Degradation of malachite green in aqueous solution by Fenton process

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ABSTRACT

In this study, advanced oxidation process utilizing Fenton's reagent was investigated for degradation of malachite green (MG). The effects of different reaction parameters such as the initial MG concentration, initial pH, the initial hydrogen peroxide concentration, the initial ferrous concentration and the reaction temperature on the oxidative degradation of MG have been investigated. The optimal reacting conditions were experimentally found to be pH 3.40, initial hydrogen peroxide concentration = 0.50 mM and initial ferrous concentration = 0.10 mM for initial MG concentration of 20 mg/L at 30 °C. Under optimal conditions, 99.25% degradation efficiency of dye in aqueous solution was achieved after 60 min of reaction.

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1. Introduction

Synthetic dyes are extensively used in many industries such as the textile, leather, paper production, food technology, etc., to color their products. For example, Malachite green (MG) is most commonly used for the dyeing of cotton, silk, paper, leather and also in manufacturing of paints and printing inks. Malachite green has properties that make it difficult to remove from aqueous solutions. Also malachite green is widely used in distilleries for colouring purposes [1]. Malachite green when discharged into receiving streams will affect the aquatic life and causes detrimental effects in liver, gill, kidney, intestine, gonads and pituitary gonadotrophic cells [2]. Therefore, the removal of color synthetic organic dyestuff from waste effluents becomes environmentally important.

In recent years, advanced oxidation processes using ozone, titanium dioxide (TiO_2), ultra violet (UV), and Fenton's reagent (H_2O_2 and ferrous ion) have received considerable attention as effective pretreatment processes of less biodegradable wastewater [3]. Among them, Fenton's reagent has been widely used because it is cost effective, easy to treat, reacts well with organic compounds and does not produce toxic compounds during oxidation.

Fenton's reaction [4] is one of the most effective methods of oxidation of organic pollutants, that are oxidatively degraded by hydroxyl radicals generated from H_2O_2 in the presence of Fe^{2+} as a catalyst [5]:

$$Fe^{2+} + H_2O_2 \rightarrow OH^{\bullet} + OH^- \qquad (1)$$
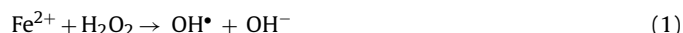
When ferrous salts are used, the hydroxyl radical is produced immediately by the rapid reaction between ferrous ion and hydrogen peroxide (Eq. (1)). With ferric salts, the hydroxyl radical is produced in a two-stage process with the slow reaction between ferric ion and hydrogen peroxide (Eq. (2)) followed by the rapid reaction between the produced ferrous ion and additional hydrogen peroxide [5,6]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^- + H^+ \qquad (2)$$
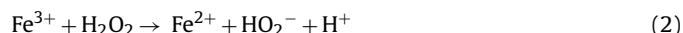
The efficiency of Fenton's process depends on H_2O_2 and Fe^{2+} concentrations and pH of the reaction. According to a previous researcher's report, pH value should be in the range of 3–5 [5,7–9].

Fenton's reagent was found to be very effective in treating various industrial wastewater components, including removal of COD and color from livestock wastewater [10], treatment of textile wastewaters with high organic load [11], cosmetic wastewaters treatment [12], alkydic resin wastewaters treatment [13], oxidation of dye-Reactive Black B [14], decolorization of an azo dye Orange G in aqueous solution [15], decolorization of C.I. Acid Yellow 23 [16] and dye wastewater [17]. Therefore, the Fenton's reagent has been applied to treat a variety of wastes such as those associated with the textile and chemical industries.

The purpose of the present work was to determine the efficiency of Fenton's reaction in the process of MG removal from aqueous solution. In the Fenton system, the definition of the optimum operational conditions such as pH, iron and hydrogen peroxide

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concentrations is important. Experiments were conducted to investigate the effects of various operating conditions on the performance of treatment system.

2. Materials and methods

2.1. Reagents

The dye, malachite green oxalate, C.I. Basic Green 4, C.I. Classification Number 42,000, chemical formula = $C_{52}H_{54}N_4O_{12}$, MW = 927.00, λ_{max} = 618 nm (measured value) was supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia. The chemical structure of malachite green oxalate is shown in Fig. 1. The Fe^{2+} ions were provided from solutions of ferrous sulfate ($FeSO_4 \cdot 7H_2O$) and the hydrogen peroxide (H_2O_2) was from stock of 30% (w/w). Both were obtained from Sigma–Aldrich (M) Sdn Bhd, Malaysia. All chemicals were of analytical grade and were used without any further purification. Deionized water was used throughout this study.

