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Comparative Advanced Oxidation Decolorization of the Triphenylmethane Dye with Dimethyl Dioxirane and Hydrogen Peroxide

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ABSTRACT

Methyl Violet (MV), a triphenylmethane dye, has been subjected to comparative studies with hydrogen peroxide and dimethyl dioxirane under optimum situations. When employing hydrogen peroxide, the photolysis process becomes slower, but the dye solutions are entirely decolored and mineralized. The decolorization rate exhibits pseudo-first-order kinetics. The effect of pH, oxidant dosage, and methyl violet concentration on the degradation is also examined. Generated o-leucoaniline,1,3-diphenylurea,2-hydroxy benzoic acid, phenol, acetone, water, carbon dioxide, and carbon monoxide are identified and measured by GC-MS analysis. These substances remain in the dye solution along with dimethyl dioxirane, which is released faster during the last stages of degradation. The degradation rates of methyl violet reached 97.9% and 65.8% within 30 mins and 180 min of reaction time using dimethyl dioxirane and hydrogen peroxide.

INTRODUCTION

The textile sector uses many chemical dyes, and the effluents produced by these industries contain a significant portion of the dye that is not used, raising concerns about environmental health. Commercial dyestuffs are sometimes difficult for wastewater treatment facilities to remove from contaminated wastewater. Even minute concentrations of dyes have an impact on aesthetic appeal, gas solubility, and water transparency. Methyl violet, also known as crystal violet or N,N,N',N',N'',N''-hexamethyl pararosaniline, is a triphenylmethane dye that is widely used in the textile industry to dye nylon, silk, wool, and cotton as well as for biological stains and paper printing (Bumpus & Brock 1988). It is utilized as an antifungal drug for dermatological infections in both human and veterinary medicine and in oral medications to treat pinworms and other tropical disorders (Casas et al. 2009).

Additionally, methyl violet is frequently used in microbiological labs as a bactericidal and antiallergenic agent and in the analysis of Gram's stain for the primary classification of bacteria and Flemming triple stain with iodine (Mittal et al. 2008). According to toxicology data, methyl violet may cause skin and eye damage, irritation, and redness with pain or swelling, whereas it may be dangerous if inhaled, eaten, or absorbed via the skin (Mittal et al. 2008, Hameed 2008). So, while methyl violet can impact the gastrointestinal tract when consumed, it can irritate the respiratory tract when inhaled (Mittal et al. 2008).

Methyl violet exhibits poor biodegradation and is labeled as a hazardous recalcitrant. The ineffective removal of methyl violet from wastewater by conventional effluent treatment systems causes it to disperse into the environment (Nelson & Hites 1980). Methyl violet and several triphenyl methane dyes are reportedly strong carcinogens, another delicate issue (Diachenko1979). Many methods have been researched to remove methyl violet from wastewater, including chemical oxidation and reduction, physical precipitation and flocculation, photolysis, adsorption, electrochemical treatment, and reverse osmosis (Azmi et al. 1998). However, these methods are expensive, very loosely applicable to various dye wastewater, and only partially effective in removing the dye, which causes waterways (Fu & Viraraghavan 2001, Selvam et al. 2003). Compared to physical and biological treatment procedures, chemical processes are less costly and environmentally friendly, produce less sludge, and are therefore seen as promising and receiving more attention.

This paper highlights research on the decolorization of Methyl violet (Fig. 1) solutions by an advanced oxidation process. The efficiency of this AOP was evaluated by using dimethyl dioxirane and hydrogen peroxide as oxidants under

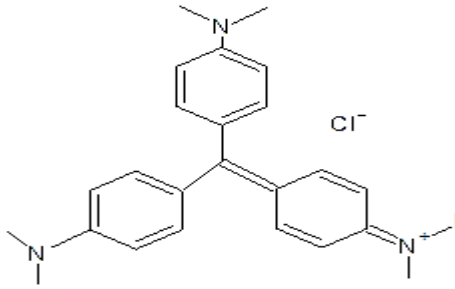


Fig. 1: Chemical structure of methyl violet.

similar situations. The effect of pH, dye concentration on the decolorization, rate of decolorization, and oxidants dosage were observed.

MATERIALS AND METHODS

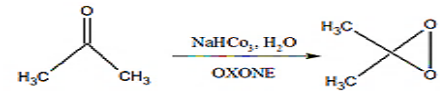
The potassium peroxymonosulfate was made available by TCI Chemicals (purity 99%). Acetone and sodium bicarbonate were supplied by Pure Chems and Merck, respectively. Hydrogen peroxide was purchased from ISOCHEM with 99% purity. Only analytical-grade substances were used for this experiment. None of the chemicals are further purified. Using an Elico Digital pH meter, the pH of the solution was determined. Because it is easily soluble in water, methyl violet dye (molecular formula $C_{24}H_{28}N_3Cl$, MW 393.95, λ=561 nm) is the dye used to symbolize organic dye. Therefore, this is made with distilled water and utilized in all studies. Due to its high water solubility, this dye is bought from S.D. fine chemicals. The decolorization of methyl violet was observed for all the optimized parameters using the instrument UV-Visible spectrophotometer (Hitachi U2910).

Preparation of an Oxidizing Agent

The solid potassium mono peroxy sulfate was added in one portion while stirring vigorously at room temperature to a 250 mL round-bottomed flask that was already filled with a mixture of water, acetone, sodium bicarbonate, and a magnetic stirring bar. This flask was also fitted with an additional funnel for solids containing this substance and was cooled using dry ice-acetone. The yellow dioxirane-acetone solution was made and deposited in the receiving flask.

Degradation Experiments

50 mL of methyl violet standard solutions (10 mg to 100 mg.L^{-1}) were prepared and used for each analysis. Every investigation was conducted at room temperature in a dark atmosphere. The dye solution's initial absorption peak was noted before the experiment began. Later the experiment was running for 30 min, 1 mL of the dye solution was taken



Equation.1. Preparation of dimethyl dioxirane.

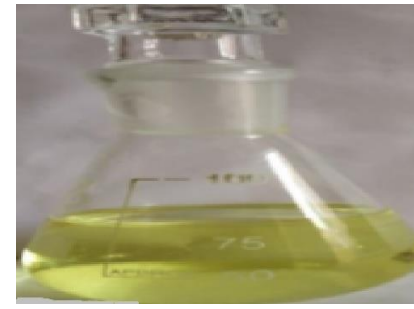
out of the reaction mixture and diluted, and the amount of dye penetration was determined. The effects of pH were investigated by adjusting the pH of the solution with 0.1 N NaOH and 0.1 N HCl. As noted, the blank trials were carried out at room temperature and in the dark. The formula (C_0- C)/C_0x100 was used for the percentage decolorization. C_0 denotes the dye solution's starting concentration, and C represents the dye solution's concentration at time t. The same was repeated as mentioned above by using hydrogen peroxide as an oxidant under sunlight.

