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Degradation of Malachite Green (MG) Under Uv and Uv With H_2O_2 Processes

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Article Details

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ABSTRACT

Advanced oxidation processes (AOPs), defined as those technologies that utilize the hydroxyl radical (OH) for oxidation, have received increasing attention in the research and development of wastewater treatment technologies in the last decades. These processes have been applied successfully for the removal or degradation of toxic pollutants or used as pretreatment to convert recalcitrant pollutants into biodegradable compounds that can then be treated by conventional biological methods. The efficacy of AOPs depends on the generation of reactive free radicals, the most important of which is the hydroxyl radical (OH). Here we summarize the formation reactions of OH and the mechanisms of dye degradation. In this study, we used methods using H2O2 and UV lamps to degrade Malachite Green where we carried out numerous trials on the Advance oxidation process. The stock solution of Malachite Green was prepared as 0.1 g/L in the first phase. Then, using the stock solution, we prepared further the standard solutions. The Vis-Spectrophotometer was then used to determine how well various solutions absorbed light. The dye was then exposed to various amounts of H2O2, and the absorption was once more measured at various time intervals. After this Malachite Green (MG) was treated with various concentrations of pH and ions and the %degradation was measured repeatedly.

DOI: Availability

INTRODUCTION

Water scarcity has become one of the most pressing global challenges, largely driven by rapid population growth, accelerated industrialization, and expanding economic development. These factors have drastically increased the demand for clean and safe water, essential for domestic consumption, agricultural activities, and maintaining ecological balance. Unfortunately, this growing demand is severely threatened by the widespread pollution of water bodies, primarily caused by the discharge of untreated or inadequately treated industrial and municipal wastewater. Among the various pollutants, dyes released from industries such as textiles, chemicals, refineries, plastics, and food processing stand out as a major environmental concern. These dyes possess complex and highly stable aromatic molecular structures that make them resistant to conventional wastewater treatment methods and natural biodegradation processes. It is estimated that about 20% of industrial wastewater pollution is due to these dyes, which have devastating effects on aquatic ecosystems. They reduce light penetration in water, thereby disrupting photosynthesis in aquatic plants, lowering oxygen levels, and adversely affecting aquatic organisms. Moreover, many dyes are toxic, carcinogenic, and capable of causing genetic mutations, posing significant health risks to humans and wildlife alike.

The persistent and hazardous nature of these dye pollutants calls for advanced and effective treatment technologies. In recent years, Advanced Oxidation Processes (AOPs) have emerged as highly promising solutions. Among these, photocatalysis and the Fenton reaction have gained considerable attention due to their efficiency in degrading complex organic contaminants. Photocatalysis involves the use of light-activated catalysts, typically titanium dioxide, which generate reactive hydroxyl radicals upon exposure to ultraviolet or visible light. These radicals attack and break down dye molecules, ultimately mineralizing them into harmless end products such as water and carbon dioxide. The Fenton process, on the other hand, employs ferrous ions and hydrogen peroxide to produce hydroxyl radicals in situ, which oxidize toxic organic compounds. Both methods not only degrade dyes effectively but also improve the biodegradability of the wastewater, making subsequent biological treatment processes more efficient. These AOPs are often integrated into wastewater treatment plants as either pre-treatment or post-treatment steps to enhance overall pollutant removal.

Alongside these advanced chemical processes, adsorption remains a widely used and effective method for dye removal. Activated carbon, known for its high surface area and adsorption capacity, is traditionally used; however, its high cost and difficulties in regeneration have motivated researchers to explore alternative adsorbents. Agricultural wastes such as banana stems, date pits, sawdust, and coconut shells have shown great potential as low-cost, sustainable adsorbents for dye removal. Utilizing these natural materials not only reduces the treatment costs but also provides a valuable avenue for managing agricultural by-products, contributing to circular economy principles.

Addressing industrial dye pollution requires not only technological solutions but also integrated water resource management strategies that emphasize decentralized governance and active stakeholder involvement. Collaborative efforts among industries, government agencies, communities, and environmental organizations are crucial to develop and enforce regulations that ensure effective wastewater treatment and prevent pollution at the source. These combined efforts are essential to protect water quality, safeguard aquatic biodiversity, and ensure the availability of clean water for future generations. In summary, tackling the challenge of dye pollution through innovative treatment technologies, sustainable materials, and robust management frameworks is vital for achieving long-term water security and supporting sustainable development in the face of increasing environmental pressures.

LITERATURE REVIEW

Faradilla et al, *(2006)* studied that some solids have been used to remove dye from aqueous solution. Various scientists Brunauer, Emmet and Teller, Langmuir, McBain and Barrer in early twentieth century studied ways to remove contaminants from liquids and gases using solids

[71].

