

Photocatalytic Degradation of Malachite Green Dye with UV/H₂O₂ System in presence of Transition Metal Ions

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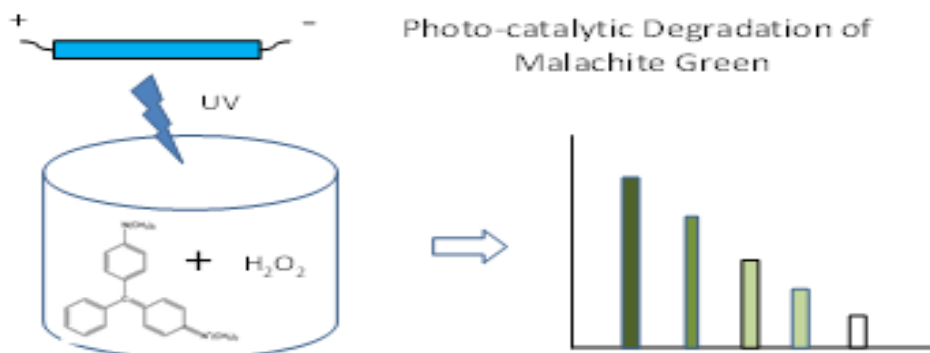
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Summary: The chemical degradation of Malachite Green dye has been studied by using UV/H₂O₂ system in presence of transition metal ions (Fe²⁺, Mn²⁺ and Ti²⁺). The degradation reaction was carried out by circulating the aqueous dye solution in a custom-made UV reactor with the help of a variable speed peristaltic pump. The effects of initial concentration of dye, concentration of Hydrogen peroxide, operating temperature, pH, Ultrasound vibrations and transition metal ions were investigated on the time required for complete degradation of the dye. It has been found that under optimum conditions the dye could be degraded in minimum possible time especially in presence of transition metals like iron. The intermediate products obtained during the degradation process were subjected to FTIR spectroscopy for structural analysis. The residue spectra did not show any band revealing the presence of any aromatic ring. To check the completion of the reaction the final residue was analyzed for total organic carbon (TOC). All such tests indicated that the dye has been completely degraded leaving no detectable residue.

Key Words: Malachite Green; Photocatalytic Degradation; UV/H₂O₂ oxidation; Textile waste; Disintegration of dye; Physio-chemical decomposition.



Introduction

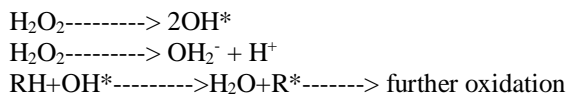
Synthetic dyes are extensively used in a number of industries like textile, leather, pulp and paper and sometime in food industries. The disposal of dyes from such industries to the environment is a serious global problem. Almost 17 to 20% fresh water pollution is caused by industrial effluents containing commercial dyes [1]. Their discharge into water bodies is toxic to aquatic life, impairs water appearance, and reduces the dissolved oxygen concentration and sunlight penetration causing ecological problems [2]. Malachite Green is one of such dyes which have industrial applications in dyeing of cotton, silk, paper, leather and drugs. This dye is also employed in distilleries for colouring purposes [3]. Industrial effluents of the concerned industries

contain considerable concentrations of the dye when drained in streams and passing by water channels. Due to its properties, Malachite Green is difficult to remove from aqueous solutions. This dye is toxic for flora and fauna and damages the aquatic life directly or indirectly when present in water channels even at very low concentrations. For aquatic life Malachite Green is notorious for causing detrimental effects on liver, gill, kidney intestine, gonads and pituitary gonadotrophic cells [4]. The toxic dye also adversely affects the livestock having either direct access to such water bodies or by grazing vegetation irrigated by contaminated water [5]. The meat and milk of such animals could be a route of the dye to human beings. Hence wastewater from an industry containing dyes

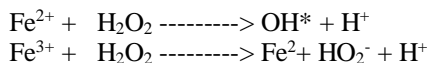
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must be treated before being discharged into the waterways for minimal environmental impacts.

