

Engineering Advanced TiO₂-nanoparticle Photocatalytic Systems for Efficient Methylene Blue Industrial Dye Degradation

Aayush Pandey
Tanglin Trust School
Singapore, Singapore
aayush.pandey@tts.edu.sg

Devendra Tiwari
Northumbria University
Newcastle, U.K.
devendra.tiwari@northumbria.ac.uk

Abstract—The contamination of aquatic ecosystems by industrial dyes is a formidable environmental crisis especially in developing regions, underscoring the need for scalable, economical and eco-friendly remediation strategies. This study explores the application and optimization of reactive oxidation species – such as H₂O₂ – on a TiO₂-nanoparticle photocatalytic system as a green technology for the dye degradation of methylene blue, a carcinogenic industrial dye. Photodegradation efficiency of the suspension improved with increasing H₂O₂ dosage, reaching a maximum decolorization efficiency of the 89.3% at 2.7 mL. The addition of H₂O₂ also close-to doubled the rate constant of photocatalysis, decreasing overall irradiation time. Given the results, it is evident the addition of oxidative species to photocatalytic systems offers a promising pathway for advancing and improving existing water treatment practices.

Keywords—photocatalysis, dye degradation, green chemistry, wastewater remediation, methylene blue

I. INTRODUCTION

According to a World Bank report, approximately 17 to 20% of industrial water pollution arises from textile dyeing and treatment. Much of this pollution is released in the form of dyes and other staining agents lost in industrial processes, dispersed into communal water systems as liquid effluent.¹ The presence of dyes in wastewater represents a significant environmental challenge for environmentalists and regulatory bodies alike, given its carcinogenic effects on organic life. It is also concerning that this issue of dye contamination is more prevalent in developing regions, where a lack of infrastructure to deal with dye waste is compounded by a reliance on primary textile industries.² With the socio-economic challenges and health risks presented, it is therefore imperative that a *sustainable* and *cost-effective* dye treatment method be established.

With growing environmental awareness, there is also a demand for environmentally-friendly technology in the removal of dyes from effluent wastewater. The photocatalytic process is considered favorable in this respect, owing to its low-cost, lack of secondary pollution, and reliance solely on energy from the sun. This reaction involves heterogenous catalysis, in which a semiconductor photocatalyst absorbs UV-light to oxidize organic pollutants – in this case dye molecules.¹⁻³ The photocatalysis mechanism also provides several advantages over other traditional remediation methods. For example, the complete degradation of organic pollutants can occur within only a few hours at room temperature, negating the need for energy-intensive high temperatures. Moreover, organic pollutants are wholly mineralized into its constituent water and carbon dioxide

molecules, thus preventing the formation of any secondary toxic products.³

While the photocatalytic process has shown significant promise in literature, it is not without its limitations. For instance, Dariani et al. [4] highlight the prolonged irradiation times required to achieve high decolorization efficiencies in MB samples, while Wiedmer et al. [5] report instances of competing substances in industrial wastewater severely hindering the oxidative capabilities of TiO₂. To overcome these challenges, this study aims to enhance the photocatalytic process by the addition and optimization of oxidative species such as hydrogen peroxide (H₂O₂). Oxidative species have the potential to accelerate the dye-degradation process by generating hydroxyl radicals, which are highly reactive and capable of oxidizing dye-molecules more rapidly. H₂O₂ in particular has also been chosen for this study due to its affordability and availability in industry as a chemical reagent. For other parameters, titanium dioxide (TiO₂) is the photocatalyst of choice for its high photocatalytic activity and extensive scientific literature, while Methylene Blue (MB) – a cationic dye commonly used in industries such as textiles, dyeing and pharmaceuticals – will be employed as the target pollutant. Therefore, this research aims to investigate the effects of H₂O₂ dosage on the photodegradation of MB and to determine the optimal dosage to maximum dye degradation.

