

## Photo Fenton Induced Decolorization Study of Malachite Green Dye Solutions

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### Abstract

*Advanced Oxidation Processes have proved their superiority over the conventional techniques in decolorizing the dye waste water due to their ability to produce highly reactive ·OH radicals. The decolorization of aqueous solutions of Malachite Green dye is studied using photo Fenton's process which involves hydrogen peroxide and Fe<sup>2+</sup> in presence of UV radiations. The combination of UV radiations with Fenton's reagent has found to enhance the rate and extent of decolorization of dye solution which may be due to the production of additional ·OH radicals by multiple pathways. Additional equivalent of ·OH radicals are formed due to photolytic conversion of Fe<sup>3+</sup> (produced due to reaction of H<sub>2</sub>O<sub>2</sub> with Fe<sup>2+</sup> ions) to Fe<sup>2+</sup>. The dye degradation using this technique has been found to be governed by the factors like initial dye concentration, quantity of hydrogen peroxide and ferrous ion and the intensity of radiation. The Photo-Fenton-Reaction has many advantages like comparatively low doses of Fe<sup>2+</sup>, higher rate of degradation, lower operational cost etc. as compared to classical Fenton-Reaction.*

*Keywords : A.O.P., photolysis, dye degradation, photo Fenton's process.*

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### Introduction

With the accidental invention of first synthetic dye, Mauthen, the synthetic dyes have dominated the then used natural dyes due to their superior characteristics like variety of shades and tones, bulk production, fastness, ease of applications and so on[1]. They almost replaced the natural dyes by the end of nineteenth century. Synthetic dyes not only impart the diverse colours, but themselves are diverse in chemical structure, characteristics and hence find themselves in variety of applications. It is estimated that around 450,000 dyes differing in chemical constitution and properties are synthesized in tremendously large quantities and are used extensively in diverse applications like textile industry, paper industry, medicines, cosmetics, food etc[2]. Around 15-20 % of the dyes used are supposed to be lost during dyeing processing, thus generating huge quantity of coloured effluents containing dyes, most of which are considered as toxic, recalcitrant and potentially carcinogenic, in varying amounts[3,4].

Unfortunately most of these effluents are released directly to main stream water sources, thereby burdening the environment with loads of contaminants. The presence of dyes, even at trace level is highly visible in water and highly undesirable [5] to aesthetic appeal as well as for sustaining aquatic life. The dyes considerably reduce the penetration of sunlight into water, causing disturbances in the photosynthetic activity. Moreover, if such water containing dyes or their degradation products get into

main stream water sources, it can induce several health hazards like diarrhea, vomiting, nausea, cancer, ulceration of skin and mucous membrane in addition to causing severe damage to liver, kidney, brain, reproductive system in human beings [6,7].

Hence, it is expected that, these dye effluents should be treated effectively before they are released into water bodies. However, the technologies that are used conventionally like physical, chemical and biological processes, are inadequate and inefficient to degrade synthetic dyes, as most of these dyes are structurally very stable and hence resistant to degradation[8-13].

Therefore, to look for the techniques that would overcome this problem effectively had been a matter of utmost priority for last few decades. The exhaustive research in this regard has lead to invention of advanced oxidation processes and various researchers have reported their effectiveness in achieving the nearly complete degradation of dyes without hampering the environment.

The advanced oxidation processes have been reported to hold promising future as these are capable of achieving almost complete degradation of dyes from waste waters [14-21]. These methods are based on the principle of generation of highly reactive hydroxyl radical ( $\cdot\text{OH}$ ) at a certain stage, which is supposed to be capable for the destruction of pollutants [22]. Owing to their high standard oxidation potential (2.8V), these  $\cdot\text{OH}$  radicals are able to oxidize almost all the organic compounds to  $\text{CO}_2$  and water.

In present work, decolorization of aqueous solutions of Malachite Green using Photo Fenton's reagent is investigated.