Conventional wastewater treatment strategies including physical, chemical and biological methods have been employed for decontamination of dye containing effluents but all such methods proved markedly ineffective for removing or degrading synthetic dyes in aqueous systems due to problems like sludge generation, operational hurdles, high retention time and cost ineffectiveness [6-8]. Chemical oxidation with hydrogen peroxide in presence of UV radiation proved itself a very promising technique for dye degradation. UV radiation from 200 to 280nm is considered responsible for dissociation of hydrogen peroxide. Mercury lamps generating 254nm resonance line are also efficient sources to oxidize hydrogen peroxide which yields hydroxyl radicals (OH[•]), which are highly powerful oxidizing species. The main oxidizing reactions that occur in UV/H₂O₂ system are as follows [9]:



UV/H₂O₂ system yields complete degradation of dye and even converts the carbon to CO₂. Several dyes employed in textile and leather industries (including azo dyes) have been effectively degraded by UV/H₂O₂ system [10-11]. An alternative approach to dissociate hydrogen peroxide, which has been found equally useful for dye degradation, is the use of Fenton's reagent (Fe²⁺/H₂O₂). Researchers have successfully employed this system using different alterations for degrading a number of dyes [12-14]. The reactions involved in this system were as follows:



The most beneficial factor in case of the application of UV/H₂O₂ system and Fenton's reagent was the complete degradation of toxic dyes to CO₂ and water because most of the conventional procedures simply decolorize the dye by breaking it into colorless intermediates which may still be toxic to aquatic life and human health. Discharge of the dye contaminated effluents in water bodies is such an acute problem that researchers are still trying to degrade the dye completely with little effort in minimum possible time leaving no toxic intermediates. A number of workers have used certain nano-materials to enhance the efficiency of the oxidizing process. Karimi et al used nano-strontium titanate as the nanophotocatalyst while

oxidizing the dye under UV irradiation [15]. Efficiency of TiO₂ modified with Sn and Eu as photocatalyst was checked by Solis-Casados and coworkers while degrading Malachite Green under solar light [16]. Antonio Zorro employed Fe-doped Titania catalysts for degrading azo dyes in visible light [17]. The effect of carbon nanotube particles was also investigated by a group of environmental researchers [18].

While investigating the effect of UV radiation along with various chemical reagents most of the researchers used UV lamp over the reaction mixture leaving a considerable air gap between the lamp and the surface of the solution which reduces the UV efficacy as air effectively absorb short range UV radiation [19-20]. Some workers employed UV lamp for the generation of ozone which served as the oxidant for the dye under study [21-23]. Literature also reports some advanced techniques for pollution removal from waste water such as biological, electrochemical, and bioelectro-chemical methods [24-26].

In this study Malachite Green has been degraded by using UV/H₂O₂ system in a custom-made UV reactor. The dye solution was circulated with the help of a peristaltic pump around the cylindrical shaped UV lamp using no gap for air. Primary parameters like initial concentration of dye, concentration of hydrogen peroxide and speed of pump were optimized by calculating the %age degradation of dye after suitable time intervals. The degradation efficiency of the experiments was calculated by using the formula:

$$\text{Degradation efficiency} = [1 - C_t/C_0] \times 100$$

Where C₀ is the initial dye concentration (mg/L) and C_t is the concentration after time t (min). The proposed method is novel in the sense that the dye has been degraded both chemically as well as by irradiating with a powerful UV radiation. The UV source is designed in such a way that there is no air gap between the lamp and the dye solution which usually diminishes the radiation in most of the cases.

Experimental

Chemicals and Equipment:

Malachite Green (Product: 34045-5T) was obtained from BDH and was used without further purification. Authentication of the dye was confirmed by plotting its λ_{max} (617.9nm) on a UV/VIS Spectrophotometer. Rest of all the reagents used were

of AnalaR Grade. Double distilled water was used throughout the work. An APEL UV/VIS Spectrophotometer, Model PD-303 equipped with glass cells was used for measuring the absorbance during each experiment of dye degradation. A multi speed peristaltic pump with silicon tubing (worked at 150 rpm) was used for the circulation of dye solution around the cylindrical UV lamp.

UV Reactor:

A tubular Phillips UV lamp Model TUV 15W G15 T8 UVC (Length 437mm & width 25mm), emitting radiation of maxima 254nm (input power 15 Watts; output $45\mu\text{W}/\text{cm}^2$) was employed as a source of UV radiation. The lamp was sealed in a glass tube of relatively wider diameter but shorter in length and with inlet and exit for dye solution. During the degradation experiments the outer tube was wrapped with an aluminum foil to avoid the atmospheric light. Fig. 1 shows the schematic diagram of the whole setup used for dye degradation.