II. BACKGROUND INFORMATION

The study by Zhang et al. [6] identifies two pathways for photocatalysis in TiO₂ solutions: (i) a superoxide-mediated route (*direct*), and (ii) a route involving electron transfer between TiO₂ particles and an excited MB dye state (*indirect*). In practical applications however, the indirect mechanism contributes more to the degradation of the dye molecule. This preference arises because the direct (superoxide) pathway is slower due to a rate-limiting step in the reaction.

A. Mechanism of Indirect Dye Degradation

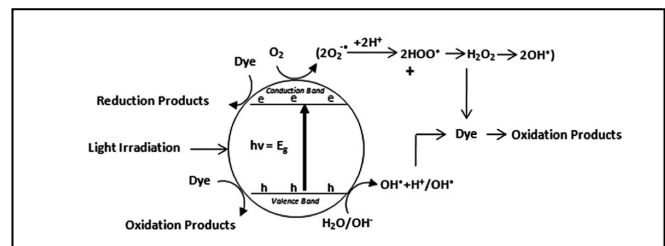
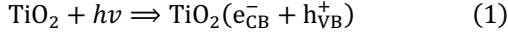


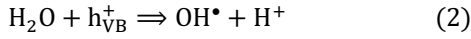
Fig. 1. Diagram representation of indirect dye degradation process

1) **Photoexcitation:** The reaction initiates when a photoelectron is promoted from the filled valence band of the

TiO₂ semiconductor to the empty conduction band due to electromagnetic irradiation. This excitation only occurs if the incident photoelectron's energy ($h\nu$) is equal to or greater than the semiconductor's band gap. The excitation process leaves an orbital hole in the valence band represented by $h\nu_{VB}^+$, generating an electron and hole pair represented by e^-/h^+ .



2) **Ionization of Water:** The holes generated in the valence band then react with water molecules adsorbed onto the surface of the semiconductor, producing hydroxyl radicals (OH^\bullet).



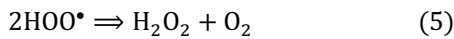
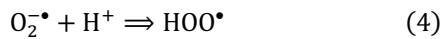
These OH^\bullet radicals are powerful oxidation agents due to the presence of unpaired electrons and can attack organic molecules such as dyes, causing them to mineralize into their constituent inorganic molecules of H_2O and CO_2 .

3) **Oxygen Ionosorption:** While the hole in the valence band reacts with water to form hydroxyl radicals, the electron in the conduction band (e_{CB}^-) reacts with dissolved oxygen in the system to form anionic superoxide radicals ($O_2^{\bullet-}$).

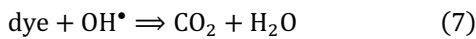


The production of the superoxide radical not only contributes to the oxidation of the dye, but also prevents electron-hole recombination from taking place. This ensures the reaction remains in the forward direction.

4) **Superoxide Protonation:** The superoxide radical ($O_2^{\bullet-}$) generated in (c) is protonated, forming hydroperoxyl radicals (HO_2^\bullet). The hydroperoxyl radicals further react to form H_2O_2 , which subsequently dissociates in solution to form more highly reactive hydroxyl radicals (OH^\bullet).



5) **Dye Mineralization:** Mineralization is the decomposition of organic compounds by an oxidizing agent into smaller inorganic compounds. Upon reacting with OH^\bullet radicals produced in (b) and (d), the dye is mineralized into its constituent molecules of CO_2 and H_2O .



B. Mechanism of Direct Dye Degradation

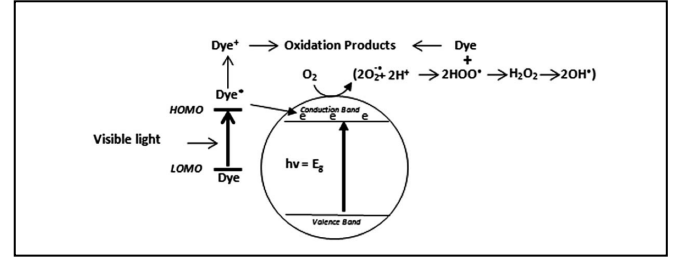
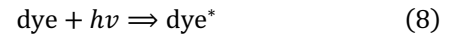
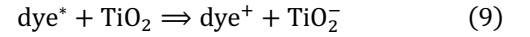


Fig. 2. Diagram representation of direct dye degradation process

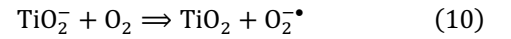
Owing to its ability to absorb visible light, another mechanism of photocatalytic dye-degradation can occur under visible ($700 \text{ nm} > \lambda > 380 \text{ nm}$) rather than UV-light.³ In this mechanism, a visible-light photon first excites the dye from the ground state (dye) to the excited state (dye*).



