BS 192: Chemistry Lab Report
Experiment 4: Photo-Catalytic Degradation of Methylene Blue

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In this experiment, we investigated the degradation of methylene blue, a common organic pollutant, under three different conditions: (1) in a dark environment with iron oxide nanoparticles (Fe_3O_4) as a photocatalyst, (2) under LED light with iron oxide nanoparticles (Fe_3O_4) as a photocatalyst, and (3) under LED light without a catalyst as a control. We analyzed the kinetics of the reactionunder these conditions, determined the molar extinction coefficient (ϵ) of methylene blue using Beer-Lambert's Law. The absorption spectra of the solutions in the different vials were recorded at regular intervals to monitor the reaction progress. The results demonstrate that the presence of a photocatalyst significantly enhances the degradation efficiency compared to the control experiments. The use of (Fe_3O_4) nanoparticles under LED light proved to be an effective approach for breaking down methylene blue in wastewater, highlighting the potential of photocatalysis in environmental remediation.

Index Terms - Photo-catalysis, Methylene Blue, Fe_3O_4 nanoparticles, UV-Vis spectroscopy, Beer-Lambert's Law, Chemical Reaction Kinetics

I. Introduction

This experiment seeks to study the degradation of organic dye contaminants, namely Methylene Blue, which is a frequent industrial wastewater contaminant. We use Fe_3O_4 nanoparticles and LED light as the photocatalyst for degrading the dye and tracking its degradation by measuring its absorption spectra. There are three vials holding different mixtures with one as the control consisting only of the dye solution. To calculate concentration from absorbance, first we do a calibration to obtain the molar extinction coefficient by Beer-Lambert's law:

$$Absorbance = \epsilon \times c \times l$$

Where ϵ is the molar extinction coefficient, c is the concentration, and l is the path length. The molar extinction coefficient (ϵ) measures how strongly a chemical species or substance absorbs light at a particular wavelength. Thus, absorbance is proportional to concentration.

This reaction is based on the principle of absorption of light by Fe_3O_4 nanoparticles by light, which results in the generation of electron-hole pairs that facilitate the breakdown of dye. The nanoparticles may also adsorb some dyes due to electrostatic interactions. The reactions involved are: [MB = Methylene Blue]

$$\mathrm{Fe_3O_4 + hv \longrightarrow Fe_3O_4\,(e^-\,(CB) + h^+(VB))} \quad (1)$$

$$\mathrm{MB + h^+(VB) \longrightarrow Oxidation\,of\,MB} \quad (2)$$

$$\mathrm{H_2O + h^+(VB) \longrightarrow OH^- + H^+} \quad (3)$$

$$\mathrm{MB + OH^- \longrightarrow CO_2 + H_2O} \quad (4)$$

A. Precautions:

- Handle all apparatus carefully.
- Wear gloves, safety glasses, and shoes.
- Avoid mixing droppers between different test tubes.
- Use chemicals with caution while following all necessary safety procedures.

II. Materials and Methods

A. Materials Required

1) Three Vials
2) Three Cuvettes
3) Three Droppers
4) Test Tubes
5) Beaker
6) Aluminum Foil
7) Strong Magnet
8) Magnetic Bead
9) Magnetic Stirrer
10) LED Torch
11) UV-Vis Absorption Spectrophotometer
12) Methylene Blue (MB) Solution (5 ppm)
13) Iron Oxide Fe_3O_4 Nanoparticles

B. Methods

1) **Part A - Study of photocatalysis reaction kinetics of methylene blue dye**
   a) Prepare the following three vials :
      i) Vial 1: 5 ml methylene blue + 5 mg of Fe_3O_4 nanoparticles. Wrap it with Aluminum foil and keep aside (Dark experiment).
      ii) Vial 2: 5 ml methylene blue + 5 mg of Fe_3O_4 nanoparticles + 1 magnetic bead. Put it under LED torch on top of the magnetic stirring bar.
      iii) Vial 3: 5 ml methylene blue: control experiment. Put it under the LED light on top of the magnetic stirring bar. (Control experiment)
   b) Record UV-Vis absorption spectra of the solution in every 10 minutes (5 readings), as given below:
      Vial 1:
      i) Put vial 1 near the magnetic post/bar to remove the Fe_3O_4 nanoparticles.
      ii) Take 2 ml of the sample in a cuvette 1 and measure the absorbance spectrum.
      iii) Pour this 2 ml back in the vial (after measurement) and keep it in dark.
      iv) Repeat above steps to take 5 readings at 10 minutes intervals each.
      Vial 2:
      i) Take vial 2 out and put it near the magnetic post/bar to remove the Fe_3O_4 nanoparticles.
      ii) Take 2 ml of the sample in cuvette 2 and measure absorbance spectrum.
      iii) Pour this 2 ml back in the vial (after measurement) and put the vial back under LED at the earliest.
      iv) Repeat above steps to take 5 readings at 10 minutes intervals each.
      Vial 3:
      i) Take 2 ml from vial 3 and measure absorbance spectrum.
      ii) Pour this 2 ml back in the vial (after measurement).
      iii) Put the vial back under LED at the earliest.
      iv) Repeat above steps to take 6 readings at 10 minutes intervals each.

