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Effect of UV Light Intensity on Methylene Blue Degradation by Fe_3O_4 Nanoparticles: A Distance-Based Study

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Abstract
Given the extensive use of synthetic dyes like methylene blue in industries such as textiles, plastics, and paper manufacturing, their environmental impact upon discharge into wastewater systems is a critical concern. These dyes are highly resistant to degradation, posing significant challenges for conventional wastewater treatment methods. As a result, innovative approaches are needed to address the persistent pollution caused by these dyes.
This paper investigates the effect of UV light intensity on the degradation of methylene blue dye using magnetite iron oxide (Fe_3O_4) nanoparticles. UV light was specifically chosen for this investigation due to its ability to activate nanoparticles and promote the generation of reactive species, which enhance the degradation process. Fe_3O_4 nanoparticles are explored for their efficiency as adsorbents to mitigate this impact. The experiment involved varying the distance of a UV light source (15, 20, 25, and 30 cm) from methylene blue dye solutions to assess how light intensity influences the degradation rate of the dye by Fe_3O_4 nanoparticles. Spectrophotometric measurements at 665 nm were used to monitor changes in dye concentration over 80 minutes.

Keywords: Methylene blue, Fe3O4 nanoparticles, UV light intensity, dye degradation, wastewater treatment, reactive oxygen species, adsorption, photocatalysis, environmental remediation, spectrophotometry.

Introduction

Synthetic dye pollution has become a critical environmental issue, with significant implications for both wildlife and human health. Annually, around 1 million tons of synthetic dyes are produced worldwide,(Tkaczyk et al.) with approximately 10-15% of these dyes discharged into the environment during manufacturing and application processes (Al-Tohamy et al.). Synthetic dyes contribute to 17-20% of industrial wastewater,(Sarkar et al.) and studies indicate that 70-80% of the synthetic dyes used in textiles are carcinogenic, mutagenic, or teratogenic (Islam et al.). These statistics highlight the urgency of developing effective dye removal methods to mitigate these environmental impacts.
One promising approach for dye removal is adsorption using nanoparticles. Fe_3O_4 nanoparticles, in particular, have shown considerable potential due to their large surface area, superparamagnetic properties, and ability to adsorb various contaminants. These nanoparticles can be easily separated from aqueous solutions using a magnetic field, making them highly practical for wastewater treatment applications. Additionally, Fe_3O_4 nanoparticles can be used in magnetic resonance imaging, drug delivery systems, as

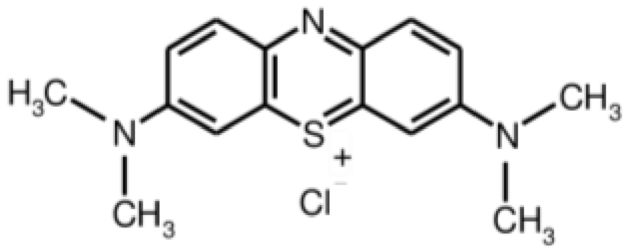
sorbents for heavy metals, as antibacterial agents, catalysts, electrochemical biosensors, shielding materials in electromagnetic interference, and for energy harvesting.

This research investigates how the intensity of light, altered by the distance (15, 20, 25, 30 cm) of a UV light lamp from the dye solution, affects the rate of degradation of methylene blue dye by Fe_3O_4 nanoparticles over 80 minutes. The intensity of UV light plays a crucial role in the activation of Fe_3O_4 nanoparticles.(Ruíz-Baltazar et al.) Under UV light irradiation, the energy absorbed by the nanoparticles can generate reactive species such as hydroxyl radicals, which significantly enhance the degradation process of dyes like methylene blue (Abdel et al.). This study focuses on quantifying the impact of different light intensities on the adsorption and degradation efficiency of Fe_3O_4 nanoparticles.

Spectrophotometric measurements at 665 nm, the lambda max for methylene blue,(Lipatova et al.) were employed to monitor changes in dye concentration. This wavelength corresponds to the maximum absorbance of methylene blue, allowing for accurate tracking of the degradation process. This approach enabled a detailed assessment of the degradation kinetics of methylene blue dye under varying UV light intensities, providing insights into the efficiency of Fe_3O_4 nanoparticles as adsorbents for dye removal in wastewater treatment.