2.2. Preparation of synthetic dye solution

The dye solution was prepared by dissolving the MG dye in deionized water to produce a stock solution of 500 mg/L. This stock solution was diluted in accurate proportions to produce solutions of different initial concentrations.

2.3. Experimental procedures

A 250-ml stoppered glass (Erlenmeyer flask) was used as a batch reactor. Batch experiments of MG degradation were performed by adding H_2O_2 to the dye solution and then the pH was adjusted to the desired value by the addition of a few drops of either 0.1N H_2SO_4 or 0.1N NaOH. Following the pH adjustment, the Fe^{2+} ions were quickly added to the dye solution. The flask was then placed in a thermostated water-bath shaker and agitation was provided at 150 rpm. The samples were taken out from the conical flask periodically using a 1-ml syringe and were analyzed immediately.

The effect of initial MG concentration $[MG]_0$ in the oxidation of MG was studied by varying the amount of $[MG]_0$ used for the experiment (20, 45, 80 and 100 mg/L), while maintaining pH, agitation speed, initial ferrous concentration $[Fe^{2+}]_0$, initial hydrogen peroxide concentration $[H_2O_2]_0$ and temperature constant at 3.40, 150 rpm, 0.05, 2.00 mM and 30 °C, respectively. The solutions were agitated in a thermostatic water-bath shaker for a period of 70–100 min.

The effect of pH on MG degradation was studied using 200 mL of 20 mg/L dye solution taken in stoppered conical flask containing 0.05 and 2.00 mM of $[Fe^{2+}]_0$ and $[H_2O_2]_0$, respectively. The pH of

the solution was varied from 2.50 to 4.00 using 0.1N H_2SO_4 and 0.1N NaOH. The solution at the respective pH was agitated in a thermostatic water-bath shaker (150 rpm) for a period of 60 min at 30 °C.

The effect of the $[Fe^{2+}]_0$ dosage on the MG degradation was also studied. To 200 mL of 20 mg/L MG solution, different $[Fe^{2+}]_0$ concentrations (0.010, 0.025, 0.050 and 0.100 mM) were added along with 2.00 mM of $[H_2O_2]_0$. The flasks were agitated in a thermostatic water-bath shaker for a period of 60 min at 30 °C. Samples were taken out from the conical flask periodically for analysis purpose.

The effect of H_2O_2 in the oxidation of MG was studied by varying the amount of H_2O_2 used for the experiment (0.50, 2.00 and 4.00 mM) with $[Fe^{2+}]_0$ of 0.10 mM. The solutions were agitated in a thermostatic water-bath shaker for a period of 60 min at 30 °C.

To study the effect of reaction temperature, 200 mL of 20 mg/L MG solution was agitated with 0.10 mM of $[Fe^{2+}]_0$ and 0.50 mM $[H_2O_2]_0$ at pH 3.40 for a period 60 min at various temperatures (30, 40 and 50 °C).

2.4. Analytical methods

The efficiency of the proposed process was evaluated by monitoring MG degradation by measuring absorbance at 618 nm using a double beam UV/vis spectrophotometer (Shimadzu, Model UV 1601, Japan). Therefore, the concentration of the MG in the reaction mixture at different reaction times was determined by measuring the absorption intensity at λ_{max} 618 nm and from a calibration curve. Prior to the measurement, a calibration curve was obtained by using the standard MG solution with known concentrations. Because the reaction continued after sampling, the measurement of absorbance of reaction solution was done within 1 min.

The degradation efficiency of MG was defined as follows:

$$\text{Degradation efficiency} = \left(1 - \left(\frac{C_t}{C_0}\right)\right) \times 100\% \qquad (3)$$

where C_0 (mg/L) is the initial concentration of MG, and C_t (mg/L) is the concentration of MG at reaction time t (min).

3. Results and discussion

3.1. Effect of the initial MG concentration

The experiments were conducted at initial concentration in the range 20–100 mg/L of $[MG]_0$, while maintaining pH, agitation speed, $[Fe^{2+}]_0$, $[H_2O_2]_0$ and temperature constant at 3.40, 150 rpm, 0.05, 2.00 mM and 30 °C, respectively. Fig. 2 shows the effect of $[MG]_0$ on its degradation by Fenton oxidation. It can be seen that the reaction time decrease with decrease in initial concentration. At 20 mg/L, the degradation efficiency was 96% at 35 min and increase to 100% after 50 min. However, lower degradation efficiencies were observed at higher initial concentrations even at longer reaction time. For example, at the first 20 min, the degradation efficient observed at initial MG concentration of 45, 80 and 100 mg/L were 47.23, 32.07 and 10.02%, respectively. This means that with constant $[H_2O_2]_0$ and $[Fe^{2+}]_0$, more hydrogen peroxide was consumed in the first 20 min because of a higher MG concentration. After 20 min, the amount of hydrogen peroxide available was smaller and the degradation of MG slowed down significantly.