The excited state dye species is further converted into a partially-oxidized cation (dye^+) by the movement of electrons from the valence band to the conduction band of the TiO₂ semiconductor.



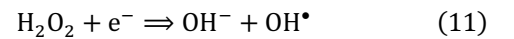
The dissolved oxygen in the system then reacts with the electrons trapped inside the structure of the semiconductor, forming superoxide radical anions ($O_2^{\bullet-}$).



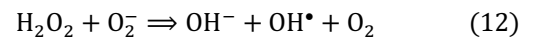
As per (4-7), these $O_2^{\bullet-}$ radicals consequently form hydroxyl radicals (OH^\bullet), which are responsible for bulk of the oxidation of the dye molecule.

C. Hydrogen Peroxide as an Oxidizing Species

H_2O_2 is considered to have a dual role in the photocatalytic process. One role is that it promotes **charge separation** – the process in which an excited electron exits the semiconductor structure to a nearby electron acceptor, responsible for creating highly-oxidizing OH^\bullet radicals.⁷



Another role is seen in (12), where H_2O_2 molecules can react with dissolved oxygen in the system to form OH^\bullet radicals, thus also increasing the rate of photo-oxidation.



However, at high H_2O_2 concentrations, the species may act as an electron-hole and OH^\bullet scavenger, essentially reversing the photo-oxidation process. Additionally, H_2O_2 may react with TiO_2 to form toxic peroxy-compounds, which also may impede photocatalytic activity inside the system.^{7,8}

III. EXPERIMENTAL

A. Materials and Engineering a Batch Reactor Setup

Methylene Blue (MB) was purchased from Charleston Scientific in solution form. Anatase Titanium Dioxide (TiO_2) was purchased from Sigma-Aldrich as a nanopowder, while 30% Hydrogen Peroxide (H_2O_2) was sourced from Merck. An improvised batch reactor setup was engineered for this study, consisting of a 250 mL glass beaker placed on a 500 rpm magnetic stirrer. The batch reactor was placed in an AdvanceLab Full Spectrum-UV Cabinet, which acted as the UV-light source. The beaker was also wrapped with shiny aluminum foil, crucially reflecting any external wavelengths of light.

B. Methodology and Spectrophotometric Technique

The methodology followed in this experiment involved adding an exact amount of TiO_2 nanopowder into Methylene Blue (MB) dissolved in 100 mL of distilled water. The suspension was then placed in the improvised batch reactor described earlier, with constant magnetic agitation to ensure complete adsorption of the dye molecules onto the photocatalyst's surface. Subsequently, discrete dosages of H_2O_2 were added to each beaker, immediately after which the suspensions were exposed to full-spectrum UV light. Absorbance readings were taken every 20 minutes from the start ($t = 0$ min) to the end ($t = 120$ min) to measure the change in MB concentration as the reaction progressed.

UV-Vis Spectrophotometry was chosen as the spectrophotometric technique to determine the change in concentration of the MB-dye solution. This would be determined through the change in absorbance at Methylene Blue's absorption peak ($\lambda = 664$ nm), which was also experimentally confirmed.

$$A = \epsilon lc \quad (13)$$

From Beer-Lambert's Law above (13), as ϵ and l are constants, it is inferred that absorbance, A , is directly proportional to concentration, c . Thus by calculating the change in absorbance given by (14), we can measure the change in concentration and therefore degradation efficiency of the dye solution.

$$\text{degradation \%} = \frac{A_0 - A_{t=120}}{A_0} \times 100 \quad (14)$$

During preliminary experiments, an issue was observed where near-constant levels of absorbance were identified at wavelengths where no absorbance was expected. This was hypothesized to be caused by solid TiO_2 particulates scattering incident light across all wavelengths, causing an overall absorbance increase. To address this, the methodology was tweaked: aliquots of the TiO_2 – MB suspension were centrifuged and the supernatant was extracted for spectrophotometric analysis. This additional step would ensure accurate, particulate-free absorbance readings.

