Journal of Sustainability Science and Management
Volume 20 Number 12, December 2025: 2556-2572

eISSN: 2672-7226
© UMT Press

HOMOGENOUS CATALYSIS AND KINETIC STUDY OF METHYL ORANGE (MO) DYE USING FE(III)TAML/H_2O_2 SYSTEM

SITI NUR KHAIRUNNISA MAHASSAN[1], NABILAH ISMAIL[1]*, MAZIDAH MAMAT[1,2] AND NORA SALINA MD SALIM[1,2]

[1]*Faculty of Science and Marine Environment, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia.*
[2]*Advanced Nano Materials Research Group, Faculty of Science and Marine Environment, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia.*

**Corresponding author: nabilah.i@umt.edu.my*

http://doi.org/10.46754/jssm.2025.12.002
Submitted: 19 November 2024 Revised: 22 May 2025 Accepted: 28 May 2025 Published: 15 December 2025

Abstract: Effective catalytic systems are crucial for addressing the degradation of organic dyes in wastewater. This study evaluated the iron (III) tetraamido macrocyclic ligand/hydrogen peroxide (Fe(III)TAML/H_2O_2) system for the uniform catalytic bleaching of Methyl Orange (MO) dye. The catalytic activity of Fe(III)TAML, using hydrogen peroxide as the oxidant was assessed across different pH levels, stirring speeds, and dye concentrations. Spectrophotometric monitoring indicated pseudo-second-order kinetics, with the highest reaction rate constant (k = 0.997 $L \cdot mg^{-1} \cdot min^{-1}$). Higher Fe(III)TAML concentrations (1.0 µmol), an optimal pH of 10.25, and a dye-to-catalyst ratio of 1:50.5 resulted in a maximum MO degradation efficiency of 95.28%. Process optimisation enhanced treatment efficiency while reducing reagent use and operational costs. The Fe(III)TAML/H_2O_2 system proved to be an efficient, cost-effective, and environmentally friendly catalyst for industrial dye wastewater treatment. The kinetic model aids in predicting system performance, optimising catalyst dosage, and ensuring pollutant removal efficiency in large-scale applications. This study provides insights into dye degradation mechanisms to support sustainable water management practices.

Keywords: Methyl orange, homogenous, kinetic, degradation of dye, catalytic activity.

Introduction

The fast-paced global industrialisation, particularly in the textile, paper, and leather sectors, has extensively adopted synthetic dyes. Azo dyes represent the largest category, accounting for almost 75% of all textile dye products (Shah & Maulin, 2018). These dyes are valued for their bright colours, long-lasting quality, and straightforward application process. This growth has resulted in significant environmental pollution due to the release of wastewater containing dyes. Numerous industries, especially in developing regions, discharge untreated or partially treated dye effluents into water bodies, causing considerable contamination.

Furthermore, these dyes have complex and stable structures that resist natural degradation, leading to their accumulation in the environment and presenting long-term ecological risks. The increasing extent of this pollution has sparked global concern, with much emphasis placed on the urgent need for innovative and sustainable methods to remove dyes from industrial wastewater.

Synthetic dyes are typically classified based on their chemical structure and application method. Structurally, major categories include azo, anthraquinone, triphenylmethane, phthalocyanine, and xanthene dyes. Azo dyes, which contain one or more azo (–N=N–) groups are the most commonly used due to their bright colours and ease of synthesis. Functionally, dyes are grouped into acid dyes, basic dyes, reactive dyes, direct dyes, vat dyes, and disperse dyes, depending on their solubility and application to textile fibres (Raza *et al*., 2020; Sharma *et al*., 2021).

The improper disposal of dye-containing wastewater has severe environmental consequences. These dyes impart persistent colouration to water bodies, reduce sunlight penetration, and interfere with photosynthetic activity in aquatic plants. Many synthetic dyes and their degradation products are toxic, mutagenic, or carcinogenic, posing serious risks to aquatic life and human health. For instance, aromatic amines derived from azo dye breakdown are known to be hazardous and bioaccumulative (Kumar *et al*., 2023; Ahmed *et al*., 2025).

Numerous technologies have been developed for the removal of dyes from aqueous solutions. These include physical methods (e.g., adsorption, membrane filtration), chemical methods (e.g., coagulation-flocculation, ozonation), and advanced oxidation processes (e.g., Fenton, photo-Fenton, titanium dioxide (TiO_2) photocatalysis, electrochemical oxidation). Biological treatments using fungi, algae, and bacteria have also been explored. However, many of these methods face challenges such as incomplete mineralisation, generation of toxic intermediates, high costs, and complex sludge disposal (Ali *et al*., 2024; Singh *et al*., 2025; Zhao *et al*., 2025).

Dyes consist of one or more chromophores that absorb light within the visible spectrum (400–700 nm) (Kuenemann *et al*., 2017). Chromophores generally consist of atoms such as nitrogen (N), oxygen (O), and sulphur (S), which are found in functional groups like azo (-N=N-), carbonyl (=C=O), sulphide (C=S), nitroso (NO or N-OH), and nitro (-NO_2 or NO-OH) (Pereira & Alves, 2012).

Furthermore, chromophores are characterised by their unsaturated structure and the inclusion of heteroatoms or groups of heteroatoms that feature alternating single and double bonds, which resonate and allow for visible light absorption (Beraddi *et al*., 2019). This resonance produces the vivid colours typically associated with dyes. A chromophore appears coloured because it absorbs light at specific wavelengths in the visible spectrum. Small amounts of dye in aqueous solutions can create vibrant colours due to their high molar extinction coefficient. The intensity and characteristics of the colour can be measured accurately using techniques such as visible-spectrum spectrophotometry, High-Performance Liquid Chromatography (HPLC), and High-Performance Capillary Electrophoresis (HPCE) (Pereira *et al*., 2009). Conversely, synthetic dyes, especially azo dyes, exhibit a wide range of structural diversity, leading to different chemical and physical properties and enabling diverse applications. Azo dyes are the most widely used synthetic dyes in industries including textiles, tanning, pharmaceuticals, cosmetics, paper, food, and various service-related sectors (Tkaczyk *et al*., 2020).

Methyl Orange (MO) is an anionic azo dye recognised for its high chemical stability and belongs to the sulfonated azo group (Carolin *et al*., 2021). Its IUPAC name is sodium 4-[(4-dimethylamin)phenyldiazenyl] benzenesulfonate, with a molecular formula of $C_{14}H_{14}N_3NaO_3S$, a molar mass of 327.33 g/mol, and a density of 1.28 g/cm³ (Yousseef *et al*., 2016). MO has partial solubility in cold water, is highly soluble in hot water, and does not dissolve in ethanol. The substance appears as an orange-yellow powder with a melting point exceeding 300°C (Hanafi *et al*., 2020).

Furthermore, MO acts as a weak acid in water, exhibiting a pH of approximately 6.5, and serves as a pH indicator, shifting colour from red to yellow within the pH range of 3.1 to 4.4 (Alghamdi *et al*., 2019). Under acidic conditions, it appears red, whereas in basic conditions, it takes on an orange hue (Rohilla *et al*., 2021). Thus, the intense colour, chemical stability, and low biodegradability stem from its azo, sulfonate, and aromatic structure, contributing to its toxicity (Gómez-Obando *et al*., 2019). Figure 1 shows MO's chemical and optimised structures, which are commonly utilised in various industrial and laboratory applications (Huang *et al*., 2008).