   NB: Start the timer when you add Fe_3O_4 nanoparticles to the solution and stop it while recording UV-Vis spectra of the solution. Do not mix up the vials.

2) **Part B - Calculation of molar extinction coefficient of methylene blue**
   Procedure of calibration with known concentrations:
   a) Take 2 ml MB solution with a concentration of 5 ppm. Record the UV-Vis spectra of the following solutions systematically (one by one):
      i) TT 1 : 2 ml MB
      ii) TT 2 : 1 ml MB + 1 ml water
      iii) TT 3 : 1 ml MB + 2 ml water
      iv) TT 4 : 1 ml MB + 3 ml water
      v) TT 5 : 1 ml MB + 4 ml water
   b) Take about 2 ml from each of the test tubes and measure their absorption spectra.
   c) Again, the water level will go down as the hydrogen gas evolves.
   d) Plot absorbance maximum with different MB concentrations.
   e) From the slope of this graph, calculate ϵ. Note that l = 1 cm.

III. Results

A. Calibration test in controlled environment:

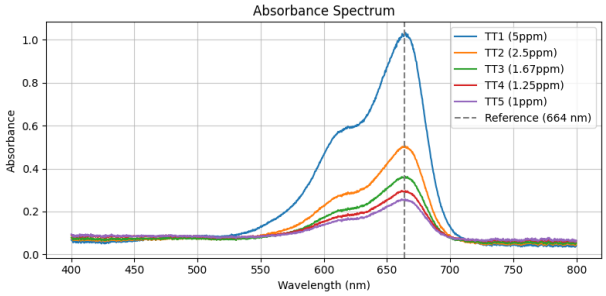

Fig. 1: Absorbance Spectrum obtained for the known concentrations of methylene blue solution.

We now should plot the absorbance at 664 nm v/s the concentration of methylene blue in ppm, which should be a straight line.

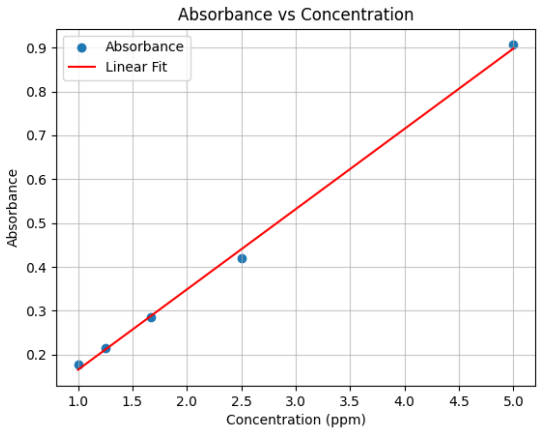

Fig. 2: Graph of Absorbance at 664 nm (maxima) v/s Concentration of melthylene blue (in ppm).

The graph demonstrates that as the Methylene Blue solution is diluted, the concentration of MB in the sample decreases. According to Beer-Lambert's law, absorbance is directly proportional to concentration. Thus, the observed decrease in absorbance with dilution reflects a reduction in MB concentration. The absorbance measured at 664 nm wavelength corresponds to the concentration of methylene blue. The path length l is set to 1 cm, and given the absorbance values

at 664 nm and the concentrations for each dilution, we can determine the molar absorptivity given by ϵ by finding out the slope of this curve, which comes out to be $0.183\ ppm^{-1}cm^{-1}$ or $183.26\ Lg^{-1}cm^{-1}$.

$$\epsilon = 0.183\ ppm^{-1}cm^{-1} = 183.26\ Lg^{-1}cm^{-1}$$

B. *Degradation of Methylene Blue:*

We used three different vial of Methylene blue and kept each of then in specific conditions.

1) Vial 1: Methylene Blue + Fe_3O_4
2) Vial 2: Methylene Blue + Fe_3O_4 + light
3) Vial 3: Methylene Blue + light

From each of these vials, we obtained different values for absorption spectra.

