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Photooxidative degradation of Malachite Green (MG) by UV/H_2O_2: Influence of operational parameters and kinetic modeling

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Abstract

The decolorization of Malachite Oxalate Green (MG), a dye containing three groups of aryls was investigated using UV radiation in the presence of H_2O_2 in a batch photoreactor at different light intensities. H_2O_2 and UV-light showed negligible effect when they were used independently. Removal efficiency of MG was sensitive to the operational parameters such as initial concentrations of H_2O_2, MG and light intensity. The semi-logarithmic graphs of the concentrations of MG versus time were linear, suggesting pseudo-first order reaction ($k_{optimum} = 1.006\ min^{-1}$). A simple kinetic model is proposed which confirms pseudo-first order reaction.

Keywords: Advanced oxidation processes (AOPs); Photooxidation; UV/H_2O_2; Malachite Green; Kinetic model

1. Introduction

Dye pollutants from textile industry are an important source of environmental contaminations. They are generally resistant to biological degradation. It is estimated that 1–15% of the dye is lost during dyeing processes and is released into wastewater [1]. This color wastewater imposes a major problem for the industry as well as a serious threat to the environment [2].

A number of chemical and physical processes such as chemical precipitation, coagulation, electrocoagulation [3], elimination by adsorption on activated carbon and reverse osmosis are applied for color removal from textile effluents. Nevertheless these processes merely transfer the contamination from one phase to another and as a consequence producing secondary wastes and leaving the problem essentially unsolved [4,5].

Recent developments of chemical treatment of wastewater resulted in a considerable improvement in the oxidative degradation of organic compounds dissolved in aqueous media [6–9]. Among these methods called advanced oxidation processes (AOPs), homogenous chemical oxidation using ultraviolet radiation (UV) in the presence of H_2O_2 seems to be a very promising technique [10–12]. Mercury lamps emitting at 254 nm being the most commonly used in order to generate effective hydroxyl radicals. The accepted mechanism for the photolysis of H_2O_2 is the cleavage of the molecule into hydroxyl radicals, which are very powerful oxidizing species. These radicals can oxidize organic compounds (RH) producing organic radicals ($R^{\bullet}$), which are highly reactive and can undergo further

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oxidation. The possible reactions, which occur during UV/H_2O_2 process, are as follows [8,13]:

$$H_2O_2 + h\nu \rightarrow 2^{\bullet}OH \quad (1)$$

$$RH + {}^{\bullet}OH \rightarrow H_2O + R^{\bullet} \rightarrow \text{further oxidation} \quad (2)$$

The above technique has several advantages such as no sludge formation in the treatment, operation at ambient temperature and also the oxygen formed in this process is useful for aerobic biological decay process [14]. Furthermore, if the operation is carried out under suitable conditions, the final products are H_2O, CO_2 and low molecular weight aliphatic acids [15].

This paper deals with the decolorization of Malachite Green using UV/H_2O_2 technique with a particular emphasis on operational conditions and kinetic modeling.

2. Materials and methods

A cationic basic dye (Basic Green 4), Malachite Oxalate Green was obtained from Panreac Co. (Espain) and used without further purification. This dye was chosen as a model compound of triarylmethane dyes. Fig. 1 displays the structure of this dye. Hydrogen peroxide (30% w/w), NaOH and HCl were products of Merck (Germany). Solutions were prepared by dissolving requisite amount of the dye in double distilled water before each experiment.

All experiments were performed in a batch photoreactor. A UV lamp (30 W, UV-C, $\lambda_{max} = 254$ nm, manufactured by Philips, Holland) was used as a radiation source and placed above a batch photoreactor of 0.5 l volume. The incident UV-light intensity was measured by a Lux-UV-IR meter (Leybold Co.).

In each experiment, 200 ml of the dye solution was used. At certain time intervals, 5 ml of sample was withdrawn, analyzed with a UV–Vis spectrophotometer (Ultrospec 2000, Biotech Pharmacia, England) and returned back to the reactor. The decolorization of MG was measured with the above-mentioned spectrophotometer at 617 nm. Calibration plot based on Beer–Lambert's law was established by relating absorbance to the concentration.