C. Determining MB Concentration & TiO_2 Loading

As recommended in comparable literature⁷⁻⁹, a Methylene Blue concentration of 6.5 mL L^{-1} will be used to model dye-effluent wastewater. An important assumption here is that the

concentration of MB is sufficiently low to adhere to Beer-Lambert's Law. This is because at high concentrations, dye molecules are closer to each other and may form oligomers, causing the relationship between absorbance and concentration to deviate from proportionality.

Regarding the ideal TiO_2 photocatalyst dosage, there is ambiguity between studies as the amount of photocatalyst can depend on various factors, such as the nature of the targeted dye, the chemical structure of the semiconductor, and the purity of the photocatalyst. For instance, Dariani et al. [4] reports an optimum TiO_2 dosage of 1 g L^{-1} , whereas Kaur and Singh [9] describe a dosage of 0.3 g L^{-1} under the same parameters. Given this ambiguity, a preliminary experiment was conducted to determine an optimum dosage for this study. TiO_2 dosages of 0.2, 0.4, 0.6, 0.8 and 1 g L^{-1} were investigated, with the concentration of MB-dye fixed at 6.5 mL L^{-1} as described earlier. Degradation Efficiency was calculated using (14), where A_0 is absorbance at $t = 0$ and $A_{t=120}$ is absorbance after 120 minutes.

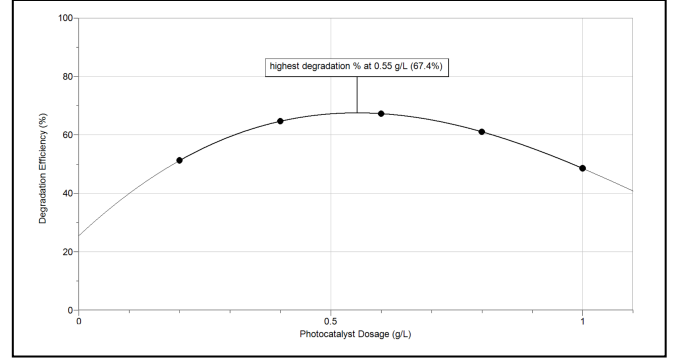


Fig. 3. Trend in Deg. Efficiency for TiO_2 dosages of 0.2 – 1 g L^{-1}

Figure 3 above illustrates the trend in degradation efficiencies for the TiO_2 dosages tested. The peak – representing the dosage with the greatest degradation efficiency – was measured to be 0.55 g L^{-1} . It is hypothesized the decrease in efficiency beyond this critical point is because of the increased cloudy-white opacity of the suspension, which may block incident UV-radiation from irradiating the semiconductor structure.

From the preliminary experiments, an optimum Methylene Blue concentration of 6.5 mL L^{-1} and Titanium Dioxide dosage of 0.55 g L^{-1} have been determined and will be used henceforth.

IV. RESULTS

A. Optimizing H_2O_2 Dosage

TABLE 1. DOSAGES OF H_2O_2 AND RESPECTIVE DEG. EFFICIENCIES

H_2O_2 Dosage (mL)	Absorbance (AU)		Efficiency (%)
	$t = 0$ min	$t = 120$ min	
0.00	0.977	0.312	68.1
1.00	0.988	0.222	77.5
2.00	0.981	0.151	84.6
3.00	0.977	0.105	89.3
4.00	0.993	0.179	82.0
5.00	0.996	0.250	74.9

From Table 1, it is seen that a H_2O_2 dosage of 3 mL achieved the highest Methylene Blue degradation efficiency with 89.3%. On the other hand, the control experiment with no additional H_2O_2 degraded the least, a considerably lower 68.1%. To approximate an optimum H_2O_2 from the results, Table 1 can be represented as a graph, with a regression curve plotted on degradation efficiency against dosage.

