetic bead:** Placed in solution to enable stirring with a magnetic stirrer.
- **Aluminium foil:** Used to cover reaction containers to prevent exposure to external light.
- **Beaker:** A general-purpose glass container used for holding solutions and mixing reagents.
- **Glass vials:** Small containers for storing reaction samples or reagents.
- **Spectrophotometer:** An instrument used to measure the absorbance of light by the solution at specific wavelengths.
- **Gloves:** Protective equipment to prevent skin contact with chemicals.
- **Protective Goggles:** Eye protection to prevent injury from chemical splashes or light exposure.
- **Droppers:** Tools for transferring small volumes of liquid reagents accurately.

B. Methodology

1) Experiment 1
   a) Prepare three vials as follows:
      i) **Vial 1:** Combine 5 ml of methylene blue (stock solution) with 5 mg of Fe_3O_4 nanoparticles.
      ii) **Vial 2:** Combine 5 ml of methylene blue (stock solution) with 5 mg of Fe_3O_4 nanoparticles and add 1 magnetic bead.
      iii) **Vial 3:** 5 ml of methylene blue (stock solution) only.
   b) Wrap Vial 1 with aluminum foil to block light and set it aside.
   c) Place Vials 2 and 3 under LED light on a magnetic stirring bar.
   d) Every 10 minutes, follow these steps to measure absorbance:
      i) **Vial 1:**
         A) Position Vial 1 near a magnetic bar to separate Fe_3O_4 nanoparticles using magnetic separation.
         B) Extract 2 ml of the solution, place it in a cuvette, and record the absorbance spectrum.
         C) Return the 2 ml sample to the vial and keep it in darkness.
      ii) **Vial 2:**
         A) Remove Vial 2 from LED light, position it near the magnetic bar for nanoparticle separation.
         B) Extract 2 ml of the solution, place it in a cuvette, and measure absorbance.
         C) Return the 2 ml sample to the vial and immediately return it to the LED light.
      iii) **Vial 3:**
         A) Remove Vial 3 from LED light.
         B) Extract 2 ml of the solution, place it in a cuvette, and measure absorbance.
         C) Return the 2 ml sample to the vial and promptly replace it under the LED light.
   e) Continue absorbance measurements every 10 minutes for each vial, for a total duration of 50 minutes.
2) Experiment 2 (Calibration using known concentrations)
   a) Begin with a methylene blue (MB) stock solution at 5 ppm concentration.
   b) Prepare test tubes with varying dilutions:
      i) **Test Tube 1 (TT1):** 2 ml of MB solution.
      ii) **Test Tube 2 (TT2):** 1 ml of MB solution with 1 ml of distilled water.
      iii) **Test Tube 3 (TT3):** 1 ml of MB solution with 2 ml of distilled water.
      iv) **Test Tube 4 (TT4):** 1 ml of MB solution with 3 ml of distilled water.
      v) **Test Tube 5 (TT5):** 1 ml of MB solution with 4 ml of distilled water.
   c) Extract 2 ml from each test tube and measure their absorbance spectra using a spectrophotometer.
   d) Plot the absorbance at the peak wavelength against MB concentrations.
   e) Determine the molar extinction coefficient, ϵ, from the slope of this plot.

IV. Results

The equations used to calculate the concentrations and molarity are given below:

$$\text{Final Concentration} = \frac{\text{Volume of MB} \times \text{Initial Concentration}}{\text{Total Volume}}$$

$$\text{Molarity (M)} = \frac{\text{Concentration (ppm)} \times 0.001 \text{ g/L}}{\text{Molecular Weight (g/mol)}}$$

The molecular weight of methylene blue is approximately 319.85 g/mol.

A. Calibration of Methylene Blue solution

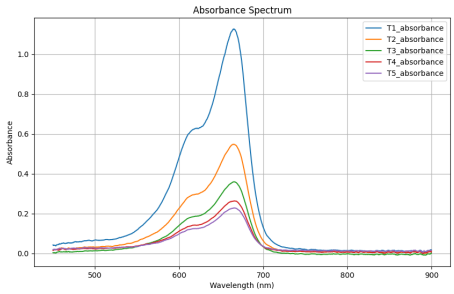

Fig. 2. Absorbance spectrum different concentrations of Methylene Blue

The concentrations of Methylene Blue in Molarity (M) are:

1) **Test Tube 1 (TT1):** 1.5632×10^{-5} M
2) **Test Tube 2 (TT2):** 7.8162×10^{-6} M
3) **Test Tube 3 (TT3):** 5.2108×10^{-6} M
4) **Test Tube 4 (TT4):** 3.9081×10^{-6} M
5) **Test Tube 5 (TT5):** 3.1265×10^{-6} M