RESULTS AND DISCUSSION

Visual Observation of the Formation of an Oxidizing Agent

Dimethyl dioxirane was initially identified through visual examination. The reaction mixture's color change indicates the formation of dimethyl dioxirane. The aqueous solution of acetone and water first turn colorless, but when sodium

2(a)



2(b)

Fig. 2: (a) Sodium bicarbonate and acetone are combined in this solution. (b) The addition of potassium peroxymonosulfate forms dimethyl dioxirane.

bicarbonate and potassium peroxymonosulfate are added, the color changes to pale yellow (Robert et al. 1985, Adam et al. 1987). Fig. 2a and 2b show the formation of dimethyl dioxirane.

Uv-Visible Spectroscopy

UV-visible (200-800 nm) examination of methyl violet dye supernatants at various period intervals revealed decolorization and a reduction in MV dye concentration. MV has a significant absorption peak at 561 nm in the UV-visible spectrum. The intensity of the primary peak dropped dramatically after oxidant treatment due to decolorization. After 30 min, the MV peak recorded at max 561 nm reduced without any change in the maximum until the full decolorization of the treated Methyl violet dye (Fig. 4). It has been reported that dye decolorization by dimethyl dioxiranemay results from dye adsorption by the oxidant or chemical degradation. For example, in chemical degradation, the primary visible light absorption peak completely disappears, as seen in our investigation and illustrated in Fig. 3a.

Similarly, no reaction occurs while using hydrogen peroxide as an oxidizing agent at room temperature. The decolorization occurs in sunlight with hydrogen peroxide as an oxidant under optimal conditions. The degradation process was monitored using UV-Visible spectroscopy at regular intervals of time. The characteristic peak slightly decreases after the completion of 3 h, which indicates that only 50% of degradation takes place at 3 h. Fig. 3b includes UV-Visible depictions of the degradation process.

A comparison of both oxidants revealed that the dimethyl dioxirane decolorized the dye solution within 30 mins. But hydrogen peroxide was not able to decolorize the dye solution completely. Only partial decolorization occurred at 3 h, which showed that dimethyl dioxirane was more powerful than hydrogen peroxide.

Fourier Transform Infrared Analysis

The FT-IR spectra of pure methyl violet (Fig. 4a) and the dye-decolorized sample (30 min) revealed a noticeable difference in the fingerprint wave number area of 1,500-500 cm^{-1}, indicating methyl violet decolorization by dimethyl dioxirane. In the FT-IR spectrum of pure methyl violet, there are distinct peaks in the region of 1,500–500 cm^{-1} that correspond to the monosubstituted and para-disubstituted aromatic ring (Fig. 4a). However, the appearance of a wave number peak at 1583.29 cm^{-1} corresponds to the C=C stretching of the aromatic ring. At 1166.66 cm^{-1}, there

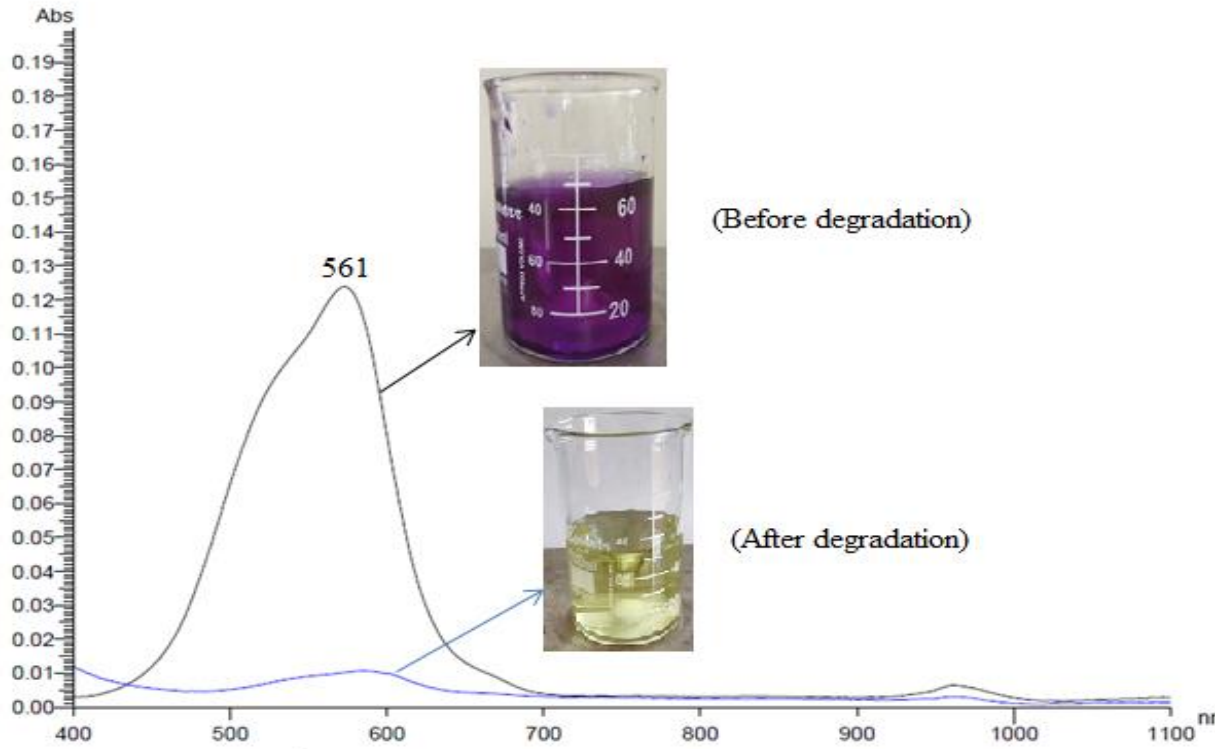


Fig. 3a: Depicts the methyl violet UV-visible spectrum under ideal conditions before and after degradation.