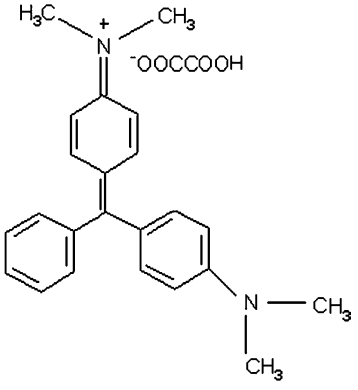


Fig. 1. Structure of MG (C.I. 42000).

3. Results and discussion

3.1. Effect of UV radiation in the presence of H_2O_2

Fig. 2 shows the concentration of MG versus time for experiments carried out with UV radiation only, hydrogen peroxide without UV radiation and UV radiation plus hydrogen peroxide. There was no observable loss of the color when the irradiation was applied in the absence of H_2O_2; the color removal was also negligible in the absence of UV radiation. The results reveal that a considerable decrease in the concentration of the dye occurs when the sample was irradiated with UV in the presence of H_2O_2. This loss is due to the formation of hydroxyl radicals, which are powerful oxidizing agents. The pH of the solution decreased at the end of the process and became slightly acidic because of the production of organic and inorganic acids [8].

3.2. Effect of the initial H_2O_2 concentration

UV irradiation of MG (10 mg l^{-1}) was carried out using different concentrations of H_2O_2. The results are shown in Fig. 3. As it can be seen, the removal efficiency increases with increasing H_2O_2 concentration, but it remained almost constant above 300 mg l^{-1}. This occurrence can be explained by the two opposing effects. With increasing H_2O_2 concentration:

(1) More hydroxyl radicals are available to attack aromatic rings and the rate of the removal increases (Eq. (1)).

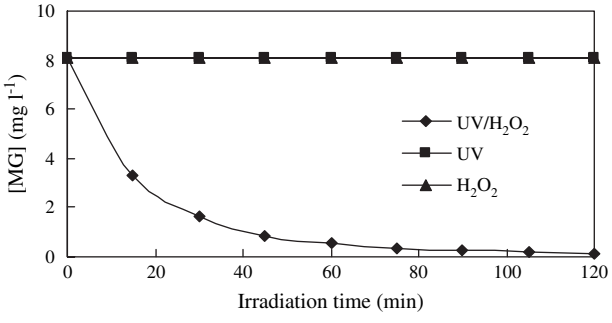


Fig. 2. Effect of UV radiation and hydrogen peroxide in oxidative decolorization of MG. $[MG]_0 = 10$ mg l^{-1}, $[H_2O_2]_0 = 50$ mg l^{-1}, $I_0 = 8.6$ W m^{-2}.

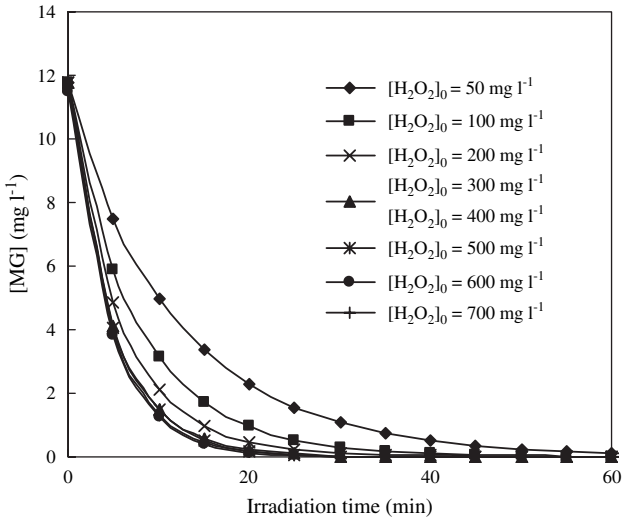


Fig. 3. Effect of initial concentration of hydrogen peroxide in oxidative decolorization of MG. $[MG]_0 = 10\ mg\ l^{-1}$, $I_0 = 8.6\ W\ m^{-2}$.

