

Light Induced Kinetic Studies of Oxidative Degradation of Malachite Green

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(Received: 15 May 2009;

Accepted: 25 October 2010)

AJC-9210

Oxidative degradation of malachite green was performed in presence of Fe(III) + H₂O₂ mixture in dark and in light. The UV radiation completely mineralized the dye molecules where the degradation rate was decreased in the order of UV > visible > dark. Malachite green molecules showed optimum colour in the pH range of 3.8-5.9. The effective Fenton activity was noticed at [H₂O₂]/[Fe(III)] ratio of 7.01. The degradation rate was positively influenced by the temperature where the activation energy degradation was estimated as 16.83 kJ mol⁻¹. A maximum 86 % degradation was achieved at 45 °C.

Key Words: Fenton's reagent, Photolysis, Degradation, Malachite green, Rate constant.

INTRODUCTION

All coloured textile dyes are recognized as a family of pollutants, highly toxic, carcinogenic and responsible for water pollution. In textile industries, 10-15 % dyes are lost to the environment without any pre-treatment¹. The release of these coloured compounds into the eco-system acts as a dramatic source of environmental pollution². The common physico-chemical treatment methods for the decolourization/degradation of dye waste-waters such as activated carbon adsorption and extraction are able to separate these pollutants forming a concentrated waste, which is also required to be treated subsequently³. Therefore, this technique is inefficient to eliminate the pollutants from water. Ozone and hypochlorite oxidations are efficient decolourizing methods but they are not desirable because of the high operating costs and the secondary pollution arising from the residual chlorine or because of unreacted intermediates^{4,5}. Other conventional processes based on biological treatment (aerobic-anaerobic) are relatively ineffective in effluent decolourization, because high molecular weight compounds are not easily degraded by bacteria⁶. The most widely used techniques to treat water soluble organic pollutants are electrochemical oxidation⁶, photocatalytic degradation⁷⁻⁹ and Fenton degradation¹⁰⁻¹². It has been reported that due to effective electron transfer from the visible light-excited dyes into Fe³⁺, which leads to regeneration of Fe²⁺ and an easy cycle of Fe³⁺/Fe²⁺, much faster degradation and mineralization of various dyes have been achieved in the photo-Fenton reaction under visible light irradiation, comparing with the Fenton reaction in the dark^{10,11,13-15}.

Recently, several reports have been published concerning degradation/decolourization of malachite green¹⁶⁻²². Many of them discussed the potential degradation route of malachite green molecules during the course of photo-Fenton reaction. In our previous study, we have discussed the photocatalytic degradation behaviour of malachite green using TiO₂ photocatalyst²³. In this study, we will discuss some undisclosed features of kinetics of malachite green- Fenton's reagent interactions. The aim of this study is to degrade malachite green using Fenton's reagent assisted by inexpensive visible light. In this report, we will illustrate the degradation performance in terms of first order kinetics and percent degradation. We will explain the effect of different components of Fenton's reagent, pH, malachite green concentration and temperature in presence and in absence of visible light.

EXPERIMENTAL

All of the chemicals were of analytical grade supplied by Merck (Germany). The electronic spectra were recorded by Shimadzu (model-160) UV-visible recording spectrometer. The concentration of malachite green (MG) molecules was determined from the spectra at 617 nm. The solutions were photolyzed using UV (320 nm) and visible (halogen lamp, 500 W) light source. When visible light source was used, a UV filter was employed to eliminate UV fraction from the visible light. The experiments were carried out under aerobic and thermostatic condition in a glass reactor where the light source was positioned 25 cm apart from the reactor. A water bath was used to maintain temperature during photolysis,

which was equipped with continuous water flow system. In order to monitor the effect of photolysis, 400 mL of reaction mixture was prepared and was equally divided into two parts placing into two similar reactors. One reactor was kept in dark and another one was placed in the photolysis reactor where approximately 10 cm² area of the reactor exposed to the light source. The solutions were prepared by taking requisite amounts of malachite green and Fe₂(SO₄)₃. The reaction was initiated by adding desired amount of hydrogen peroxide. The pH of the solutions was controlled either by using dilute HCl or by using dilute NaOH. In order to monitor the change in UV-visible spectra or concentration of malachite green molecules, 2 mL of the reaction mixture was withdrawn with a regular interval from the reactor and after measuring the spectra, the test solution (2 mL) was returned to the reactor as soon as possible to maintain the constancy of the volume of the reaction mixture in the reactor.