B.H Hameed et al) carried out adsorption of methylene blue by bamboo-based activated carbon. Bamboo was used to make activated carbon by physiochemical activation with potassium hydroxide and carbon dioxide. Adsorption models and kinetic studies were also conducted and it was found that pseudo-second-order model best described the process [72].

I.D. Mall, et al (2005) studied the removal of malachite green dye from aqueous solution using bagasse fly ash and analyzed kinetic and adsorption isotherm models. Adsorption was carried out in batch processes and the effects of various parameters were analyzed. Adsorption followed pseudo-second-order kinetics [73].

Ewa Lorenc-Grabowska et al (2006) conducted experiments on adsorption of Congo Red using bituminous coal-based mesoporous activated carbon. Mesopores contribute 52 to 83% to the total pore volume. The adsorption was best described by pseudo-second-order model and the Langmuir equation. The monolayer adsorption was found to increase with increase in mesopore volume [74].

R.A Shawabkeh et al, (*2007)* performed study of adsorption of phenol and Methylene Blue by activated carbon from pecan shells. Activated carbon is prepared from pecan shells by chemical activation with phosphoric acid. Then it is treated with sodium dodecyl sulfate to prepare the surface for adsorption. The results indicated good removal of phenol and Methylene Blue dye by pecan shells [75].

M.I. El-Khairy et al, (*2008*) studied the adsorption of Malachite green dye by rattan sawdust at 30oC. Results indicated that rattan sawdust can be used as low, cost adsorbent source. Two isotherms Freundlich and Langmuir were analyzed and the best fit model was found to be Langmuir isotherm model. Adsorption kinetics was predicted by pseudo-first – order model. For a short period of time the adsorption rate was controlled by film diffusion, at longer adsorption period pore-diffusion controls the rate [76].

Mi-Hwa Baek et al, (*2009*) studied feasibility of using degreased coffee beans as adsorbent for removing Malachite Green dye was evaluated by Mi-Hwa Baek, Christianah Olakitan Ijagbemi, Se-Jin O, Dong-Su Kim. Rate kinetics, adsorption isotherms and thermodynamic properties were also evaluated for the purpose [77].

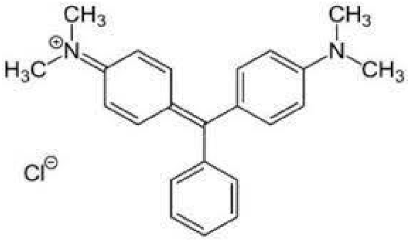
M. Anbia et al, (*2011*) removed Malachite Green dye from wastewater was studied by using mesoporous carbon adsorbent. Mesoporous carbon was synthesized and effects of various conditions 5 such as dye concentration, adsorbent dose, contact time and pH were observed, the adsorption isotherms and rate kinetics were also determined [78].

Shabudeen et al, (*2011*) removed Malachite Green present in aqueous solution by use of solid agricultural waste, was studied. Agricultural solid waste, Kapok hull was activated by Sulphur acid (1:1 ratio) and batch kinetic and isotherm experiments were performed to determine the sorption and desorption characteristics. The experimental parameters affecting rate of adsorption were initial dye concentration, carbon dose, agitation time, particle size, and temperature and pH variation. The adsorption isotherm models and rate kinetics were established for the process. Adsorption rate constants, diffusion rate constants, interparticle diffusion constants and diffusion coefficients were also determined. It was found out that interparticle diffusion is the rate limiting step.

METHODOLOGY EXPERIMENTAL WORK:

Malachite Green (MG)

TABLE 1: MALACHITE GREEN (MG)

Name	Property
Malachite Green (MG)	Dye
Molecular Formula	C23H26ClN2
Molecular Size	0.8 nm – 1.58 nm
Molecular Weight	364.92 g/mol
Solubility in water	60 mg/ml
Pka	10.3
Maximum Wavelength	617 nm
Ionic strength	0.1
Molecular Structure	

DISTILLED WATER

Distilled water was used for the preparation of stock solutions and various diluted solutions.

HYDROGEN PEROXIDE (H_2O_2)

Hydrogen peroxide, a reactive oxygen species, is the simplest compound that slowly decomposes into water and elemental oxygen when exposed to light. Different concentrations of 30% pure H_2O_2 were used in the experiments.

HYDROCHLORIC ACID (HCL)

HCl plays a significant role in the treatment of dye-containing wastewater and in chemical reactions aimed at breaking down dyes. Different concentrations of HCl with 30% purity were employed.