3.2. Effect of pH

To study the effect of pH on degradation of MG by Fenton oxidation and to find the optimal pH of reaction mixture, a series of experiments were conducted at different pH values 2.5, 3.00, 3.4 and 4.00, whereas the $[MG]_0$, $[Fe^{2+}]_0$ and the $[H_2O_2]_0$ were
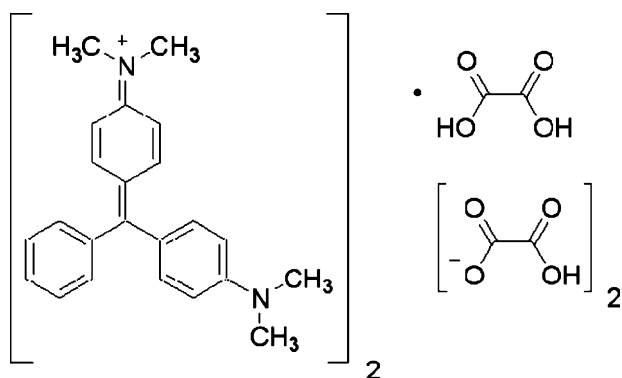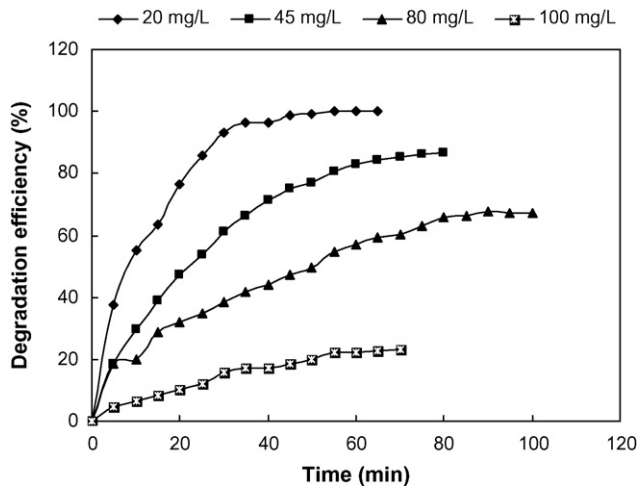

Fig. 1. Chemical structure of malachite green.

Fig. 2. Effect of initial MG concentration on the degradation of dye during Fenton oxidation treatment. Reaction conditions: $[H_2O_2]_0 = 2$ mM, $[Fe^{2+}]_0 = 0.05$ mM, pH 3.40 and temperature = 30 °C.

Fig. 4. Effect of initial Fe^{2+} concentration on the degradation of MG during Fenton oxidation treatment. Reaction conditions: $[dye]_0 = 20$ mg/L, $[H_2O_2]_0 = 2.00$ mM, pH 3.40 and temperature = 30 °C.

maintained at 20 mg/L, 0.05 and 2.00 mM, respectively. The results (Fig. 3) given indicated that the degradation of MG was significantly influenced by the pH of the solution and the optimal solution pH was observed at 3.40. A similar result was reported for the degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process [18]. The decoloration efficiency increases from 38.29 to 93.22% as a consequence of the pH value increase from 2.50 to 3.4 within 30 min. Further increase in the pH value from 3.4 to 4.0 was detrimental to the oxidation process as the decoloration efficiency decreased from 93.22 to 30.89%. The drop in efficiency at high pH values may be due to the precipitation of $Fe(OH)_3$. In this form, iron decomposes H_2O_2 into oxygen and water [19], and consequently the oxidation rate decreases because less hydroxyl radicals are available.

The measured final pH values after 60 min of reaction were 2.43, 2.90, 3.30, and 3.98 for an initial pH of 2.50, 3.0, 3.40, and 4.00, respectively. The observed drop in the final solution pH with initial pH values may be due to the generation of HSO_4^- and NO_3^- and carboxylic acid during mineralization of dye [18].