RESULTS AND DISCUSSION

Malachite green-Fe³⁺ interaction and effect of pH:

Malachite green (MG) is a cationic dye (Fig. 1), which exhibits maximum absorption in the UV-visible absorption spectrum at 617 nm. This dye has methyl amine groups, thus the potential malachite green-Fe³⁺/Fe²⁺ interactions were investigated prior to monitoring of Fenton's effect. It has been observed that when Fe₂(SO₄)₃ was added to malachite green solution at 0.5-2.0 molar ratio, no change in the absorption spectrum was observed even after several days. The spectra of malachite green solutions were also recorded in presence of Fe(NO₃)₃ or FeCl₃ instead of Fe₂(SO₄)₃, at different pH but no observable complexation was noticed. This indicates that structure of malachite green was stable with all the Fe(III) systems. Fig. 2 shows the dependency of decolourization of malachite green molecules on pH at

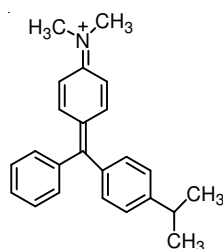


Fig. 1. Molecular structure of malachite green

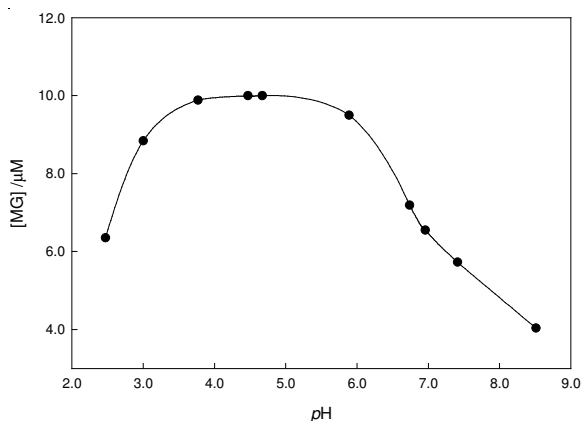


Fig. 2. Influence of pH on decolourization of malachite green molecules (10 μM) at 617 nm

617 nm. The Fenton and photo-Fenton reactions are strongly pH dependent. The pH value controls the generation of hydroxyl radicals and thus the oxidation efficiency²³. At lower pH conditions (pH < 3.0), reaction is retarded by three ways; (i) hydrogen peroxide becomes stable because of oxonium ion (H₃O₂⁺) formation, which severely reduce its reactivity with ferric/ferrous ion, (ii) some complex species, such as [Fe(H₂O)₆]³⁺ and [Fe(H₂O)₆]²⁺ formed in this pH range hinders the catalytic regeneration of Fe(II)/Fe(III) species and (iii) the scavenging effect of the ·OH by H⁺ is enhanced in this pH range²². All these facts consequently should lower the degradation efficiency of malachite green molecules at sufficiently acidic condition. Meanwhile, at pH above 3.3, the rate of degradation of organic molecules should be decreased because of precipitation of Fe(III) as hydroxide. Under this concern, before applying Fenton's reagent to the reaction system, the stability of the UV-visible spectrum was checked at variable pH. However, the maximum active colour of malachite green molecules was noticed in the pH range between 3.8 and 5.9 as shown in Fig. 2. Beyond this pH range, malachite green molecules might have changed its structural geometry, which was reflected as auto-decolourization of the malachite green molecules. Such an unusual decolourization thus attributed a bar to measure the absolute concentration of malachite green beyond the said pH range. Therefore, this observation made us narrow to evaluate the degradation performance in a wide range of pH. Hence, pH 3.8 is selected to explore the degradation behaviour of malachite green throughout the whole study.