IONS

Stock solutions of various ions, including sodium carbonate (Na_2CO_3), sodium hydrogen carbonate ($NaHCO_3$), sodium sulphate (Na_2SO_4), potassium nitrate (KNO_3), and sodium chloride (NaCl), were prepared and used as catalysts.

IRON

Different concentrations of iron solutions, obtained from iron sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), were used for the Fenton and photo-Fenton processes.

VIS-SPECTROPHOTOMETER

A Vis-Spectrophotometer (Model 721) was used to measure the absorbance of solutions.

UV LAMP

A UV lamp (Mercury lamp manufactured by Philips, Germany) was utilized for the photocatalytic degradation of the dye.

METHOD

PHOTOCHEMICAL DEGRADATION

A 100 mg/L stock solution of Malachite Green (MG) was prepared using distilled water. Standard solutions with concentrations of 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L, 25 mg/L, and 30 mg/L were then prepared by diluting the stock solution with distilled water. The absorbance of these solutions was measured using a Vis-Spectrophotometer at a wavelength of 617 nm. Dye concentrations were determined from the calibration curve constructed at the wavelength corresponding to the maximum absorbance.

PHOTOCATALYTIC DEGRADATION PROCESS

The experiments were conducted in a reaction chamber equipped with a UV lamp. In the first step, the dye solution was treated with different concentrations of H_2O_2 under UV irradiation, and the average concentration of H_2O_2 was recorded. In the next step, the dye was treated with varying concentrations of HCl under UV light, and absorbance measurements were taken at different time intervals. Subsequently, the dye was exposed to different concentrations of ions (sodium carbonate, sodium bicarbonate, sodium nitrate, sodium chloride), and absorbance was noted over time. Finally, the Fenton and photo-Fenton processes were performed, wherein Malachite Green was treated with iron (Fe) solutions, and the absorbance was measured using the Vis-Spectrophotometer.

RESULTS AND DISCUSSION:

CALIBRATION CURVE

The various solutions were prepared with various Malachite Green (MG) concentrations of 5, 10, 15, 20, 25 and 30 mg/l. By using a Vis Spectrophotometer at a wavelength of 617 nm, we determined the absorbance of these concentrations and obtained the calibration curve depicted in figure 1. For the unknown dye concentration in various solutions, we obtained a straight-line equation from which we calculated the effects of different ions, PH and ferrous ion on percentage degradation of Malachite Green (MG).

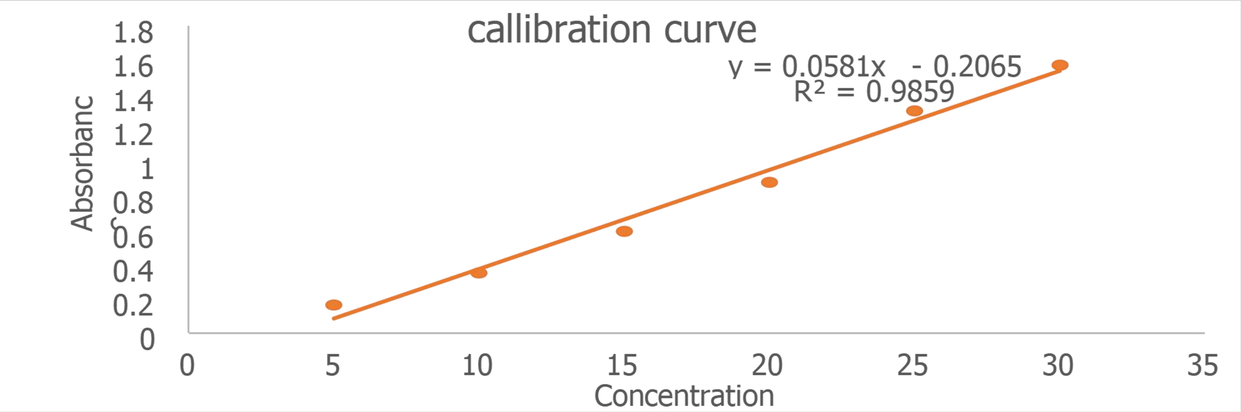


FIGURE 1: CALIBRATION CURVE FOR THE ABSORBANCE OF MALACHITE GREEN (MG)

EFFECT OF INITIAL CONCENTRATION OF MALACHITE GREEN (MG)

In order to find the percent of dye degradation caused by UV irradiation without a catalyst, numerous experiments with varying dye concentrations were undertaken after choosing an appropriate concentration of Malachite Green (MG). The following table 2 shows the various concentrations of Malachite Green (MG) and their absorbance. The 10 mg dye was selected for further experiments.