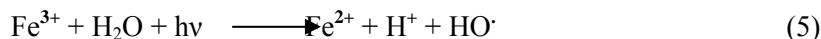
The use of Photo-Fenton reagent ( $\text{H}_2\text{O}_2 / \text{Fe}^{2+} / \text{UV}$ ) is well established and has been successfully utilized to treat wastewater and soil [23-28]. This method has been found to be superior to Fenton or Fenton-like reagents, since it involves interaction of UV radiation with Fenton's reagent. This technique has shown positive results in removing pollutants from natural and industrial waste water and increasing the biodegradability of dyes that are encouraging. This process is also being used as a pre-treatment method to decrease the toxicity of waste water [29,30].

In general the dye degradation using this technique has been found to be governed by the factors like initial dye concentration, quantity of hydrogen peroxide and ferrous ion and the intensity of radiation. When compared to Fenton's reaction or  $\text{H}_2\text{O}_2/\text{UV}$  technique, the photo Fenton reaction has shown overall more dye degradation which may be due to the production of  $\cdot\text{OH}$  radicals by multiple pathways.

### **Mechanism of Photo Fenton's Reaction**

The  $\cdot\text{OH}$  are generated in photo Fenton process through the photolysis of  $\text{H}_2\text{O}_2$  ( $\text{H}_2\text{O}_2/\text{UV}$  rays) and Fenton reaction ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ). In photo Fenton process, additional equivalent of  $\cdot\text{OH}$  are formed due to photolytic conversion of  $\text{Fe}^{3+}$  produced to  $\text{Fe}^{2+}$ .





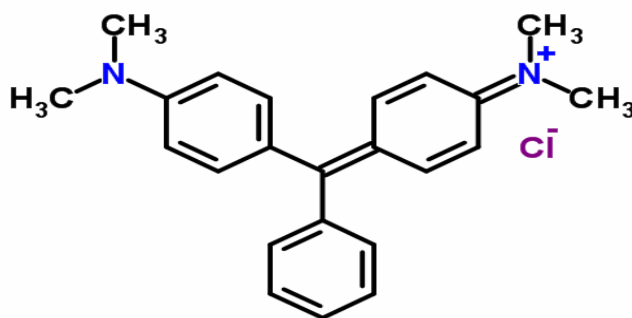
The hydroxyl radicals formed in Eq.(5) react with organic species in similar manner as in Eq.(3) to promote their oxidation thus enhancing the rate and extent of degradation. As the photolysis of  $\text{Fe}(\text{OH})_2$  regenerates  $\text{Fe}^{2+}$  ions, photo Fenton's reaction would need less dosages of  $\text{Fe}^{2+}$  compared to conventional Fenton's process. In addition to this, photo-Fenton-Reaction shows many advantages such as higher rate of dye degradation, lower operational cost due to low chemical consumption, etc in comparison with the classical Fenton-Reaction .

The present communication explores the possibility of decolorization of Malachite Green dye aqueous solutions using photo Fenton's reagent. Malachite Green dye is used extensively for dyeing leather, wool, cotton, jute, paper, certain fibers etc. and for such purposes it has been produced in large quantities and extremely variable qualities. Malachite Green and its metabolites and breakdown products may not be completely removed by wastewater treatment and may be present in sufficient amounts in effluents from industry or waste water treatment plants or other sources.

## Experimental

### Materials

All chemicals used were of AR grade. The Malachite Green was procured from HiMedia and was used without any further purification. All the solutions were prepared afresh using double distilled Water.  $\text{H}_2\text{O}_2$ ( 30% ) solution was used as a source of  $\text{H}_2\text{O}_2$  .