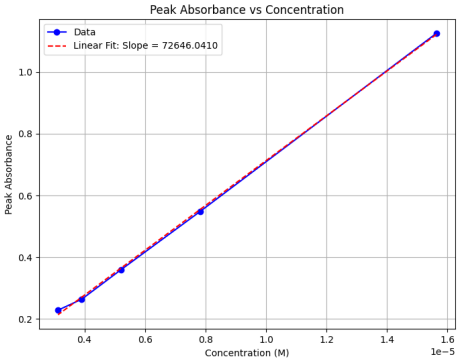

Fig. 3. Peak Absorbance for different concentrations of Methylene Blue

According to the Beer-Lambert Law, the ϵ can be calculated by evaluating the gradient of the plot. From Fig. 3 , the calculated value of ϵ=$7.26 \times 10^4\,\text{M}^{-1} \cdot \text{cm}^{-1}$

B. Vial 1 (5 ml methylene blue (stock solution) + 5 mg of Fe_3O_4 nanoparticles)

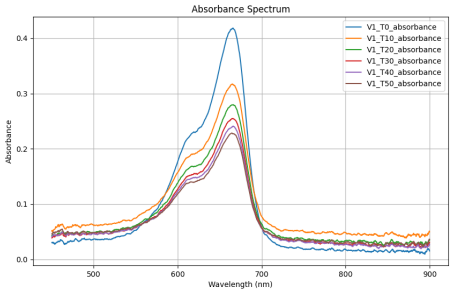

Fig. 4. Absorbance spectrum for vial 1

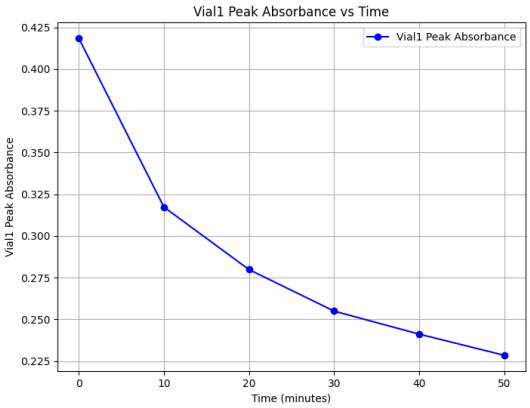

Fig. 5. Absorbance v/s Time for Vial 1

C. Vial 2 (5 ml methylene blue (stock solution) + 5 mg of Fe_3O_4 nanoparticles+ + 1 magnetic bead)

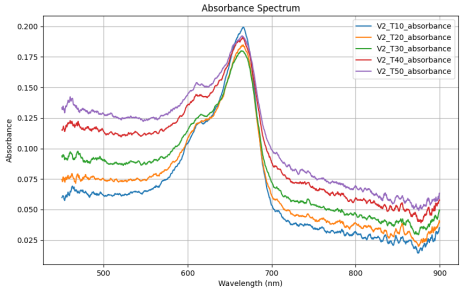

Fig. 6. Absorbance spectrum for vial 2

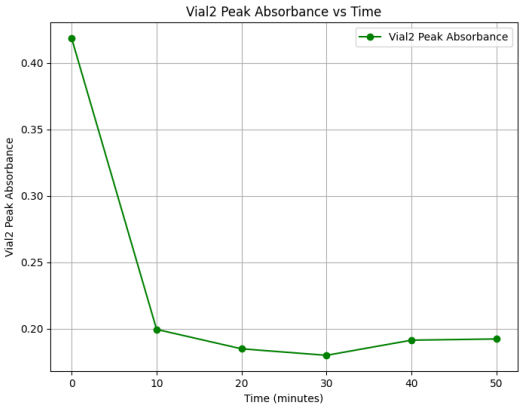

Fig. 7. Absorbance v/s Time for Vial 2

D. Vial 3 (5 ml methylene Blue solution, kept in light)

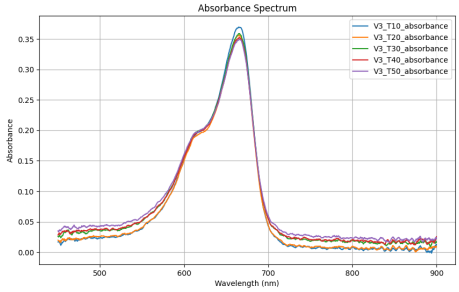

Fig. 8. Absorbance spectrum for vial 3

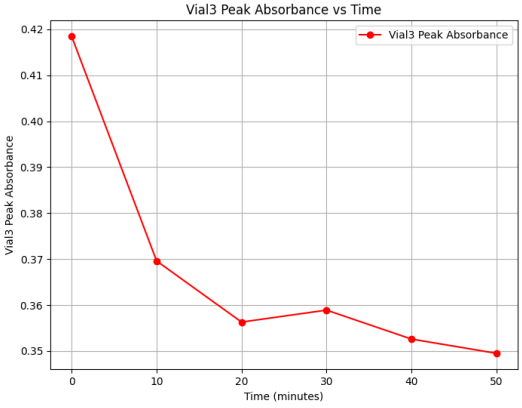

Fig. 9. Absorbance v/s Time for Vial 3

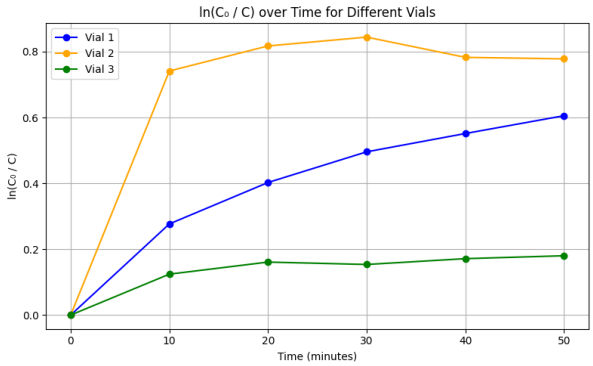

Fig. 10. $ln(C_0/C)$ v/s Time for different vials

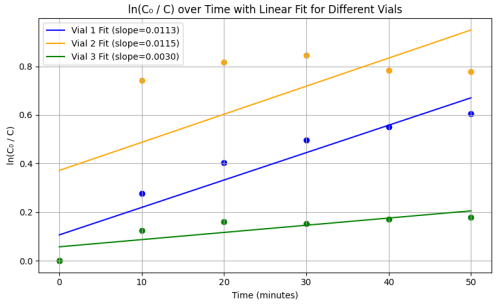

Fig. 11. $ln(C_0/C)$ v/s Time for different vials (linear fit)

TABLE I
METHYLENE BLUE CONCENTRATION (PPM) IN DIFFERENT VIALS OVER TIME

Time (minutes)	Vial 1 (ppm)	Vial 2 (ppm)	Vial 3 (ppm)
0	1.842595	1.842595	1.842595
10	1.397026	0.877929	1.627295
20	1.231919	0.813648	1.568737
30	1.122288	0.792074	1.580185
40	1.061528	0.842266	1.552447
50	1.005612	0.846229	1.538798

TABLE II
ABSORBANCE VALUES FOR DIFFERENT VIALS OVER TIME

Time (minutes)	Vial 1	Vial 2	Vial 3
0	0.4185	0.4185	0.4185
10	0.3173	0.1994	0.3696
20	0.2798	0.1848	0.3563
30	0.2549	0.1799	0.3589
40	0.2411	0.1913	0.3526
50	0.2284	0.1922	0.3495

TABLE III
LN(C_0/C) FOR DIFFERENT VIALS OVER TIME

Time (minutes)	Vial 1	Vial 2	Vial 3
0	0.0000	0.0000	0.0000
10	0.2768	0.7413	0.1242
20	0.4026	0.8174	0.1609
30	0.4958	0.8442	0.1536
40	0.5514	0.7828	0.1713
50	0.6055	0.7781	0.1801

$$\text{Amount of Degradation} = C_0 - C_t$$

The amount of degradation of Methylene Blue in each of the vials is as follows:

1) Vial 1: 0.836983 ppm
2) Vial 2: 0.996366 ppm
3) Vial 3: 0.303797 ppm