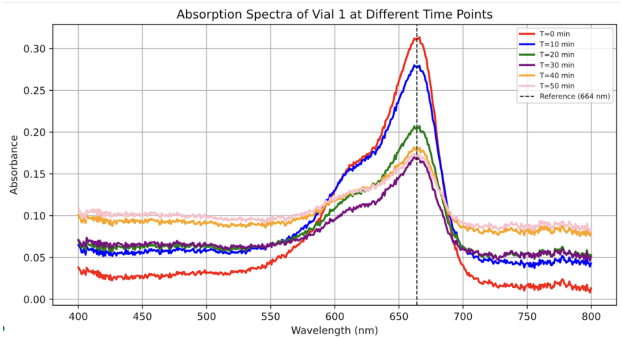

Fig. 3: Absorption spectra for vial 1.

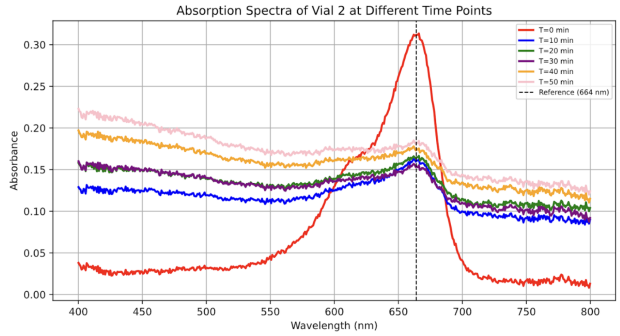

Fig. 4: Absorption spectra for vial 2.

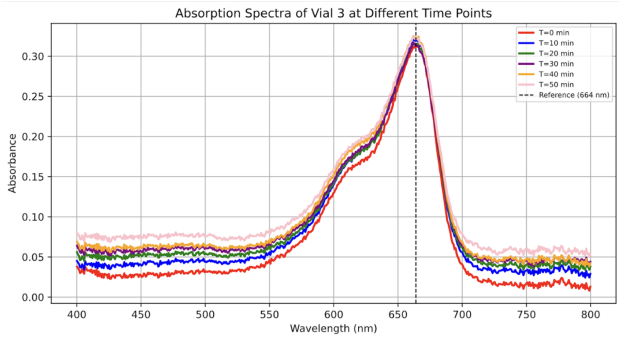

Fig. 5: Absorption spectra for vial 3.

We see that absorption with respect to time time is seen to be decreasing the fastest for Vial 2, while Vial 1 undergoes a slow reaction and vial 3 barely shows signs of change. This is due to the fact that neither vial 1 nor 3 have the ideal conditions for degradation that are present, namely, the presence of Fe_3O_4 and light simultaneously.

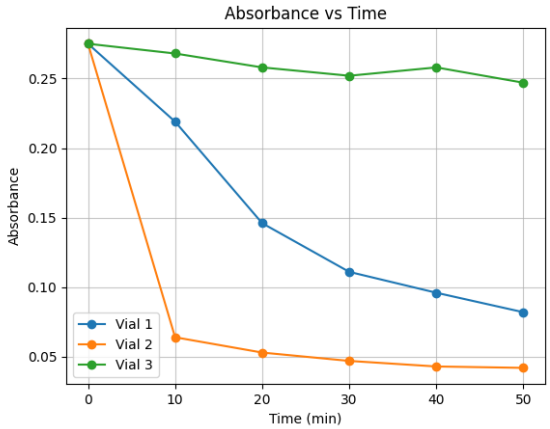

Fig. 6: Graph of Absorbance vs Time (in min) for the 3 vials.

Now we shall attempt to find out the value of $log(C_o/C_i)$ using the value of ϵ we determined to find out the rate at which the degradation reaction occurs. This will also give us a pictorial representation of the difference in rates of reaction across all the three vials.

Rearranging the equation for Beer-Lambert Law, we can use the following equation to find out the concentrations:

$$C = \frac{A}{\epsilon \times L}$$

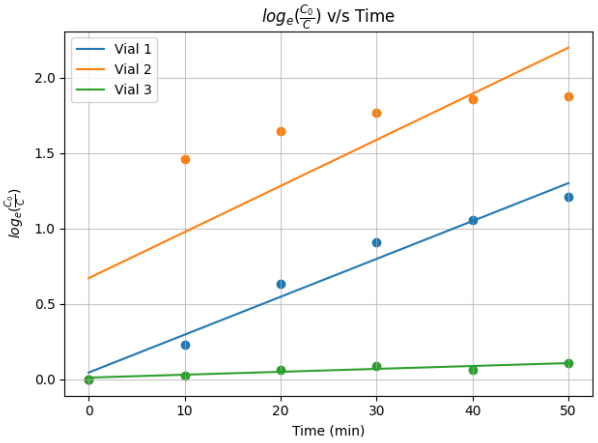

Fig. 7: Graph of $log(C_o/C_i)$ vs Time (in min) for the 3 vials along with the best line fit.