3.3. Effect of the initial Fe^{2+} concentration

To study the role of initial concentration of Fe^{2+} on the degradation of MG by Fenton oxidation, a series of experiments
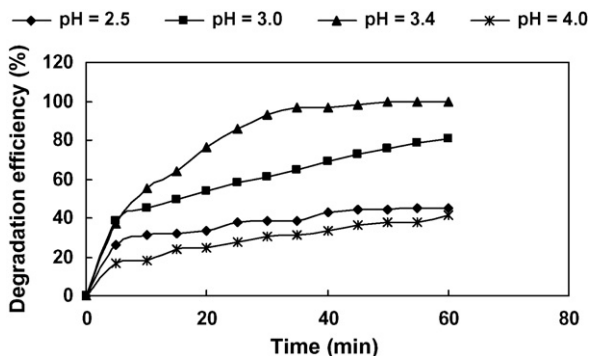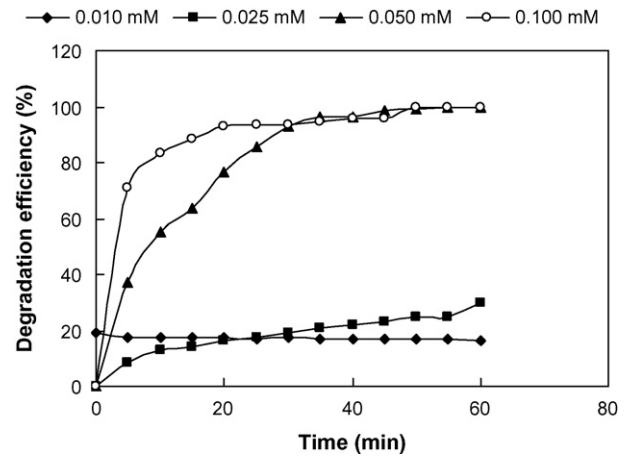
were conducted with different $[Fe^{2+}]_0$ from 0.01 to 0.10 mM and the results obtained are presented in Fig. 4. The degradation efficiency of MG was significantly changed over the $[Fe^{2+}]_0$ value of 0.01–0.10 mM. The lowest degradation efficiency (16.58%) was recorded at $[Fe^{2+}]_0$ value of 0.01 mM after 60 min reaction time, while the highest degradation efficiency (100%) was recorded at $[Fe^{2+}]_0$ value of 0.10 mM after 55 min reaction time.

Many studies reported in literature have revealed that the use of a much higher concentration of Fe^{2+} could lead to the self-scavenging of $^\bullet OH$ radical by Fe^{2+} (Eq. (4)) [20,21] and induce the decrease in degradation rate of pollutants:

$$^\bullet OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad k_4 = 4.3 \times 10^8 \, M^{-1} \, s^{-1} \quad (4)$$
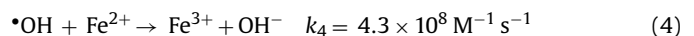
3.4. Effect of the initial H_2O_2 concentration

To study the effect $[H_2O_2]_0$ on MG degradation, the experiments were conducted at initial MG concentration of 20, 0.10 mg/L $[Fe^{2+}]_0$ at 30 °C. The effect of $[H_2O_2]_0$ was studied in the range of 0.5–4 mM as shown in Fig. 5. As expected, the increase in $[H_2O_2]_0$ accelerated the dye decolorization at the beginning of the reaction. The decoloration efficiency increased from 85.59 to 87.72% as a consequence of increasing H_2O_2 dosage from 0.5 to 4.0 mM at 10 min. This can be explained by the effect of $OH^\bullet$ radicals produced additionally. However, it can be seen from

Fig. 3. Effect of pH on the degradation of MG during Fenton oxidation treatment. Reaction conditions: $[dye]_0 = 20$ mg/L, $[H_2O_2]_0 = 2$ mM, $[Fe^{2+}]_0 = 0.05$ mM and temperature = 30 °C.
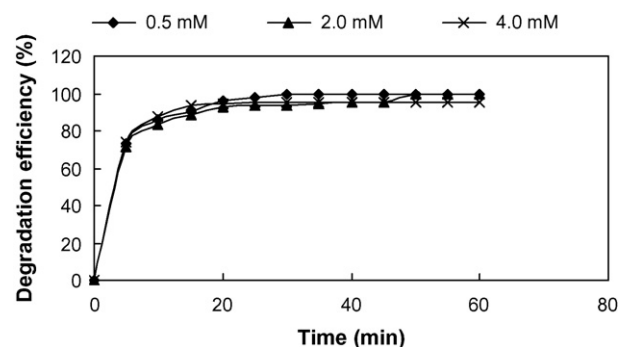

