Impact of Humic Acid on the Removal of Malachite Green Dye by Peroxymonosulfate (KHSO$_5$)

[1]**Ajayi A. A. &** [2] **Ukonu C. U.**

Department of Science Laboratory Technology
Federal Polytechnic Ilaro, Ogun State.
E-mail: adetola.ajayi@federalpolyilaro.edu.ng

Abstract

Numerous dyes contain a heterocyclic structure and are not highly biodegradable. This indicates that they do not biodegrade as effectively as they ought to in commercial sewage treatment systems. This paper examines the role of humic acid and the degradation process of Malachite Green Dye (MG) in the vast industrial world, which has contaminated natural water sources and posed a risk to humans and microbes. A remedy to this problem has been identified, which is an oxidation technique for removing MG from water. The findings demonstrated that, at Peroxymonosulfate (PMS) concentration more than 1.0 mM, malachite green at 50 mg/L could be successfully degraded (> 90 %). Humic acid has a complex role to play in the degradation of PMS, as it interacts with both MG and PMS to create sulfate radicals, while Cl$^-$ interacts with PMS and sulfate radicals to activate them.

Key words: Malachite Green, Peroxymonosulfate, Humic acid, UV-VIS Spectrophotometer

Introduction

It is essential to maintain water quality in order to protect the environment and human health. Wastewater contains a wide range of pollutants, including heavy metals, dyes, phenols, polychlorinated biphenyls (PCBs) pesticides and dyes (Ya et al., 2018; Shindhal et al., 2021). Malachite green, a type of organic dye, is particularly hazardous due to its intense colors, adverse effects on human health and contribution to the increase of Chemical Oxygen Demands (CODs) in water bodies (Sherugar et al., 2022). Malachite green is widely used in industries such as textiles, printing and dye manufacturing, as well as in plastics, pharmaceuticals and photography. However, its complex chemical structure makes it difficult to treat with conventional biological methods (Ya et al., 2018; Sherugar et al., 2022). To address this issue, chemical remediation techniques have become increasingly popular in wastewater treatment, particularly AOPs (advanced oxidation processes) using peroxymonosulphate or persulfate which are highly effective against a variety of pollutants, including dyes and PCBs (Sulyman & Gierak 2020). In addition, the large-scale implementation of heat and radio activation can be challenging. Previous studies suggest that organic compounds can be used to activate PMS/ persulfate/chemical oxidation without the use of synthetic chemicals (Ya et al., 2018; Semião, Haminiuk & Maciel 2020; Shindhal et al., 2021). These organic compounds are naturally occurring in the water and soil and are derived from natural sources. This is a new investigation. The paper presents a method for degrading Malachite green in the form of oxidative wastewater without the use of an additional activator and includes humic acid in the process. The aim of this series of experiments is to elucidate the effects of various concentrations of PMS in the degradation of Malachite green when the humic acid is present.

Materials and Method

Chemicals

All the chemicals such as malachite green, humic acid, peroxymonosulfate, sodium hydrogen, sulfuric acid, ethanol, and sodium chloride were acquired from Sigma Aldrich and utilized without further modification.

Experimental Procedures and Analysis

Using Ya et al., 2018 method, batch examinations were performed at room temperature using a 50 ml tube containing wastewater containing malachite green. The pH was adjusted using 0.2 M nitric acid (HNO$_3$) and sodium hydroxide (NaOH) and the final pH values were assessed with a pH meter. The oxidative reaction was administered on a recirculating shaker at a velocity of 100 revolution per minute, in a shady environment. At regular duration, approximately 20 ml of samples were put up from the tube to be analyzed. An ethanol (C$_2$H$_5$OH) scavenger was added immediately to the sample, and the samples were then positioned in the UV-VIS Spectrophotometer Cell for

the purpose of determining the maximum absorption at 670nm of the dye. Equation 1 was used to calculate the dye removal efficiency. In the equation 1 C_1 represent the original malachite green concentration where C_2 is the final malachite green concentration after the reaction. The examinations were retested three times, with the removal efficiency determined as the mean of the first three measurements, thus ensuring that relative errors were kept below 6 %.

