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Influence of some Reaction Parameters on Photo Fenton Degradation of Malachite Green Under Visible Irradiation

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Abstract
The photo degradation of Malachite Green (M.G) was investigated using Photo-Fenton process under 60 watts Tungsten visible irradiation. In order to determine optimum condition, the operating parameters such as initial dye concentration, pH, H_2O_2 dosage and Fe^{2+} dosage, have been investigated. The experimental results showed that at pH of 2, H_2O_2 and Fe^{2+} concentrations of 12mM and 0.5mM, respectively within 15min irradiation time, the optimum degradation was found to be 94% which is nearly complete degradation. Total Organic Carbon (TOC) analysis showed nearly complete mineralization of the dye molecules with efficiency (65%). The kinetics of the Fenton process followed pseudo second order kinetics with rate constants of 0.062LMol^{-1}min^{-1}. Therefore, pH, H_2O_2, Fe^{2+} and MG concentrations influence photo-Fenton degradation of MG under visible irradiation.

Keywords: Malachite green; Fenton; Mineralization; Photocatalysis.

INTRODUCTION

Currently there is a great concern expressed massively in the media on the critical issue of water pollution, these involves the improper disposal of industrial waste, sewage disposal, oil spillage on domestic water bodies. All these different sources of water pollution contain hazardous mixtures of mainly organic and inorganic compounds which have adverse effect on environment, aquatic and human health (Soon & Hameed, 2011). The discharge of waste water containing dyes in the environment is a powerful source of esthetic and agitation in aquatic life(Nandi & Patel, 2017). More than 10,000 different types of dyes and more than 800,000 tons per year are produced worldwide and about 11-15% of the dyes are disposed off to the environment after dyeing process (Sun *et al.*, 2007). Presently, more thern 25% of the total world population suffer from healthy and hygienic water problem (Mezohegyi *et al.*, 2010). There is need for treatment of such contaminants before discharging to remove a wide variety of toxic, refractory organic compounds (Basavarajappa *et al.*, 2020). Advanced oxidation processes (AOP), have the ability to oxidize almost all complex organic contaminants into smaller molecules, complete mineralization of the compounds into CO_2, water and inorganic ions such as SO_4^{2-}, NO_3^- and N_2 is possible (Klamerth *et al.*, 2010). Among these AOP's Fenton process as reported by Henry John Horstman (H.J.H) Fenton 1894, the process uses H_2O_2 and ferrous ions to generate hydroxyl radical(Chacó *et al.*, 2006). Photo Fenton process is one of the important process to generate hydroxyl radicals, and has been widely used to degrade pollutants because it rapidly and non selectively oxidize

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organic contaminant into carbon dioxide, water and other inorganic ions (Zheng *et al.,* 2007). Malachite green (MG) is an organic compound that is used as a dyestuff and controversially as an antimicrobial in aquaculture. MG is traditionally used as a dye for materials such as silk, leather, and paper. it has also been used as anti bacterial to treat saprolegnia (Raducan *et al.,* 2008). MG is transformed in organisms to leucomalachite green, which accumulates in the tissues of exposed organisms from where it can easily get into the human food chain. Both clinical and experimental observations reported so far revealed that MG is a multi-organ toxin (Srivastava *et al.,* 2004). The demonstration of processes that can remove this compound from aqueous solutions is therefore desirable. In this paper, we optimized the effectiveness of photo Fenton process on MG dye removal under visible irradiation.

EXPERIMENTAL

Chemical

Malachite dyes containing approx. 95% was obtained from sigma Aldrich, H_2O_2 (40%w/v) from Globa Chemie, $FeSO_4.7H_2O$ (99%) Sigma Aldrich, H_2SO_4, NaOH (99.0% and 96%) Ideal scientific. Deionized water was used throughout the investigations. The reagents were used as received without any purification.

Experimental Procedure

The experiments were carried out with 100mL dye solution prepared in appropriate concentrations using deionized water. The solutions pH was adjusted to the desired level using sulfuric acid and sodium hydroxide, which were measured by pH meter. During the experiment 5mL sample of suspensions were withdrawn at regular time intervals and analyzed using UV-Vis spectrophotometer. Each of the experiments was replicated three more times.