1) Methylene blue dye ($C_{16}H_{18}ClN_3S$)

Methylene blue is a synthetic dye extensively used in various industries, including textiles, plastics, and paper manufacturing, for its distinctive blue colour. (Oladoye et al.) Its chemical structure comprises a phenothiazine core with a central nitrogen atom, making it a thiazine dye. (Wainwright and Crossley). Due to its stable molecular configuration, methylene blue is highly resistant to degradation, posing environmental challenges when released into industrial wastewater. (Hamad and Idrus)Consequently, effective treatment methods are imperative to mitigate its environmental impact before discharge.



Chemical structure of methylene blue

2) Magnetite iron- oxide nanoparticles (Fe_3O_4)

Magnetite iron-oxide nanoparticles (Fe_3O_4) are a type of magnetic nanoparticle extensively used in environmental remediation for their ability to catalyse the degradation of pollutants (M. Liu et al.). These nanoparticles serve as efficient photocatalysts for the degradation of methylene blue, a common synthetic dye found in industrial wastewater (Dwivedi et al.). The Fe_3O_4 nanoparticles, with their cubic inverse spinel structure, exhibit superparamagnetic properties, which allow them to be easily manipulated and recovered using external magnetic fields(Nguyen et al.). When exposed to UV light, these nanoparticles generate reactive oxygen species (ROS) that break down methylene blue molecules, reducing their environmental impact (Bashir et al.). Precise control over experimental conditions is needed to achieve maximum efficiency in pollutant removal.

Methodology

Independent Variable	Dependent Variable
The UV lamp was positioned at different distances (15 cm, 20 cm, 25 cm, 30 cm) from the round-bottom flask containing the methylene blue dye solution. These varying distances allow us to assess adsorption at different light intensities.	The variation in absorbance at 665 nm of the methylene blue solution, measured using a spectrophotometer, indicates the extent of degradation of the dye by Fe3O4 nanoparticles over a period of 80 minutes.

Materials required

The experimental setup included a bar magnet, a Vayinato 50 watt UV lamp, and a round-bottom flask. The chemical reagents involved were $FeCl_2$, $FeCl_3$, NH_4OH, and methylene blue dye. Spectrophotometric measurements were taken using a Spectrophotometer.

Procedure

Fe_3O_4 nanoparticles were synthesised using the co-precipitation by adding 100 mmol of $FeCl_3$ and 50 mmol of $FeCl_2$ to 200 cm³ of distilled water in a round-bottom flask, stirring at 300 rpm for 50 minutes at 75°C. Chilled NH_4OH was added, then stirred at 500 rpm for 90 minutes. The nanoparticles were collected with a magnet, and dried for two days. A 10 ppm methylene blue solution was prepared by diluting 10 mg of methylene blue in 100 cm³ of distilled water to 100 ppm, then further diluting it tenfold. This solution was divided into five flasks (20 cm³ each), and initial absorbance at 665 nm was measured. After returning the solutions to the flasks, 0.05 grams of Fe_3O_4 nanoparticles were added and stirred gently. A Vayinato 50 watt UV lamp was used for all samples to ensure consistent light intensity. Absorbance readings at 665 nm were taken at 20, 40, 60, and 80 minutes with the UV lamp placed at 15, 20, 25, and 30 cm distances. There was also a control group which had no UV lamp, in order to keep the nanoparticles unactivated.

Magnetite iron oxide nanoparticles (Fe_3O_4) possess several advantageous properties that make them highly effective for adsorption applications in environmental remediation. Their large surface area provides active sites for the adsorption of pollutants, ensuring a higher rate of interaction with contaminants like methylene blue (X. Liu et al.). Additionally, the small volume of these nanoparticles allows them to be easily dispersed in aqueous solutions, maximising their contact with the dye molecules(Singh et al.). Fe_3O_4 nanoparticles also exhibit superparamagnetic properties, which enable their easy separation from solutions using an external magnetic field(Nguyen et al.).

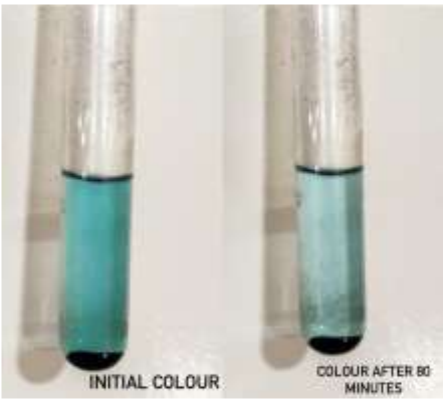
This approach was chosen because co-precipitation is a straightforward and efficient method for synthesising Fe_3O_4 nanoparticles, ensuring high purity and uniform size distribution, which are crucial for consistent experimental results.(Besenhard et al.) The use of UV light to activate the nanoparticles was selected due to its effectiveness in generating reactive oxygen species that enhance the degradation of methylene blue. (Bashir et al.)