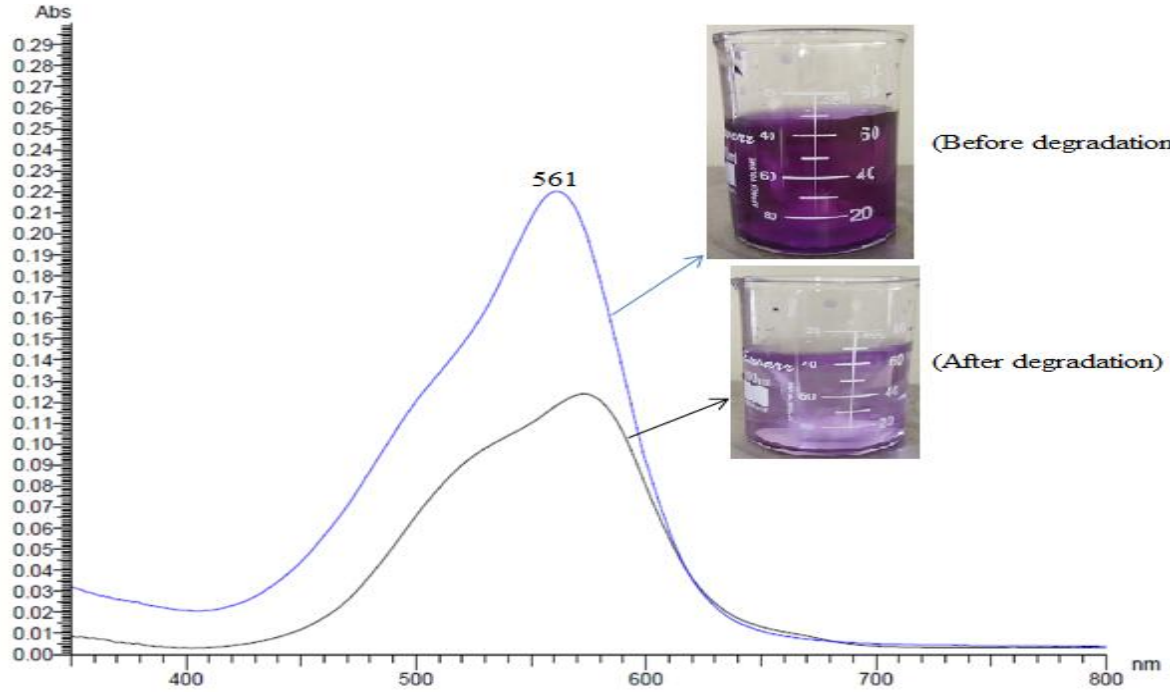


Fig. 3b: Demonstrates the UV-Visible spectra of methyl violet before and after their degradation in the presence of sunlight.

is also a peak for aromatic C-N stretching vibrations. At 2924.95 cm^{-1}, the C-H asymmetric stretching vibration was seen, while at 3160.93 cm^{-1}, the free -NH_2 group displayed an amide antisymmetric stretching vibration. The peak indicated a C=C stretching bend at 1666.28 cm^{-1}. Peaks at 1166.66 and 1113.70 cm^{-1} relate to the C-O stretch. The benzene ring bending is correlated with the peaks at 758.62 and 725.30 cm^{-1}. After degradation, the FT-IR spectrum of the decolorized MV products (Fig. 4b) showed characteristic peaks at 3,435.88 cm^{-1} for hydrogen bonding, 2,074.66 cm^{-1}, 1,633.49 cm^{-1} for -C-C- stretching, 1,116.65 cm^{-1} for -C-O- stretching. After decolorization, the IR spectra of methyl violet show various suppressed peaks.

Furthermore, the disappearance of many peaks at 758, 725, and 991 cm^{-1} shows that the ring has been lost. FT-IR spectrum analysis reveals different absorption bands for methyl violet dye before and after the advanced oxidation process. The findings demonstrated a considerable structural shift, which can be validated by comparing before and after degradation spectral images.

Similarly, The FT-IR spectra of pure methyl violet (Fig. 5a) and the dye-decolorized sample (3 h) revealed a noticeable difference in the fingerprint wave number of 1,500-500 cm^{-1}, indicating methyl violet decolorization by hydrogen peroxide. The presence of specific peaks to the fingerprint wave number region of 1,500-500 cm^{-1} represents the monosubstituted and para-disubstituted benzene rings in the FT-IR spectrum of pure methyl violet (Fig. 4a). In contrast, the presence of a wave number peak at 1583.29 cm^{-1} represents the C=C stretching of the benzene ring. There is also a peak for aromatic C-N stretching vibrations at 1166.66 cm^{-1}. C-H asymmetric stretching vibration was observed at 2924.95 cm^{-1}, while the free -NH_2 group showed amide antisymmetric stretching vibration at 3160.93 cm^{-1}. The peak at 1666.28 cm^{-1} indicated a C=C stretching bend. Peaks corresponding to the C-O stretch are located at 1166.66 and 1113.70 cm^{-1}. The peaks at 758.62 and 725.30 cm^{-1} correlate to benzene ring bending. After degradation, the FT-IR spectrum of the decolorized MV products (Fig. 5b) showed more same characteristic peaks at 3444.60 cm^{-1} corresponding to OH stretching, 2077.48 cm^{-1}, and 1632.95 cm^{-1} for aromatic C-H bending, 1423.75 cm^{-1} for OH bending, 1279.80 cm^{-1} and 1216.54 cm^{-1} correspond to C-O stretching, 703 cm^{-1} for C=C stretching.

The major bands disappeared in FTIR spectra by using dimethyl dioxirane. Complete decolorization occurs in methyl violet using dimethyl dioxirane as an oxidant. Whereas using hydrogen peroxide as an oxidant, many peaks remain the same, and no complete decolorization occurs at reaction time. The result confirmed that dimethyl dioxirane is a more powerful oxidant than hydrogen peroxide.