Effect of irradiation: Fig. 3 shows the concentration changes of malachite green molecules under different conditions. The change of absorption spectrum took place during degradation of malachite green molecules by Fenton's and photo-Fenton processes. The N-demethylation of the malachite green molecule and the cleavage of the conjugated structure forming benzophenone derivatives (BPD) have been described as the main photodegradation mechanisms of malachite green in many different photooxidative processes¹⁷. In the consecutive pathway of Fenton and photo-Fenton degradation of malachite green molecules, several intermediates are generated which are finally mineralized due to the action of hydroxy and perhydroxy radicals^{19,24-28}.

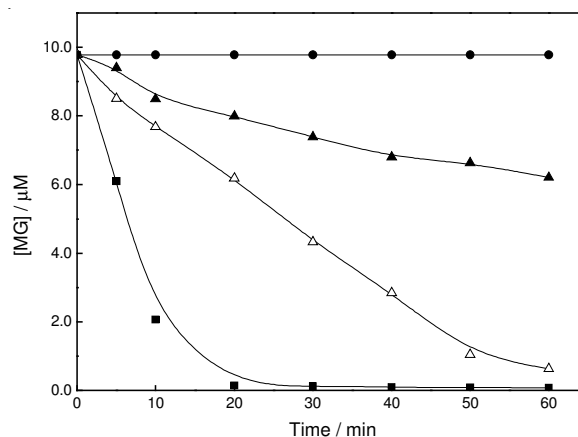
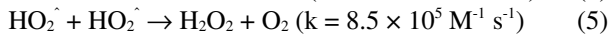
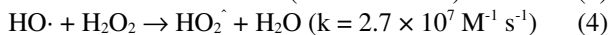
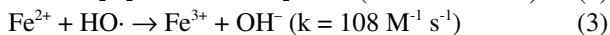
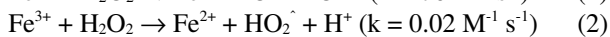
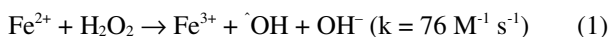


Fig. 3. Influence of irradiation on degradation of malachite green. (●) UV (absence of Fenton's reagent); (▲) dark; (Δ) Visible light; (■) 320 nm UV. [MG] = 10 μM, [Fe(III)] = 60 μM and [H₂O₂] = 235 μM, pH = 3.8, reaction time = 1 h, 29 °C

The mechanism of Fenton's oxidation process is established, which is reported in the literature¹³



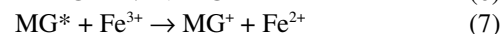
Malachite green molecules are degraded rapidly since the catalytic system ($\text{H}_2\text{O}_2 + \text{Fe(II)/Fe(III)}$) persistently generates oxidizing radicals and the rapid degradation is more pronounced in presence of photons. Table-1 summarizes the experimental results under different irradiation conditions using similar chemical environment. In the absence of Fenton's reagent, even in the presence of UV radiation, malachite green decolourization/degradation was not noticed. When Fenton's reagent was applied, the absorption peak at 617 nm was diminished and finally disappeared indicating the degradation of malachite green molecules. No new absorption band appeared both in the visible and UV region especially band for any aromatic moiety and $\text{Fe}^{2+}/\text{Fe}^{3+}$ complexes. The concentration of malachite green molecules decayed exponentially as like as a first order reaction therefore the relative catalytic reduction has been explained in terms of first order reactions in this report. Here, the rate constant (k) was calculated on the assumption that the concentration of malachite green (C) expresses a first order reaction, *i.e.*, $C = C_0 \exp(-kt)$, where C_0 is the initial concentration of malachite green and ' t ' is time (min). The reduction performance is therefore discussed as in terms of k_d (dark), k_v (visible) and k_{uv} (UV). A maximum rate constant (k) was obtained in presence of UV irradiation ($49.82 \times 10^{-3} \text{ min}^{-1}$) followed by visible light irradiation $24.26 \times 10^{-3} \text{ min}^{-1}$ and the minimum effect was obtained in the dark ($7.21 \times 10^{-3} \text{ min}^{-1}$) under same experimental condition as shown in Fig. 3. In the dark, only 15.48 % degradation was obtained, which was increased to 93.53 and 99.9 % in presence of visible and UV radiation, respectively at 29 °C. This results indicates that the degradation efficiency was decreased in the order of UV > visible > dark.