(2) Above $300\ mg\ l^{-1}$ hydroxyl radical efficiently reacts with H_2O_2 and produces $HO_2^{\bullet}$ (Eq. (3)).

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \quad (3)$$

Since $HO_2^{\bullet}$ radicals are not as reactive as $^{\bullet}OH$, enhancement of $HO_2^{\bullet}$ radicals leads to a negligible contribution in the dye destruction [16].

3.3. Effect of the initial MG concentration

The effect of dye concentration on the decolorization efficiency was monitored at different concentrations of the dye and presented in Fig. 4. It can be seen that

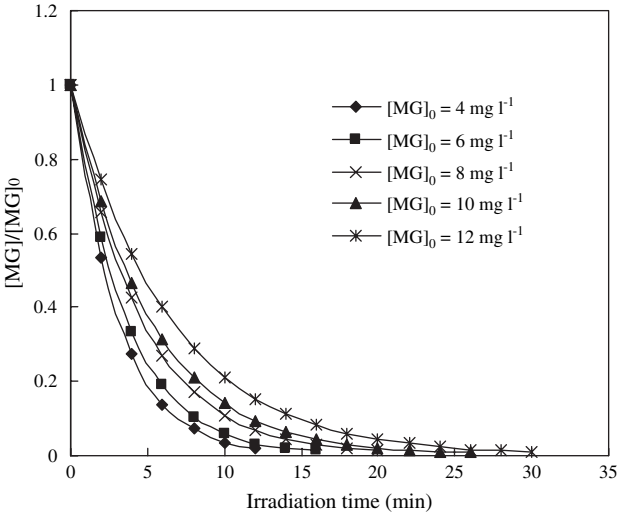


Fig. 4. Effect of initial concentration of MG in oxidative decolorization of dye. $[H_2O_2]_0 = 300\ mg\ l^{-1}$, $I_0 = 8.6\ W\ m^{-2}$.

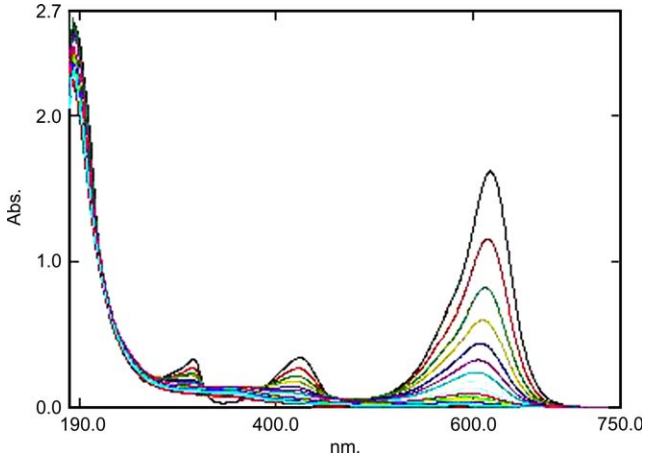
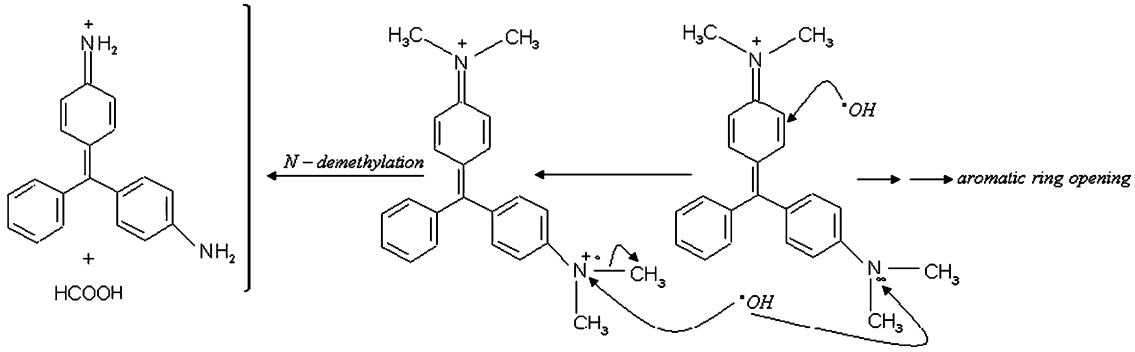