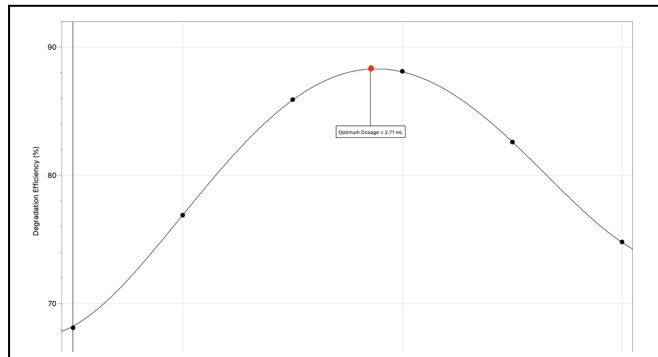


Fig. 4. Hydrogen Peroxide dosage against Deg. Efficiency

Figure 4 illustrates a cubic regression modelling the non-linear relationship between H_2O_2 dosage and degradation efficiency for the MB – TiO_2 suspension in this study. The optimum dosage, in red, represents a predicted dosage for which there will be the highest degradation efficiency. As suggested by the regression model, this critical H_2O_2 dosage is 2.70 mL for a MB-wastewater solution of 100 mL. In generic terms, this is a H_2O_2 concentration of 27 mL L^{-1} with a predicted degradation efficiency of 89.3%.

The results clearly establish that until a certain “critical” dosage, general increases in the volume of oxidizing species improve the photocatalytic degradation efficiency of Methylene Blue. After this “critical” point however, efficiency begins to pitfall with excess H_2O_2 dosage. Interestingly, these results are supported by several studies in literature. For example, Jian-xiao et al. [10] determined an optimum oxidative species concentration of 24 mL L^{-1} to maximize photocatalytic activity. Moreover, the study also reported the phenomena of diminishing efficiencies past an optimum point, with decolorization at dosages greater than 4 mL reported as even less effective than systems without any added H_2O_2 whatsoever.

This paper theorizes the cause of this diminishing phenomenon to be the hole-scavenging nature of H_2O_2 at high concentrations, as described in **2.B**. At such concentrations, the OH^\bullet radicals produced from the decomposition of H_2O_2 readily recombine with electron-hole pairs rather than oxidizing the dye, thus impeding photocatalytic activity in the photocatalyst-dye system.

B. Effect of H_2O_2 Dosage on Rate Constant

One valuable path of inquiry is to study how H_2O_2 dosage affects the rate constant of the reaction. This can suggest how oxidative species affect the speed of the photocatalytic reaction, allowing for faster and more efficient treatment of dye wastewater. To determine the rate constant, the natural

logarithm of the change in Methylene Blue concentration will be plotted against irradiation time.

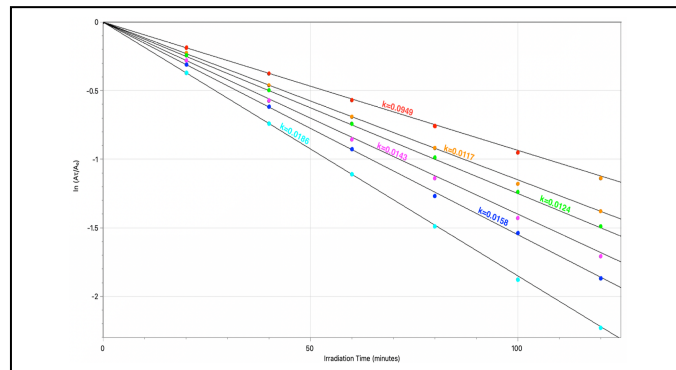


Fig. 5. First-Order Kinetics to Calculate Rate Constant

Figure 5 above illustrates irradiation time, t , plotted against $\ln \frac{A_t}{A_{t=0}}$. There is a strong direct proportionality between these two variables for all H_2O_2 dosages, which is characteristic of *first-order kinetics*. This conclusion is also supported in literature, such as by Ajmal et al. and Wiedmer et al., who also established first-order kinetics in these parameters. Given the first-order nature of the reaction, the rate constant will therefore be the absolute value of the gradient. This is also shown by (15) below, where k is the rate constant, A_0 and A_t are the initial and final MB concentrations, and t is the irradiation time.