By varying the distance of the UV lamp, we could systematically study the effect of light intensity on the degradation process, providing detailed insights into the efficiency of Fe_3O_4 nanoparticles under different conditions. Spectrophotometric measurements at 665 nm allowed precise monitoring of the methylene blue concentration, ensuring accurate assessment of the degradation kinetics.

During the synthesis and experimental procedures involving Fe_3O_4 nanoparticles and methylene blue degradation, several safety precautions were strictly adhered to ensure safety. Personal protective equipment, including lab coats, goggles, and nitrile gloves, were worn at all times to prevent direct contact with chemicals. The synthesis of nanoparticles and handling of chemicals were conducted in a well-ventilated room to avoid inhalation of any harmful fumes. The NH_4OH, being a strong base, was handled with extra care, and all spills were neutralised immediately using appropriate neutralising agents. The UV lamp, which was used to activate the nanoparticles, posed a risk of UV exposure; therefore, the lamp was operated with a UV-shield, and direct eye or skin exposure was avoided. Additionally, proper magnetic handling techniques were employed to safely collect the nanoparticles, and all waste materials, including methylene blue solutions, were disposed of according to hazardous waste disposal regulations. These measures ensure a safe working environment and minimise any potential health risks.

Ethical considerations were also taken into account throughout the study. The use of methylene blue, a potentially harmful dye, was kept to a minimum necessary for experimental accuracy, and efforts were made to ensure that any release into the environment was avoided. Additionally, the data was accurately recorded and reported, and that all findings were presented honestly and transparently..

Drying of nano-particles after synthesis



Colour change observed after 80 minutes

<u>Raw data</u>

Absorbance (absorbance unit) when UV lamp is at a distance of 15 cm

Trial / time	1	2	3	4	5
0	1.483	1.512	1.473	1.534	1.509

20	1.189	1.232	1.343	1.187	1.310
40	1.156	1.184	1.192	1.021	1.102
60	1.112	1.099	1.104	0.985	1.897
80	1.087	1.046	1.001	0.650	0.903

Absorbance (absorbance unit) when UV lamp is at a distance of 20 cm

Trial / time	**1**	**2**	**3**	**4**	**5**
0	1.479	1.513	1.545	1.497	1.478
20	1.326	1.297	1.391	1.296	1.394
40	1.282	1.199	1.272	1.163	1.211
60	1.204	1.177	1.198	1.112	1.175
80	1.194	1.197	1.191	1.129	1.107

Absorbance (absorbance unit, ± 0.001 au) when UV lamp is at a distance of 25 cm

Trial / time	**1**	**2**	**3**	**4**	**5**
0	1.538	1.483	1.523	1.489	1.537
20	1.315	1.312	1.336	1.311	1.289
40	1.211	1.205	1.214	1.208	1.266
60	1.213	1.227	1.189	1.164	1.192
80	1.206	1.184	1.171	1.177	1.135

Absorbance (absorbance unit) when UV lamp is at a distance of 30 cm

Trial / time	**1**	**2**	**3**	**4**	**5**
0	1.532	1.605	1.479	1.536	1.521
20	1.344	1.291	1.312	1.429	1.347
40	1.281	1.217	1.171	1.394	1.218
60	1.197	1.199	1.273	1.293	1.206
80	1.176	1.205	1.198	1.207	1.192

Absorbance (absorbance unit) when no UV lamp is employed

Trial / time	1	2	3	4	5
0	1.527	1.584	1.606	1.583	1.492
20	1.465	1.493	1.519	1.505	1.434
40	1.402	1.491	1.481	1.493	1.388
60	1.391	1.439	1.427	1.438	1.395
80	1.389	1.394	1.402	1.446	1.363

Calculation of average absorbance and concentration

The average absorbance at different time intervals was determined by calculating the mean absorbance value from the five trials conducted at each interval. This was done by summing all absorbance values at a specific time point and dividing by five. To calculate the concentration of methylene blue at different time intervals, the Beer-Lambert law(Swinehart) was applied. According to this law, , where A is the average absorbance, Ɛ is the molar absorption coefficient *($M^{-1}cm^{-1}$ from methylene blue*), c is the molar concentration, and l is the path length of light. There is a linear decline in the concentration of methylene blue dye under UV light. To find the rate of degradation, the gradient of the best-fit line is determined.