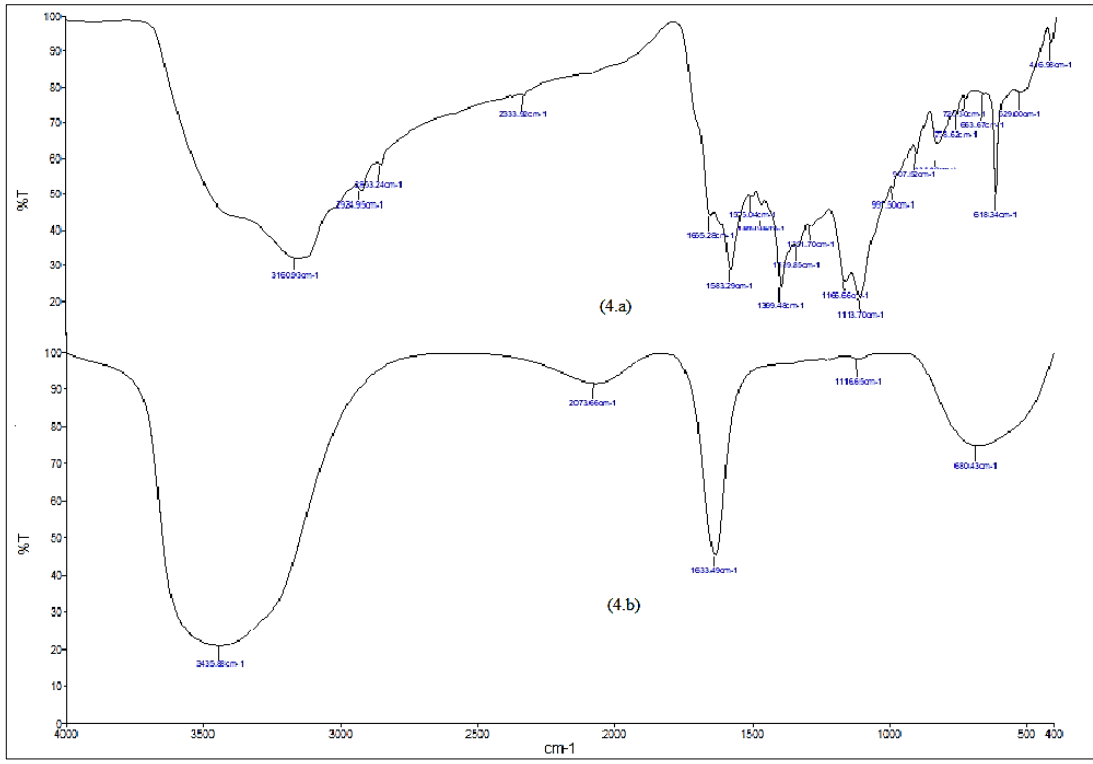


Fig. 4a: Shows the before-degradation FTIR spectra of pure methyl violet. 4b: Shows the after-degradation FTIR spectrum of methyl violet using dimethyl dioxirane.

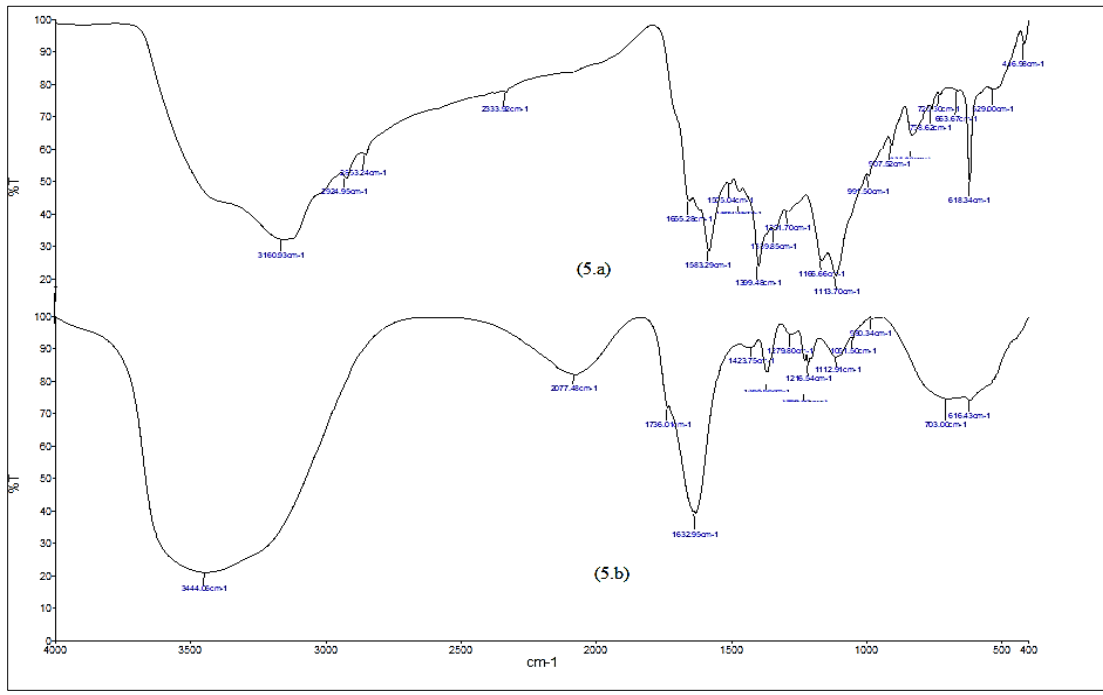
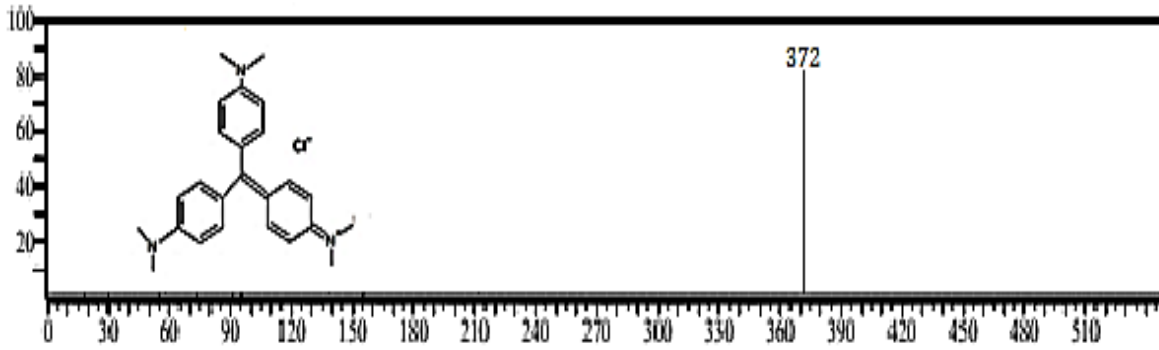
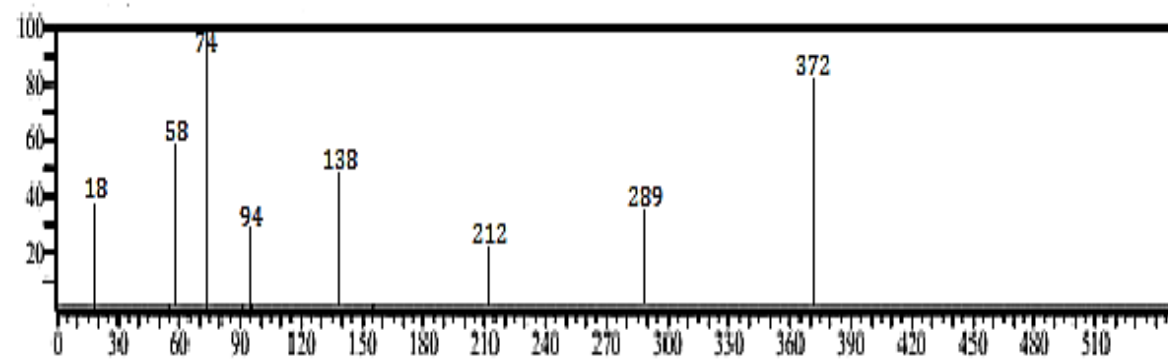


Fig. 5a: Shows the before-degradation FTIR spectra of pure methyl violet. 5b: Shows the after-degradation FTIR spectrum of methyl violet using hydrogen peroxide.