Structure of Malachite Green Dye

### Methodology

The stock solution of Malachite Green dye was prepared by dissolving 10 mg of dye in 50 ml of doubly distilled water. In order to study the effect of photo Fenton's reagent on the rate and extent of decolorization, an appropriate concentration of dye solution was selected having medium absorbance. The stock solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was prepared as a source of  $\text{Fe}^{2+}$  while 30%  $\text{H}_2\text{O}_2$  solution ( Merck ) was used as a source of  $\text{H}_2\text{O}_2$  with appropriate dilutions. The sample solutions were prepared by transferring

10 ml each of this selected dye concentration to 50 ml beakers followed by addition of conc.  $\text{H}_2\text{SO}_4$  so as to maintain pH of sample solutions in required acidic range. It was then followed by the addition of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  solution such that firstly the concentration of  $\text{H}_2\text{O}_2$  was kept constant and  $\text{Fe}^{2+}$  concentration was varied and then vice-versa. Decolorization of the sample solutions was carried out by exposing them to various doses of UV rays by placing them in UV reactor, having Hg lamp (12 W) as a source of UV rays. The decoloration was followed as a function of decrease in absorbance of irradiated samples and was measured on Spectronic-D20 spectrophotometer at  $\lambda_{\text{max}}$  of 619 nm.

## Results and Discussion

### Calibration plot

The calibration curve for Malachite Green dye (as shown in Fig.1.) is prepared so as to determine the concentration of Malachite Green dye remaining in solution after irradiation, by plotting absorbance values against concentration of dye solutions. The calibration curve between concentration and corresponding absorbance was found to be linear with regression coefficient of 0.99 at 619 nm.

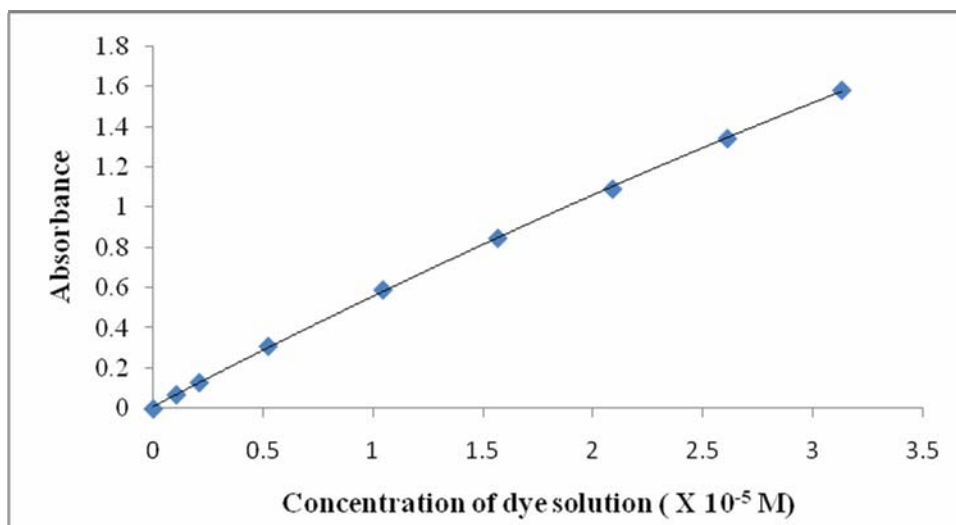


Figure 1 Calibration plot of Malachite Green dye

### Decolorization study

Concentration of both,  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  plays a vital role in degradation of dye as evident from the following discussion.

### Effect of $\text{H}_2\text{O}_2$ on rate and extent of decolorization

In the present study, it was observed that UV rays or  $\text{H}_2\text{O}_2$  either alone or in combination were ineffective in bringing about the effective decolorization ( Fig.2). Fenton's reagent alone when employed was found to decolorize the dye solutions to a satisfactory level, but the efficiency of Fenton's reagent was found to

enhance when coupled with UV rays. This could be attributed to generation of additional  $\cdot\text{OH}$  radicals as per the equation (5) mentioned earlier.

