Experiment 5
Degradation of an organic pollutant in water using LED light and a photocatalyst

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CONTENTS

I. INTRODUCTION

In this experiment, we aim to investigate the degradation of organic dye pollutants, specifically Methylene Blue, a common contaminant in industrial wastewater. We utilize Fe_3O_4 nanoparticles and LED light as a photocatalyst to degrade the dye and monitor its degradation by measuring its absorption spectra. The setup involves three vials with different mixtures, including one serving as a control containing only the dye solution. To get concentration from absorbance, we first do a calibration to find the molar extinction coefficient using Beer-Lambert's law:

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

Where ϵ is the molar extinction coefficient, l is the path length, and c is the concentration.

The principle behind this reaction involves the absorption of light by the Fe_3O_4 nanoparticles, resulting 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]

$$Fe_3O_4 + h\nu \longrightarrow Fe_3O_4\,(e^-(CB) + h^+(VB)) \tag{2}$$

$$MB + h^+(VB) \longrightarrow Oxidation\,of\,MB \tag{3}$$

$$H_2O + h^+(VB) \longrightarrow OH^- + H^+ \tag{4}$$

$$MB + OH^- \longrightarrow CO_2 + H_2O \tag{5}$$

Safety Precautions:

i Wear gloves, eyeglasses, and toe-covered shoes before entering the lab.

ii Handle all apparatus with care. Avoid mixing droppers between different test tubes.

iii Use chemicals with caution while following all necessary safety procedures.

II. EXPERIMENT DETAILS

A. Apparatus

1) Test tubes
2) Aluminium foil
3) LED torch
4) Magnetic bead
5) Beaker
6) UV-Vis absorption spectrophotometer
7) Three vials
8) Magnetic stirrer
9) Strong magnet

B. Materials

1) Methylene Blue
2) Fe_3O_4 nanoparticles

C. Procedure

1) Experiment 1

i For the preparation of calibration, we first take variable concentrations of Methylene Blue in five test tubes.

a) TT1: 2 ml Methylene Blue
b) TT2: 1 ml Methylene Blue + 1 ml water
c) TT3: 1 ml Methylene Blue + 2 ml water
d) TT4: 1 ml Methylene Blue + 3 ml water

e) TT5: 1 ml Methylene Blue + 4 ml water

ii Now take 2 ml of solution from each test tube 1-5 and plot their absorbance vs. concentration graph from the UV-Vis absorption spectra.

iii Calculate the molar extinction coefficient (ϵ) by taking $l = 1\,cm$ and taking the slope from the graph.

2) Experiemnt 2

i Get three vials ready.

a) In the first one, mix 5 ml of Methylene Blue with 5 mg of Fe_3O_4 nanoparticles.

b) In the second one, mix the same Methylene Blue and Fe3O4 nanoparticles and add a magnetic bead.

c) The third one has Methylene Blue.

ii Wrap the first vial with aluminum foil and set it aside.

iii Put the second and third vials on the magnetic stirrer under a bright LED light.

iv Every 10 minutes, do the following

a) Take the first vial near the magnet to move the particles to the side. Then, take 2 ml of the liquid, measure its absorption spectrum, and put it back in the vial in the dark.

b) Take the second vial near the magnet to move the particles to the side. Then, take 2 ml of the liquid, measure its absorption spectrum, put it back in the vial, and put it back under the LED light as soon as possible.

c) Take 2 ml of the liquid from the third vial, measure its absorption spectrum, put it back in the vial, and put it back under the LED light as soon as possible.

III. Results and Calculations

A. Calibration for ϵ

We took five test tubes with a different Methylene Blue concentration and observed their absorption spectra.

1 2 ml Methylene Blue [$C_{MB} = 5ppm$]

2 1 ml Methylene Blue + 1 ml distilled water [$C_{MB} = 2.5\,ppm$]

3 1 ml Methylene Blue + 2 ml distilled water [$C_{MB} = 1.667\,ppm$]

4 1 ml Methylene Blue + 3 ml distilled water [$C_{MB} = 1.25\,ppm$]

5 1 ml Methylene Blue + 4 ml distilled water [$C_{MB} = 1ppm$]

The absorption spectra for all test tubes in one graph are as follows:

We observe a peak at 665 nm, which corresponds to Methylene Blue. Plotting the absorbance vs. concentration for this wavelength and computing the slope, we obtain the value of ϵ.

1) Calculations

$$A = \epsilon \times c \times l \tag{6}$$

Where ϵ is the molar extinction coefficient, l is the path length, and c is concentration.