6a



6b

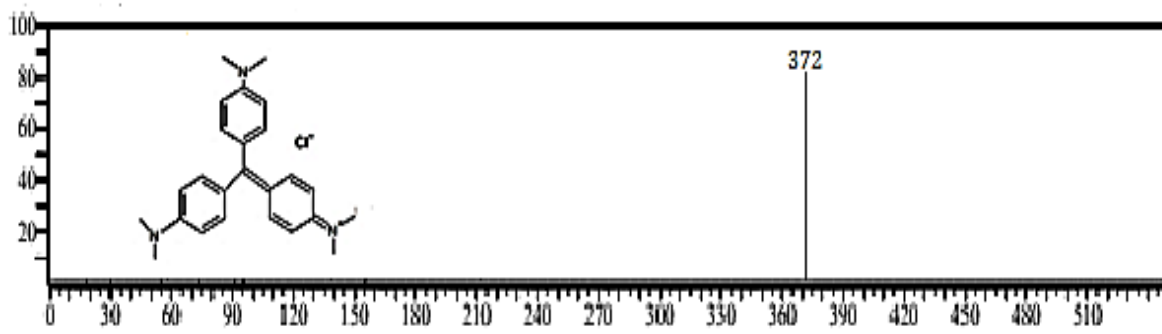
Fig. 6a & b: Shows the mass spectrum of before and after decolorization of methyl violet using dimethyl dioxirane as an oxidizing agent.

Mass Spectroscopy

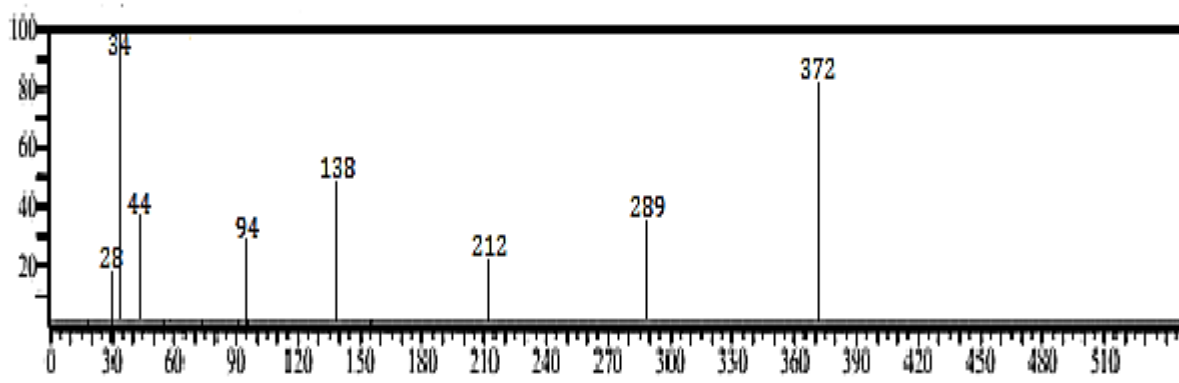
Fig. 6a depicts the mass spectra of the pure dye Methyl violet. Fig. 6e depicts the possible breakdown pathways of methyl violet dye using dimethyl dioxirane at room temperature. The MV dye's N-demethylation and the fragmentation of the chromospheric group as a result of the loss of heterocyclic conjugation and subsequent intermediate alkylation initially resulted in oxidative intermediate intermediates. In the second oxidation stage, heterocyclic species were added to the quinoid molecule, which caused the aromatic rings to open and carboxylic acids to be produced. The subsequent ring-opening processes may have produced (CH$_3$)2CO and H$_2$O as end products (Hunge et al. 2021, Ju et al. 2011). The corresponding spectra are determined by the molecular ions M+ = 372.2 u. A progressive loss of CnH2n groups indicates the typical degradation of methyl violet with dimethyl dioxirane at normal temperature (Fig. 6b). MV detected seven degradation products with m/z values of 289.4 u, 212.2 u, 138.1 u, 94.1 u, 74.0 u, 58.0 u, and 18.0 u.

Fig. 6c depicts the mass spectra of the pure dye Methyl violet. Fig. 6f depicts the potential pathways for methyl violet dye degradation utilizing hydrogen peroxide in the presence of sunlight. The N-demethylation of the MV dye results in the production of oxidized intermediate products, which in turn causes the cleavage of the chromosphere structure due to the loss of aromatic conjugation and subsequent intermediate hydroxylation. The second process involved opening aromatic rings and forming carboxylic acids, while the first stage involved the degradation of hydroxylated species in producing the quinoid molecule. The ring-opening processes persisted, and CO_2 and CO may have been the final products of deterioration. The corresponding spectra are characterized by molecular ions, M+ = 372.2 u. Under sunlight, the usual breakdown of methyl violet with hydrogen peroxide is characterized by a gradual loss of CnH$_2$n groups (Fig. 6d). At m/z = 289.4 u, 212.2 u, 138.1 u, 94.1 u, 44.0 u, 34.0 u, and 28.0 u, MV produced seven degradation products.