Fig. 5. Effect of initial H_2O_2 concentration on the degradation of MG during Fenton oxidation treatment. Reaction conditions: $[MG]_0 = 20$ mg/L, $[Fe^{2+}]_0 = 0.10$ mM, pH 3.40 and temperature = 30 °C.
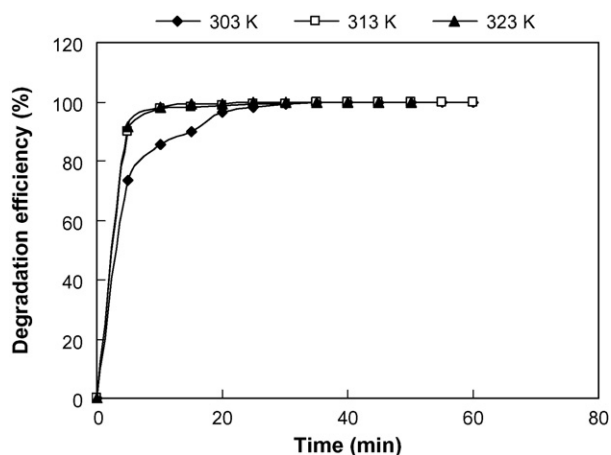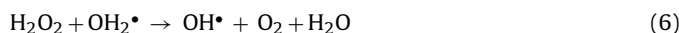
Fig. 6. Effect of temperature on the degradation of MG during Fenton oxidation treatment. Reaction conditions: $[dye]_0 = 20\,mg/L$, $[H_2O_2]_0 = 0.50\,mM$, $[Fe^{2+}]_0 = 0.100\,mM$ and pH 3.40.

the figure that after a period of 35 min there was no significant increase in degradation efficiency % on increasing the $[H_2O_2]_0$. After a reaction time of 50 min, with a 0.50, 2.00 and 4.00 mM of H_2O_2, % degradation of 99.66, 99.51 and 95.69, respectively, were obtained.

Aravindhan et al., [22] explained this phenomenon and stated that the addition of H_2O_2 is known to increase the rate of dye degradation by allowing an enhancement in the quantum yield of formation of hydroxyl radical. Consequently, the degradation rate is expected to be enhanced. But at high dosage, H_2O_2 is a powerful $OH^\bullet$ scavenger:

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O \tag{5}$$

$$H_2O_2 + OH_2^\bullet \rightarrow OH^\bullet + O_2 + H_2O \tag{6}$$

$$HO_2^\bullet + OH^\bullet \rightarrow H_2O + O_2 \tag{7}$$

Thus, the addition of higher concentration of H_2O_2 did not improve the degradation. This could be due to the fact that hydroperoxyl radicals ($HO_2^\bullet$) was generated in the presence of excess of H_2O_2. Although $HO_2^\bullet$ promotes radical chain reactions and is an effective oxidant itself, its oxidation potential is much lower than that of $OH^\bullet$. The hydroperoxyl radicals are much less reactive and do not contribute to the oxidative degradation of organic substrates, which occur only by reaction with $OH^\bullet$ [23,24].

3.5. Effect of temperature

In order to study the effect of reaction temperature on the degradation of MG a series of experiments were conducted at different temperatures; 30, 40 and 50 °C and the results are shown in Fig. 6. From Fig. 6, it can be seen that the degradation efficiency of MG increased from 85.59 to 98.14% as a consequence of increasing the temperature from 30 to 50 °C within the first 10 min of oxidation process. This is because higher temperature increased the reaction rate between hydrogen peroxide and any form of ferrous/ferric iron (chelated or not), thus increasing the rate of generation of oxidizing species such as $^\bullet OH$ radical or high-valence iron species [18]. After a reaction time of 20 min, the increase in the % degradation of MG is only marginal on increasing the temperature.

4. Conclusions

The examined Fenton's reaction was found to be very efficient for removing MG from aqueous solutions. The optimal operation parameters for the Fenton oxidation of MG were 0.50, 0.10 mM, 20 mg/L, 3.40 and 30 °C for $[H_2O_2]_0$, $[Fe^{2+}]_0$, $[MG]_0$, pH and temperature, respectively. Under these conditions, 99.25% degradation efficiency of MG in aqueous solution was achieved after 60 min of reaction. Excessive hydrogen peroxide may favor the formation of less reactive radicals and detard the decoloration rate of MG.

Acknowledgement

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