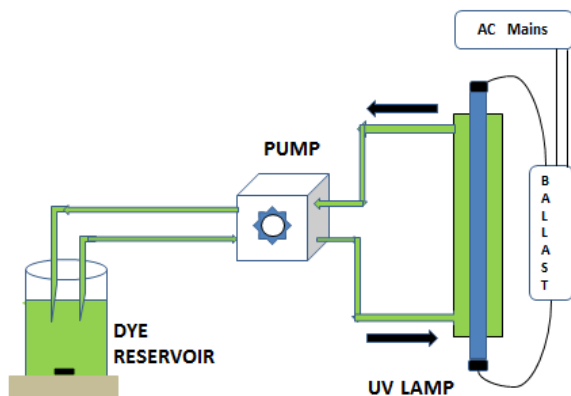


Fig. 1: Experimental setup for degradation of Malachite Green.

Stock solution of Malachite Green (1000 mg/L) was prepared by dissolving 0.5g of dye in 500ml of deionized water. The dye solution was stirred for 6 hours at 60°C for complete hydrolysis. To avoid any degradation due to solar light the solution was kept in dark and working solutions were prepared time to time by appropriate dilution of the stock solution. In order to calculate the %age efficiency a calibration graph was prepared by plotting the absorbance values of 10 to 100 mg/L solutions against dye concentration. To check the effect of various parameters, 100 mg/L solution was normally employed. A certain volume (500 ml) was taken in the dye reservoir, stirred constantly and circulated around the tubular UV lamp till the dye become colorless and absorption

approached to zero. The time consumed for decolourization of the dye solution was used as a measure of efficacy of the process.

Analytical Tabulation

The degradation efficiency of the proposed method was monitored by measuring the absorbance of Malachite Green at 618 nm using an APEL UV/VIS Spectrophotometer, Model PD-303 equipped with glass cells after each experiment. In order to measure the concentration of the dye, a calibration graph was prepared by measuring the absorbance of the standard solutions at 618nm on the spectrophotometer and plotting against dye concentration. The degradation efficiency of malachite Green was calculated by using the following equation:

$$\text{Degradation Efficiency} = [1 - (C_f/C_o)] \times 100$$

where C_o was the initial concentration and C_f was the final concentration of Malachite green.

Results and Discussion

Calibration Graph

To find out the concentration of Malachite Green in solution, a calibration graph was prepared by measuring the absorbance of the aqueous standard solutions under standard conditions at 618nm employing an APEL UV/VIS Spectrophotometer, Model PD-303 and plotting against dye concentration (10 to 100 mg/L). The calibration graph is shown in Fig. 2.

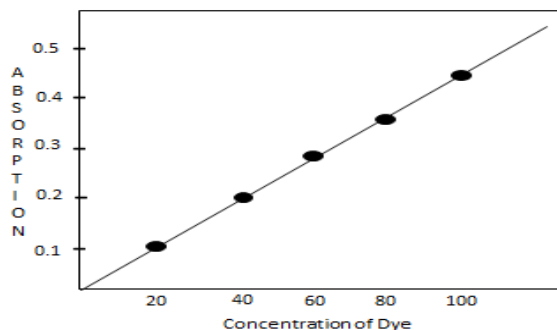


Fig. 2: Calibration graph.

Effect of initial concentration of the dye

Effect of Initial concentration of Malachite Green was investigated by calculating the degradation efficiency of 250 ml solutions of different concentrations (25, 50 & 75 mg/L). During these

experiments rest of all the parameters such as temperature (room temperature), pH (5.6), and concentration of H₂O₂ (0.5ml of 33%) were kept constant. No additional stirring was applied during the experiments and no additional metal ions were added. Time taken by the same volumes of solutions of different concentrations to reach at constant absorption value was employed as a measure of degradation efficiency. It was observed that degradation efficiency was significantly high at lower concentrations of the dye. Efficiency dropped from 96% to 52% when concentration was increased from 25 to 75 mg/L. The effect is shown in Fig. 3.

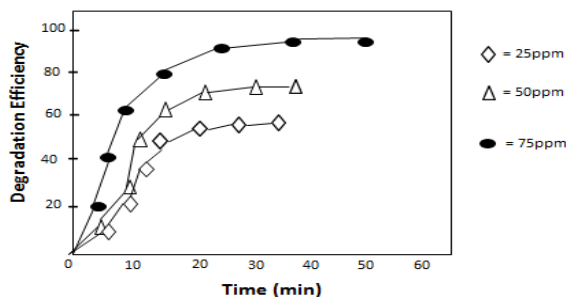


Fig. 3: Effect of Initial Concentration of Dye.