Fig. 5. Spectral changes of MG during photooxidative decolorization in the presence of H_2O_2 at 2 min intervals. $[MG]_0 = 10\ mg\ l^{-1}$, $[H_2O_2]_0 = 300\ mg\ l^{-1}$, $I_0 = 8.6\ W\ m^{-2}$.

photooxidation efficiency decreased as initial dye concentration is increased at the same concentration of H_2O_2. This can be postulated by considering that, the molar extinction coefficient of the dye at $\lambda < 260$ nm is very high, so that a rise in its concentration induces an inner filter effect and hence the solution becomes more and more impermeable to UV radiation.

3.4. Spectral changes of MG during photooxidation

Fig. 5 shows the changes in absorption spectra of MG during UV/H_2O_2 process at different irradiation times. The decrease in the absorption peak of MG at $\lambda = 617$ nm indicates a rapid degradation of the dye. Complete removal of the initial green color was observed after 20 min of irradiation. It is interesting to note from Fig. 5 that the absorption of the visible band at 617 nm decreases and a hypsochromic shift occurred simultaneously with increasing irradiation time and the maximum absorption wavelength shifts from 617 to 605 nm at 6 min of irradiation time. The hypsochromic shift process is an *N*-demethylation process [17]. With further irradiation time a new band started to form at 350 nm. It may be interpreted that poly-aromatic rings are destroyed at initial stages of the process and the produced aromatic rings display absorption in UV region, which gradually decreases by increasing irradiation time. Saquib and Muneer [2] detected the formation of benzophenone derivatives, *p*-aminobenzoic acid and aniline as intermediate reaction products resulted from reaction of a triphenylmethane dye with hydroxyl radicals. Therefore we conclude that the photooxidative degradation of MG occurs via two competitive processes: *N*-demethylation and destruction of the conjugated structure (Scheme 1).



Scheme 1. The degradation mechanism of MG with hydroxyl radicals via two competitive processes: *N*-demethylation and destruction of the conjugated structure.

3.5. Kinetic modeling

The following simplified mechanism may interpret the decolorization process of MG with $^{\bullet}OH$ in the presence of radical scavengers (S).

$$MG + {}^{\bullet}OH \xrightarrow{k_1} P \tag{4}$$

$$S_i + {}^{\bullet}OH \xrightarrow{k_i} P_i \tag{5}$$

In the above equation S_i are the scavenger molecules such as intermediates, excess H_2O_2 and $^{\bullet}OH$ or $HO_2^{\bullet}$ [18].

The corresponding kinetic equations for MG and $^{\bullet}OH$ are:

$$\frac{d[MG]}{dt} = -k_1[{}^{\bullet}OH][MG] \tag{6}$$

$$\frac{d[{}^{\bullet}OH]}{dt} = \phi I_a - k_1[{}^{\bullet}OH][MG] - \sum_i k_i[{}^{\bullet}OH][S_i] \tag{7}$$

As a consequence the steady state concentration of hydroxyl radicals can be described by Eq. (8), which is obtained by solving Eq. (7) for $[{}^{\bullet}OH]_{ss}$.