$$\frac{C_1 - C_2}{C_1} \times 100\% \dots\dots\dots\dots. 1$$
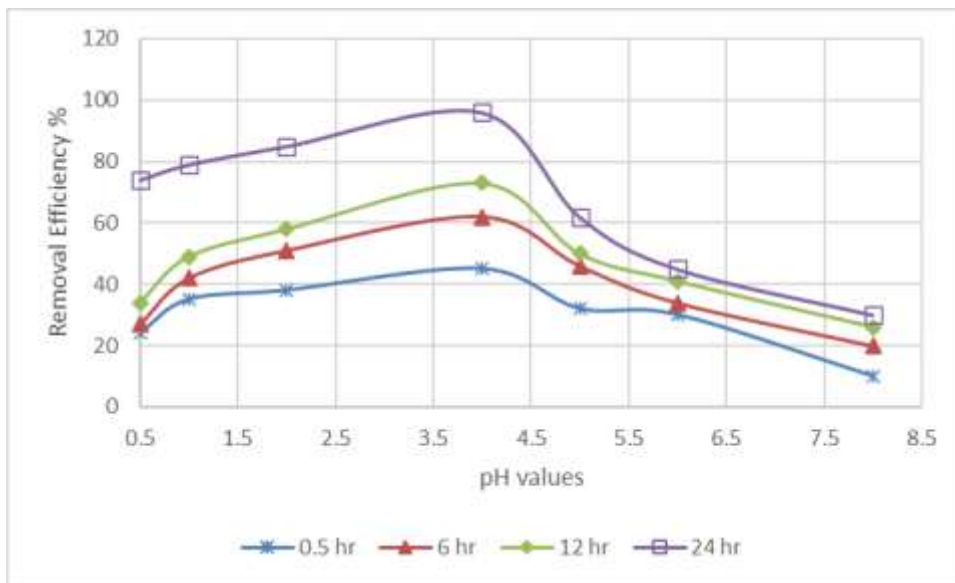
Results and Discussion

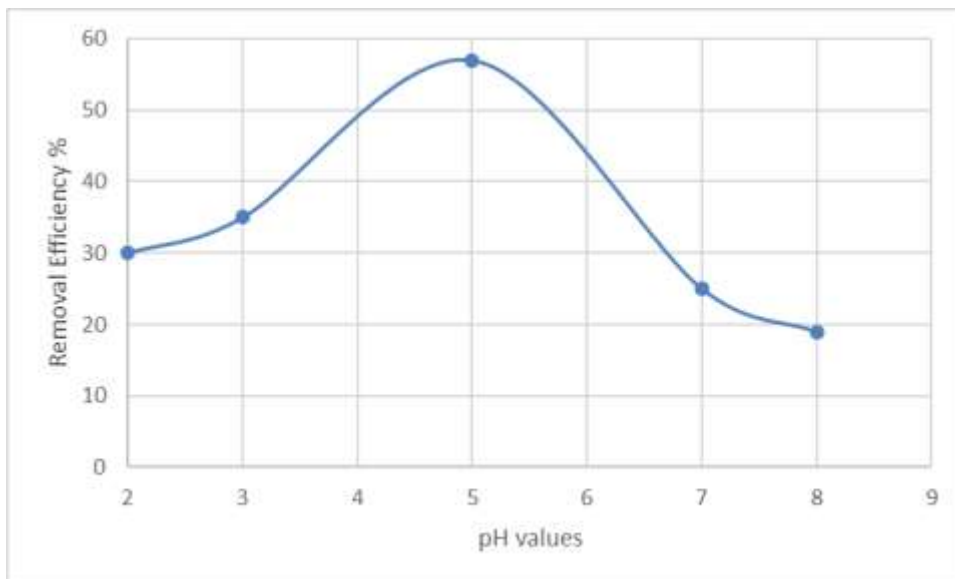Figure 1: The impact of pH on the removal of 50 mg/L malachite green using 1.0 mM PMS and at different reaction time.

Figure 2: The impact of pH on the removal of 50 mg/L malachite green using 0.5 mM at 24 hours

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The Transformation of Malachite green using PMS Across Varying pH Levels.

The process of PMS-induced transformation leads to changes in malachite green across a range of pH levels. Peroxymonosulfate (PMS) serves as a potent acidic oxidant, efficiently oxidizing malachite green without requiring any activator. Figure 1 displays the impact of solution pH values (ranging from 0.5 to 8) and reaction time (0.5 to 24 hours) on the degradation process. Within the initial half-hour, malachite green concentration decreased significantly for all pH values except pH 8.0. After 24 hours, the degradation efficiency reached an impressive 74 % to 95 % under all conditions. Remarkably, the reaction time held greater sway on the degradation efficiency of malachite green, rather than the initial pH value. An intriguing finding emerged at a reaction time of 6 hours and a pH of 8, where the dye's degradation efficiency substantially dropped. This aligned with prior research attributing it to the self-decomposition of PMS in alkaline conditions (Ya et.al., 2018; Semião, Haminiuk & Maciel, 2020). However, at 12 hours and 24 hours of reaction time, the degradation efficiency significantly improved, with the final pH measured at 4. This observation suggested that the decomposition of malachite green led to a decrease in pH, impeding the self-decomposition of PMS.