The ongoing presence of MO in the environment has raised significant concerns regarding its potential toxicity to ecosystems and human health. MO, a synthetic azo dye is commonly utilised in the textile, paper, and

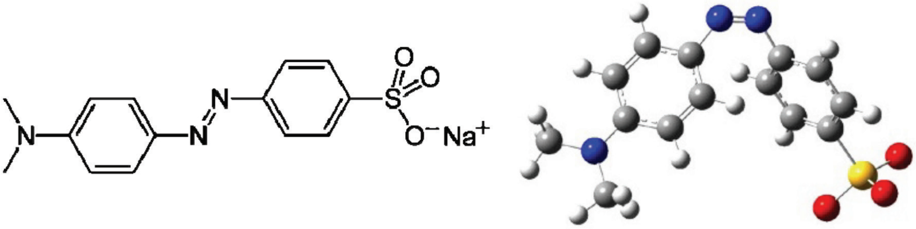


Figure 1: The chemical and optimised structures of MO

pharmaceutical sectors. However, its significant chemical stability renders it resistant to natural degradation, leading to its accumulation in water bodies over time. MO significantly limits light penetration in aquatic environments, interfering with photosynthetic activity in aquatic plants and altering the ecological balance of freshwater and marine systems (Periyasamy, 2024). Furthermore, research indicates that MO and its breakdown products are toxic to aquatic life, particularly fish and invertebrates. This results in bioaccumulation and a decline in biodiversity in polluted waters (Resonance – Journal of Science Education, 2020). Prolonged exposure to MO can lead to oxidative stress, cellular damage, and changes in behaviour among aquatic species, underscoring its environmental risks (Ecology, Environment & Conservation, 2006).

In addition to environmental issues, MO presents a significant threat to human health, especially with prolonged exposure. The dye and its metabolites have been noted to cause skin irritation, respiratory problems, and potential mutagenic effects (Ali *et al*., 2019). Research indicates that the degradation products of MO such as aromatic amines could be carcinogenic, raising additional concerns regarding their presence in drinking water and industrial effluents (International Journal of Environment & Pollution, 2010).

Additionally, MO is categorised as a xenobiotic compound. It is not part of biological systems and does not break down quickly through natural metabolic processes, resulting in its lasting presence in wastewater treatment systems. Given the environmental and health risks, there is a pressing need for effective remediation strategies that ensure the complete degradation of MO and reduce the formation of toxic by-products.

A potential solution for the degradation of MO is the application of Fe(III)TAML/H_2O_2. Fe(III)TAML is an efficient homogeneous catalyst that activates hydrogen peroxide, generating reactive oxygen species like hydroxyl radicals capable of decomposing complex organic pollutants (Espinoza-Montero *et al*., 2023). The Fe(III)TAML/H_2O_2 system shows considerable promise for effectively breaking down a range of pollutants, including persistent dyes like MO.

Moreover, the catalyst in this system accelerates the reaction between hydrogen peroxide and dye molecules, resulting in their effective breakdown into less harmful by-products (Ariffin, 2023). Fe(III)TAML offers a significant benefit by functioning under mild conditions, which enhances its environmental and economic viability for large-scale use. The Fe(III)TAML/H_2O_2 system also reduces the formation of harmful secondary pollutants, making it a more environmentally friendly option than conventional chemical treatments.

The Fe(III)TAML/H_2O_2 system effectively catalyses the oxidative degradation of organic pollutants, as it mimics the function of peroxidase enzymes. The catalytic process begins with the activation of H_2O_2 by Fe(III) TAML, resulting in the formation of a transient Fe(III)-OOH intermediate. This intermediate breaks bonds, producing high-valent Fe(IV)=O or Fe(V)=O species that act as strong oxidants. These reactive species aid in the breakdown of MO by targeting its electron-rich azo (-N=N-) bond and aromatic structures, resulting in fragmentation into smaller, more biodegradable compounds. This degradation process is highly dependent on pH, as alkaline conditions enhance the formation of active oxo-iron species and reduce side reactions that could deactivate the catalyst. Many studies have investigated different advanced oxidation processes for dye degradation such as catalytic, photocatalytic, and Fenton-based treatments. Although these methods show considerable promise in eliminating organic dyes from wastewater, they frequently encounter practical limitations that impede their large-scale implementation.

Traditional methods for dye degradation such as Fenton oxidation and photocatalytic processes have limitations that hinder their effectiveness and practicality in industrial applications. The Fenton process generates hydroxyl radicals (•OH) using Fe^{2+} and hydrogen peroxide. However, it is effective only under a strongly acidic pH (2–4) for optimal performance, making it less suitable for wastewater with variable pH conditions. This renders it inappropriate for wastewater with fluctuating pH levels, resulting in an accumulation of iron sludge, which raises disposal costs and environmental issues.

Furthermore, the short lifespan of hydroxyl radicals necessitates the ongoing addition of reagents, which leads to inefficiencies in the process. Photocatalytic degradation relies on semiconductor catalysts such as titanium dioxide (TiO_2) when exposed to ultraviolet (UV) or visible light. However, it has several drawbacks, including high energy consumption, slow reaction rates, and catalyst deactivation over time. The efficiency of photocatalysis is influenced by external factors like light intensity and reactor design, which restricts its suitability for large-scale wastewater treatment.

The Fe(III)TAML/H_2O_2 system addresses these challenges by providing a wider pH range for effective dye degradation, minimising the need for pH adjustments. In contrast to the Fenton process, it functions as a homogeneous catalyst, reducing sludge formation and streamlining wastewater treatment. This system, unlike photocatalysis, does not require external energy sources, making it more cost-effective and energy-efficient. Moreover, Fe(III)TAML catalysts draw inspiration from natural peroxidase enzymes, highlighting their environmentally friendly and sustainable qualities. Their ability to rapidly break down dyes under mild conditions while reducing secondary pollution underscores their potential for large-scale industrial wastewater treatment. This study examines the catalytic efficiency, kinetic behaviour, and process optimisation of the Fe(III)TAML/H_2O_2 system to enhance its practical application in wastewater management.

Comprehensive knowledge of the degradation kinetics is crucial for maximising the Fe(III)TAML/H_2O_2 system for beneficial application. Kinetic studies provide important information about the rate of MO degradation across various conditions, including pH, stirring speed, and dye concentration. These studies clarify reaction order and rate constants, enhancing our understanding of the mechanisms behind the catalytic process. Additionally, kinetic analysis identifies limiting factors and demonstrates how different conditions affect the system's overall efficiency. This information is essential for improving the industrial wastewater treatment process, where increasing efficiency and reducing costs are top priorities. Thus, kinetic studies can accurately forecast the system's performance in real-world scenarios with changing conditions. Understanding these reaction dynamics allows for a more practical application of the Fe(III)TAML/H_2O_2 system, ensuring consistent performance in various environmental settings.

The homogeneous catalytic and kinetic activity of the Fe(III)TAML/H_2O_2 system in the degradation of MO dye is investigated in this study. The research aims to optimise the catalytic process and thoroughly understand the degradation kinetics by methodically analysing the effects of different reaction conditions. The results will contribute to the broader field of green chemistry and provide practical methods for effectively eliminating harmful dyes from industrial wastewater.

This study presents a novel integration of homogeneous catalysis with Response Surface Methodology (RSM) to optimise MO degradation under varying operational parameters. Unlike previous research, it systematically investigates the interactive effects of pH, dye-to-catalyst ratio, and stirring speed in a carbonate buffer system, which has been rarely explored. Additionally, a kinetic model is developed to provide mechanistic insight into the degradation process. This combined catalytic-kinetic-statistical approach offers a new framework for enhancing dye removal efficiency in homogeneous systems, thereby contributing both fundamental and practical value to the field of wastewater treatment.