$$k = \left| \frac{\ln(A_t/A_0)}{t} \right| \quad (15)$$

TABLE 2. H_2O_2 DOSAGE AND RESPECTIVE RATE CONSTANTS

H_2O_2 Dosage (mL)	Rate Constant, k (min^{-1})
0.00	0.0949
1.00	0.0124
2.00	0.0158
3.00	0.0186
4.00	0.0143
5.00	0.0177

From Table 2, it can be inferred that an increase in H_2O_2 dosage increases the rate constant of the reaction – and therefore the speed of photodegradation – until a certain point after which the rate constant begins to plateau. Similar to the earlier data, k is also the highest at the H_2O_2 dosage of 3 mL, where the rate of reaction is almost twice as fast as the control experiment. These results signify that a Methylene Blue dye sample with an optimum H_2O_2 dosage degrades nearly twice as fast as one without any H_2O_2 added.

This conclusion is particularly significant given that long irradiation times for efficient dye degradation is a significant limitation of photocatalysis and its scope of applications in real-world contexts. For example, Dariani et al. [4] – whose study did not consider the use of H_2O_2 or any other oxidative species to speed-up the reaction – reported an irradiation time of 180 minutes to reach 90% decolorization. Compared to the 124 minutes recorded in this study, this represents a close-to 50% decrease in irradiation time to reach 90%

decolorization. These findings are particularly significant in making the photocatalytic route faster and more efficient, and therefore more effective as a solution to wastewater remediation.

V. CONCLUSION

The motivation of this study was to engineer a novel TiO₂-nanoparticle photocatalytic system for efficient Methylene Blue degradation through the addition of hydrogen peroxide (H₂O₂) as an oxidative species. The study sought to observe the effects of H₂O₂ on the degradation efficiency and rate constant of photocatalysis, as well as to identify a dosage where degradation efficiency could be maximized.

The study found a positive, non-linear relationship between the dosage of H₂O₂ and the degradation efficiency, up to a certain, critical dosage after which the H₂O₂ was hypothesized to be in excess and impeded with the degradation process. This study determines this optimum dosage to be 2.70 mL, with a corresponding degradation efficiency of 89.3%. On the other hand, efficiency of the control experiment (no added H₂O₂) was merely 68.1%. This close to 21% enhancement emphasizes the significant extent to which the addition of an oxidizing species can benefit the photocatalysis process as a solution to the dye-wastewater problem.

By creating a kinetic profile of the reaction, first-order kinetics was established and hence, the rate constant was calculated at all different H₂O₂ dosages. As expected, the rate constant at H₂O₂ = 3 mL was the largest with a value of 0.0186 min⁻¹. This was almost twice as large as the control, confirming H₂O₂'s advantageous dual-role of increasing both the efficiency and rate of dye-degradation. This is of immense value to dye-effluent treatment applications, as two of the most significant limitations of photocatalysis are namely its slow rate of reaction and relative degradation efficiency when compared to other more common, less environmentally-friendly methods of dye remediation.

ACKNOWLEDGMENT

The author thanks Dr. Devendra Tiwari of Northumbria University for his guidance and support throughout this research project. Thanks are also extended to the staff and facilities at Tanglin Trust School, including Dr. Claire Buckland from the Department of Chemistry, for their valuable assistance during this research endeavor.