It can be observed that the amount of degradation of methylene blue is higher in Vial 1 and Vial 2 than in Vial 3 where there is absence of catalyst.

The reaction rate constants of the vials are as follows:

1) Vial 1: 0.0113 s^{-1}
2) Vial 2: 0.0115 s^{-1}
3) Vial 3: 0.0030 s^{-1}

$$k(Vial2) > k(Vial1) > k(Vial3)$$

Here, k is the rate constant of each vial. The graph of ln(C_0/C) vs. time indicated that the reaction followed first-order kinetics, with Vial 2 showing the highest rate of degradation.

V. Conclusion

This experiment successfully demonstrated the photocatalytic degradation of Methylene Blue facilitated by iron oxide (Fe_3O_4) nanoparticles under light exposure. The findings indicated that the greatest degradation occurred in the vial with both magnetic beads and Fe_3O_4 nanoparticles under LED light, followed by the vial containing only nanoparticles (kept in the dark). The least degradation was observed in the control vial without a catalyst.

Methylene Blue concentrations were quantified using Beer-Lambert's Law, and the molar extinction coefficient (ϵ) was calculated to support the analysis. These results highlight the potential of photocatalytic processes, specifically with Fe_3O_4 nanoparticles, as an effective approach for the removal of organic dyes from industrial wastewater, offering a promising solution for sustainable water treatment.

VI. Precautions & Challenges

- Ensure the use of gloves, safety goggles, and other necessary protective equipment.
- When moving vials from light or dark conditions for absorbance measurements, do so promptly to prevent ongoing reactions from affecting the results.
- Carefully label and keep track of vial numbers and solutions to avoid confusion during data collection.

VII. Acknowledgment

We would like to express our sincere gratitude to lab staff at IIT Gandhinagar for their invaluable guidance and support throughout this experiment. Special thanks to the laboratory staff for providing the necessary equipment and ensuring a smooth experimental process. We also extend our appreciation to our group members for their teamwork and contributions. Lastly, we acknowledge IIT Gandhinagar for providing the resources and facilities to conduct this experiment.

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