TABLE 2: EFFECT OF INITIAL CONCENTRATION OF MALACHITE GREEN (MG)

CONC (mg)	Abs 1	Abs 2	Average
5	0.172	0.154	0.163
10	0.392	0.308	0.35
15	0.726	0.463	0.5945
20	0.97	0.793	0.8815
25	1.116	1.484	1.3

30	1.431	1.704	1.5675

4.3 Effect of various Concentrations of H_2O_2 on Degradation of Malachite Green (MG)

Malachite Green (MG) degradation was conducted in relation to H_2O_2 concentration. H_2O_2 was used in two distinct concentrations (10mM and 15mM). At 15 minutes, degradation was observed to range from 69 to 79%. The result is displayed in figure 2. In all experiments we used a fixed dye concentration of 30 mg/L.

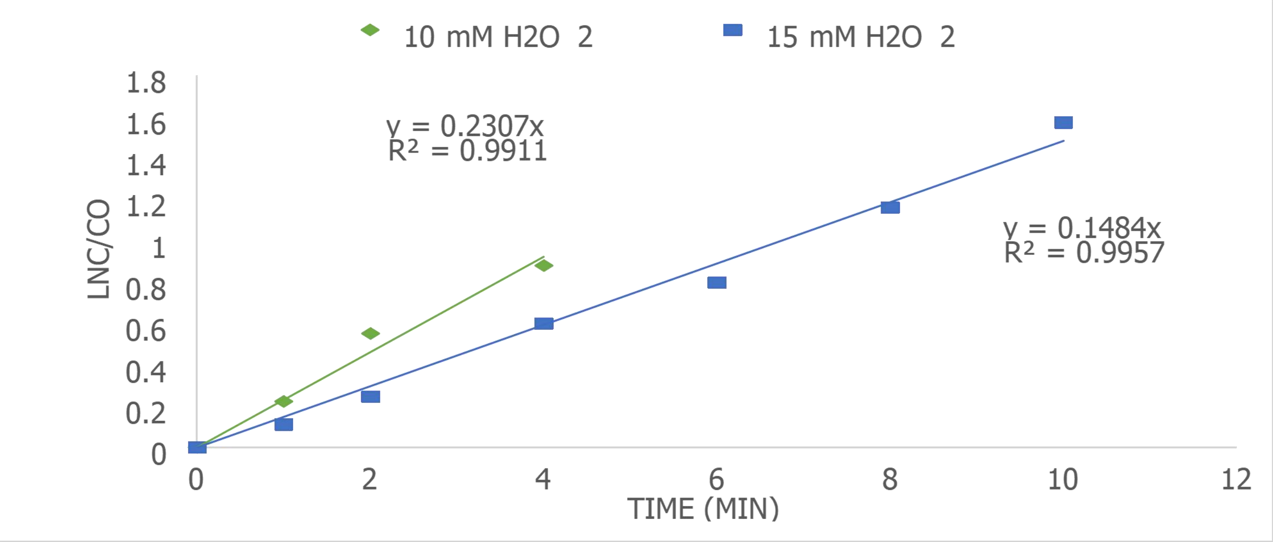


FIGURE 2: EFFECT OF H2O2 ON DEGRADATION OF MALACHITE GREEN (MG)

EFFECT OF DIFFERENT PH ON DEGRADATION OF MALACHITE GREEN (MG)

Studies on the effects of pH_3 and pH_{11} revealed that the breakdown of Malachite Green (MG) was significantly accelerated by pH_3 solutions. Malachite Green (MG) degraded 68% at pH_{11} and 85% at pH_3. Both HCl and NaOH impact the dye degradation possibly by altering the dye's molecular structure. The outcome is represented in figure 3.