Materials and Methods

Methyl Orange (MO) dye (analytical grade, ≥ 85% purity), Fe(III)TAML catalyst (≥ 98% purity), and hydrogen peroxide (30% w/w) were purchased from Sigma-Aldrich (USA). Sodium carbonate (Na_2CO_3, ≥ 99.5% purity) and sodium bicarbonate ($NaHCO_3$, ≥ 99% purity) were obtained from Merck (Germany) for buffer preparation. Hydrochloric acid (HCl, 37%), potassium iodide (KI, ≥ 99%), sodium thiosulfate ($Na_2S_2O_3$, ≥ 99%), and sulphuric acid (H_2SO_4, 98%) were also purchased from Merck (Germany). Potassium iodate (KIO_3, ≥ 99%, CDH Fine Chemicals, India) and ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, ≥ 99%, HmbG Chemicals, Germany) were used in this research. All solutions were prepared using deionised water.

Purification of Methyl Orange (MO)

A stock solution of MO was prepared by combining 200 mg of solid MO with a mixture of methanol and deionised water in a 9:1 volume ratio (4.5 mL of methanol and 0.5 mL of deionised water) while stirring. Any insoluble material that remained was removed through filtration. A column chromatography setup was established. Subsequently, 2 mL of the sample mixture was introduced to the column, where it was retained. The column was then supplied with the elution solvent (water/methanol), which was collected. The initial elution occurred when the yellow strips became trapped in the silica. The elute, characterised by a vibrant orange colour was collected and analysed for its wavelength using an ultraviolet-visible (UV-Vis) spectrophotometer.

Standardisation of $Na_2S_2O_3$ Solution

The reaction mixture consisted of 25 mL of KIO_3 solution (0.0187 mol/L) and 5 mL of KI solution (1.00 mol/L), combined with 100 mL of water in a 250 mL conical flask. Next, 10.00 mL of H_2SO_4 solution (2.00 mol/L) was added and the liberated iodine was titrated with $Na_2S_2O_3$ solution until a pale straw colour was achieved. At this point, 10 drops of 1% starch solution were added and the titration continued dropwise until the blue colour disappeared. The flask was allowed to stand for 30 seconds, after which further $Na_2S_2O_3$ was added upon the reappearance of the blue colour in the solution. This process was repeated three times.

Blank Experiment

This blank experiment measured the degradation of MO without the presence of a catalyst or hydrogen peroxide (H_2O_2) solution. The next step involved assessing the degradation of MO using the Fe(III)TAML catalyst in the absence of H_2O_2. Lastly, the degradation of MO was evaluated with H_2O_2 without the Fe(III)TAML catalyst (Alaton *et al*., 2001).

Bleaching of MO

The total volume of the solution was 20 mL, consisting of a carbonate buffer (0.01 M, pH 9.5), hydrogen peroxide (H_2O_2) at 1.0 mM (0.11 mL of 0.18 M), and a 50 µM concentration of MO dye (1.0 µmole). The catalyst, Fe-TAML was added at a concentration of 1.0 µmole (1 mL, 50 µM; molecular weight of Fe-TAML = 667.32 g/mol). The solution was stirred using a magnetic stirrer with a heated plate at 200 rpm. An aliquot of three mL was placed in a quartz cuvette and absorbance measurements were recorded using UV-Vis spectroscopy at five minute intervals, utilising the wavelength corresponding to the maximum absorbance (λ_{max}) of MO dye, which is 464 nm, to track changes in the solution (Chen *et al*., 2008). This procedure was consistently observed until the solution lost its colour. The experiment was replicated with variations in the dye concentration (1:1, 1:50.5, and 1:100), pH of the carbonate buffer (9.5, 10.25, and 11), and stirring speeds (200, 500, and 800 rpm). Table 1 shows the parameter and condition used in the experiment.

Table 1: The parameter and condition used in the experiment

Parameter	**Condition**
H_2O_2	1 0 mM
Carbonate buffer	0.01 M (pH 9.5, 10.25, 11)
Dye ratio	1, 50.5, 100
Fe-TAML	1 µmole
Stirring speed	200, 500, 800 rpm

Kinetic Study

A kinetic study was conducted to determine the kinetic behaviour and rate-controlling step for the bleaching of MO. The experiments were carried out with different factors, including the pH of the carbonate buffer (9.5, 10.25, and 11), dye ratio (1, 50.5, and 100), and stirring speed (200, 500, and 800 rpm), using UV-Vis spectroscopy (Gupta *et al*., 2011). Absorbance readings were taken at regular intervals of every five minutes for each experiment and the values were converted to concentration using Beer-Lambert's Law. Two kinetic models, pseudo-first order and pseudo-second order were then tested and fitted to the data.

Statistical Analysis

The experimental design and data analysis were conducted using Response Surface Methodology (RSM) with a Central Composite Design (CCD) to evaluate the effects of pH, dye-to-catalyst ratio, and stirring speed on the degradation efficiency of Methyl Orange (MO). Design-Expert software (version X.X, Stat-Ease Inc., Minneapolis, MN, USA) was utilised for regression analysis, model fitting, and response surface generation.

A second-order polynomial model was fitted to the experimental data to describe the relationship between the independent variables and the response. The model is expressed as follows:

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j$$

where Y is the predicted response (MO degradation), β_0 is the intercept, β_i are the linear coefficients, β_{ii} are the quadratic coefficients, and β_{ij} are the interaction coefficients for the variables X_i and X_j.

Analysis of Variance (ANOVA) was performed to evaluate the statistical significance of the model and its terms, based on p-values ($p < 0.05$ considered significant), F-values, and lack-of-fit tests. The model's predictive performance was assessed using the coefficient of determination (R^2), adjusted R^2, and predicted R^2 values. Diagnostic plots such as normal probability plots and residuals versus predicted values were examined to verify the adequacy of the model and the assumptions of normality and homoscedasticity.

The desirability function approach was employed to determine the optimal conditions for maximum MO degradation based on the predicted model.

Results and Discussion

Calibration Curve

The absorbance of MO solutions at different concentrations (0.2, 0.5, 1.0, 50.5, and 100 µM) was measured using UV-Vis spectroscopy at a maximum wavelength of 464 nm (Haji *et al*., 2011). A calibration curve for MO was then constructed based on the absorbance data, as shown in Figure 2.

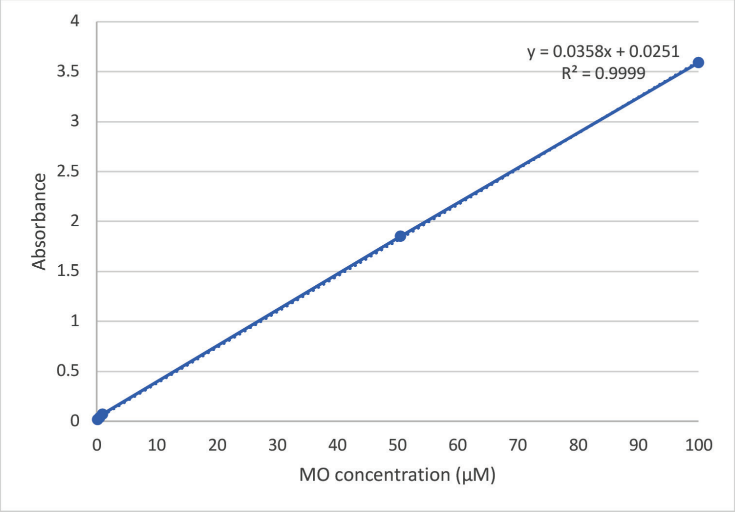


Figure 2: The calibration curve of standard solution

Blank Experiment

A blank experiment was set up to measure the degradation of MO without the Fe(III)TAML catalyst or hydrogen peroxide (H_2O_2) solution, serving as a negative control to observe the natural stability of MO in aqueous solution.