Analytical Method

The UV-Vis spectra of dyes were recorded from 400 to 800 nm using a UV-VIS spectrophotometer (Perkine Elmer UV Winlab) with a spectrometric quartz cell (1 cm path length). The maximum absorbance wavelength (λmax) of Malachite green is found at 621nm. Therefore, the concentration of the dyes in the reaction mixture at different reaction times were determined by measuring the absorption intensity at λmax = 621nm and from a calibration curve. Solution pH, dye concentration and catalyst loading were investigated for the photo catalytic degradation performance in terms of TOC removal and degradation efficiency of Malachite green was calculated as follows

$$\text{Performance } \% = \left(1 - \frac{C_t}{C_o}\right) \times 100 \quad \text{..... (1)}$$

Where C_o is the initial concentration or TOC of MG, and C_t is the concentration or TOC of MG at reaction time t.

RESULTS AND DISCUSSION

Preliminary Studies

Each of the background processes of the photo-Fenton (irradiation, H_2O_2 and Fe^{2+}) has the potential to singly cause the degradation of MG. The effect of these parameters on the degradation at different conditions of the reaction, the dark-Fenton (Dark/Fe^{2+}/H_2O_2) gives 41% degradation followed by H_2O_2/UV, 33% degradation and Fe^{2+}/UV, 9%. This showed that in the presence of light Fenton process is more effective in the degradation of MG.

Total Organic Carbon (TOC) Analysis

In assessing the degree of mineralization reached during the photo catalytic treatment, the formation of CO_2 and inorganic ions is generally determined. However, in the presence of real wastewaters the monitoring of inorganic ions and CO_2 gives only a global estimation on the well functioning of the treatment, but does not provide information on the real decay of the contaminant. In such cases the determination of total organic carbon (TOC) of the irradiated solution is generally used for monitoring the mineralization of the dye. Total mineralization has been observed for the degradation of MG dye, and it was found that the optimum TOC percentage remove was 65% after 15 minutes irradiation time (Ibrahim & Gaya, 2020).

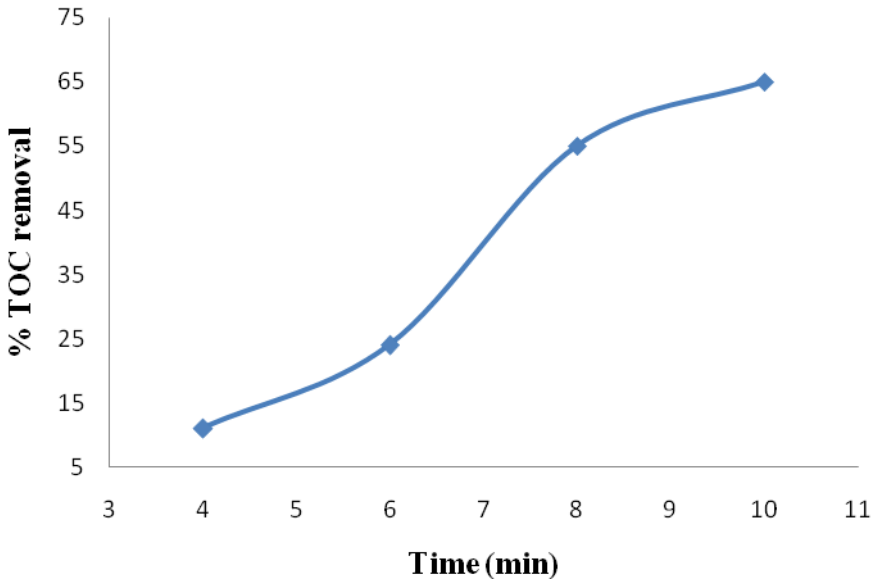

Figure 1: Total Organic Carbon removal of MG, by photo Fenton process.

