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

Study the degradation of Methylene Blue and factors affecting it

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I. Introduction

In this experiment, we are going to study the degradation of organic dye molecules commonly used in dye industries. They are present in industrial wastewater and act as an organic pollutant. We will study the reaction's kinetics and analyse the photocatalyst's effectiveness in the dye's degradation.

Our experiment involves 3 Vials: one containing Methylene blue in the dark, the second containing Methylene blue and nanoparticles kept in light, and the third one containing Methylene blue kept in light.
The values for the concentration is calculated using the Beer lambert's law which states that:

$$\text{Absorbance} = \epsilon \times c \times l \tag{1}$$

where ϵ is the molar extinction coefficient, which is the property of the molecule under observation, c is the concentration, and l is the path length. For a given setup, ϵ and l are constants.

In order to calculate the value of epsilon we have first conducted the experiment of calibration using known concentration of Methylene Blue. The reactions involved are as follows:
MB represents Methylene Blue

$$\begin{gathered}\mathrm{Fe_3O_4} + \mathrm{h}\mu \longrightarrow \mathrm{Fe_3O_4}\,(e^-(\mathrm{CB}) + h^+(\mathrm{VB}) \\ \mathrm{MB} + h^+(\mathrm{VB}) \longrightarrow \text{Oxidation of MB} \\ \mathrm{H_2O} + h^+(\mathrm{VB}) \longrightarrow \mathrm{OH} + \mathrm{H^+} \\ \mathrm{MB} + \mathrm{OH} \longrightarrow \mathrm{CO_2} + \mathrm{H_2O}\end{gathered}$$

The photocatalyst promotes the reaction by absorbing light which results in the generation of electron-hole pairs that facilitate the degradation of dye.

II. Materials

A. Chemicals

1) Methylene blue
2) Iron Oxide Nanoparticles (Fe_3O_4)
3) Distilled water

B. Apparatus

1) UV-Vis absorption spectrophotometer
2) Pasteur pipette
3) LED torch
4) Two Test tubes
5) Three Cuvette
6) Aluminum foil
7) Magnetic stirring bar
8) Magnetic bead
9) Three vials

III. Safety Measures

1) Handle the chemicals carefully and do not interchange the droppers between different test-tubes.
2) The gloves and the glasses should be worn throughout the experiment
3) Handle the lab apparatus with care.

IV. Procedure

A. Calibration with known concentrations:

1) Prepare five test tubes (TT) with different concentrations of methylene blue (MB). The five test tubes should have the following concentrations:
   i TT 1: 2 ml Methylene Blue
   ii TT 2: 1 ml Methylene Blue + $1ml$ water
   iii TT 3: 1 ml Methylene Blue + $2ml$ water
   iv TT 4: 1 ml Methylene Blue + $3ml$ water
   v TT 5: 1 ml Methylene Blue +$4mL$ water
2) Measure the absorption spectra of $2mL$ of each test tube using a UV-Vis spectrophotometer.
3) Plot the absorbance at the peak $(664nm)$ with the corresponding Methylene Blue concentrations.
4) Calculate the molar extinction coefficient (ϵ) from the slope of the graph. The path length (l) is taken as $1cm$.

B. Methylene Blue degradation

1) Setting up:

1) Prepare three vials with the following details:
   i Vial 1 : $5ml$ MB solution + $5mg$ Fe_3O_4 nanoparticles
   ii Vial 2 : $5ml$ MB solution + Fe_3O_4 nanoparticles + 1magnetic bead
   iii Vial3 : $5ml$ MB solution only.
2) Wrap vial 1 with aluminum foil and set it aside.
3) Put vial2 and 3 under the LED light on top of the magnetic stirring bar.
4) In every 10 minutes, do the following:

i Take vial 1 and, using a magnetic post/bar, move the nanoparticles to one side of the vial. Then, using a Pasteur pipette, take 2ml of the sample and measure the absorbance spectrum(t_0). After measuring the absorbance, pour the $2ml$ back and keep it in the initial position.

ii Take vial 2 out and put it near the magnetic post/bar to move the nanoparticles. Then, after $10mins$, take $2ml$ of the sample and measure the absorbance spectrum. Pour this $2ml$ back in the vial and put the vial back under LED at the earliest.