Further investigation explored the effect of pH on the degradation of malachite green at a relatively low PMS concentration (0.5 mM). Figure 2 revealed a similar trend as with 1.0 mM PMS, but the malachite green degradation efficiencies remained below 60%. The pH value had minimal impact on the degradation efficiency when it was below 6 but notably decreased when the pH value exceeded 7. This indicates that the self-decomposition of PMS became significant at low PMS concentrations. Considering that extreme pH values rarely occur in natural wastewater systems, the study concluded that the pH's effect was negligible in this malachite green degradation process. Subsequent investigations maintained pH values around 7.0 ± 0.2 to mimic natural water conditions and ensure high degradation efficiencies (Ya et al., 2018; Semião, Haminiuk & Maciel, 2020).
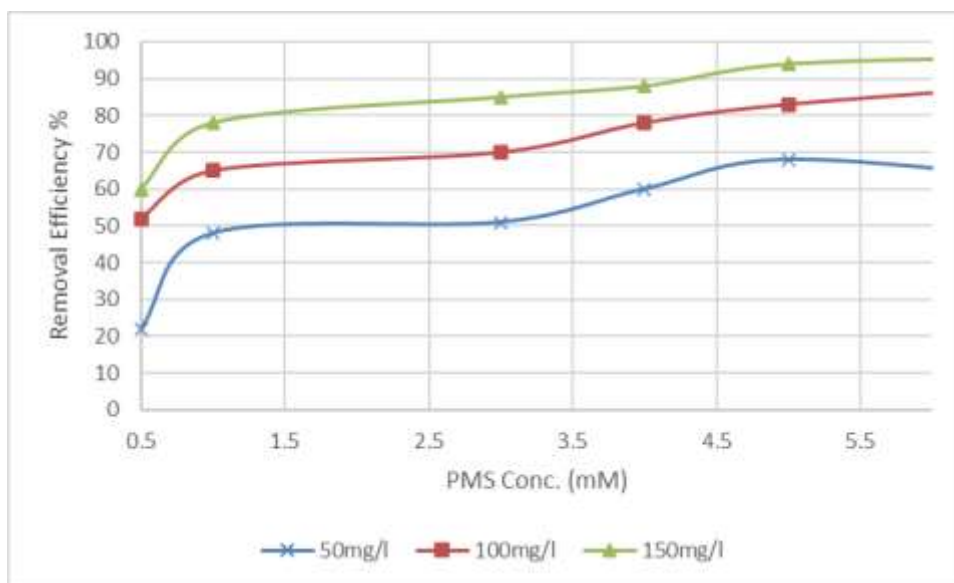

Figure 3: Removal of different concentrations of malachite green using PMS at different concentrations for 24 hours

The Impact of PMS Concentration on the Degradation of Malachite Green.