EFFECT OF pH

The effect of pH on the degradation of MG is shown in **Figure 2**. The results indicated that pH significantly affected the degradation of MG. The experiments were carried out at different pH that varied from 2 to 12. The reaction reached it is maximum in 15min at the pH value of 2 to 12 and constant dose of Fe^{+2} (0.5mM) and H_2O_2 (4mM). The percentage degradation decreased with increase in pH (2 - 12) from 89% to 71% respectively. The decrease in the efficiency of degradation of Malachite green is as a result of increase in pH the iron precipitate as hydroxide at higher pH, which resulted in a reduction in the OH radical Production and transmission of the radiation (Chen *et al.,* 2015).

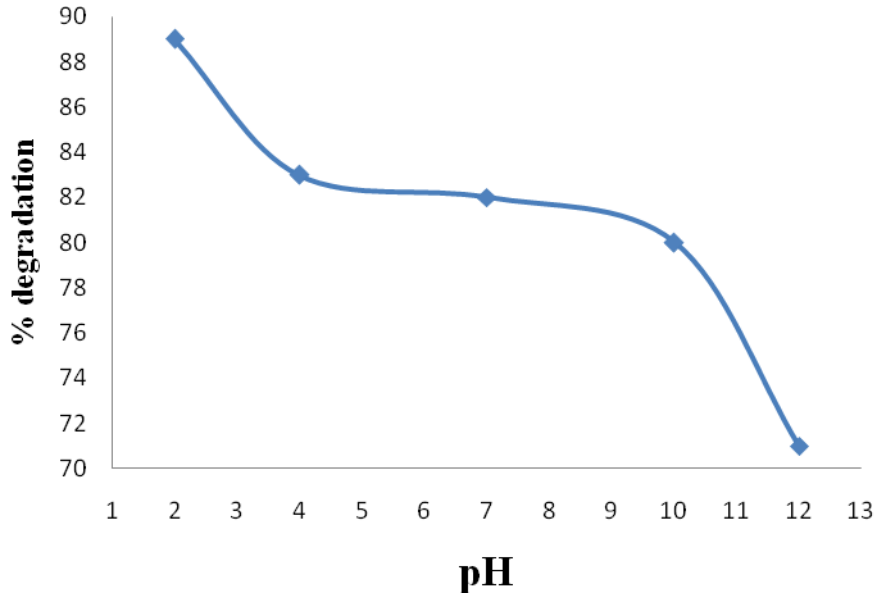

Figure 2: Percentage degradation of MG, at MG concentration (2ppm), Fe^{2+} (0.5mM), H_2O_2 (4mM) at different pH values

EFFECT OF Fe^{2+}

The effect of Fe^{2+} concentration on the degradation of malachite green by photo Fenton process was studied by varying the concentration of Fe^{2+}, keeping the other reaction parameters constant. F**igure 3** shows that the degradation of malachite green decreases with increase in the concentration of Fe^{2+} from 88 to 79% for 0.5 to 2.5mM respectively. The decrease in degradation efficiency of malachite green with increase in concentration of Fe^{2+} is because Fe^{2+} undergoes the following reaction (Equation 2).

$$\cdot OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad \text{(2)}$$

Thus in the presence of Fe^{2+}, $\cdot OH$ radicals are easily converted into OH^-, thereby decreasing their concentration and thus less degradation of the dye solution is observed (Ibrahim & Gaya, 2020).