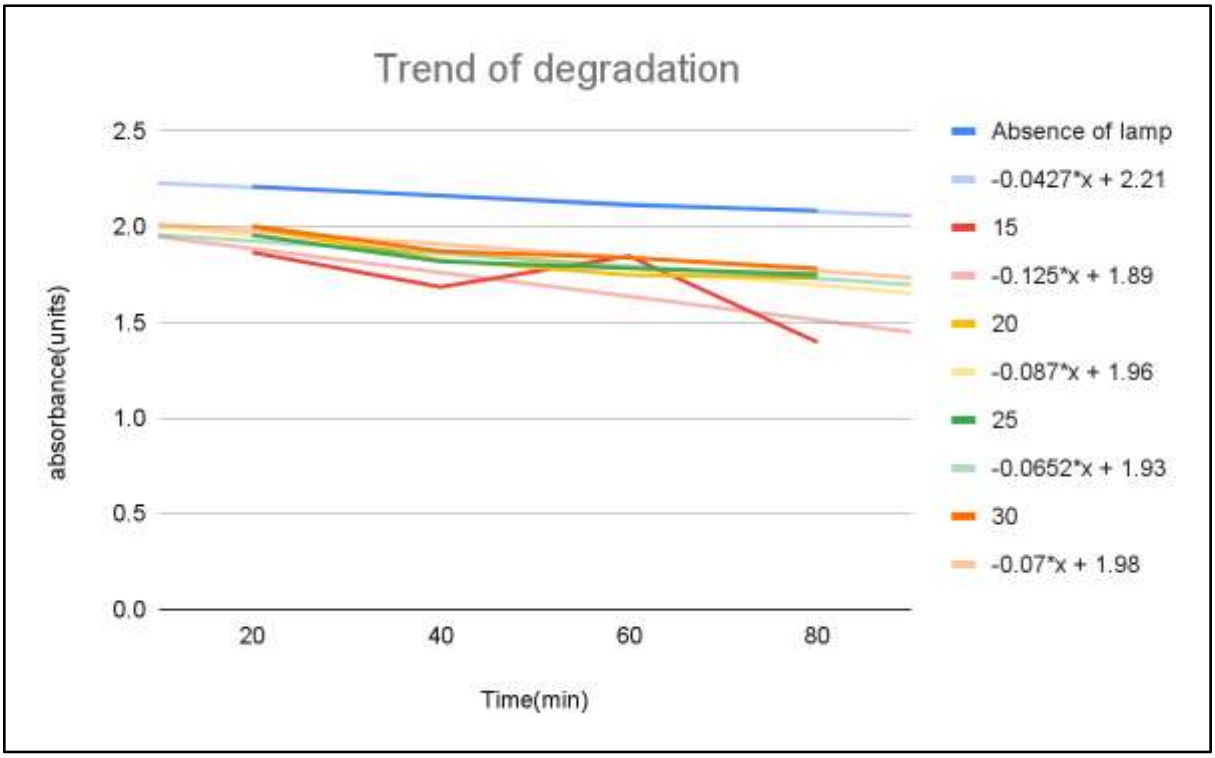
Average of absorbance readings

Distance of lamp/ Time	Absence of lamp	15	20	25	30
0	1.5584	1.5022	1.5024	1.514	1.5346
20	1.4832	1.2522	1.3408	1.3126	1.3446
40	1.451	1.131	1.2254	1.2208	1.2562
60	1.418	1.2394	1.1732	1.197	1.2336
80	1.3988	0.9374	1.1636	1.1746	1.1956

Average of Concentration ($\mu mol/dm^3$) readings

Distance of lamp / Time	Absence of lamp	15	20	25	30
0	2.322503726	2.238748137	2.2390462	2.25633383	2.287034277

20	2.210432191	1.866169896	1.998211624	1.956184799	2.003874814
40	2.162444113	1.685543964	1.826229508	1.819374069	1.872131148
60	2.113263785	1.84709389	1.748435171	1.78390462	1.838450075
80	2.084649776	1.397019374	1.734128167	1.75052161	1.781818182



Trend of degradation

Distance from light source	Trend of degradation
Absence of lamp	-0.0573
15 cm	-0.17
20 cm	-0.126
25 cm	-0.118
30 cm	-0.118