The methyl violet dye reacts with dimethyl dioxirane, giving mineralization products such as acetone and water,

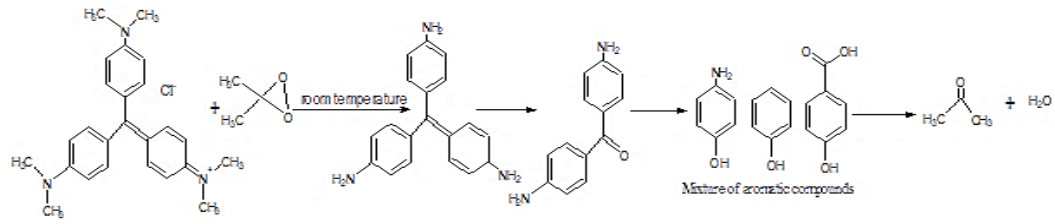


6.c

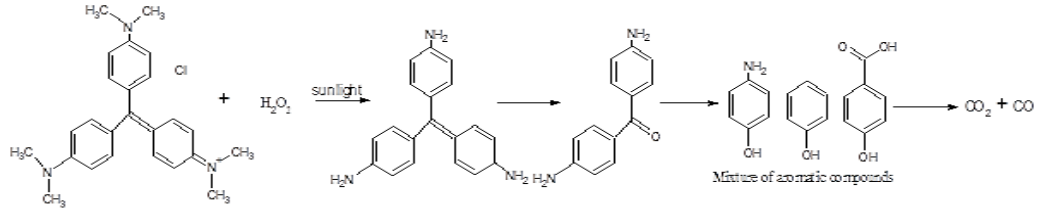


6.d

Fig. 6c & d: Shows the mass spectrum of before and after decolorization of methyl violet using hydrogen peroxide as an oxidizing agent.



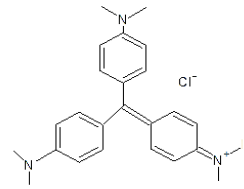
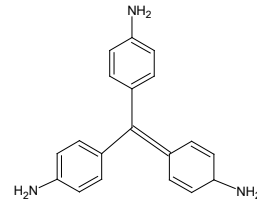
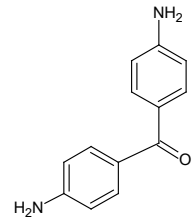
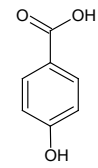
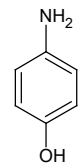
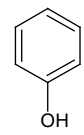
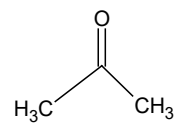
6.e



6. f

Fig. 6e & f: Possible pathways for degradation of methyl violet using dimethyl dioxirane and hydrogen peroxide as oxidizing agents.

Table 1: De-methylated intermediates of the methyl violet dye, including their chemical names, chemical structures, and m/z values.

Chemical name	Structure	m/z Value
[4-[bis[4-(dimethylamino) phenyl] methylidene]cyclohexa-2,5-dien-1-ylidene]-dimethyl azanium(Methyl violet dye)		372.52
o-Leucoaniline		289.37
1,3-Diphenylurea		212.24
2-Hydroxy benzoic acid		138.12
4-amino phenol		109.13
Phenol		94.11
Acetone		58.07
Water	H_2O	18.01
Carbon dioxide	CO_2	44.00
Carbon monoxide	CO	28.01

which is harmless to humans and the environment. Similarly, methyl violet reacts with hydrogen peroxide, releasing harmful products like carbon dioxide and carbon monoxide. Compared to hydrogen peroxide, dimethyl dioxirane is more powerful and eco-friendly.

Effect of pH

Using dimethyl dioxirane, the impact of pH in the range of 3-9 is investigated for a 10 mg.L^{-1} (50 mL) methyl violet dye solution. According to Fig. 7a, acidic pH=5 showed the highest decolorization efficacy. Good decolorization efficiency is attained at acidic and neutral pH levels because the anionic methyl violet dyes readily adsorb to the positively charged dimethyl dioxirane. Similarly, the impact of pH in the range of 3–9 is investigated using hydrogen peroxide and a 10 mg.L^{-1} (50 mL) methyl violet dye solution. According to Fig. 7b, the acidic pH=7 environment had the highest decolorization efficacy. Hydrogen peroxide does not exhibit greater efficacy at the same pH; only a small percentage of decolorization occurs over a period of time.

Effect of Oxidant

By varying the concentration of the oxidizing agent from 100 to 1000 μL for the 10 mg.L^{-1} methyl violet dye solution illustrated in Fig. 8a, the appropriate amount of dimethyl dioxirane oxidant for effective methyl violet decolorization was found. Dyes continue to degrade up to a point at which the rate of decolorization starts to decline when the oxidizing agent concentration is raised to 500 μL. This is because adding 500 μL of dimethyl dioxirane to the dye solution caused the rate of decolorization to slow down, and the number of active sites needed for dye decolorization increased as the concentration of oxidizing agent increased. This is demonstrated by the fact that more active sites are needed for dye decolorization, which rises with an increase in the concentration of the oxidizing agent, and that the decolorization process gradually slows down after adding

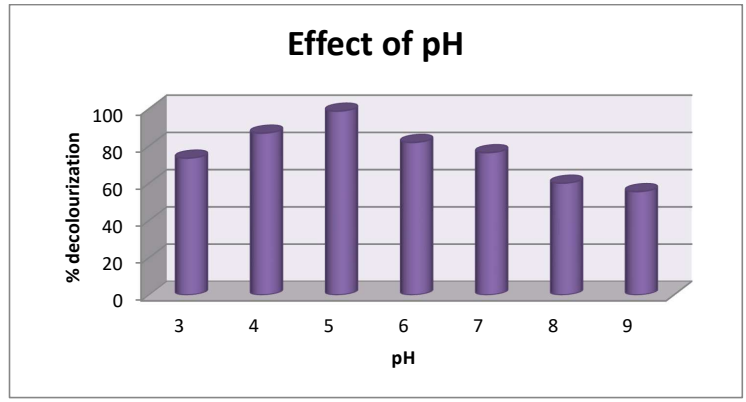


Fig. 7a: 10 mg.L^{-1} methyl violet dye solution, 500 µL of dimethyl dioxirane, pH varied from 3 to 9, under room temperature.

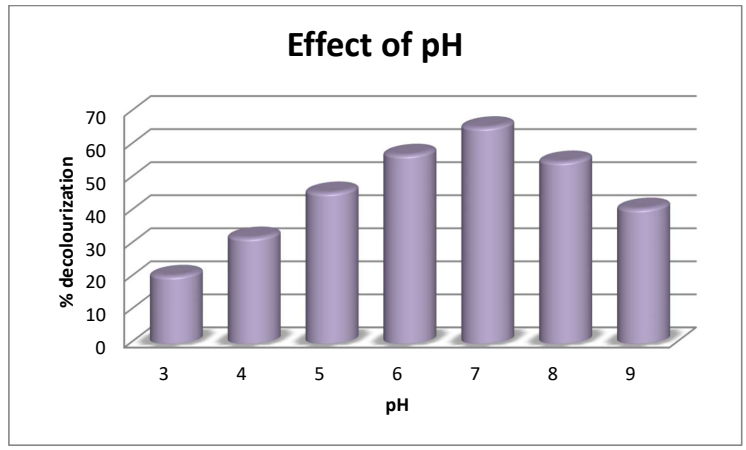


Fig. 7b: 10 mg.L^{-1} methyl violet dye solution, 5mL of hydrogen peroxide, pH varied from 3 to 9, under sunlight.