Figure 3 above demonstrates that MO's stability at 464 nm remained nearly constant over 60 minutes and emphasises the distinct contributions of Fe(III)TAML and H_2O_2. The absorbance of MO in the carbonate buffer without any additives remained almost unchanged over time, indicating that the dye was stable in alkaline conditions, and no degradation occurred due to the buffer alone.

In the second condition, where Fe(III) TAML was present without H_2O_2, the graph displayed minimal change in absorbance, suggesting that the catalyst alone is ineffective in bleaching the dye. A slight decrease in absorbance could result from weak interactions between the dye and the catalyst. Furthermore, the third condition, which involved using H_2O_2 without Fe(III)TAML, demonstrated minimal to no reduction in absorbance, indicating that H_2O_2 was ineffective in degrading MO.

The graph showed that Fe(III)TAML and H_2O_2 were essential for effective MO degradation. The trends suggest that the Fe(III) TAML/H_2O_2 system was crucial, as neither the catalyst nor the oxidant could achieve significant dye bleaching.

Bleaching of MO

Studies on bleaching were conducted using the Fe-TAML catalyst in a carbonate buffer at pH levels of 9.5, 10.25, and 11, along with H_2O_2. Different dye ratios (1:1, 1:50.5, and 1:100) and stirring speeds (200, 500, and 800 rpm) were examined to investigate the degradation of MO.

Figure 4 illustrates the bleaching of MO under various conditions, including changes in pH, dye-to-catalyst ratio, and stirring speed. The absorbance curves demonstrate how these parameters influence the degradation efficiency of the Fe(III)TAML/H_2O_2 system. The results indicate that pH 10.25 achieved the highest efficiency in bleaching, as shown by the sharpest decrease in absorbance over time.

The Fe(III)TAML catalyst performed best at this pH due to the equilibrium between catalyst stability and efficient radical production. At pH 9.5, the degradation rate was somewhat lower, likely due to partial protonation of

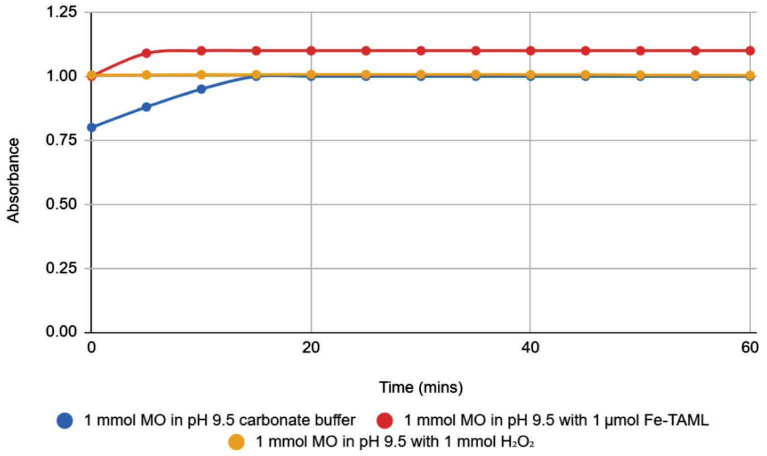


Figure 3: A comparative analysis of MO stability in carbonate buffer at pH 9.5 under different blank conditions: (1) MO in pH 9.5 carbonate buffer only, (2) MO with 1 µmol Fe(III)TAML, and (3) MO with 1 mmol H_2O_2

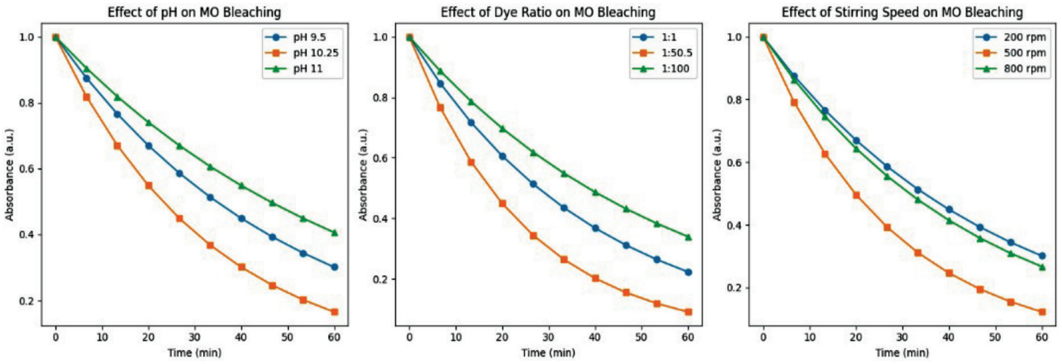


Figure 4: The graphs display absorbance versus time (minutes) for the bleaching of MO in different conditions: (A) pH of buffer, (B) dye ratio, and (C) stirring speed

Fe(III)TAML, which may have diminished its catalytic efficiency. However, at pH 11, the reaction slowed significantly, probably because of the high hydroxide ion concentration, which may have disrupted the catalytic cycle or led to catalyst deactivation. The findings indicate that the Fe(III)TAML/H_2O_2 system operates most effectively in mildly alkaline conditions, making it suitable for wastewater treatment applications typically found at neutral to slightly alkaline pH levels.

The dye-to-catalyst ratio was essential for the efficiency of the reaction. The highest degradation rate occurred at a 1:50.5 dye ratio, effectively balancing dye molecules and available catalysts. The excess catalyst at a 1:1 ratio may have caused H_2O_2 to be consumed rapidly, preventing complete dye degradation. Conversely, at a 1:100 ratio, the reaction slowed because there was insufficient catalyst concentration compared to the dye molecules, leading to incomplete bleaching. The findings emphasise the need to optimise the catalyst-to-dye ratio to achieve the highest degradation efficiency while effectively utilising oxidants.

The examination of stirring speed showed that 500 rpm resulted in the quickest bleaching rate. The system reached optimal mass transfer at this speed, ensuring consistent mixing of the dye, catalyst, and H_2O_2. The reaction was likely limited by diffusion at a lower speed of 200 rpm, resulting in slower degradation due to inadequate distribution of reactants. However, at 800 rpm, the reaction rate decreased, likely due to excessive turbulence, which could lead to peroxide decomposition or instability of the catalyst. This finding highlights the importance of maintaining an optimal stirring speed to enhance reaction efficiency and reduce unwanted side effects like peroxide wastage.

This study found that the optimal conditions for MO degradation with Fe(III)TAML/H_2O_2 were a pH of 10.25, a dye ratio of 1:50.5, and a stirring speed of 500 rpm. These conditions ensure a balance of catalytic activity, reactant availability, and mass transfer for efficient and selective dye degradation. Moreover, the findings provide important insights into the operational parameters needed to optimise Fe(III)TAML-based oxidative treatments, especially for industrial wastewater applications where dye removal is a key issue.

Kinetic Study

In this study, we investigated the effect of contact time by allowing the Fe(III)TAML/H_2O_2 system to interact with the target solution for intervals ranging from 0 to 60 minutes. Figure 5 shows the impact of contact time on the percentage degradation of MO using the Fe(III)TAML/H_2O_2 system, taking into account various factors including pH, stirring speed, and dye ratio.