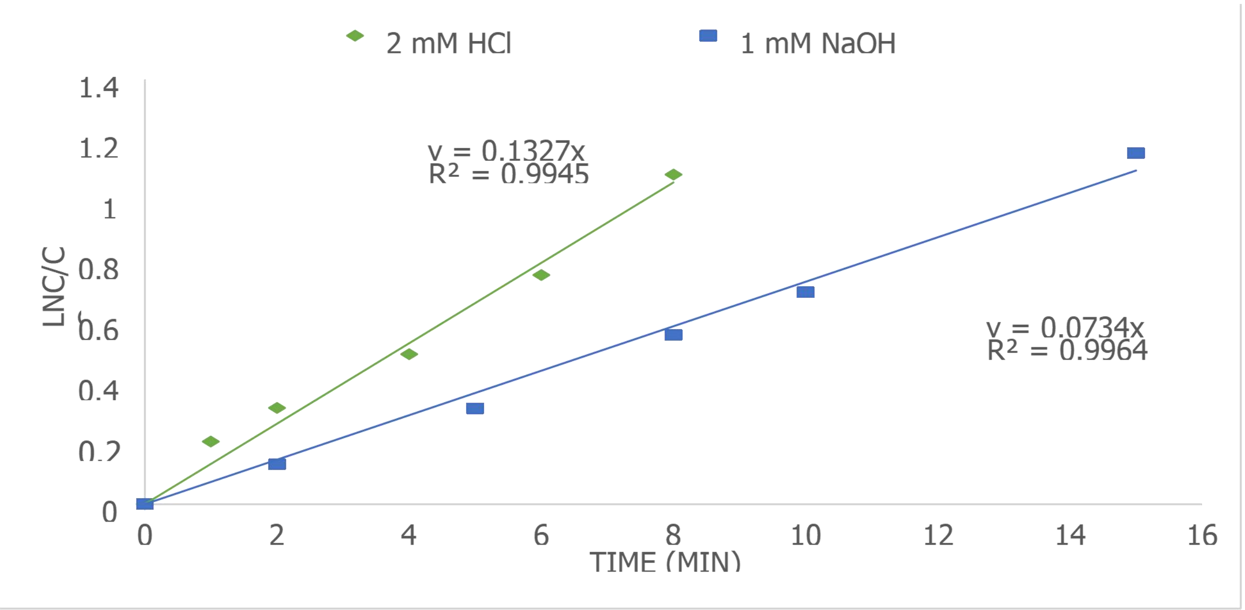


FIGURE 3: EFFECT OF PH ON DEGRADATION OF MALACHITE GREEN (MG)

EFFECT OF CARBONATE ION ON DEGRADATION OF MALACHITE GREEN (MG)

To study the effect of ions on the degradation of Malachite Green (MG), different concentrations of carbonate ions were treated with H_2O_2. At 0.5 mM and 1 mM, carbonate ion's impact on dye degradation was noted. The amount of dye remained the same at 10 mg. According to Figure 4, the percentage of degradation also rose from 60% to 74% when the carbonate ion concentration was increased from 0.5 mM to 1mM.

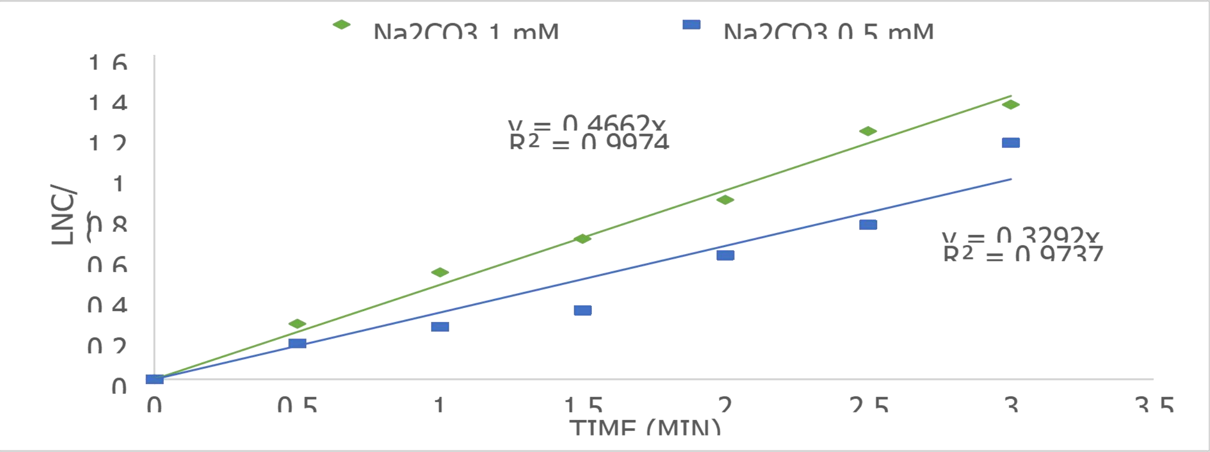


FIGURE 4: EFFECT OF CARBONATE ION ON DEGRADATION OF MALACHITE GREEN (MG)

EFFECT OF SULPHATE ION ON DEGRADATION OF MALACHITE GREEN (MG)

Under UV and H_2O_2, the impact of Sulphate ions on the percentage of Malachite Green (MG) degradation was studied. Three and five mM of Na_2SO_4 were used to treat with Malachite Green (MG). At 2 mM, dye degradation was 57%, but at 5 mM of Na_2SO_4, it was 76%.