iii similarly after $10mins$, Take $2ml$ from vial 3 and measure the absorbance spectrum. Pour this $2ml$ back in the vial and put the vial back under LED at the earliest

2) Determination of concentration from absorbance:

1) To determine the concentration of Methylene Blue in the samples, we will use Beer-Lambert's law. The equation for Beer-Lambert's law is:

$$\text{Absorbance} = \epsilon \times c \times l \tag{2}$$

Where ϵ is the molar extinction coefficient, which is the property of the molecule under observation and was calculated in the previous part of the experiment, c is the concentration, and l is the path length which is taken to be $1cm$. For a given setup, ϵ and l are constants.

V. Observations and Calculations

A. Calibration to find the value of ϵ

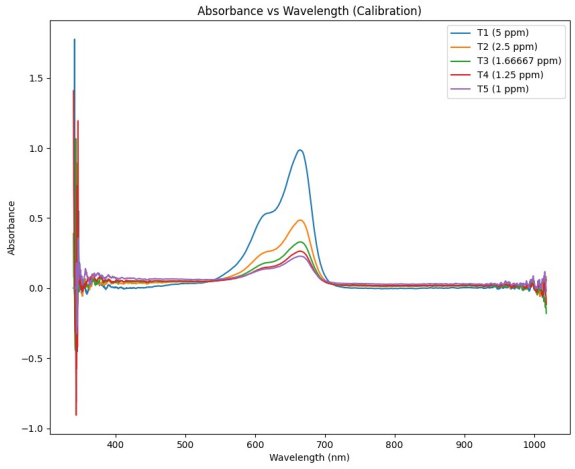


Fig. 1: Absorbance Spectrum of each Iteration

This graph illustrates that as the solution is diluted, the quantity of Methylene Blue (MB) in the sample diminishes. The absorbance reading at 664 nm represents MB concentration, and according to Beer-Lambert's law, absorbance is directly related to concentration. Therefore, the decrease in absorbance upon dilution indicates a reduction in concentration. Given the value of l (= 1cm), the values of absorbance at 664 nm, and the concentrations of each iteration, we can find out the value of ϵ.

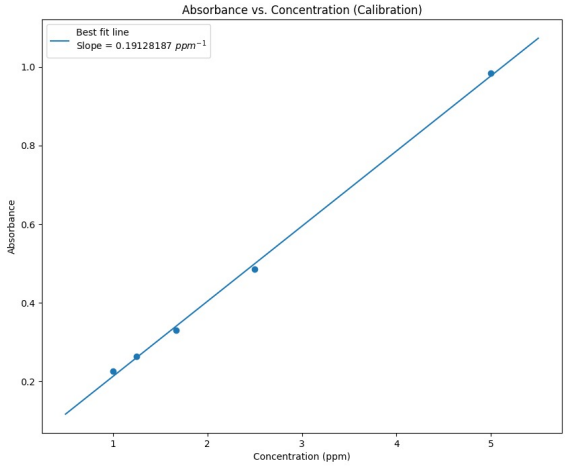


Fig. 2: Graph of Absorbance at 664 nm v/s concentration of MB in M for calibration phase.

Wavelength	Concentration	Absorbance
664.546	5	0.9863
664.546	2.5	0.4855
664.546	1.666666667	0.3369
664.546	1.25	0.2642
664.546	1	0.2278

Referring to the formula:

$$\epsilon \times c \times l = \text{Absorbance}$$

From the above graph (Fig. 2) we get the value of Epsilon as 0.19128 $\text{ppm}^{-1}cm{-}1$