Slope of graph = $\frac{A}{c} = \epsilon$

From the graph,

$$Slope = \epsilon \times l = 0.187759\,ppm^{-1} \tag{7}$$

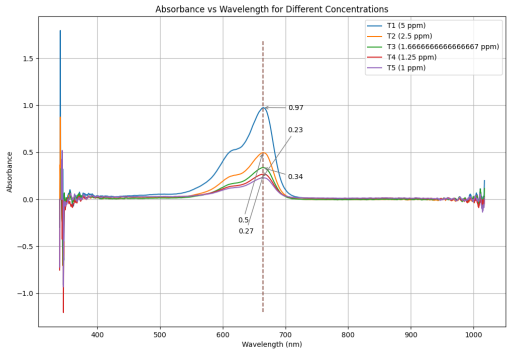


Fig. 1: Absorbance vs. Wavelength (Calibration)

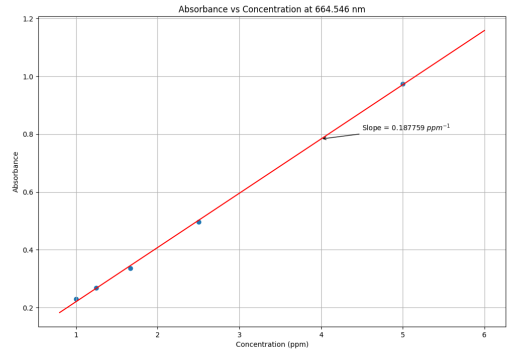


Fig. 2: Absorbance vs. Concentration (Calibration)

$$\implies \epsilon = 0.187759\,ppm^{-1}\,cm^{-1} \tag{8}$$

B. Methylene Blue degradation

We took three vials to study the degradation of Methylene Blue with different starting conditions:

i Vial 1: Methylene Blue + nanoparticles of Fe_3O_4

ii Vial 2: Methylene Blue + nanoparticles of Fe_3O_4 + light

iii Vial 3: Methylene Blue + light

We plot the graph of absorbance vs. wavelength for each vial with samples taken at intervals of 10 minutes.

1) Vial Graphs

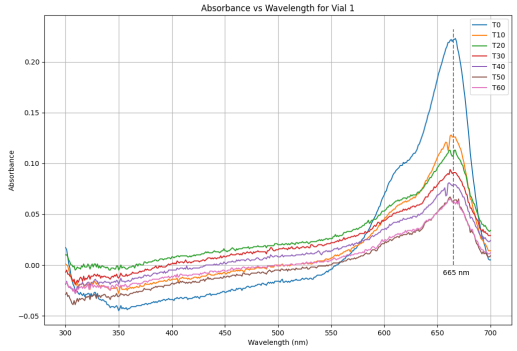


Fig. 3: Absorbance vs. Wavelength for vial 1

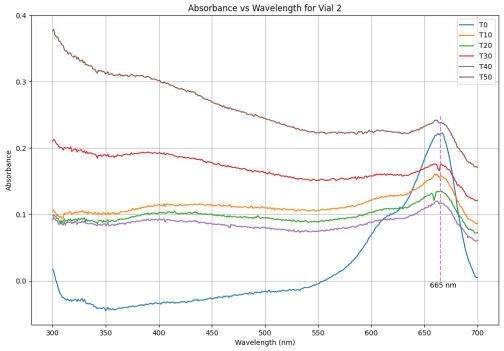


Fig. 4: Absorbance vs. Wavelength for vial 2

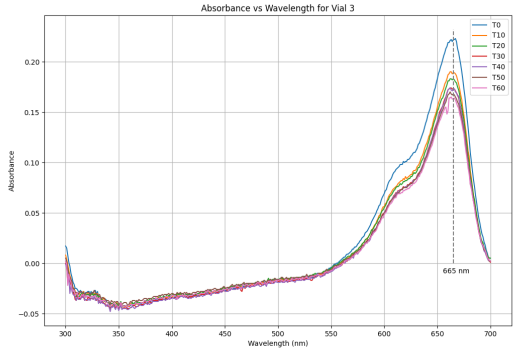


Fig. 5: Absorbance vs. Wavelength for vial 3

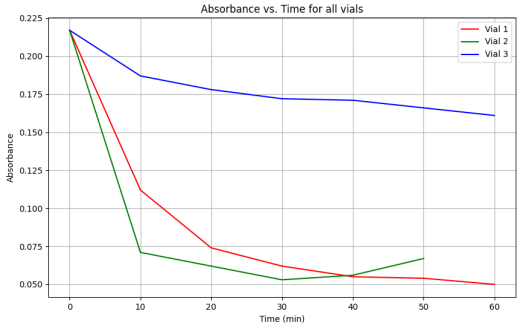


Fig. 6: Absorbance vs. Time for all vials

We focus on the absorbance value at 665 nm. We see a clear decrease with time for vial 1 and vial 2, whereas, for vial 3, absorbance decreases slowly. For vial 2, at lower wavelengths, there is an increase in absorbance because of Rayleigh scattering due to the presence of Fe_3O_4 nanoparticles.

$$Scattering \propto \frac{1}{\lambda^4} \tag{9}$$

To account for this, we will consider absorbance value to be,

$$Abs = Abs_{665nm} - Abs_{700nm} \tag{10}$$

2) Calculations

Timepoint (min)	Absorbance	Concentration (ppm)
0	0.217	1.1557
10	0.112	0.5965
20	0.074	0.3941
30	0.062	0.3302
40	0.055	0.2929
50	0.054	0.2876
60	0.050	0.2663

TABLE I: Concentrations for Vial 1

We observe a decrease in concentration values for vial 1.