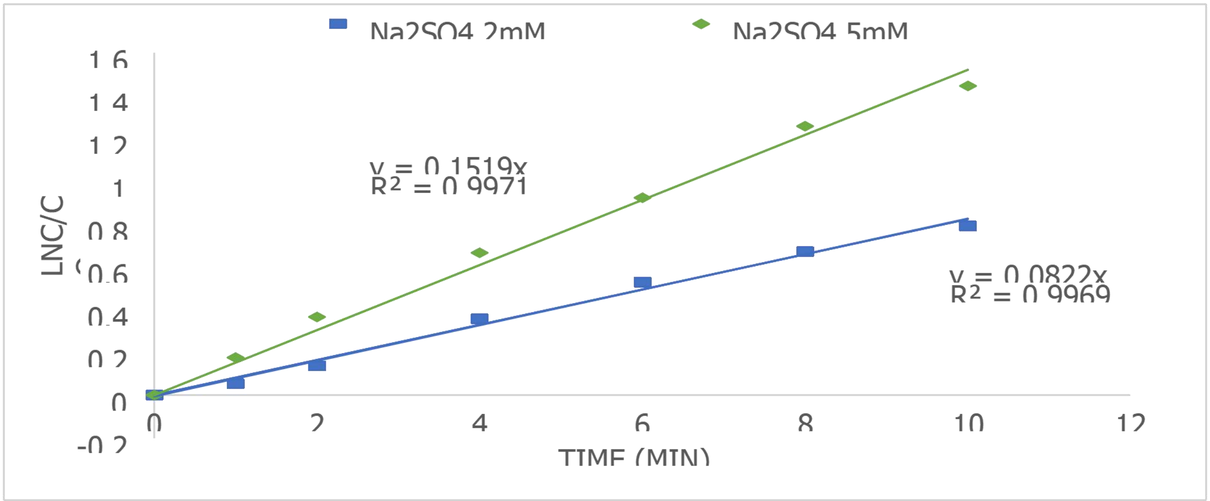


FIGURE 5: EFFECT OF SULPHATE ION ON DEGRADATION OF MALACHITE GREEN (MG)

EFFECT OF CHLORIDE ION ON DEGRADATION OF MALACHITE GREEN (MG)

Under UV and H2O2 conditions, the impact of chloride on the % degradation of Malachite Green (MG) was studied. Three and five mM of NaCl were used to treat Malachite Green (MG). At 3 mM and 5 mM of NaCl, dye degradation was 59% and 73%, respectively

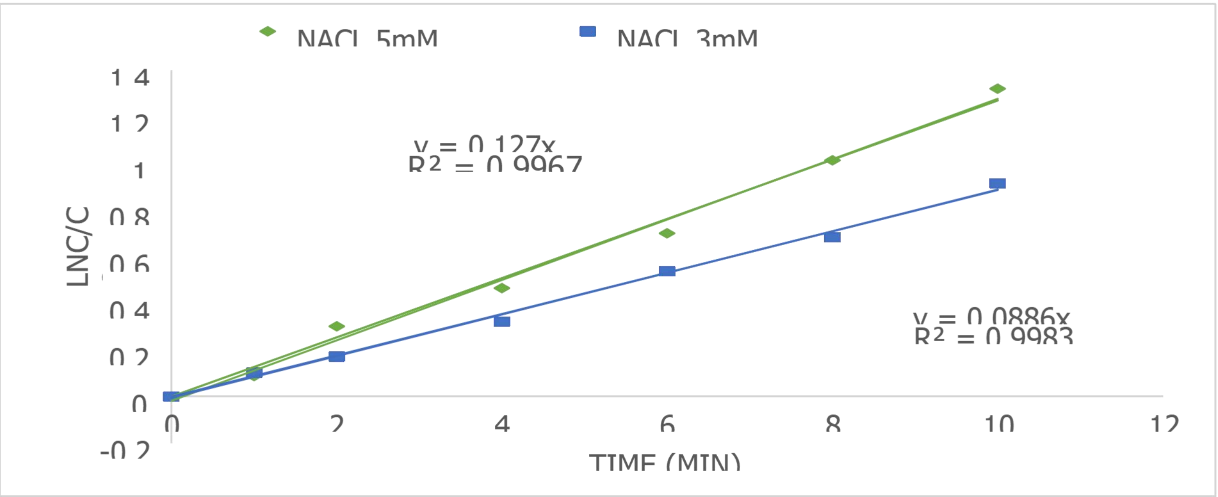


FIGURE 6: EFFECT OF CHLORIDE ION ON DEGRADATION OF MALACHITE GREEN (MG)

EFFECT OF BICARBONATE ION ON DEGRADATION OF MALACHITE GREEN (MG)

It was studied that how the bicarbonate ion affected the rate of degradation of Malachite Green (MG). When 1mM and 3mM of bicarbonate ion were used to treat Malachite Green (MG), the percentage of degradation was recorded that ranges from 56% to 68%.