$$[{}^{\bullet}OH]_{ss} = \frac{\phi I_a}{k_1[MG] + \sum_i k_i[S_i]} \tag{8}$$

also

$$I_a = I_0 f_{H_2O_2}\left[1 - \exp\left(-2.3l(\varepsilon_{H_2O_2}[H_2O_2] + \varepsilon_{MG}[MG])\right)\right] \tag{9}$$

$$f_{H_2O_2} = \frac{\varepsilon_{H_2O_2}[H_2O_2]}{\varepsilon_{H_2O_2}[H_2O_2] + \varepsilon_{MG}[MG]} \tag{10}$$

In Eq. (9), I_0 is the incident UV-light intensity, l is the optical path length of the system, $\varepsilon_{H_2O_2}$ and ε_{MG} are the molar extinction coefficients for H_2O_2 and MG, respectively. Since MG and H_2O_2 have a high absorbance in the early stages of the process, it can be written as:

$$1 - \exp(-2.3l(\varepsilon_{H_2O_2}[H_2O_2] + \varepsilon_{MG}[MG])) \approx 1 \tag{11}$$

$$[{}^{\bullet}OH]_{ss} = \frac{\phi I_0 f_{H_2O_2}}{k_1[MG] + \sum_i k_i[S_i]} \tag{12}$$

By inserting the above expression into Eq. (7) the following overall rate law is deduced:

$$-\frac{d[MG]}{dt} = \frac{k_1 \phi I_0 f_{H_2O_2}}{k_1[MG] + \sum_i k_i[S_i]}[MG] \tag{13}$$

If the concentration of the substrate is to be high, so that $k_1[MG] \gg \sum_i k_i[S_i]$, and the overall rate expression simplifies to a zero order reaction rate:

$$-\frac{d[MG]}{dt} = \phi I_0 f_{H_2O_2} \tag{14}$$

But in the present study the concentration of MG is lower than that of H_2O_2, hence $k_1[MG] \ll \sum_i k_i[S_i]$, and the overall rate expression simplifies to a pseudo-first order reaction rate:

$$-\frac{d[MG]}{dt} = \frac{k_1 \phi I_0 f_{H_2O_2}}{\sum_i k_i[S_i]}[MG] \tag{15}$$

or

$$-\frac{d[MG]}{dt} = k_{ap}[MG] \tag{16}$$

The above equation corresponds to a first order reaction. The semi-logarithmic graphs of the concentration of MG versus time yields a straight line, indicating

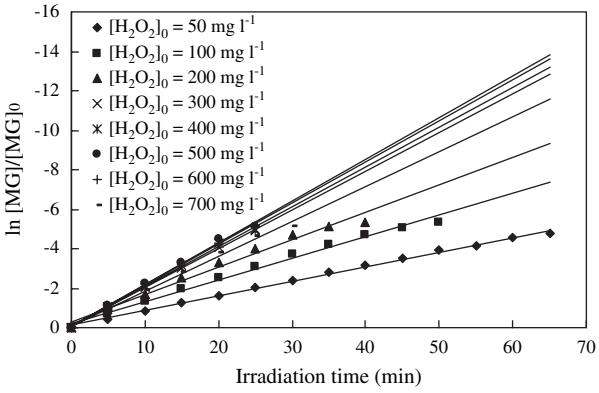


Fig. 6. Derivation of pseudo-first order rate constants of MG at different initial concentrations of H_2O_2. $[MG]_0 = 10\ mg\ l^{-1}$, $I_0 = 8.6\ W\ m^{-2}$.

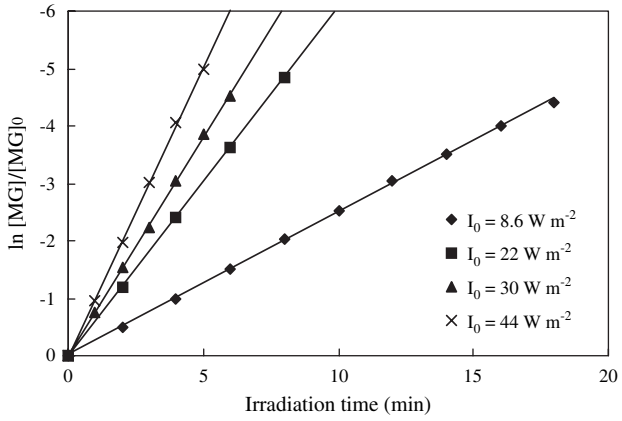


Fig. 7. Derivation of pseudo-first order rate constants of MG at different light intensities. $[MG]_0 = 10\ mg\ l^{-1}$, $[H_2O_2]_0 = 300\ mg\ l^{-1}$.