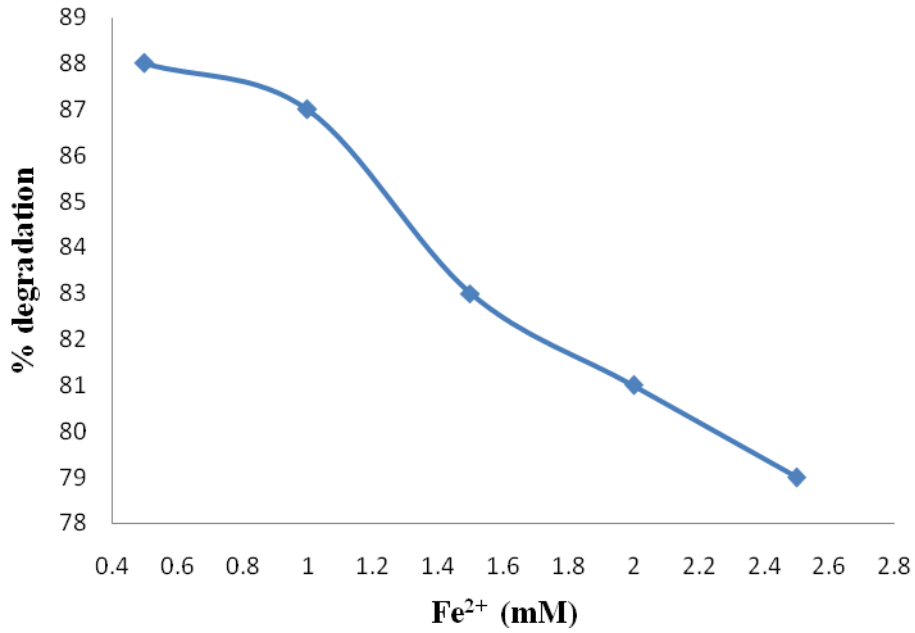

Figure 3: Percentage degradation of MG, at MG [2ppm], H_2O_2 [4mM], and pH value 2 at different Fe^{2+}concentration.

EFFECT OF H_2O_2

The effect of H_2O_2 on malachite green degradation by photo Fenton process was studied by varying the concentration of H_2O_2, keeping the other reaction conditions constant. **Figure 4** shows that the degradation of malachite green increase with increase in H_2O_2 from 88 to 94%. The increase in the degradation rate is due to increase in the number of ·OH produce by H_2O_2, and the ·OH is attacked the dye and degrade it (Ibrahim & Gaya, 2020).

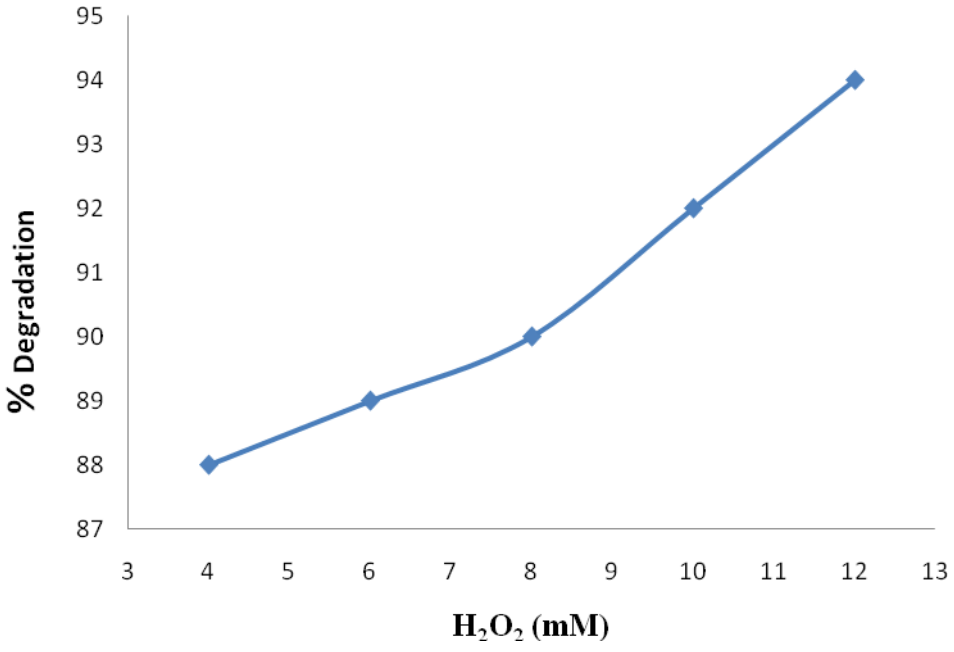

Figure 4: Percentage degradation of MG, at MG concentration (2ppm) and Fe^{2+} (0.5mM) at pH value 2 at different H_2O_2 concentration.