B. Methylene Blue degradation

The Absorbance vs Wavelength plots for all three vials are as follows

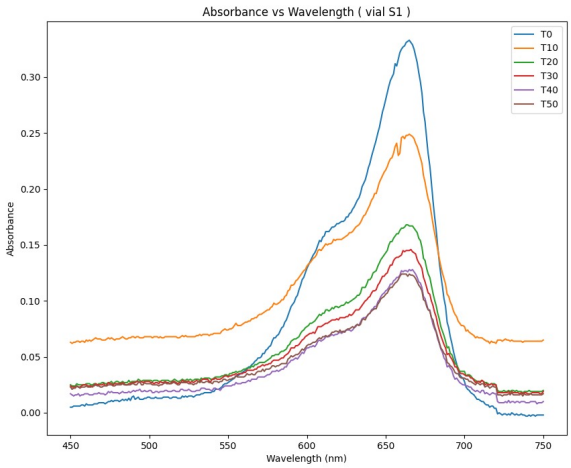
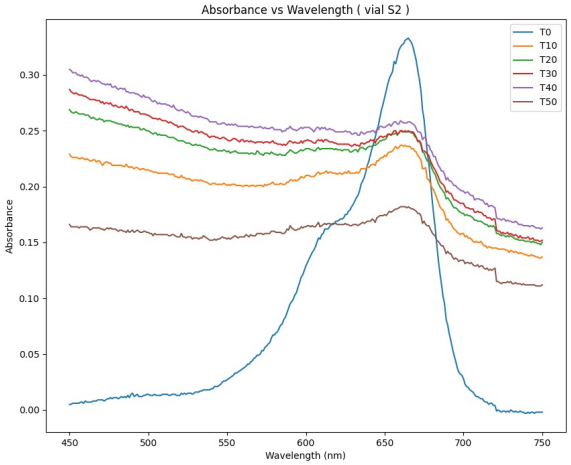


Fig. 3: Absorbance v/s Wavelength for Vial 1



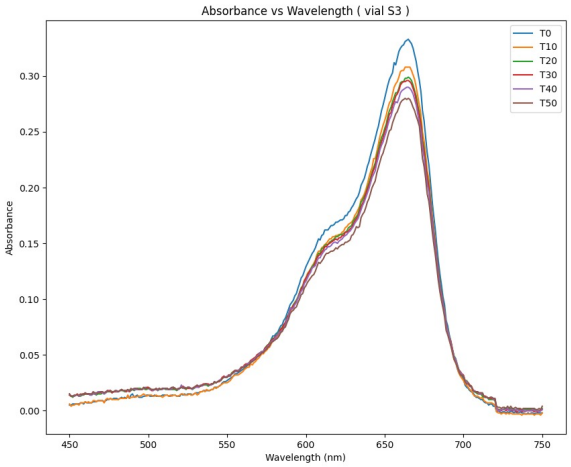


Fig. 5: Absorbance v/s Wavelength for Vial 3

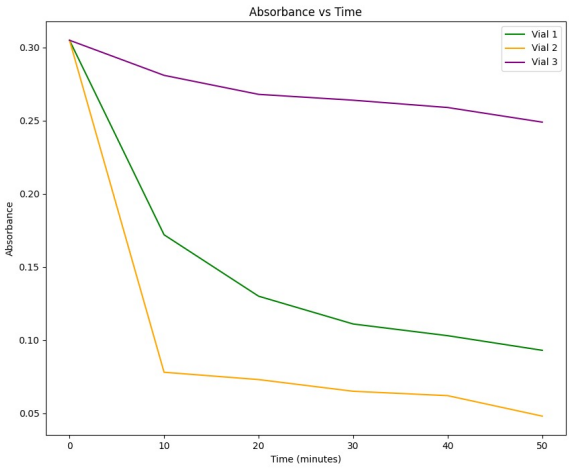


Fig. 6: Absorbance vs time for all vials

Timepoint (in minutes)	Absorbance	Concentration (ppm)
0	0.305	1.5945
10	0.172	0.8992
20	0.13	0.6796
30	0.111	0.5803
40	0.103	0.5385
50	0.093	0.4862

TABLE I: Concentrations from Vial 1

We can see a decrease in the values of concentrations as the time decreases, which means the solution is degrading.

Timepoint (in minutes)	Absorbance	Concentration (ppm)
0	0.305	1.5945
10	0.078	0.4078
20	0.073	0.3816
30	0.065	0.3398
40	0.062	0.3241
50	0.048	0.2509

TABLE II: TABLE 2: Concentrations for Vial 2

However, In the case of vial 2, it is observed that the change in the conecentration within the same time interval is more, indicating a faster rate of degradation due to the presence of the catalyst and light.