Discussion

The spectrophotometric measurements revealed a notable decrease in absorbance at 665 nm, which corresponds to the reduction in methylene blue concentration. The data indicated that the closer the UV light source was to the solution, the greater the degradation of methylene blue. Specifically, the

degradation rates were calculated to be -0.17, -0.126, -0.118, and -0.118 mol/dm³/min at distances of 15 cm, 20 cm, 25 cm, and 30 cm from the UV light source, respectively. In comparison, the degradation rate was -0.0573 mol/dm³/min in the absence of UV light.
To determine the rate of degradation, the average absorbance values at different time intervals were plotted, and the gradients of the best-fit lines were calculated. The data showed a clear trend of decreasing absorbance over time, with the steepest decline observed at the shortest distance of 15 cm. This indicates that the intensity of UV light plays a crucial role in the activation of Fe_3O_4 nanoparticles and the subsequent generation of reactive oxygen species, which are responsible for breaking down methylene blue molecules. In the control group, where no UV light was used, the methylene blue concentration remained relatively high, highlighting the necessity of UV light for activating the Fe_3O_4 nanoparticles. The variation in degradation rates at different light intensities aligns with previous studies that show a direct correlation between UV light intensity and dye adsorption efficiency. As the degradation rate was markedly influenced by the light intensity, which affected the nanoparticles' activation energy.
Despite efforts to control experimental conditions, several limitations persisted. Systematic errors, such as scratches on the cuvettes and interference from nanoparticles during light absorption measurements, were unavoidable. Additionally, anomalies in spectrophotometer readings, such as occasional increases in absorbance, likely resulted from these systematic errors. Moreover, the experiment was constrained by the availability of equipment and resources. In future studies. expanding the range of light intensities and incorporating advanced analytical techniques could provide a more comprehensive understanding of the process.
This study underscores the potential of Fe_3O_4 nanoparticles as effective adsorbents for dye removal under UV light, offering a promising approach for addressing synthetic dye pollution in wastewater treatment. Continued research and optimization are necessary to fully realise the potential of Fe3O4 nanoparticles in environmental applications.

Further Scope

This research has identified several potential approaches. For instance, utilising natural sunlight as a UV light source instead of a UV lamp. This would allow for the examination of the degradation process under more environmentally relevant conditions and assess the practical feasibility of this method in real-world scenarios. Additionally, employing turbidity tests instead of spectrophotometric measurements could offer a more straightforward and cost-effective means of monitoring water clarity and the degradation of methylene blue. This approach could simplify the procedure while still providing valuable data on the effectiveness of Fe_3O_4 nanoparticles. Exploring the use of different nanoparticles, such as titanium dioxide (TiO_2) or zinc oxide (ZnO), could provide comparative insights into the efficiency of various photocatalysts in dye degradation. By considering these alternative approaches, the scope of this research can be significantly broadened, potentially leading to more efficient and practical solutions.

Conclusion

This investigation sought to determine the effect of UV light intensity on the degradation rate of methylene blue dye using Fe_3O_4 nanoparticles. The degradation increased with higher light intensity. This finding emphasises the critical role that light intensity plays in the efficiency of the degradation process.
The enhanced degradation rate under higher light intensities can be attributed to the increased energy available for the activation of Fe_3O_4 nanoparticles, leading to more effective generation of reactive oxygen

species that break down the dye molecules. This relationship highlights the importance of optimising UV light conditions to maximise the performance of Fe_3O_4 nanoparticles in wastewater treatment.

While the study demonstrates the potential of Fe_3O_4 nanoparticles as effective adsorbents for dye removal under UV light, it also underscores the necessity of optimising light intensity for efficient wastewater treatment. Given the significant environmental hazards posed by synthetic dyes, which account for 17-20% of industrial wastewater and are often carcinogenic, mutagenic, or teratogenic, the findings of this study offer valuable insights into developing more effective dye removal strategies. Future research should consider extended exposure times, varying nanoparticle concentrations, and advanced analytical techniques to gain a deeper understanding of the degradation kinetics and mechanisms.

Additionally, an expanded range of light intensities and different dye types should be investigated to comprehensively evaluate the applicability of Fe_3O_4 nanoparticles in real-world wastewater treatment scenarios. These improvements will help establish a more robust understanding of the interaction between nanoparticles and synthetic dyes, ultimately contributing to the development of effective solutions for mitigating synthetic dye pollution and its environmental impact.

In conclusion, the rate of degradation of methylene blue by Fe_3O_4 is notably enhanced under higher light intensities. This study provides a promising approach for addressing synthetic dye pollution in wastewater treatment, highlighting the need for continued research and optimization to fully realise the potential of Fe_3O_4 nanoparticles in environmental applications.

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