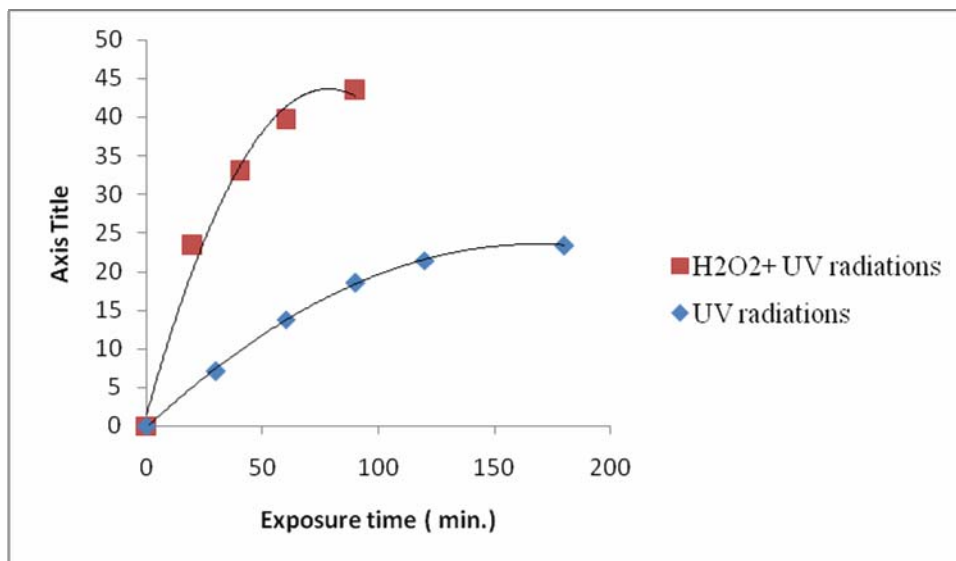


Figure 2 Decolorization using a) UV rays only and (b)  $\text{H}_2\text{O}_2$ + UV rays

The concentration of hydrogen peroxide plays a vital role in dye degradation as described in many studies [31-35]. As concentration of hydrogen peroxide increases, the degradation of dyes also increases. This can be explained on the basis that, the amount of oxidant present in the reaction system is higher for the same initial concentration of dye and catalytic ferrous ions.

Figure 3 depicts the effect of  $\text{H}_2\text{O}_2$  concentration on the extent of photo Fenton induced decolorization of dye solutions. It can be seen from the graph that, increase in  $\text{H}_2\text{O}_2$  concentration (keeping all other parameters constant), increases the rate of decolorization.

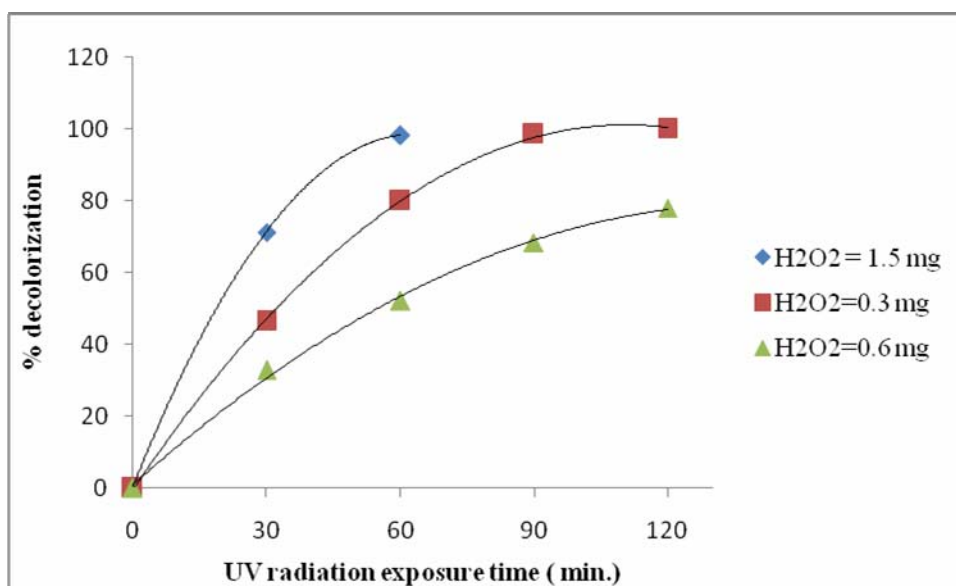


Figure 3 Effect of  $\text{H}_2\text{O}_2$  concentration on rate and extent of decolorization