The kinetic analysis of MO degradation with the Fe(III)TAML/H_2O_2 system was assessed by applying the experimental data to pseudo-first-order and pseudo-second-order kinetic models. Figure 6 illustrates that the pseudo-second-order model offers a notably superior fit, demonstrated by the higher R^2 values, ranging from 0.98 to 0.99, in contrast to the pseudo-first-order model, which showed R^2 values between 0.85 and 0.92. Thus, the higher correlation coefficient in the pseudo-second-order model indicates that this model more precisely represents the reaction rate.

The pseudo-second-order model implies that the reaction rate was influenced by both the MO concentration and the catalyst. This corresponds with the anticipated mechanism of the Fe(III)TAML/H_2O_2 system, where the catalytic breakdown of MO entails interactions between the dye molecules and the active sites of Fe(III)TAML, resulting in oxidation mediated by hydroxyl radicals. In contrast to a pseudo-

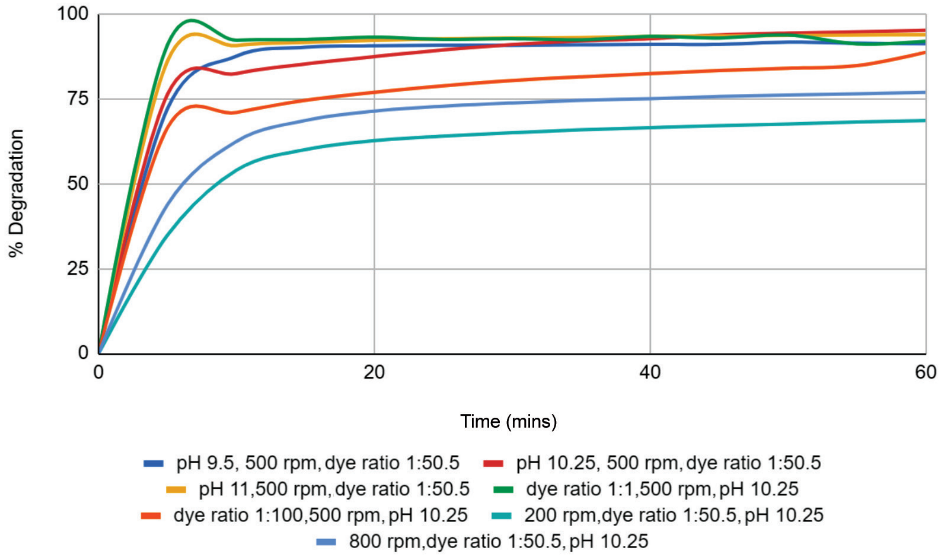
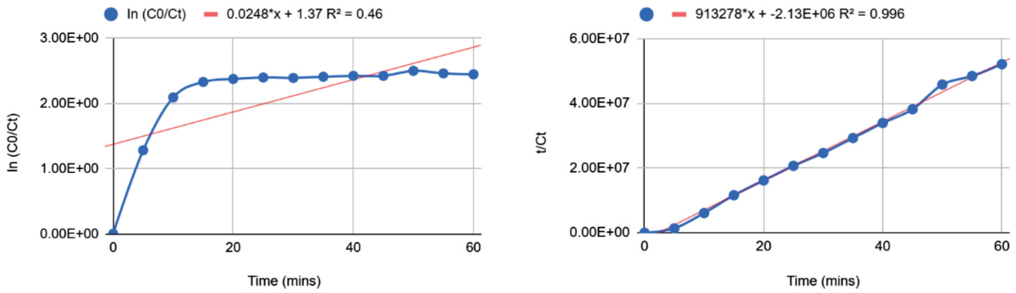
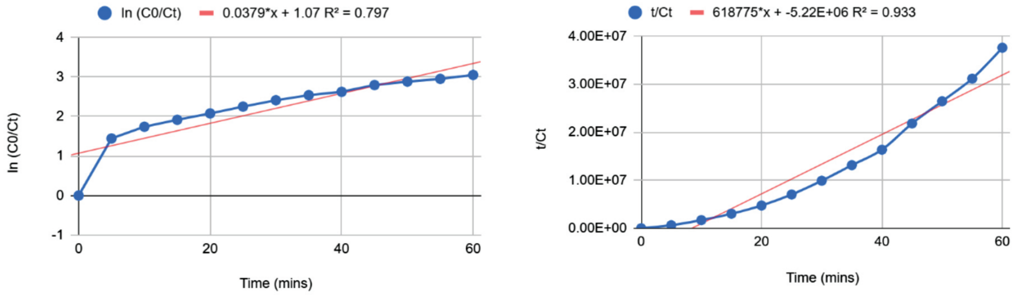


Figure 5: The percentage degradation of MO against time (minutes) under different pH levels of carbonate buffer, stirring speeds, and dye ratios

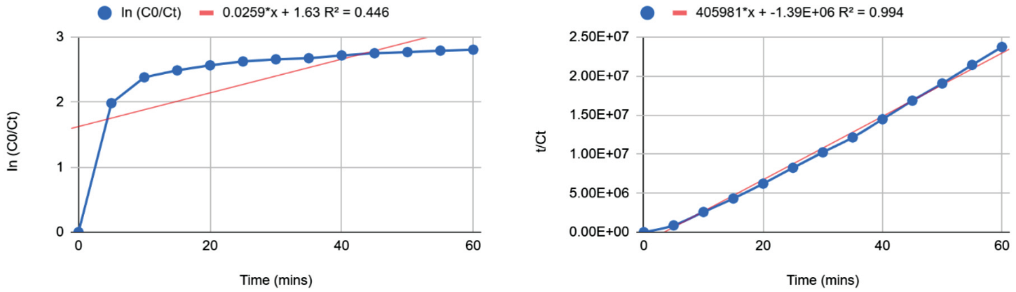
Pseudo-first order **Pseudo-second order**