TABLE-1
INFLUENCE OF ON FENTON DEGRADATION OF
MALACHITE GREEN (MG) MOLECULES

Oxidation process	$k \times 10^{-3}$ (min^{-1})	$t_{1/2}$ (min)	Degradation (%)
Fenton process in dark	7.21	96.11	15.48
Fenton process in visible light	24.26	28.56	93.53
Fenton process in UV (320nm)	49.82	13.91	99.90

[MG] = 10 μM , [Fe(III)] = 60 μM and [H₂O₂] = 235 μM , pH = 3.8,
Reaction time = 60 min, 29 °C

The accelerated reduction of malachite green molecules in presence of visible light can be explained the by photo excitation mechanism as discussed in reference^{29,30}. The ferrous ions are oxidized to ferric ions to generate oxidizing species hydroxyl radicals [reaction (1)]. Therefore a robust catalytic effect is attained if the regeneration of Fe(II) species can be accelerated. Because of long π -conjugation, malachite green molecules were probably able to be oxidized by transferring one electron to Fe(III) followed by photo-excitation to generate adequate Fe(II) as per the following equations 6-7.



Therefore, because of dynamic cycle $\text{Fe(II)} \rightarrow \text{Fe(III)} \rightarrow \text{Fe(II)}$, substantial hydroxyl radical were produced in presence of visible light by increasing the degradation rate.

Almost 100 % degradation of malachite green molecules was attained in presence of UV irradiation within 1 h. At pH 3.8, a part of ferrous iron would exist as the form of Fe(OH)^{2+} whose photolysis under UV illumination could directly produce $\cdot\text{OH}$ radicals and Fe^{2+} .



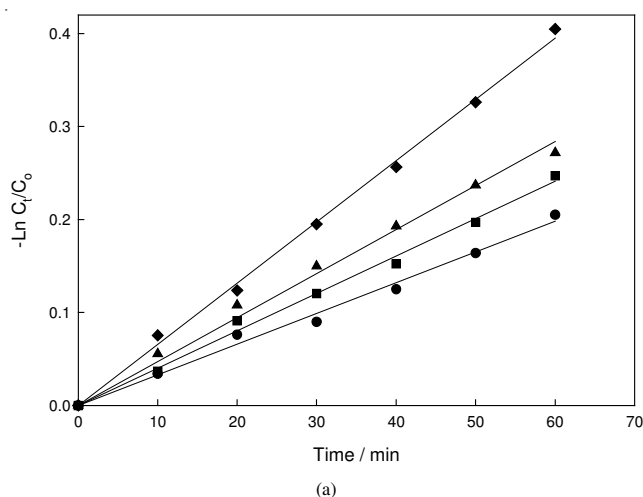
Moreover, UV radiation can produce hydroxyl radicals by homolytic fission of hydrogen peroxide, which must have strengthen the degradation process^{26,28}.



In presence of UV, all of the reactions (6-9) contributed to attain fast degradation of malachite green molecules. However, the use of UV radiation is cost effective. In order to minimize the cost, the use of inexpensive visible light is advisable. Therefore, the rest of the study has been focused on the use of visible light source.

Influence of H₂O₂, Fe(III) and malachite green concentration: According to Fenton mechanism, two most inevitable components of dye degradation are Fe(II)/Fe(III) and H₂O₂. In the catalytic pathway of degradation, Fe(II) and Fe(III) species are recycled as $\text{Fe(II)} \rightarrow \text{Fe(III)} \rightarrow \text{Fe(II)}$ with the action of H₂O₂. Therefore, the exploration of degradation of organic compounds at variable Fe(II)/Fe(III) and H₂O₂ concentrations reserves great importance.

Fig. 4 shows the effect of H₂O₂ concentration on degradation rate at pH 3.8 when 10 μM malachite green was employed for degradation in presence of 40 μM Fe(III) under irradiation and non-irradiation conditions. The apparent rate constant (both k_d and k_v) was increased with the increase of H₂O₂ concentration. However, the effect of H₂O₂ concentration in dark attained a steady state at 94-282 μM range though the photolysis rate (k_v) was increased almost linearly. Further increase of H₂O₂ from this concentration, k_d was significantly increased in dark like k_v , suggesting the involvement of hydrogen peroxide in the rate determining step of radical generation ($\cdot\text{OH}/\text{OOH}$).