Timepoint (in minutes)	Absorbance	Concentration (ppm)
0	0.305	1.5945
10	0.078	1.4690
20	0.073	1.4011
30	0.065	1.3802
40	0.062	1.3540
50	0.048	1.3017

TABLE III: Concentration for Vial 3

There is not much change in the concentration of vial 3 indicating a slower rate of dye degradation due to the absence of the catalyst.

The graph shown below is a plot of $ln(C_0/C)$ vs time (t)

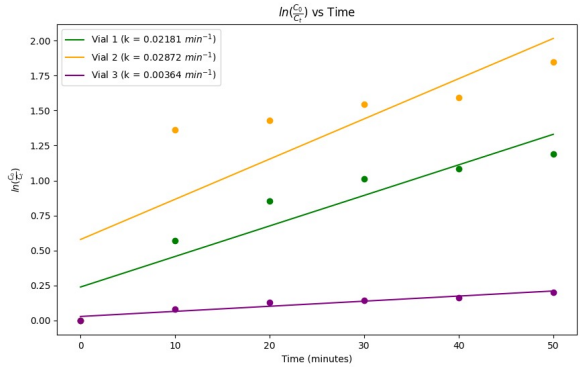


Fig. 7: $ln(C_0/C)$ for all three vials

The straight lines in the above graphs indicate that the reaction follows first-order kinetics. The rate constant for this reaction can be found by calculating the slope of the best-fit line.

Vials	k (min-1)
1	0.02181
2	0.02872
3	0.00364

TABLE IV: Values of rate constant for all the vials

From the above table, we observe that the rate of reaction in vial 2 is the fastest and for vial 3 it's the slowest that is:

$$k_{vial3} < k_{vial1} < k_{vial2} \tag{3}$$

The amount of Methylene Blue degraded after 20 minutes is as follows:
Vial 2 contains Methylene Blue and catalyst kept in light = 1.2129 ppm Vial 2 contains Methylene Blue and no catalyst kept in light = 0.1934 ppm

VI. Conclusion

In conclusion, Fe_3O_4 nanoparticles are an effective photocatalyst when combined with LED light to degrade water's Methylene Blue (MB) pollutants. Three distinct vial setups are used for the experiments. Vial 1 The combination of catalyst and Methylene Blue resulted in the most evident deterioration. Vial 2 (additional magnetic beads) and vial 3 (only Methylene Blue) followed suit. Vial 1 was kept in the dark with aluminium foil, whereas LED lights initially illuminated Vial 2, containing Methylene Blue and Fe_3O_4 and Vial 3, containing Methylene Blue. Readings were taken from all three vials. Each vial's absorbance was measured after every ten minutes. Methylene Blue concentration calibration and degradation kinetics analysis demonstrated that the catalyst's presence and concentration significantly influenced the reaction rate. This highlights the role of Fe_3O_4 nanoparticles in the degradation of Methylene Blue. The plots of $ln(C_0/C)$ vs time, where C_O represents the starting concentration, and C is the concentration at t time, indicate that the reaction follows first-order kinetics. The slope of this graph gives the value of Rate constant(k) for the reaction, which comes out to be 0.02181 for vial 1, 0.02872 for vial 2 and 0.00364 for vial 3. Thus, the experiment shows that both nanoparticles and light are necessary for the degradation of Methylene Blue

VII. Author Contributions

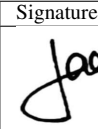
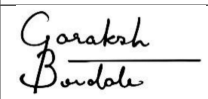
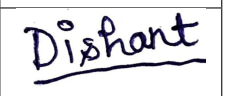
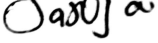
Name	Roll number	Contribution	Signature
Faayza Vora	23110109	Introduction, Safety measures, Material, Graphs,Apparatus, compiling of the report, Handeled the Vial 2 in the lab.	
Goraksh Bendale	23110118	Performed calibration experiment in lab, Observation and calculations for the calibration experiment	
Dishant Tanmay	23110100	Proceedure, Handeled the vial 3 and the timer in the lab	
Hriday Pandya	23110136	Observations, Calculations, handeled vial 2 in the lab , Compiling of the report	
Haravath Saroja	23110127	Conclusion, Performed Calibration experiment in the lab	

TABLE V: Author's Contribution