500 μL of dimethyl dioxirane to the methyl violet dye solution. Approximately 98.42% of the dye is decolored after 500 µL in 30 min.

Similarly, the optimum amount of hydrogen peroxide for efficient methyl violet decolorization was determined by adjusting the oxidant concentration from 1 to 10 mL for 10 mg.L^{-1} of methyl violet dye solution shown in Fig. 8b. With 5 mL of hydrogen peroxide. Methyl violet dye can be fully decolored; beyond that, the decolorization rate starts to decline. As the oxidant concentration rises, the active sites needed for dye decolorization also increase. However, if too much oxidant has been added to the dye solution, the suspension becomes turbid, which reduces sunlight penetration. The photo decolorization process slows down due to the dye solution's decreased exposure to sunshine (Hu et al. 2003 & Soroosh et al. 2019). At the same time, just 12% of the dye was decolored with hydrogen peroxide at room temperature. This demonstrates that the dye is resistant to self-photolysis and that a supporting catalyst is required for effective methyl violet decolorization. With 5 mL, approximately 75.59% of the dye is decolored in 180 min. To decolorize the dye solution in sunlight, more hydrogen peroxide is required.

Effect of Initial Dye Concentration

The maximum dye decolorization effectiveness is assessed using 500 µL of dimethyl dioxirane at an ideal pH of 5 by operating at room temperature to determine the best concentration of methyl violet dye. The dye concentration is varied between 10-100 mg.L^{-1}. Within 30 min, 10 mg.L^{-1} of the methyl violet dye had approximately 97.9% of its color removed. Without a supporting catalyst, dimethyl dioxirane can ably decolorize 10-100 mg.L^{-1} of methyl violet dye solution under room temperature. About 26.8% of 100 mg.L^{-1}

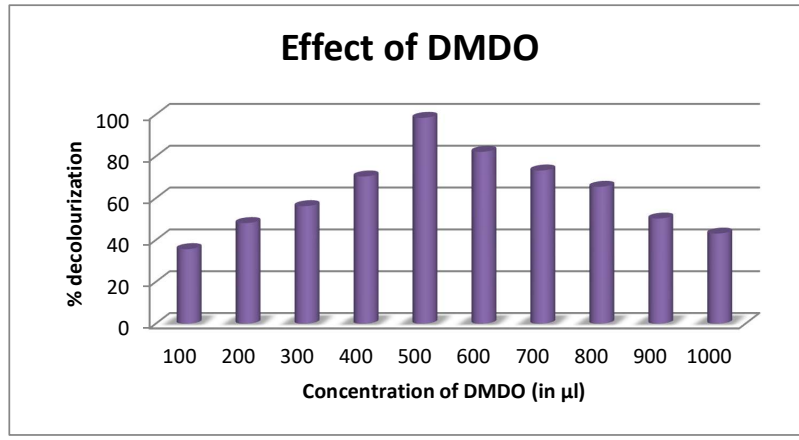


Fig. 8a: 10 mg.L^{-1} methyl violet dye solution, dimethyl dioxirane dosage varied from 500 µL to 1000 µL, pH = 5, under room temperature.

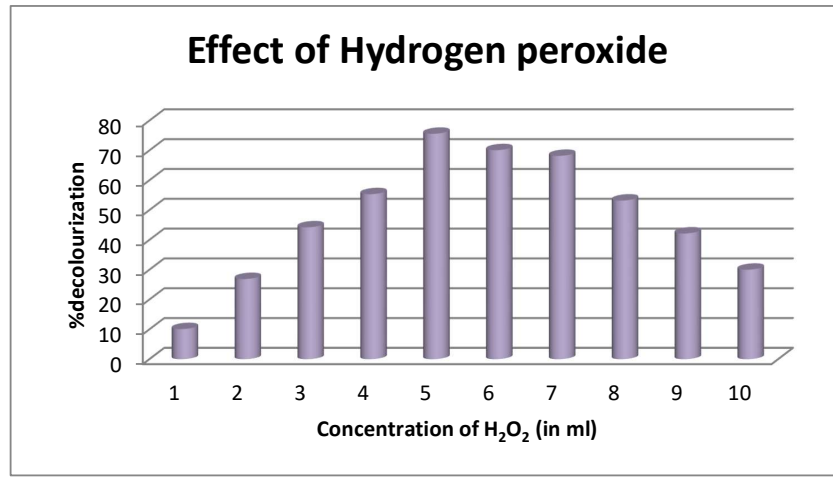


Fig. 8b: 10 mg.L^{-1} methyl violet dye solution, hydrogen peroxide dosage varied from 1mL to 10 mL, pH = 5, under sunlight temperature.

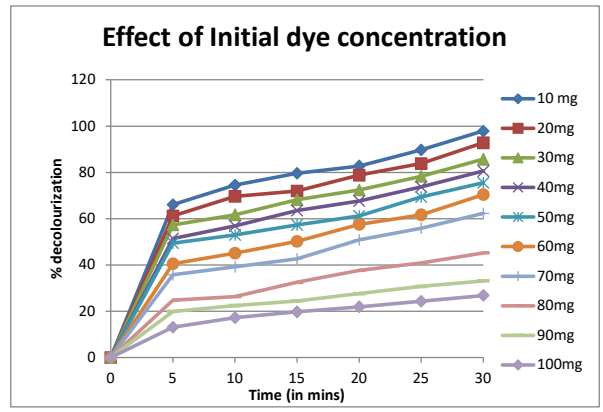


Fig. 9a: 500 µL of dimethyl dioxirane, pH=5, initial methyl violet dye concentration varied from 10 mg.L^{-1} to 1000 mg.L^{-1}, under room temperature.

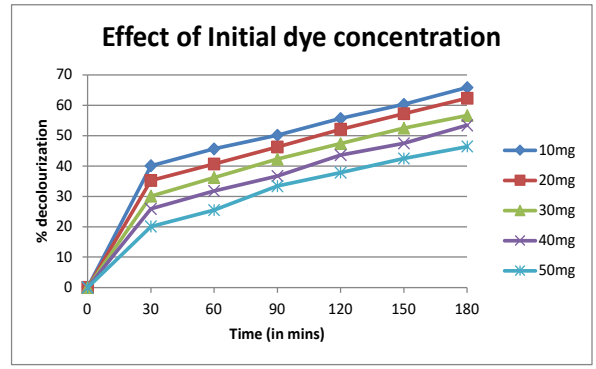


Fig. 9b: 5 mL of hydrogen peroxide, pH=7, initial methyl violet dye concentration va from 10 mg.L^{-1} to 50 mg.L^{-1} under sunlight.

of methyl violet dye can be decolorized within 30mins as shown in Fig. 9a.