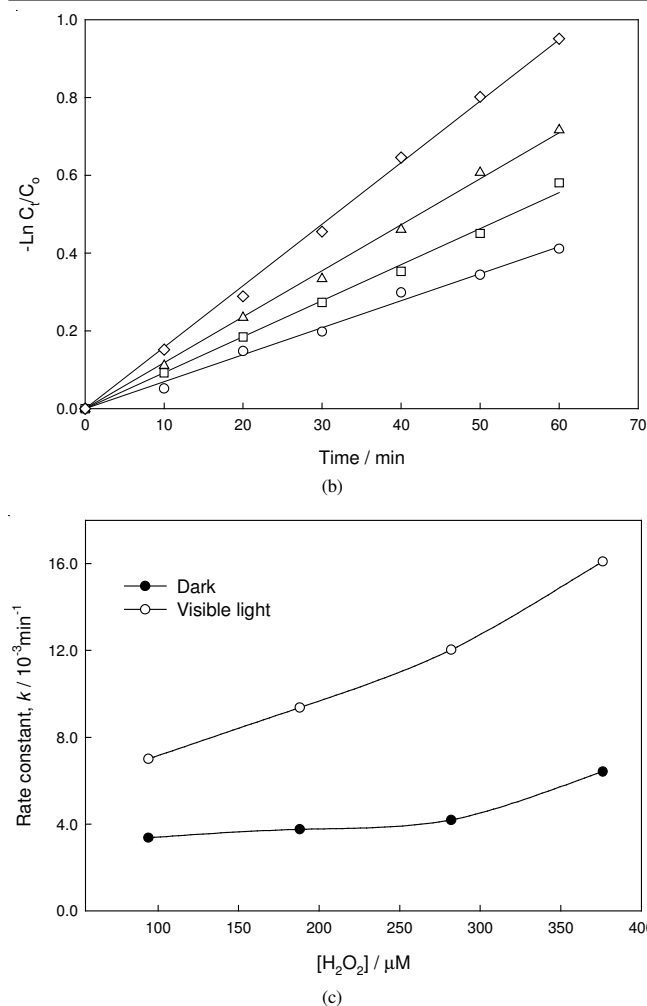


Fig. 4. First order degradation of malachite green in (a) dark (block symbol) and in (b) visible light (open symbol) at various H_2O_2 concentration. H_2O_2 concentration: (●/○) 94.0 μM ; (■/□) 188.0 μM ; (▲/△) 282.0 μM ; (◆/◇) 376.0 μM . Fig. 4c exhibits the dependency of H_2O_2 concentration on rate constant. $[MG] = 10 \mu M$, $[Fe(III)] = 40 \mu M$

Based on mechanism of Fenton's oxidation process, reaction (2) is identified as the slowest step *i.e.*, the rate determining step. However, in present case, the ratio, $[H_2O_2]/[Fe(III)] = 7.05$ (at fixed $Fe(III)$; 40 μM), was effective in attaining rapid degradation rate in the dark where the significant photo effect was also observed. In order to explore more about this ratio, we next studied the effect of $[Fe(III)]$ at a fixed 94 μM H_2O_2 concentration in the range of 20-100 μM . Fig. 5 shows the effect of $Fe(III)$ concentration at fixed H_2O_2 and malachite green concentrations. The reaction rate was increased monotonically both in dark and in presence of visible light but at 80 μM ; the degradation rate tended to be steady. This means that above $[H_2O_2]/[Fe(III)] = 1.18$ (at fixed H_2O_2 ; 94 μM), the $Fe(III)$ species had the insignificant effects on degrading malachite green molecules. Next, we explored the influence of malachite green concentration on degradation extent in the concentration range 4-10 μM with constant hydrogen peroxide and $Fe(III)$ concentration ($[H_2O_2] = 94 \mu M$ and $[Fe(III)] = 20 \mu M$) as shown in Fig. 6. The extent of degradation was decreased almost linearly with the increase of malachite green concentration in the dark. At very low malachite green concentration (10 μM), the highest photo effect was noticed. However, as the malachite green