Effect of Concentration of Hydrogen Peroxide

Effect of concentration of Hydrogen Peroxide was studied by determining the degradation efficiency of 250ml dye solution of 25 mg/L initial concentration. Concentration of hydrogen peroxide was varied from 0.5 to 1.5ml/250ml of 33% solution. During these experiments rest of all the parameters such as temperature (room temperature) and pH (5.6), were kept constant. No additional stirring was applied during the experiments and no additional metal ions were added. Time taken by the 250 ml dye solutions with varying concentrations of hydrogen peroxide to reach at constant absorption value was used a measure of degradation efficiency. The Effect of hydrogen peroxide concentration is shown in Fig. 4.

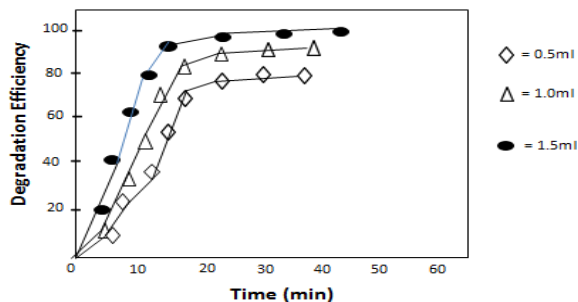


Fig. 4: Effect of Concentration of Hydrogen peroxide.

Effect of pH

Effect of pH on the degradation efficiency of Malachite Green was checked by adjusting the dye solution (25mg/L) at four different values (3, 5, and 7). The pH value was maintained with dilute solutions of hydrochloric acid and sodium hydroxide. The effect could not be checked above pH value because Malachite Green starts showing its behavior like acid-base indicator. The experiment was repeated at room temperature with constant concentration of 1.5ml H₂O₂ (33%)/250ml. No additional stirring was conducted during the experiments and no additional metal ions were added. The time taken by the 250 ml dye solutions of different pH values to reach at constant absorption value was taken as a measure of degradation efficiency. The Effect of change in solution pH is shown in Fig. 5.

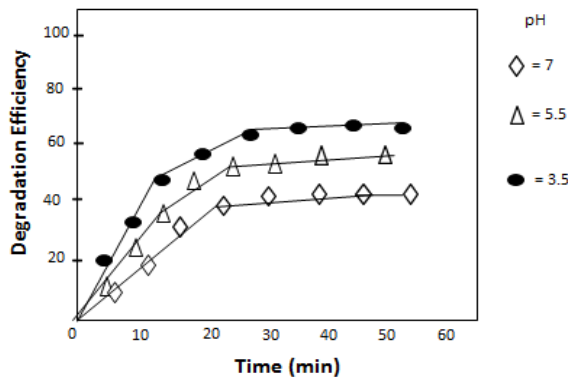


Fig. 5: Effect of PH.

Effect of Extra Stirring and Ultrasonification:

To check the degradation of Malachite Green the dye solution was circulated through the UV reactor with the help of a peristaltic pump for certain time periods till the final absorption reached to a constant value. In order to make the degradation process faster, additional stirring with the help of a mechanical stirrer and ultrasonification by employing an ultrasound bath were employed. But it was observed that none of the additional agitation could produce any significant effect on the degradation efficiency of the dye under any set of conditions. Hence it can be safely concluded that in present setup the additional stirring has no marked effect on degradation process.

Effect of temperature

To check the effect of temperature on degradation of Malachite Green, the dye solution was proceeded through different temperatures. The

temperature was maintained by placing the solution reservoir in a water bath with controlled temperature. Rest of the conditions like pH(4.0) and H₂O₂ concentration (1.5ml of 33%/250 ml dye solution of 25mg/L) were kept constant. Temperature of working solutions was varied from 298K to 318K. As shown in Fig. 6 that a slight increase has been found in degradation efficiency by increasing the temperature of dye solution. It can be safely concluded that degradation reaction proceeds a little faster at elevated temperatures.

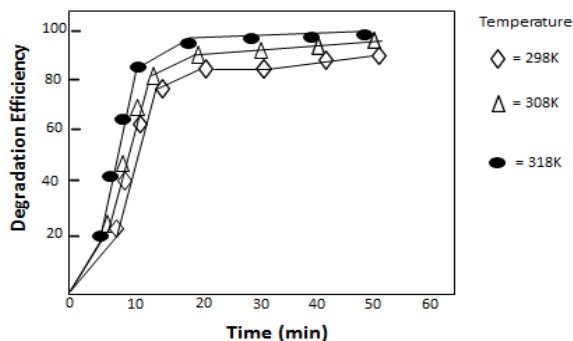


Fig. 6: Effect of Temperature.