Figure 3 shows how malachite green is degraded under various concentrations (50 -150 mg/L) of PMS. As the concentration of PMS rises in each of the experiments, so does malachite green degradation efficiency. However, there is a slight variation in the degradation curve based on the initial concentration of PMS. When the PMS dosage is 0.5 mM, it is not very effective in degrading relatively large concentrations (i.e conc. greater than 50 mg/L). However, when the PMS is increased (1.0 mM-2.5 mg/L) the degradation efficiency increases by 30 % and 42 %, respectively, for 100 and 150 mg/L. When 5 mg/L of PMS is added to the malachite green concentration, the degradation efficiencies increase to 72 % and 94 % respectively. Surprisingly, at very high concentrations (100mg/L or 150mg/L) there is no significant improvement in degradation efficiency. This behavior may be due to the fact that PMS is competitively consumed by intermediates (Ya et al., 2018; Semião et al., 2020).
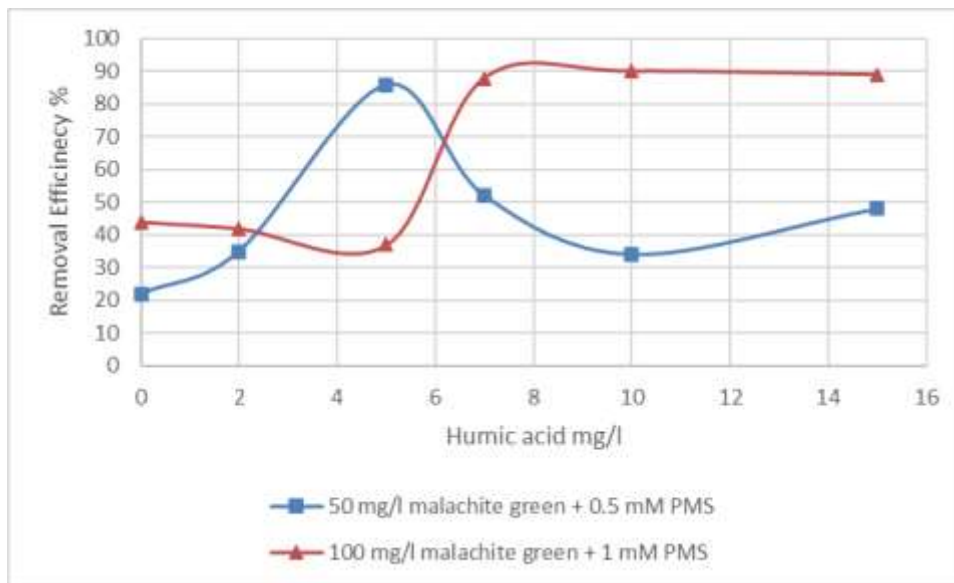
Figure 4a: The influence of humic acid on the removal of malachite green using various PMS concentrations for 24 hours
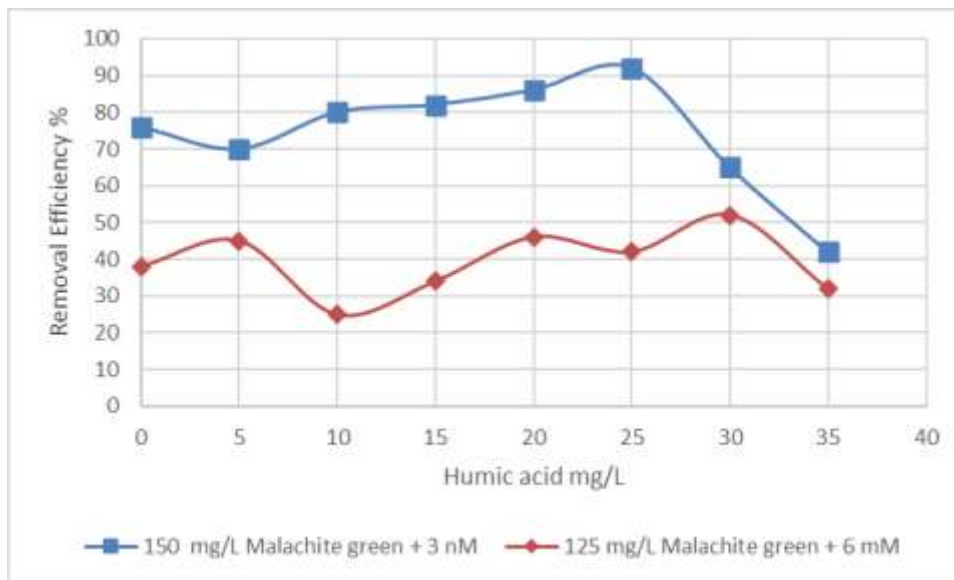

Figure 4b: The influence of humic acid on the removal of malachite green using various PMS concentrations for 24 hours

The Impact of Humic Acid at Various PMS Concentrations.

Humic acids are naturally present in water, usually between 0.1 and 20 mg/L (Shindhal et al, 2021) Previous studies have shown that humic acids can mess with water purification because they can chelate it (Hassan & Carr, 2021; Shindhal et al., 2021). In this study, humic acid was found to act as a catalyst for persulfate, which can be used to break down PCBs.

Our earlier research demonstrated that when the amount of PMS was less than 2 mM with malachite green concentration of 50 mg/L or greater, the removal efficiency for malachite green remained below 70% (Fig. 4a).

When humic acid was present at a concentration of less than 2 mg/L, its impact on removal efficiency was not significant for all designs of malachite green. However, when 5 mg/L humic acid was added to the solution, the

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removal rate of a 50 mg/L malachite green diluent increased from 22 to 85 %. Additionally, for a 100 m/L malachite green diluent with 1 mg/L PMS, 7 or 15 mg/L humic acid significantly increased the degradation rate from 42 % to over 89 %. In Figure 4b, 30 mg/L humic acid was found to be effective in degrading 125 mg/L malachite green at an efficiency of approximately 84 %, compared to 35 mg/L humic acid at an efficiency of 32 %. In a 150 mg/L malachite green effluent containing 6 mg/L PMS, 25 mg/L humic acid resulted in a maximum degradation rate of 98%, which was greater than the rate of degradation observed when humic acid was only present. It should be noted that in some cases, humic acid did not have a beneficial effect on the degradation of malachite green; this can be seen in Fig. 4b.

Conclusion

This paper provides approach to remove malachite green blue within effluents with the aid of peroxymono sulfate, without the use of any extra activators. The findings ascertain that malachite green can be degraded with high concentrations of PMS, eliminating the need for additional activators. On the other hand, at low levels of PMS, degradation efficiency was significantly reduced, particularly when the pH above 7.0. Humic acid plays a key role in activating PMS, which in turn produces sulfate radicals. However, the efficiency of the degradation process may be limited due to competing reactions between the two substances, particularly when high levels of PMS are present. All in all, this research suggests that complex reactions occur in synergistic fashion within malachite green wastewater systems, resulting in a multifactorial degradation mechanism. This paper aims to provide valuable insights on how to effectively control methylene blue degradation in wastewater with a low-cost oxidizer.

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