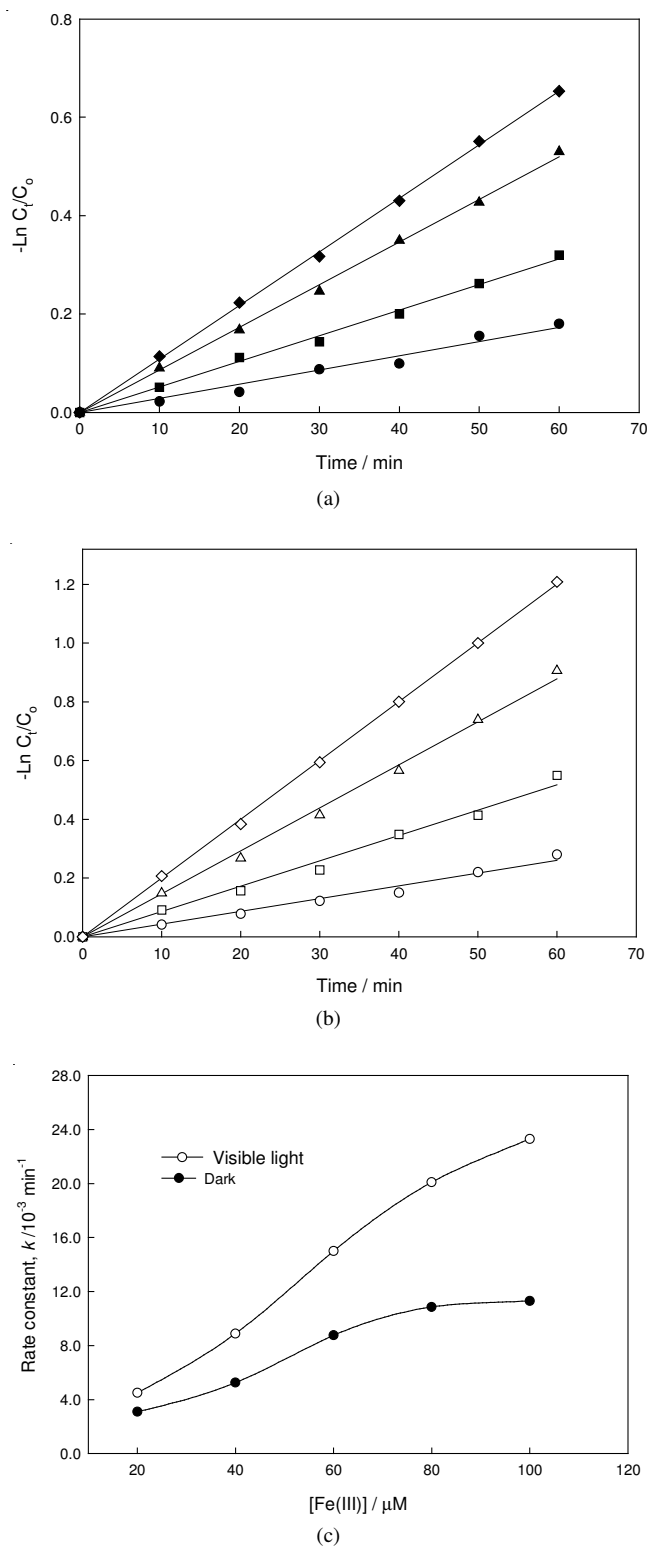


Fig. 5. First order degradation of malachite green in (a) dark and in (b) visible light at various $Fe(III)$ concentration. $Fe(III)$ concentration: (●/○) 20.0 μM ; (■/□) 40.0 μM ; (▲/△) 60.0 μM ; (◆/◇) 80.0 μM . Fig. 5c exhibits the dependency of $Fe(III)$ concentration on rate constant. $[MG] = 10 \mu M$, $[H_2O_2] = 94 \mu M$, $pH = 3.8$

concentration was increased the photo effect was decreased, which might be because of deactivation of excited malachite green molecules retarded the rate of reaction (6,7). The decrease of degradation extent with concentration suggests that degra-