Similarly, only 65.8% of dye decolorization took place within 180 min using hydrogen peroxide under sunlight at pH 7, as shown in Fig. 9b. Whereas, under room temperature, only 12% of the dye decolorization took place with hydrogen peroxide. This demonstrates strongly that the dye is resistant to self-photolysis and needs a supporting catalyst for efficient decolorization of methyl violet. Hydrogen peroxide can be able to decolorize only 50 mg.L^{-1} of dye solution within 180 min. It takes more time to decolorize the dye solution compare to dimethyl dioxirane.

Kinetic Studies

The graph of *ln* (C/C_0) vs. reaction time was plotted using the extinction plot. Fig. 10a and 10b show a 10 mg.L^{-1} methyl violet dye solution with 500 µL of dimethyl dioxirane and 5 mL of hydrogen peroxide. The slope is employed to determine the reaction rate constant of the plot. The reaction's rate constant was determined using equation (2) (Yadav et al. 2019).

$$ln\frac{C_0}{C} = k.t \quad (2)$$

C0 denotes the initial dye concentration, Ct is the dye concentration at time t, and k denotes the constant reaction rate.

Studies from earlier work demonstrate that concerning pollutant concentration, most oxidation processes follow pseudo-first-order kinetics (Bhargav et al. 2007, Eftaxias et al. 2001, Garg et al. 2010, Santos et al. 2004). The dimethyl dioxirane and hydrogen peroxide rate constant are 0.0144, 0.003, and the R^2 value is 0.9896, 0.9733. All the data points arranged along a straight line confirmed the result.

CONCLUSION

In conclusion, we have presented the comparison study results between hydrogen peroxide and dimethyl dioxirane. Dimethyl dioxirane is produced via a standard chemical process. The removal percentage was the preferred outcome. This study optimized the decolorization of methyl violet

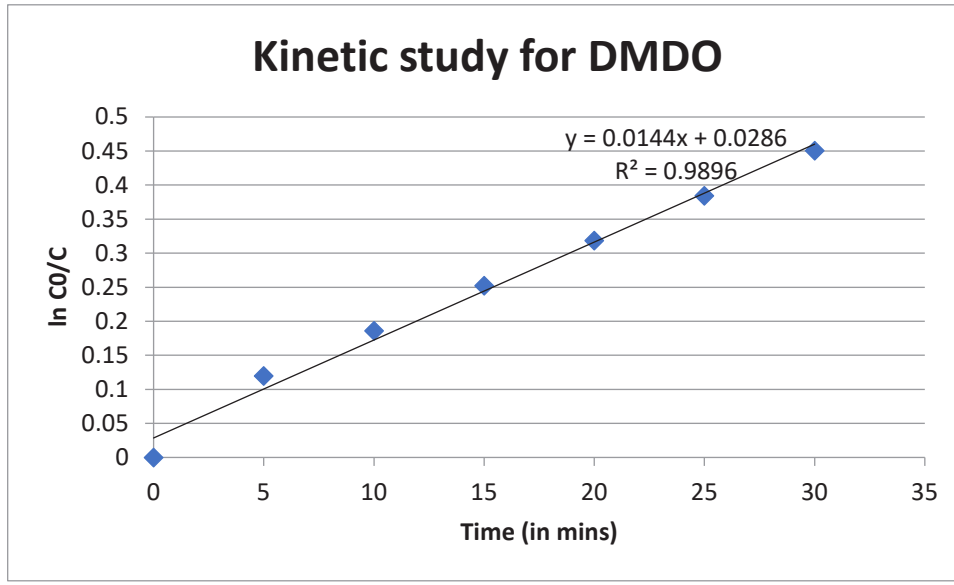


Fig. 10.a: The plot of lnC0/C Vs. Time for 10 mg.L^{-1} of methyl violet dye solution.

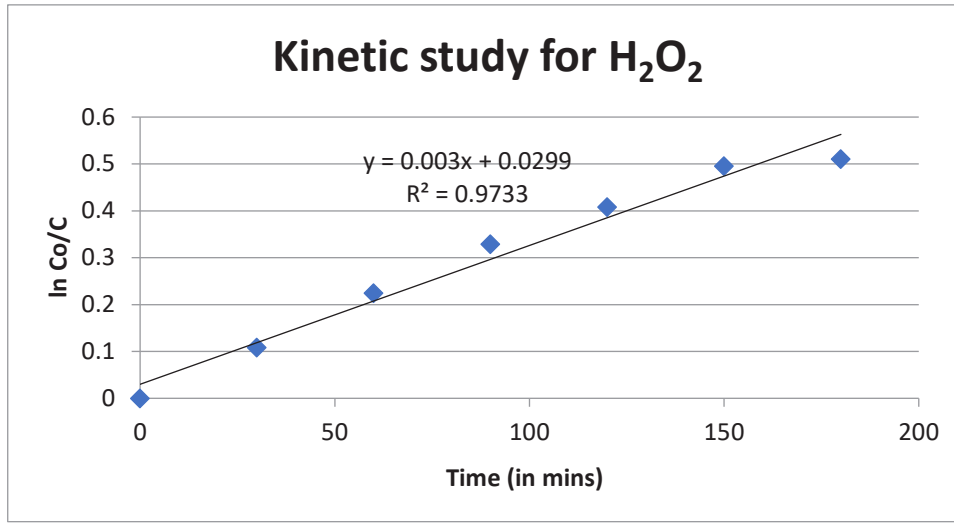


Fig. 10.b: The plot of lnC0/C Vs. Time for 10 mg.L^{-1} of methyl violet dye solution.

dyes by efficient advanced oxidation using a dimethyl dioxirane and hydrogen peroxide system under ambient temperature and sunlight. Initial dye concentration, solution pH, and oxidant dosage were considered variant factors. Decolorization efficiencies of 97.9 % and 65.8% were achieved within 30 and 180 min of reaction time under optimum conditions for methyl violet. Results indicate that, when compared to hydrogen peroxide, the dimethyl dioxirane oxidation process is a viable and affordable method for dye removal from textile industry effluents. The end product, such as acetone and water, is produced by employing dimethyl dioxirane as an oxidant to decolorize methyl violet. The dye decolorization process takes less than hydrogen peroxide as an oxidant. Compared to hydrogen peroxide, dimethyl dioxirane is a powerful, safe, affordable, and environmentally friendly oxidant.

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