REFERENCES

- [1] S. Dutta, B. Gupta, S. Kumar Srivastava, and A. Kumar Gupta, "Recent advances on the removal of dyes from wastewater using various adsorbents: a critical review," *Materials Advances*, vol. 2, no. 14, pp. 4497–4531, 2021, doi: <https://doi.org/10.1039/D1MA00354B.J>.
- [2] Lellis, C. Z. Fávaro-Polonio, J. A. Pamphile, and J. C. Polonio, "Effects of textile dyes on health and the environment and bioremediation potential of living organisms," *Biotechnology Research and Innovation*, vol. 3, no. 2, pp. 275–290, Jul. 2019, doi: <https://doi.org/10.1016/j.biori.2019.09.001>. K. Elissa, "Title of paper if known," unpublished.
- [3] Rafiq *et al.*, "Photocatalytic degradation of dyes using semiconductor photocatalysts to clean industrial water pollution," *Journal of Industrial and Engineering Chemistry*, vol. 97, pp. 111–128, May 2021, doi: <https://doi.org/10.1016/j.jiec.2021.02.017>. Y. Yorozu, M. Hirano, K. Oka, and Y. Tagawa, "Electron spectroscopy studies on magneto-optical media and plastic substrate interface," *IEEE Transl. J. Magn. Japan*, vol. 2, pp. 740–741, August 1987 [Digests 9th Annual Conf. Magnetism Japan, p. 301, 1982].
- [4] R. S. Dariani, A. Esmaili, A. Mortezaali, and S. Dehghanpour, "Photocatalytic reaction and degradation of methylene blue on TiO₂ nano-sized particles," *Optik*, vol. 127, no. 18, pp. 7143–7154, Sep. 2016, doi: <https://doi.org/10.1016/j.ijleo.2016.04.026>.
- [5] D. Wiedmer, E. Sagstuen, K. Welch, H. J. Haugen, and H. Tiainen, "Oxidative power of aqueous non-irradiated TiO₂·H₂O₂ suspensions: Methylene blue degradation and the role of reactive oxygen species," *Applied Catalysis B: Environmental*, vol. 198, pp. 9–15, Dec. 2016, doi: <https://doi.org/10.1016/j.apcatb.2016.05.036>.
- [6] F. Zhang, J. Zhao, T. Shen, H. Hidaka, E. Pelizzetti, and N. Serpone, "TiO₂-assisted photodegradation of dye pollutants II. Adsorption and degradation kinetics of eosin in TiO₂ dispersions under visible light irradiation," *Applied Catalysis B: Environmental*, vol. 15, no. 1–2, pp. 147–156, Jan. 1998, doi: [https://doi.org/10.1016/S0926-3373\(97\)00043-X](https://doi.org/10.1016/S0926-3373(97)00043-X).
- [7] I. Poullos and I. Aetopoulou, "Photocatalytic Degradation of the Textile Dye Reactive Orange 16 in the Presence of TiO₂ Suspensions," *Environmental Technology*, vol. 20, no. 5, pp. 479–487, May 1999, doi: <https://doi.org/10.1080/09593332008616843>.
- [8] A. Ajmal, I. Majeed, R. N. Malik, H. Idriss, and M. A. Nadeem, "Principles and mechanisms of photocatalytic dye degradation on TiO₂-based photocatalysts: a comparative overview," *RSC Adv.*, vol. 4, no. 70, pp. 37003–37026, 2014, doi: <https://doi.org/10.1039/c4ra06658h>.
- [9] S. Kaur and V. Singh, "TiO₂ mediated photocatalytic degradation studies of Reactive Red 198 by UV irradiation," *Journal of Hazardous Materials*, vol. 141, no. 1, pp. 230–236, Mar. 2007, doi: <https://doi.org/10.1016/j.jhazmat.2006.06.123>.
- [10] L. V. Jian-xiao, C. Ying, X. Guo-hong, Z. Ling-yun, and W. Su-fen, "Decoloration of methylene blue simulated wastewater using a UV-H₂O₂ combined system," *Journal of Water Reuse and Desalination*, vol. 1, no. 1, pp. 45–51, Mar. 2011, doi: <https://doi.org/10.2166/wrd.2011.019>.