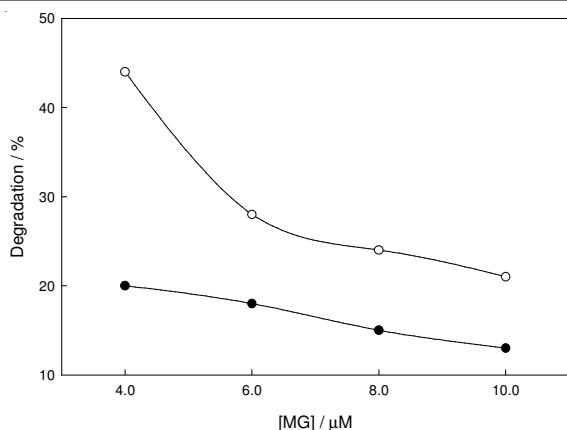


Fig. 6. Influence of malachite green concentration on extent of degradation. [Fe(III)] = 20 μM and [H₂O₂] = 94 μM, pH = 3.8, reaction time = 1 h

degradation rate was proportional to the evolution rate of hydroxyl peroxide radicals implying that activity of each of the radicals was terminated when it attacked the malachite green molecules.

Effect of temperature: Finally, we measured the effect of temperature on degradation in the dark. Fig. 7 shows the spectral changes at 45 °C and the inset shows the logarithm of rate constant on reciprocal of absolute temperature. The effect of temperature on rate constants, k_d , for malachite green degradation was studied at different temperatures of 20, 28, 36 and 45 °C under identical experimental conditions of chemicals. As the temperature was increased, the rate of degradation was increased proportionately. A maximum of 86 % degradation was attained at 45 °C within 1 h. The effect was not measured at higher than this temperature to avoid potential H₂O₂ decomposition. The increased degradation rate with temperature suggests that reaction (1) and or (2) were positively influenced by the temperature increase. However the real mechanism of temperature dependency was not clearly understood from our experiments. Since, there is a rate determining step involved (reaction 2) in the Fenton's process, we applied so called Arrhenius equation to evaluate activation energy. From the slope of the least square best fit line of the $\ln k_d$ versus reciprocal of absolute temperature as shown in the inset of Fig. 7, the estimated activation energy was 16.83 kJ mol⁻¹.

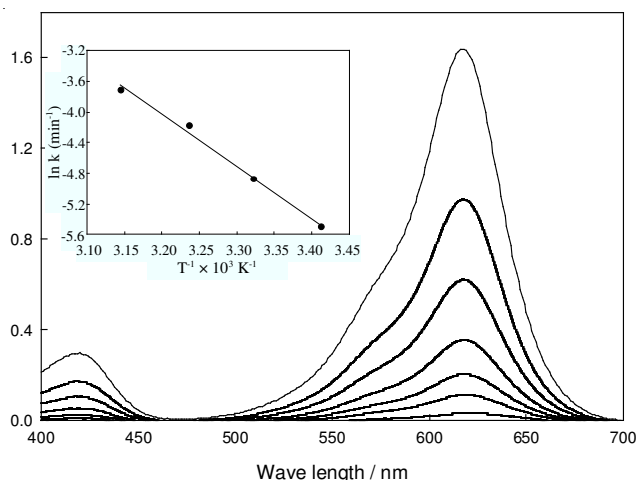


Fig. 7. Change of absorption spectra of malachite green at 45 °C recorded at 10 min intervals. The inset shows the linear fit of Arrhenius plot. [MG] = 10 μM, [Fe(III)] = 60 μM and [H₂O₂] = 235 μM, pH = 3.8

Conclusion

The maximum active colour of malachite green molecules was noticed in the pH range between 3.8 and 5.9. Using Fenton's reagent, the degradation rate was measured in a wide range of H₂O₂ and Fe(III) concentration. The UV and visible light accelerated the degradation rate by exciting the dye molecules and producing sufficient OH radicals in the order of UV > visible > dark. A rate determining step is involved in degrading malachite green molecules having activation energy of 16.83 kJ mol⁻¹.

ACKNOWLEDGEMENTS

The authors deeply remember the contribution of Prof. Abu Jafar Mahmood, Department of Chemistry, University of Dhaka, Bangladesh. The authors also acknowledged the kind helps from Dr. M. Mominul Islam of BUET, Dhaka. The University Grants Commission of Bangladesh (UGC) is acknowledged for financial assistance. The authors also admit the helps from Kumamoto University, Japan.

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