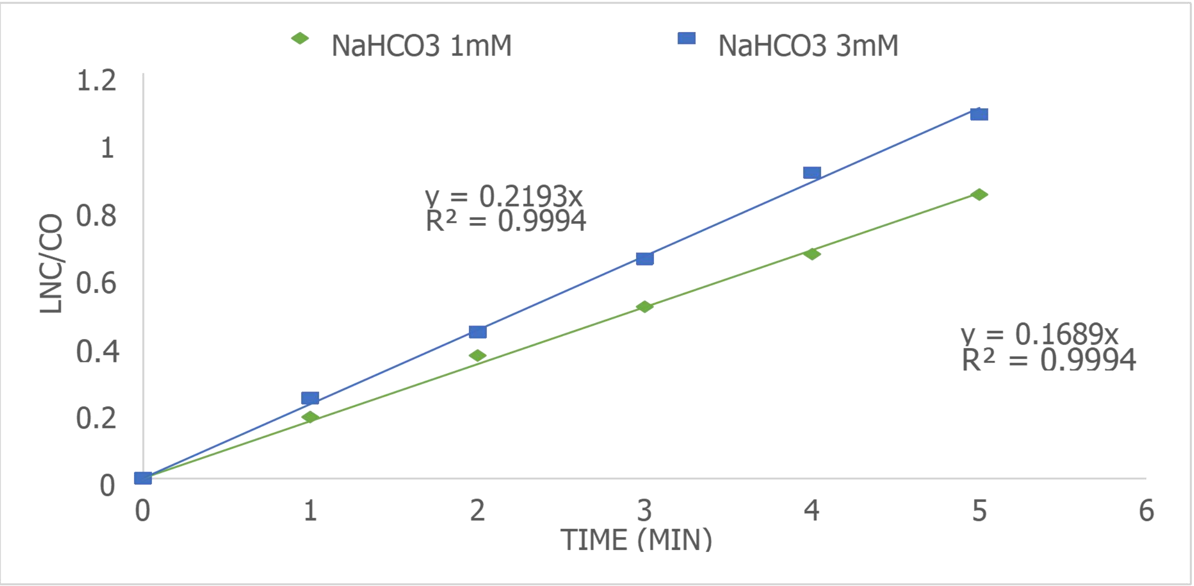


FIGURE 7: EFFECT OF BICARBONATE ION ON DEGRADATION OF MALACHITE GREEN (MG)

EFFECT OF NITRATE ION ON DEGRADATION OF MALACHITE GREEN (MG)

Malachite Green (MG) was treated with potassium nitrate and kept under UV at different interval of time. The percentage degradation of Malachite Green was noted for different concentration. The %degradation of Malachite Green was 61% at 2 mM of KNO_3 while 68% at 5mM.