Timepoint (min)	Absorbance	Concentration (ppm)
0	0.217	1.1557
10	0.071	0.3781
20	0.062	0.3302
30	0.053	0.2823
40	0.056	0.2983
50	0.067	0.3568

TABLE II: Concentrations for Vial 2

We see a sharp decrease in concentration values for vial 2 because we had Fe_3O_4 and light acting on it. Also, we could not obtain the absorption spectrum for T = 60 min because of high Rayleigh scattering.

Timepoint (min)	Absorbance	Concentration (ppm)
0	0.217	1.1557
10	0.187	0.9960
20	0.178	0.9480
30	0.172	0.9161
40	0.171	0.9107
50	0.166	0.8841
60	0.161	0.8575

TABLE III: Concentrations for Vial 3

We do not see a large decrease in concentration values, indicating a low percentage of dye degradation.

Now, we plot the graph of $ln(\frac{C_0}{C_t})$ vs t for all vials,

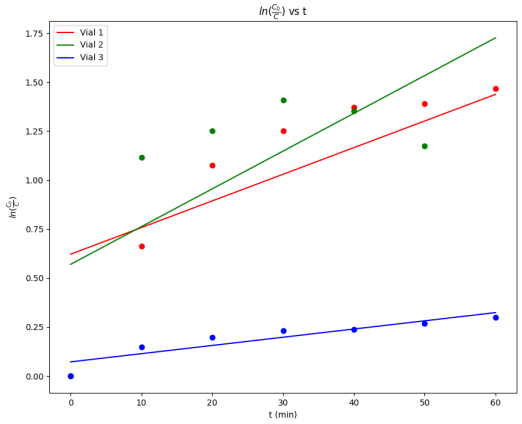


Fig. 7: $ln(\frac{C_0}{C_t})$ vs t for all vials

These straight-line graphs indicate first-order kinetics. We can calculate the rate constant for the reaction under the conditions of three vials via the slope of the curve as,

$$k = \frac{1}{t} ln(\frac{C_0}{C_t}) \tag{11}$$

Vial	k (min^{-1})
1	0.0136
2	0.0193
3	0.0042

TABLE IV: Rate constant for different vials

We observe that,

$$k_{vial2} > k_{vial1} > k_{vial3} \tag{12}$$

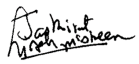
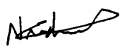
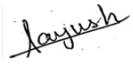
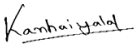
Amount of Methylene Blue degraded in 20 minutes:

Vial 2 [Methylene Blue + Catalyst] = $0.8255\ ppm$
Vial 3 [Methylene Blue + No Catalyst] = $0.2077\ ppm$

IV. Conclusion

In this experiment, we first got the value of the molar extinction coefficient. Then, we examined the kinetics of degradation of Methylene Blue dye in the presence and absence of the catalyst. We had three vials, one having Fe_3O_4 nanoparticles wrapped in aluminum foil [Vial 1], one without the nanoparticles but kept under LED light [Vial 3], and one with the nanoparticles as well as kept under LED light [Vial 2]. After observing the UV-Vis absorption spectra for these vials in fixed intervals of time, we found out that the rate of degradation is fastest in vial 2, and it is high in vial 1, but it is low or negligible in vial 3. However, the high rate of degradation in vial 1 is not because of a decrease in the concentration of Methylene Blue but because of the adsorption of Methylene Blue particles onto the Fe_3O_4 nanoparticles. We also calculated the dye's degradation amount in twenty minutes, both with and without catalyst. Those results indicate that nanoparticles are essential for the effective degradation of Methylene Blue dye, and there is no effective degradation just being kept under LED light.

V. Author Contribution

Name	Contribution	Signature
Jaskirat Singh Maskeen (23110146)	Document structure, Results, Calculations and Conclusion.	
Nishchay Bhutoria (23110222)	Introduction and Safety precautions.	
Aayush Bundel (23110005)	Experimental details.	
Kavya Lavti (23110164)	Experimental details	
Kanhiyalal (23110155)	Absent	

Everyone present, contributed equally in the lab.