EFFECT OF MALACHITE GREEN CONCENTRATION

The effect of malachite green concentration was studied by taking different concentrations and of it and keeping the other reaction parameters constant. The M.G concentration is one of the important parameters in photo-Fenton processes. The effect of initial dye concentration in these processes is shown in **Figure 5**. The figure clearly revealed that the increase in dye concentration decreases the degradation rate. Increase of dye concentration from 2mg/dm^3 to 10mg/dm^3 decreased the degradation from 81% to 52%. Hydroxyl radical is mainly responsible for dye degradation and its concentration remains constant for all dye concentrations. The increase in dye concentration increases the number of dye molecules and not the HO· concentration and so the degradation rate decreases, and this increasing number of MG dye molecule also obstructs the penetration of photons entering into the solution, therefore less production of OH radical (Adepu *et al.,* 2017).

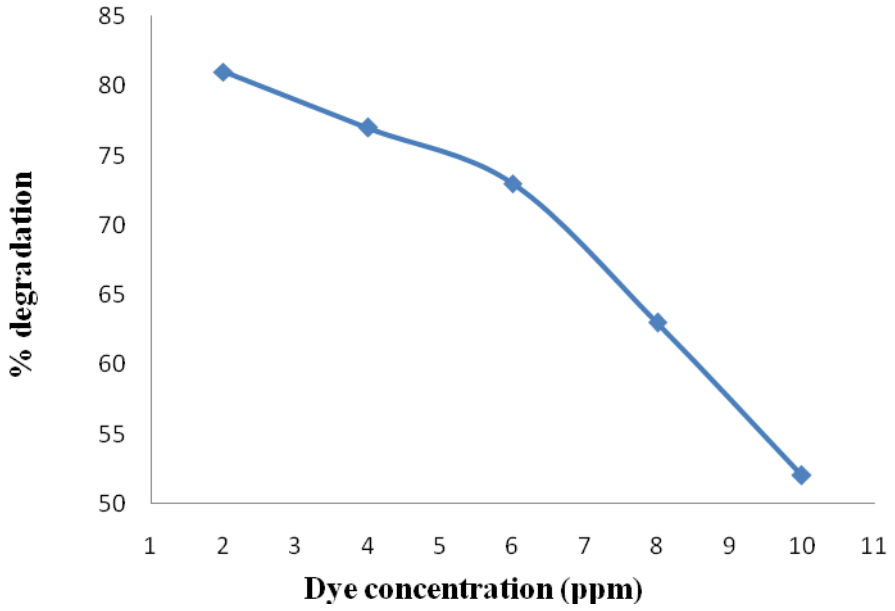

Figure 5: Percentage degradation of MG, at different concentration of MG, H_2O_2 (4mM), pH 2, Fe^{2+} (0.5mM).

Kinetics Studies

The kinetics studies was carried out for more knowledge of degradation MG dye solution, the optimum oxidation processes described in terms of Pseudo first and second order Kinetics by plotting the graphs; for pseudo first order kinetics the graph of $\ln C_t$ *vs* t as seen in equation 3 while for pseudo second order, the graph of $1/C_t$ *vs* t see equation 4, the kinetics of MG follows Pseudo second order kinetics because it has higher correlation coefficient (R^2) of 0.811 and the rate constant (k) value of 0.062 calculated from the slope of the graph as in Table 1, this happens due to higher R^2 value than its corresponding first order value R^2 = 0.734 with rate constant (k) 0.066.

$$\ln C_t = -k_1 t + \ln C_0 \qquad 3$$

$$\frac{1}{C_t} = k_2 t + \frac{1}{C_o} \qquad 4$$

Table 1: Summary of Kinetic study for Photo Fenton process

Order of the reaction	R^2 value	K value
Pseudo first order	0.734	0.066
Pseudo second order	0.811	0.062

CONCLUSION

The Photo-degradation of malachite green via photo Fenton reagent has been taken into consideration. The results showed that the degradation rate of malachite green was greatly accelerated by the photo Fenton process and the combination of homogeneous system light/ H_2O_2 / Fe^{2+} produced the highest photochemical degradation percentage (94%) of malachite green. The degradation rate was influenced by pH of solution and the amount of hydrogen peroxide and iron salt. The optimum condition for the photo degradation of malachite green in the light/ H_2O_2 / Fe^{2+} system were observed at pH 2, with original Fe^{2+} concentration of 0.5mM and H_2O_2 concentration of 12mM. The degradation followed pseudo second order kinetics, and Total Organic Carbon removal up to 65%.

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