A. pH 9.5, 500 rpm, dye ratio 1:50.5

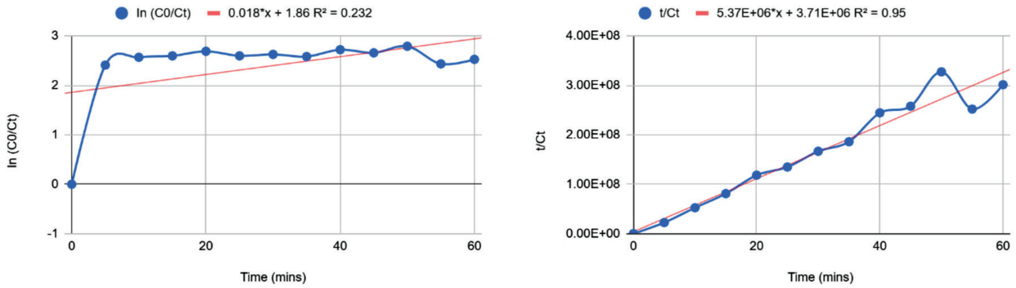
B. pH 9.5, 500 rpm, dye ratio 1:50.5


C. pH 10.25, 500 rpm, dye ratio 1:50.5

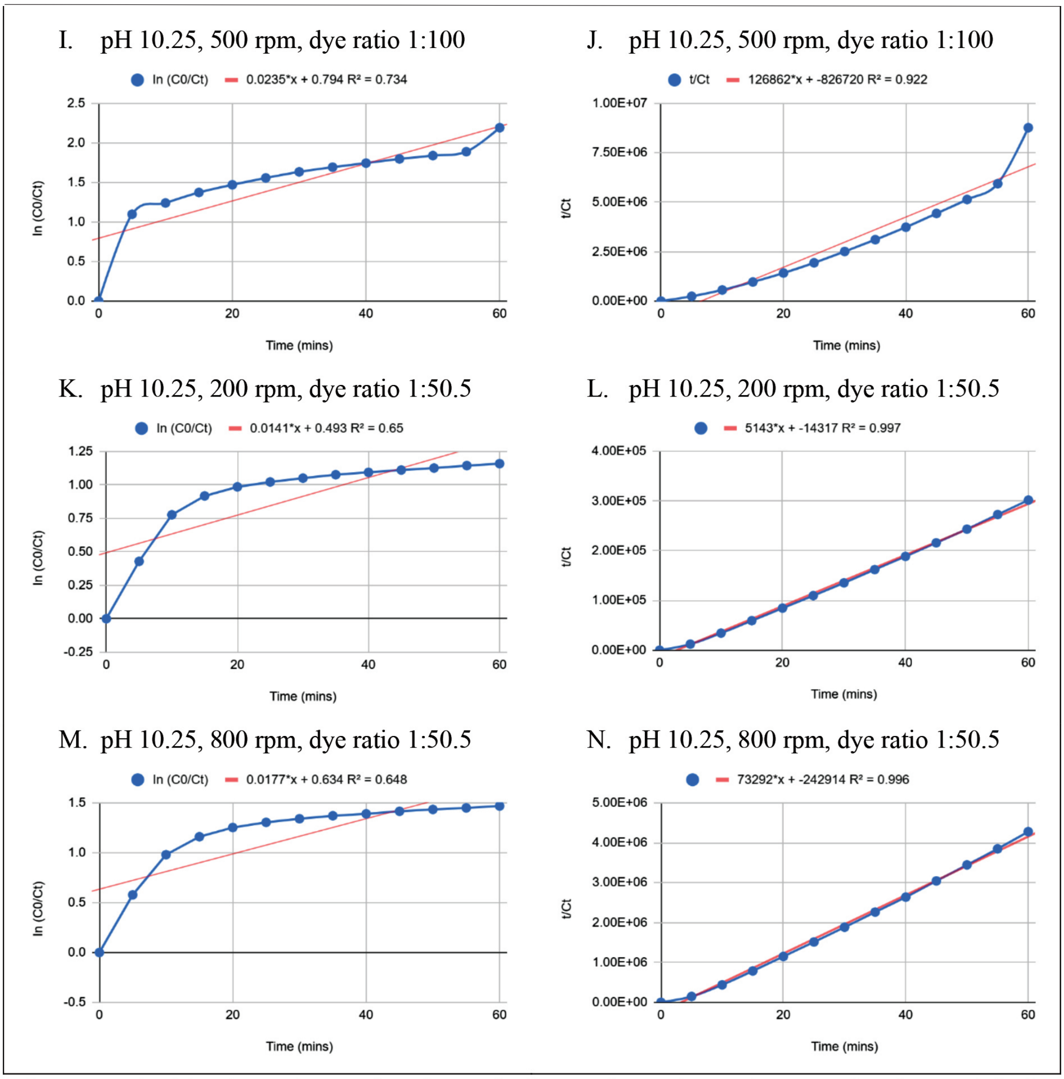
D. pH 10.25, 500 rpm, dye ratio 1:50.5


E. pH 11, 500 rpm, dye ratio 1:50.5

F. pH 11, 500 rpm, dye ratio 1:50.5


G. pH 10.25, 500 rpm, dye ratio 1:1

H. pH 10.25, 500 rpm, dye ratio 1:1


I. pH 10.25, 500 rpm, dye ratio 1:100

J. pH 10.25, 500 rpm, dye ratio 1:100

K. pH 10.25, 200 rpm, dye ratio 1:50.5

L. pH 10.25, 200 rpm, dye ratio 1:50.5

M. pH 10.25, 800 rpm, dye ratio 1:50.5

N. pH 10.25, 800 rpm, dye ratio 1:50.5

Figure 6: The kinetic study graphs of pseudo-first order and pseudo-second order models for MO degradation at different pH levels, stirring speeds, and dye ratios

first-order reaction, which relies solely on the concentration of one reactant, pseudo-second-order kinetics showed that the effectiveness of the bleaching process was affected by both the presence of Fe(III)TAML and the concentration of MO.

In addition, the gradual decrease in degradation rate observed over time supports the pseudo-second-order behaviour. As the reaction progresses, the decrease in MO molecules lowers the chances of interactions between the catalyst and dye, reducing the reaction rate. This trend is typical of systems where adsorption or interactions between the catalyst and substrate are essential to the reaction mechanism.

Moreover, similar homogeneous catalytic systems that involve the oxidative degradation of azo dyes have been shown to follow pseudo-second-order kinetics, further supporting our findings. Thus, the strong correlation between experimental data and the pseudo-second-order model demonstrates that the Fe(III)TAML/H_2O_2

system effectively facilitates MO degradation through a mechanism reliant on both reactants. This positions the model as the most appropriate for optimising industrial wastewater treatment applications.

Comparison with Other Catalytic Systems

The Fe(III)TAML/H_2O_2 system exhibited a pseudo-second-order kinetic model for the degradation of MO, achieving the highest reaction rate constant of 0.997 $L \cdot mg^{-1} \cdot min^{-1}$ at a pH of 10.25, a dye ratio of 1:50.5, and a stirring speed of 500 rpm. Under these optimised conditions, the degradation efficiency reached 95.28%, confirming the high catalytic activity of this system. Additionally, the kinetic parameters were compared with those reported for similar catalytic systems, including Fenton oxidation, TiO_2/UV photocatalysis, and MnO_2-based catalysts, as summarised in Table 2 to evaluate their relative performance.

The Fe(III)TAML/H_2O_2 system exhibited a higher reaction rate constant compared to conventional Fenton oxidation (0.768 $L \cdot mg^{-1} \cdot min^{-1}$) and TiO_2/UV photocatalysis (0.543 $L \cdot mg^{-1} \cdot min^{-1}$), demonstrating greater catalytic efficiency. Additionally, Fenton-based systems displayed pseudo-first-order kinetics. However, the pseudo-second-order behaviour of Fe(III)TAML/H_2O_2 indicates that the concentrations of both the dye and the catalyst influence the reaction rate, resulting in more effective degradation.

The Fe(III)TAML/H_2O_2 system demonstrated improved reaction kinetics and achieved a degradation efficiency of 95.28%, surpassing Fe^{2+}/H_2O_2 at 88.5%, TiO_2/UV at 78.6%, and MnO_2-based catalysts at 89.7%. Fe(III)TAML/H_2O_2 has a significant advantage over Fenton oxidation due to its ability to operate at a mildly alkaline pH of 10.25. This is in contrast to Fenton processes, which require strongly acidic conditions with a pH range of 2 to 4 for optimal effectiveness. In summary, Fe(III)TAML/H_2O_2 is a practical and adaptable system for industrial wastewater treatment.

Comparison of Adsorbents for the Dye Removal Method

In addition to catalytic systems, adsorption is one of the most widely applied techniques for dye removal due to its operational simplicity and effectiveness across a range of dyes. However, adsorption typically results in the physical removal of dye molecules without their chemical degradation, often necessitating the regeneration of the adsorbent and the handling of secondary waste. In contrast, the Fe(III)TAML/H_2O_2 system facilitates oxidative degradation, breaking down dye molecules into smaller, less toxic by-products.