From Fig. 7, we can see that the graph is almost linear. Therefore, we can say that the degradation of methylene blue

follows first order kinetics. The rate of a first order reaction is given by:

$$r = \frac{dC}{dt} = -k \cdot C$$
$$\implies \frac{dC}{C} = -k \cdot dt$$
$$\implies ln(\frac{C_o}{C}) = k \cdot t$$

where k is the rate constant of the reaction. To calculate this rate constant, we can find out the slope of the best fit line for each vial in Fig. 7. The rate constants for the reaction under different conditions are:

Vial	Rate Constant (k)
Vial 1	$k = 0.025\ min^{-1}$
Vial 2	$k = 0.031\ min^{-1}$
Vial 3	$k = 0.002\ min^{-1}$

TABLE I: The rate constant values for the reaction in each vial (under different conditions)

Hence, we can see that the rate constants for the vials under different conditions follow the relation:

$$k_{vial3} < k_{vial1} < k_{vial2}$$

C. Readings and Calculations:

Vial	Time (mins)	Absorbance	Concentration (in ppm)	$\ln(\frac{C_0}{C})$
Vial 1	0	0.275	1.502	0
	10	0.219	1.196	0.228
	20	0.146	0.798	0.633
	30	0.111	0.606	0.907
	40	0.096	0.524	1.052
	50	0.082	0.448	1.210
Vial 2	0	0.275	1.502	0
	10	0.064	0.350	1.458
	20	0.053	0.290	1.646
	30	0.047	0.257	1.767
	40	0.043	0.235	1.856
	50	0.042	0.229	1.879
Vial 3	0	0.275	1.502	0
	10	0.268	1.464	0.026
	20	0.258	1.409	0.064
	30	0.252	1.377	0.087
	40	0.247	1.409	0.064
	50	0.213	1.349	0.107

TABLE II: Absorbance, Concentration and $\ln(\frac{C_0}{C})$ for each vial at each time interval.

At t = 0, the concentration is 1.502 ppm in all three vials.

- At t = 30 mins, the concentration of methylene blue in vial 2 is 0.257 ppm, hence the concentration degraded by 1.245 ppm in 30 mins in presence of the catalyst and with exposure to light.
- At t = 30 mins, the concentration of methylene blue in vial 3 is 1.377 ppm, hence the concentration degraded by 0.125 ppm in 30 mins in presence with exposure to light and absence of the catalyst.

Hence, the amount of degradation of methylene blue in 30 mins is much greater when the photocatalyst and light are both present in comparison to when the light is present but the photocatalyst is not. This highlights the importance of the photocatalyst for the reaction to occur.

Concentration	Absorbance
5 ppm	0.905
2.5 ppm	0.419
1.67 ppm	0.285
1.25 ppm	0.215
1 ppm	0.178

TABLE III: Concentration and Absorbance values used for calibration and finding out ϵ

IV. Conclusion

In this experiment, we calculated the concentration of Methylene Blue at different intervals for three different vials. We can conclude that maximum degradation was observed in the vial 2 (Fe_3O_4 + light) due to the combined effect of light absorption and the presence of Fe_3O_4 magnetic nanoparticles. The second maximum degradation was observed in the vial 1 (Fe_3O_4 dark), where it contains nanoparticles of the Fe_3O_4 facilitate degradation in absence of the light. Most negligible degradation was observed in the vial 3 (only light) in absence of catalyst.

This experiment proved Beer-Lambert's law by plotting the calibration curve of absorbance v/s concentration which allows us to determine the molar coefficient (ϵ) of Methylene Blue. The calibration plot using a test tube(TT1 - TT5) helped to determine the molar coefficient of Methylene Blue.

$$\epsilon = 0.183\ ppm^{-1}cm^{-1} = 183.26\ Lg^{-1}cm^{-1}$$

V. Author Contributions

1) Akshit Chhabra, 24110026
   - Performed the experiment and conducted the procedure for vial 1 in degradation of methyl blue.
   - Completed the 'Abstract' and 'Author Contributions' sections and compiled, formatted the report on LaTeX.
2) Rayan Talukder, 24110294
   - Performed the experiment and assisted in the calibration tests in controlled environment.
   - Completed the 'Results' section.
3) Rhythem Soni, 24110296
   - Performed the experiment and conducted the procedure for vial 2 in degradation of methyl blue.
   - Completed the 'Introduction' section and assisted in the 'Materials and Methods' section.
4) Rishi Soni, 24110297

- Performed the experiment and assisted in the calibration tests in controlled environment.
- Completed the 'Conclusion' section.

5) Roshia Shweta, 24110304
   - Performed the experiment and conducted the procedure for vial 3 in degradation of methyl blue.
   - Assisted in the 'Materials and Methods' section.

REFERENCES

[1] BS 192 Chemistry Lab Manual