Effect of Transition Metal Ions:

Effect of three metal ions Fe⁺², Mn⁺² and Ti⁺⁴ was investigated on the photocatalytic degradation of Malachite Green. 2.5 ml of 100mg/L solutions of these metal ions were added in 250ml of dye solution (25mg/L) containing 1.5ml of 33% H₂O₂ solution. Rest of the conditions were similar for all the solutions. The effect is shown in Fig. 7. Addition of Fe (II) reduced the absorption as soon as the iron solution was added. This was probably due to the Fenton's process which degraded the dye in short time. Next was Ti (IV) which enhanced the degradation efficiency considerably. In case of Mn (II) no appreciable effect was observed. The effect of metal ions is shown in Fig. 7.

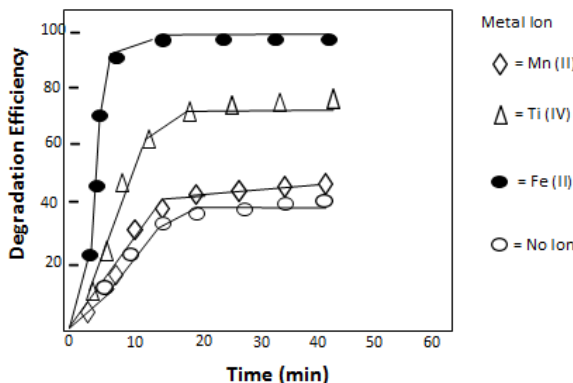


Fig. 7: Effect of Metal Ions.

Residue Analysis

An attempt was to analyze the residue after complete degradation of Malachite Green. The colorless liquid was heated to dryness on a low flame and the residue was analyzed for functional groups and any phenyl group by FTIR. No appreciable band of any functional group or aromatic ring was shown by the spectra which showed that a complete degradation of the dye took place due to UV/H₂O₂ treatment. Similarly, the residue did not produce any smoky flame when burned on an oxidizing Bunsen flame which revealed the absence of aromatic carbon.

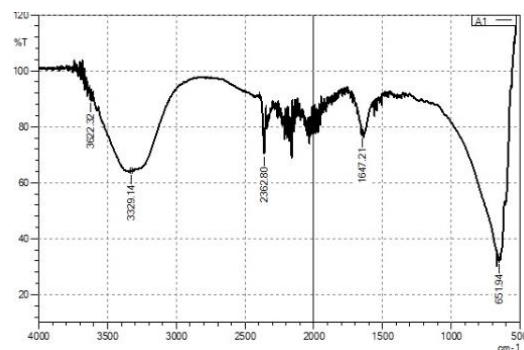


Fig. 8: FTIR of Malachite Green before degradation.

Spectra of Malachite green dye solution before degradation (A1) and solid residue (A5) left after degradation of the dye were studied in order to make the comparison and to reveal the changes taking place in the structure of dye with the passage of time and exposure to UV and other oxidizing reagents.

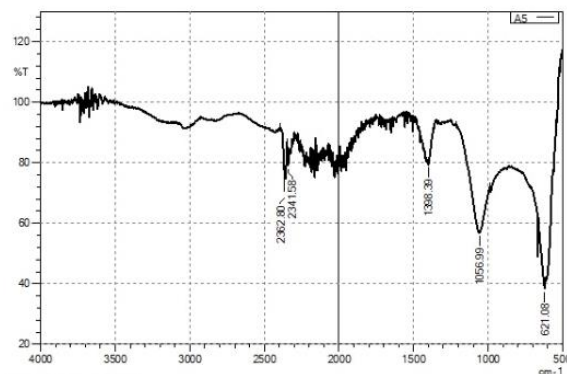


Fig 9: FTIR spectra of solid residue left after degradation of malachite green

In case of Malachite green presence of aromatic group is indicated by the peak at 1647cm⁻¹. Appearance of peak at 2362cm⁻¹ indicates the stretching vibration due to asymmetric C-H.

Appearance of two peaks at 3329cm⁻¹ and 3622cm⁻¹ correspond to O-H and N-H stretching.

In case of solid residue, peak at 1056cm⁻¹ indicating C-O bending, and at 2341 and 2362cm⁻¹ show the presence of C-H disappearance of other peaks indicate the breakage of the aromatic ring structure and absence of nitrogen groups from the molecule, thereby, supporting the dye degradation.

Conclusion

It can be safely concluded from this work that commercial dye Malachite Green can be effectively degraded by treating with hydrogen peroxide under UV irradiation. The degradation efficiency can be enhanced by optimizing the conditions like pH, temperature, and concentration of hydrogen peroxide. The degrading process can be further accelerated by adding a small quantity of Fe (II) salt. The degradation process is adequately safe, considerably fast, and environmentally friendly.

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