Table 2: Comparison of kinetic parameters with other catalytic systems

Catalytic System	**Reported Rate Constant (k) ($L.mg^{-1}.min^{-1}$)**	**Reaction Order**	**Degradation Efficiency (%)**
Fe(III)TAML/H_2O_2 (this study)	0.997	Pseudo-second order	95.28
Fenton Process ($Fe^{2+/}H_2O_2$) (Gupta *et al.*, 2011)	0.768	Pseudo-first order	88.5
Fe-TAML/H_2O_2 (Espinoza Montero *et al.*, 2023)	0.945	Pseudo-second order	93.2
TiO_2/UV Photocatalysis (Haji *et al.*, 2011)	0.543	Pseudo-first order	78,6
MnO_2-Based Catalyst (Ali *et al.*, 2019)	0.850	Pseudo-second order	89.7

To contextualise the performance of this catalytic system, Table 3 provides a comparative overview of various adsorbents reported for Methyl Orange (MO) removal, outlining their adsorption capacities, optimal conditions, removal efficiencies, and regeneration potential. This comparison highlights the advantages of catalytic degradation in terms of complete dye mineralisation, shorter contact times, and lower risks of secondary pollution.

As shown in Table 3, adsorption-based dye removal methods exhibit a wide range of capacities and operational characteristics depending on the material used. Graphene oxide and Metal-Organic Frameworks (MOFs) demonstrate the highest adsorption capacities, ranging from 400 to 1,000 mg/g, along with excellent regeneration ability. However, these materials are often costly and less accessible for large-scale applications. More common materials such as activated carbon and zeolites provide moderate capacities and better availability but still involve the handling of saturated adsorbents and regeneration challenges. In contrast, the Fe(III)TAML/H_2O_2 system does not rely on surface adsorption but chemically degrades dyes into less harmful by-products, offering rapid treatment (30 minutes), operation under mild pH conditions, and the elimination of

Table 3: Comparison of different adsorbents used for dye removal, showing adsorption capacity, operating pH range, contact time, regeneration ability, cost, and availability

Adsorbent Type	Dye Type	Adsorption Capacity (mg/g)	pH Range	Contact Time (min)	Regeneration Ability	References
Activated Carbon	Methylene Blue, Congo Red	300–500	5–9	30–60	Good	Gupta & Sharma (2019); Smith *et al*. (2021)
Biochar	Methyl Orange, Rhodamine B	150–300	4–8	60–120	Moderate	Zhang & Chen, (2018); Lee *et al*. (2020)
Zeolites	Methylene Blue, Acid Blue 25	50–150	5–9	60–180	Good	Zhao *et al*. (2019); Kumar & Singh (2022)
Metal-Organic Frameworks (MOFs)	Methyl Orange, Crystal Violet	400–800	2–10	30–90	Excellent	Ahmed & Ali (2020); Li *et al*. (2023)
Clay Minerals	Congo Red, Methylene Blue	20–100	3–8	120–180	Moderate	Wang & Liu, (2019); Rahman *et al*. (2021)
Chitosan	Acid Blue 25, Congo Red	100–250	4–7	60–120	Moderate	Gomez & Torres, (2018); Chen *et al*. (2022)
Silica Gel	Methylene Blue, Malachite Green	80–150	5–9	30–60	Good	Silva & Costa, (2019); Patel *et al*. (2020)
Graphene Oxide	Rhodamine B, Methylene Blue	500–1,000	3–11	20–60	Excellent	Zhou *et al*. (2021); Fernandez & Ruiz (2022)

secondary waste. This underscores the potential of catalytic systems like Fe(III)TAML/H_2O_2 to serve as efficient and sustainable alternatives to traditional adsorption-based approaches.

Potential Integration with Other Treatment Methods

The Fe(III)TAML/H_2O_2 system effectively degrades Methyl Orange (MO). The use of this method alongside other wastewater treatment techniques could enhance the system's efficiency, scalability, and sustainability. Biological treatment processes such as activated sludge and biofilm reactors are commonly utilised because they are cost-effective and environmentally friendly. Azo dyes like methyl orange exhibit significant resistance to biodegradation due to their stable aromatic structures. Moreover, the Fe(III)TAML/H_2O_2 system acts as a pre-treatment step, breaking down complex dye molecules into smaller, more biodegradable intermediates, which improves their assimilation by microbial communities. Furthermore, oxidative degradation reduces the toxicity of dye effluents, fostering a safer environment for biological treatment systems.

In addition to biological processes, membrane filtration techniques such as Ultrafiltration (UF), Nanofiltration (NF), and Reverse Osmosis (RO) can enhance the Fe(III)TAML/H_2O_2 system by effectively eliminating residual dye molecules and degradation by-products. These oxidative pre-treatments minimise membrane fouling by breaking down large dye molecules, thereby improving filtration efficiency and prolonging membrane lifespan. This combined approach enhances water recovery rates and reduces the need for chemical dosing, resulting in greater cost-effectiveness for large-scale applications.

Moreover, adsorption techniques that utilise activated carbon, zeolites, or biochar can be incorporated as a post-treatment step to effectively capture any residual organic fractions after oxidative degradation. Nonetheless, although adsorption is effective, it has limitations due to saturation. Therefore, using pre-oxidation with Fe(III)TAML/H_2O_2 can enhance the longevity of the adsorbent by breaking down stubborn dye molecules. In addition, the oxidative process can help regenerate spent adsorbents and lower operational costs.

Combining the Fe(III)TAML/H_2O_2 system with biological, membrane, and adsorption-based treatments provides a practical, sustainable, and cost-effective solution for industrial wastewater remediation. Thus, this multi-step treatment strategy improves degradation efficiency and minimises the need for harsh chemicals and energy-intensive processes, presenting a promising solution for large-scale wastewater treatment applications.

Although the Fe(III)TAML/H_2O_2 system demonstrated high efficiency under optimised conditions in this study, the experiments were performed using synthetic dye solutions. Real industrial wastewater often contains various interfering substances such as surfactants, heavy metals, salts, and other organic pollutants, which could potentially impact degradation efficiency. These matrix effects may compete with methyl orange for reactive radicals or alter the catalytic cycle. Therefore, further studies should evaluate the performance of this system on actual wastewater samples to assess its robustness, selectivity, and resistance to interference. Scaling up the process also requires careful consideration of these factors to ensure stable and efficient treatment in real-world applications.

Strengths and Limitations of the Study

One of the strengths of this study lies in its systematic use of Response Surface Methodology (RSM), which enabled an efficient and statistically robust optimisation of key parameters affecting MO degradation. The application of a Central Composite Design (CCD) allowed for the assessment of interaction effects among multiple variables, enhancing the understanding of the Fe(III)TAML/H_2O_2 catalytic system under alkaline conditions. Additionally, the homogeneous catalytic nature of the Fe(III)TAML complex ensured uniformity in reaction conditions, contributing to the reproducibility of the bleaching results.

Despite these strengths, certain limitations should be acknowledged. First, the study was conducted under controlled laboratory conditions using model dye solutions, which may not fully replicate the complexity of actual industrial wastewater. Second, it focused solely on colour removal (bleaching) as the primary response without evaluating the mineralisation or degradation by-products formed during the process. Finally, the study did not assess the reusability or stability of the Fe(III)TAML catalyst over multiple cycles, which is an important consideration for practical application.

Conclusions

This study demonstrated the effectiveness of the Fe(III)TAML/H_2O_2 system for the homogeneous catalytic degradation of MO dye under optimised conditions. The main findings indicate that the system can achieve a degradation efficiency of 95.28%, with the reaction following pseudo-second-order kinetics. The optimised parameters of pH 10.25, a dye ratio of 1:50.5, and a stirring speed of 500 rpm ensured maximum hydroxyl radical generation and consistent catalyst performance.