reaction of pseudo-first order. Eqs. (10) and (15) indicate that k_{ap} is a function of H_2O_2 concentration. The apparent reaction rate constants (k_{ap}) for decolorization of MG using different amounts of H_2O_2 as obtained from semi-logarithmic graphs of MG concentration versus time (Fig. 6) are given in Table 1. The results in Table 1 reveal that k_{ap} increases with increasing the amount of H_2O_2 and reaches to an almost constant value above optimum concentration. This result is in good agreement with kinetic model.

3.6. The effect of UV-light intensity

The influence of UV-light intensity on the decolorization of MG has been monitored by varying the UV-light intensities from 8.6 to 45 $W\ m^{-2}$. The results are shown in Figs. 7 and 8. It appears that with increasing the light intensity the decolorization rate increases. This increase is due to the enhanced production of hydroxyl radicals. At low UV power the rate of photolysis of H_2O_2 are limited and at high UV power more hydroxyl radicals are formed, upon the photodissociation of H_2O_2, hence decolorization rate increases.

As shown in Fig. 8, a linear relation exists between pseudo-first order reaction rates and UV light intensities, which is also in a good agreement with proposed model (Eq. (15)). These results indicate that the employed light intensities in this study are in the low range [19,20].

4. Conclusions

UV/H_2O_2 process showed to be a powerful method for decolorization of MG. The removal efficiency was sensitive to operational parameters. For decolorization of MG ($10\ mg\ l^{-1}$), an optimum dose of H_2O_2 ($300\ mg\ l^{-1}$) at the light intensity of 45 $W\ m^{-2}$ was found to give a rate constant of $1.006\ min^{-1}$, beyond the critical dose of H_2O_2 the oxidation rate reached a plateau. On the basis of proposed kinetic model pseudo-rate constant (k_{ap}) is affected with varying initial concentration of MG and H_2O_2. Pseudo-rate constant (k_{ap}) decreases as the initial concentration of MG increases but it increases with increasing the amount

Table 1
Pseudo-first order rate constants for decolorization of MG ($10\ mg\ l^{-1}$) by UV-light ($8.6\ W\ m^{-2}$) in the presence of various amounts of hydrogen peroxide

No.	$[H_2O_2]_0$ ($mg\ l^{-1}$)	k_{ap} (min^{-1})	R^2
1	50	0.0739	0.9972
2	100	0.1093	0.9909
3	200	0.1388	0.9834
4	300	0.1964	0.9990
5	400	0.2027	0.9970
6	500	0.2112	0.9945
7	600	0.2086	0.9979
8	700	0.1765	0.9946

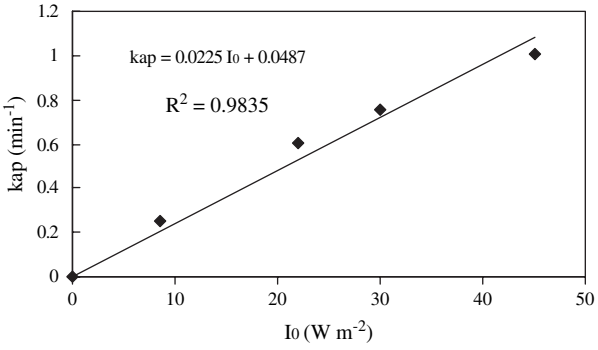


Fig. 8. Relation between light intensity and pseudo-first order reaction rate constant.

of H_2O_2 and remains almost constant above an optimum value. These findings are in a very good agreement with kinetic model.

Acknowledgements

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