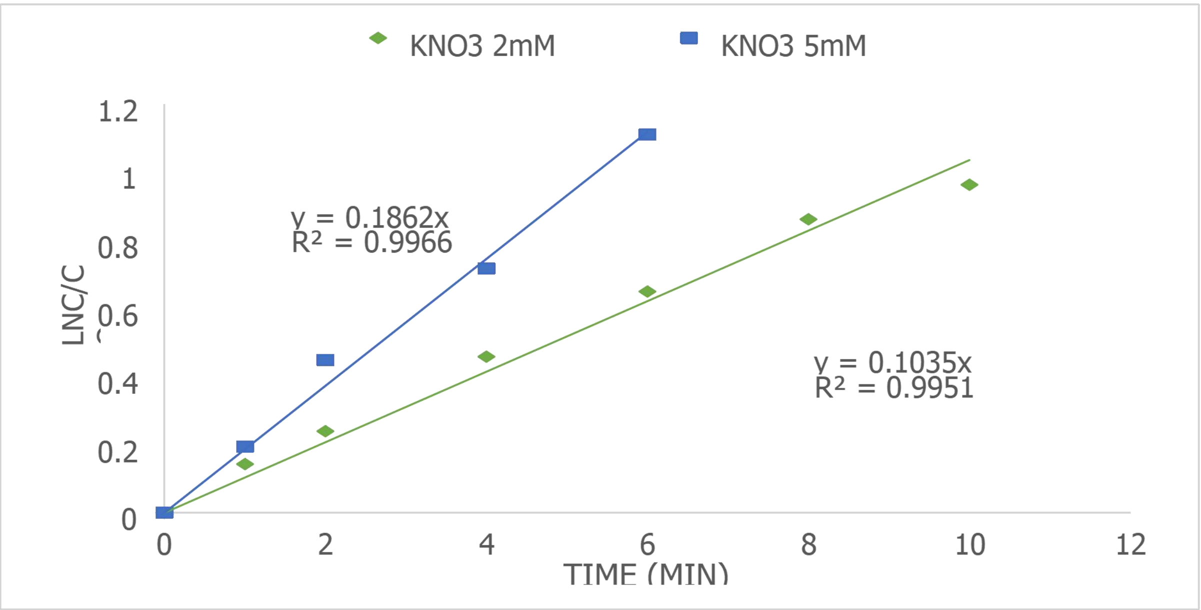


FIGURE 8: EFFECT OF NITRATE ION ON DEGRADATION OF MALACHITE GREEN (MG)

EFFECT OF FERROUS ION ON DEGRADATION OF MALACHITE GREEN (MG) IN THE PRESENCE AND ABSENCE OF HCL

Under UV and H_2O_2, the impact of ferrous ions on the percentage of Malachite Green (MG) degradation was studied. 0.5 mg/l iron at neutral pH and 0.5 mg/l iron with HCl were used to treat Malachite Green. 81% of the dye was maximally degraded with 0.5 mg/L of iron, compared to 95% with 0.5 mg/L of iron.

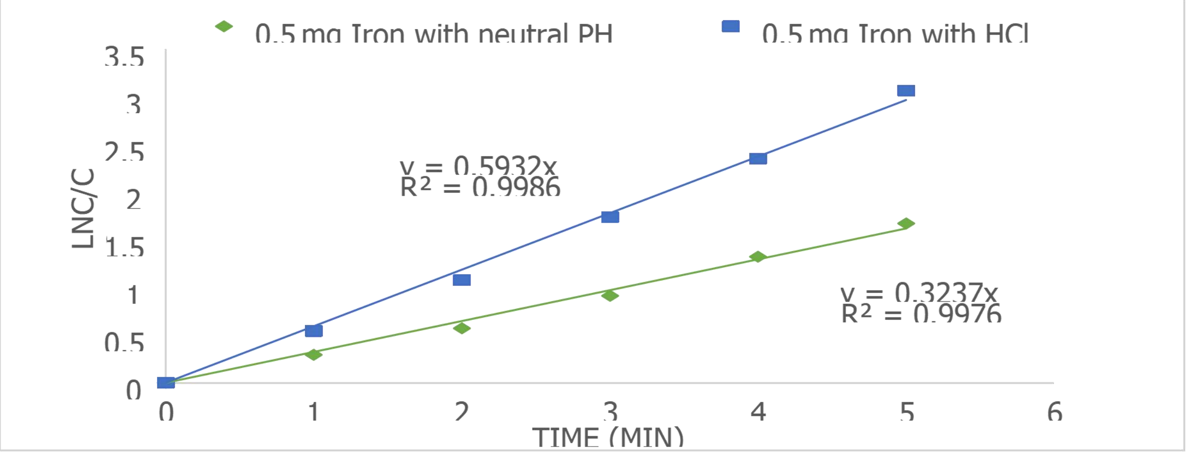


FIGURE 9: EFFECT OF FERROUS ION ON DEGRADATION OF MALACHITE GREEN (MG)

CONCLUSION

Malachite Green (MG) stock solution was prepared as a 100m mg/L solution. The average concentration from the standard solution was then chosen for the subsequent steps. After the absorbance of various Malachite Green (MG) concentrations was measured by a Vis Spectro photometer (Model 721). The degradation that observed in the presence of H_2O_2 was 77 to 86%. After this Malachite Green (MG) was further treated with various concentrations of H_2O_2 and kept under UV light. The degradation of Direct Black 22 after being treated with HCl and NaOH in the following step was 71% for NaOH and 87% for HCl. The degradation of Direct Black 22 was then measured after treatment with various ions, and it ranged from 60 to 74% with Na_2CO_3, 56 to 68% with $NaHCO_3$, and 61 to 68% with KMO_3, 69 to 79% with H_2O_2, 56 to 73% with NaCl, 57 to 76% with Na_2SO_4, 68% with NaOH, 85% with HCl and the maximum degradation was observed by treating Malachite Green (MG) with various concentration of ferrous ion with HCl and without HCl which was 81 to 95%.

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