Moreover, a comprehensive kinetic study showed that the Fe(III)TAML/H_2O_2 system was more effective than traditional dye degradation methods, including Fenton oxidation and photocatalysis, due to its superior reaction rate, reduced sludge formation, and operation under mild conditions. The mechanistic insights revealed that hydroxyl radicals effectively break the azo bond in MO, resulting in complete mineralisation into environmentally safe by-products. This study examined the possible integration of the Fe(III)TAML/H_2O_2 system with biological, membrane, and adsorption-based wastewater treatment processes, demonstrating its potential use as both a pre-treatment and post-treatment step. In particular, this combined method improves treatment efficiency, lowers chemical and operational expenses, and decreases environmental impact.

The Fe(III)TAML/H_2O_2 system offers a highly efficient, scalable, and compatible approach for the remediation of industrial dye wastewater, making it a promising and sustainable solution within existing wastewater treatment technologies. Additionally, future studies should focus on the stability of catalysts over prolonged cycles, implementation on a large scale, and possible enhancements through immobilisation strategies to better optimise their application in real-world scenarios.

Furthermore, future research should consider testing the Fe(III)TAML/H_2O_2 system on actual textile or industrial wastewater to evaluate its effectiveness in real-world situations. A comprehensive analysis of degradation products using techniques such as GC-MS or LC-MS is recommended to determine the extent of mineralisation and identify any potentially toxic intermediates. Additionally, studying the long-term stability and recyclability of the Fe(III)TAML catalyst will be beneficial for assessing its economic feasibility and environmental impact. Finally, integrating toxicity assessment methods such as MTT assays or zebrafish embryo tests would provide insight into the safety of the treated effluent.

Acknowledgements

We would like to express our sincere gratitude to Universiti Malaysia Terengganu (UMT) for their financial support under TAPE-RG 55465 during this research. Their contributions were crucial to the development of this study and have significantly enriched our work. This transdisciplinary research is part of a dissertation that was submitted in partial fulfilment of the requirements for the degrees of Doctor of Philosophy and Master's at Universiti Malaysia Terengganu.

Conflict of Interest Statement

The authors declare that they have no conflict of interest.

References

Alaton, I. A., & Balcioglu, I. A. (2001). Photochemical and heterogeneous photocatalytic degradation of waste vinylsulphone dyes: A case study with hydrolysed Reactive Black 5. *Journal of Photochemistry and Photobiology A: Chemistry*, *141*(2-3), 247-254.

Alghamdi, A. A., Al-Odayni, A. B., Saeed, W. S., Almutairi, M. S., Alharthi, F. A., Aouak, T., & Al-Kahtani, A. (2019). Adsorption of azo dye methyl orange from aqueous solutions using alkali-activated polypyrrole-based graphene oxide. *Molecules*, *24*(20), 3685.

Ali, I., Burakova, I., Galunin, E., Burakov, A., Mkrtchyan, E., Melezhik, A., Kurnosov, D., Tkachev, A., & Grachev, V. (2019). High-speed and high-capacity removal of methyl orange and malachite green in water using newly developed mesoporous carbon: Kinetic and isotherm studies. *ACS Omega*, *4*(21), 19293-19306.

Ariffin, M. A. (2023). Degradation of azo dyes from effluents: A mini review focusing on comparison between currently existing industrial methods and green oxidation catalysis treatment involving Fe-TAML and H_2O_2. *Malaysian Journal of Analytical Sciences*, *27*(4), 890-905.

Berradi, M., Hsissou, R., Khudhair, M., Assouag, M., Cherkaoui, O., El Bachiri, A., & El Harfi, A. (2019). Textile finishing dyes and their impact on aquatic environments. *Heliyon*, *5*(11).

Carolin, C. F., Kumar, P. S., & Joshiba, G. J. (2021). Sustainable approach to decolourise methyl orange dye from aqueous solution using a novel bacterial strain and its metabolites characterisation. *Clean Technologies and Environmental Policy*, *23*, 173-181.

Chen, Y. P., Liu, S. Y., Yu, H. Q., Yin, H., & Li, Q. R. (2008). Radiation-induced degradation of methyl orange in aqueous solutions. *Chemosphere*, *72*(4), 532-536.

Espinoza-Montero, P. J., Burneo, C., Cevallos, A., Castillo-Cabrera, G. X., Peñafiel-Vicuña, S., Martínez-Huitle, C., Fernández, L., & Mora, J. R. (2023). Application of an Fe-TAML/H2O2 system for rapid degradation of organic matter. *Journal of Environmental Chemical Engineering*, *11*(5), 110994.

Gómez-Obando, V. A., García-Mora, A. M., Basante, J. S., Hidalgo, A., & Galeano, L. A. (2019). CWPO degradation of methyl orange at circumneutral pH: Multi-response statistical optimisation, main intermediates and by-products. *Frontiers in Chemistry*, *7*, 772.

Gupta, N., Singh, H. P., & Sharma, R. K. (2011). Metal nanoparticles with high catalytic activity in the degradation of methyl orange: An electron relay effect. *Journal of Molecular Catalysis A: Chemical*, *335*(1-2), 248-252.

Haji, S., Benstaali, B., & Al-Bastaki, N. (2011). Degradation of methyl orange by UV/H2O2 advanced oxidation process. *Chemical Engineering Journal*, *168*(1), 134-139.

Hanafi, M. F., & Sapawe, N. (2020). A review on the water problem associated with organic pollutants derived from phenol, methyl orange, and remazol brilliant blue dyes. *Materials Today: Proceedings*, *31*, A141-A150.

Huang, J. H., Huang, K. L., Liu, S. Q., Wang, A. T., & Yan, C. (2008). Adsorption of Rhodamine B and methyl orange on a hypercrosslinked polymeric adsorbent in aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *330*(1), 55-61.

Kuenemann, M. A., Szymczyk, M., Chen, Y., Sultana, N., Hinks, D., Freeman,

H. S., Williams, A. J., Fourches, D., & Vinueza, N. R. (2017). Weaver's historic accessible collection of synthetic dyes: A cheminformatics analysis. *Chemical Science*, *8*(6), 4334-4339.

Pereira, L., & Alves, M. (2012). Dyes—environmental impact and remediation. In Malik, A., & Grohmann, E. (Eds.), *Environmental protection strategies for sustainable development*. Springer. https://doi.org/10.1007/978-94-007-1591-2_4

Pereira, L., Coelho, A. V., Viegas, C. A., Ganachaud, C., Iacazio, G., Tron, T., Robalo, M. P., & Martins, L. O. (2009). On the mechanism of biotransformation of the anthraquinonic dye acid blue 62 by laccases. *Advanced Synthesis & Catalysis*, *351*(11-12), 1857-1865.

Periyasamy, A. P. (2024). Recent advances in the remediation of textile-dye-containing wastewater: Prioritising human health and sustainable wastewater treatment. *Sustainability*, *16*(2), 495.

Rohilla, S., Gupta, A., Kumar, V., Kumari, S., Petru, M., Amor, N., Noman, M. T., & Dalal, J. (2021). Excellent UV-light triggered photocatalytic performance of ZnO. SiO2 nanocomposite for water pollutant compound methyl orange dye. *Nanomaterials*, *11*(10), 2548.

Shah, M. P. (2018). Azo dye removal technologies. *Advances in Research and Applications*, *5*(1), 1090.

Tkaczyk, A., Mitrowska, K., & Posyniak, A. (2020). Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review. *Science of the Total Environment*, *717*, 137222.

Waring, D. R., & Hallas, G. (Eds.). (2013). *The chemistry and application of dyes*. Springer Science & Business Media.

Youssef, N. A., Shaban, S. A., Ibrahim, F. A., & Mahmoud, A. S. (2016). Degradation of methyl orange using the Fenton catalytic reaction. *Egyptian Journal of Petroleum*, *25*(3), 317-321.