### Effect of Ferrous Ion Concentration [Fe<sup>2+</sup>]

Fig.4 represents the effect of ferrous ion concentration (keeping all other parameters constant) on the extent of dye degradation. It is clear that with an increase in the concentration of iron, dye degradation also increases to a point where further addition of iron becomes inefficient. The optimum amount of iron catalyst is characteristic of Fenton's reagent, although its exact amount varies from dye to dye solution.

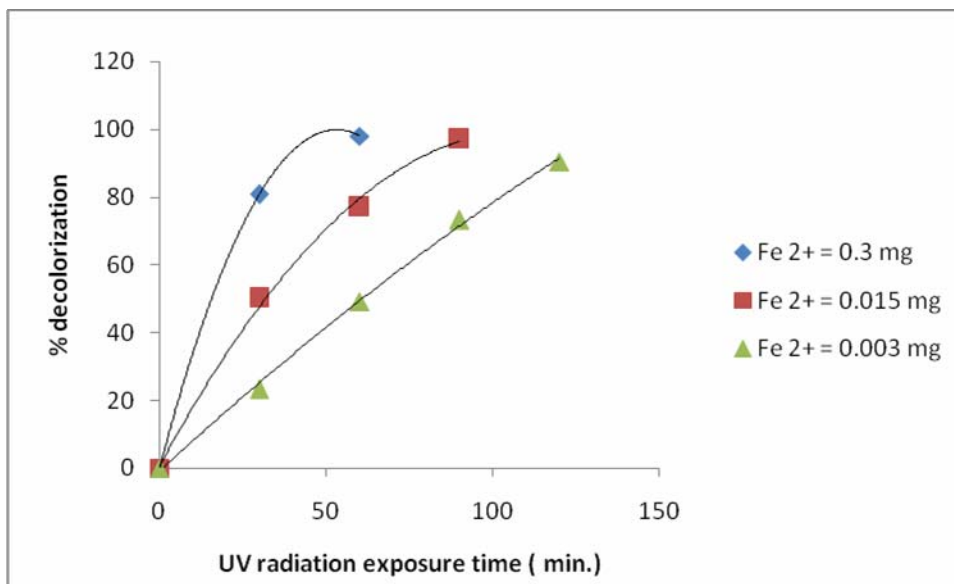


Figure 4 Effect of ferrous ion concentration on rate and extent of decolorization

The influence of ferrous ions in dye degradation is similar to the one for hydrogen peroxide. When Fenton concentration increases, the degradation of dye also increases, because the amount of catalyst present in the reaction system is higher for the same initial concentration of dye and hydrogen peroxide [36].

The very low extent of decolorization of dye using UV rays alone in this study may be due to fact that the energy of UV rays alone is unable to produce OH<sup>•</sup> radicals in the required proportion or produce <sup>•</sup>OH radicals at a such slow rate that it is unable for destruction of dye molecules .

### Conclusion

In the present study, the decoloration of Malachite Green dye solutions was achieved effectively using photo Fenton reagent. The degradation rate and extent increased with increase in concentration of H<sub>2</sub>O<sub>2</sub> (when other parameters were kept constant) and similar was the observation for Fe<sup>2+</sup> concentration (when other parameters were kept constant). Thus, decolorization of dye containing effluents can be achieved effectively by using photo Fenton's advanced oxidation process. This process has some major advantages over conventional Fenton's reagent like higher rate of degradation, low operational cost owing to reduced requirement of chemicals, generation of low quantity of sludge etc.

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