

**PHOTODEGRADATION OF MALACHITE GREEN OXALATE (MGO) BY
FENTON-LIKE AND PHOTO-FENTON-LIKE SYSTEMS**

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**DISSERTATION SUBMITTED AS PARTIAL FULFILMENT FOR THE
DEGREE OF BACHELOR OF SCIENCE HONOURS**

**INDUSTRIAL CHEMISTRY PROGRAMME
SCHOOL OF SCIENCE AND TECHNOLOGY
UNIVERSITI MALAYSIA SABAH**

2005



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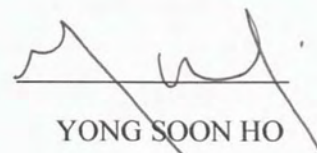
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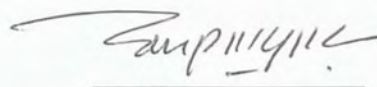


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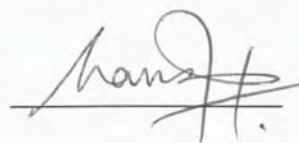
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ACKNOWLEDGEMENTS

First of all, I would like to express my gratitude to my project supervisor, Mr. Moh Pak Yan for his guidance and precious information along the progress of project I and project II in order to fulfill my qualification for Degree of Science and Technology in Industrial Chemistry.

Besides that, I would like to thank Professor Dr. Marcus Jopony as well because organized the work schedule, timetable for the progress of our final project and inform us about the essential parts of the project in class. I also not forget to thank laboratory assistant Mr. Sani and Mr. Muhin for their commitment during my laboratory work.

Lastly, I would like to thank my family, all my friends and course mates who have giving important advice and moral support to me in effort to complete this project.



ABSTRACT

The effect of operational parameters, namely Fe^{3+} and UV light on the degradation of MGO in Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) and photo-Fenton-like (UV/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2$) systems were investigated. The Fe^{3+} concentration was varied to give different $\text{Fe}^{3+}:\text{H}_2\text{O}_2$ ratio (1:20, 1:40, 1:100, 1:200 and 1:400). The degradation of MGO was followed by measuring the absorbance at $\lambda=365$ nm. The results showed that higher concentration of Fe^{3+} gives the higher degradation of MGO. On the other $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ system showed higher degradation degree if compared to $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system.



ABSTRAK

Kesan parameter operasi iaitu Fe^{3+} dan cahaya UV telah diuji terhadap tahap degradasi bagi MGO dengan menggunakan sistem Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) dan system foto-Fenton-like (UV/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2$). Pelbagai kepekatan Fe^{3+} telah digunakan untuk memberikan nisbah $\text{Fe}^{3+} : \text{H}_2\text{O}_2$ yang berbeza (1:20, 1:40, 1:100, 1:200 dan 1:400). Degradasi MGO adalah diikuti dengan pengukuran nilai penyerapannya pada $\lambda=365$ nm. Keputusan menunjukkan bahawa semakin tinggi kepekatan ion Fe^{3+} , semakin tinggi penguraian dan pelunturan larutan MGO. Dalam pada itu, sistem $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ menunjukkan kesan penguraian yang lebih tinggi jika dibandingkan dengan sistem $\text{Fe}^{3+}/\text{H}_2\text{O}_2$.



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LIST OF SYMBOLS, UNITS AND ABBREVIATIONS

MGO	Malachite Green oxalate
%	percentage
AOPs	advanced oxidation processes
$\text{Fe}^{3+}/\text{H}_2\text{O}_2$	Fenton-like system
$\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$	photo-Fenton-like system
Fe^{3+}	ferric ion
H_2O_2	hydrogen peroxide
$\cdot\text{OH}$	hydroxyl radical
UV	ultra-violet light source
nm	nanometer
ml	millilitre
Abs	absorbance
$\%D_{\text{Abs}}$	percentage of degradation degree
mol/L	mole per litre
g/L	gram per litre
Kg/L	kilogram per litre
μL	micro litre
mg	milligram
λ	wavelength



CHAPTER 1

INTRODUCTION

1.1 An Overview on Treatment of Textile Wastewater

Wastewaters from textile and dye industries are highly coloured with significant amount of auxiliary chemicals. The discharge of these wastewater introduced intensive colour and toxicity to aquatic environment causing serious environmental problem (Muruganandham and Swaminathan, 2004).

Many conventional wastewater treatment methods such as flocculation by chemical reagent, activated carbon absorption and biological treatment had been used for treating the textile waste effluents but becoming ineffective or merely transfer the dye from water to solid. Hence, the advanced oxidation processes (AOPs) have been proposed in recent years as alternatives to the conventional treatment methods (Ince and Tezcanli, 1999).



Advanced oxidation processes (AOPs) is one of the chemical oxidation process that offers a highly reactive, non-specific oxidant namely hydroxyl radicals ($\bullet\text{OH}$), capable of destroying wide range of organic pollutants in water and wastewater (Kavitha and Palanivelu, 2005). Ince and Tezcanli (1999), reported that the advantages of AOPs over conventional chemical oxidation processes is due to the absence of kinetic limitations, and the generation of highly reactive free radicals, which are 10^6 to 10^9 times faster than the strongest chemical oxidant like ozone and hydrogen peroxide.

Fenton's reagent is the mixture of H_2O_2 and ferrous ion (Fe^{2+}), that able to generate hydroxyl radicals (Neyens and Baeyens, 2002). Fe^{3+} can also react with H_2O_2 in the so-called Fenton-like reaction regenerating Fe^{2+} and thus, supporting the Fenton process (Torrades *et al.*, 2003). Arslan-Alaton and Gurses (2004), stated that the reaction of H_2O_2 with ferric (Fe^{3+}) and ferrous (Fe^{2+}) iron in acidic aqueous solutions which are among the most common homogeneous systems and potential sources of hydroxyl generation.

Fenton-like reaction offer a cost effective source of hydroxyl radicals and it is easy to operate and maintain if compare to the other AOPs (Neamtu *et al.*, 2003). According to Lee *et al.* (2003), the Fenton reaction ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and Fenton-like reaction ($\text{Fe}^{3+}/\text{excess H}_2\text{O}_2$), have been widely applied in the treatment of non-biodegradable wastewater in the field of advanced oxidation processes (AOPs). However, Fenton systems (Fenton reaction and Fenton-like reaction) have two limitations, there are large production of iron sludge and slow reduction of ferric ion



by H_2O_2 . So, illumination of the system by UV-visible was suggested to overcome the limitations of the Fenton system.

Photo-Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$) and Photo-Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$) systems is one of the advanced oxidation processes (AOPs), where iron salts serves as photocatalysts and H_2O_2 as an oxidizing agent (Ghaly *et al.*, 2001). Fe^{3+} catalyses hydrogen peroxide decomposition. In the absence of light (Fenton-like system) and of complexing ligands other than water, the mechanism of H_2O_2 decomposition in acidic solution involves the formation of hydroperoxyl radicals ($\text{HO}_2\cdot$) and $\cdot\text{OH}$. Upon irradiation by UV (photo-Fenton-like system), Fe^{3+} can promote the photooxidation of organic compounds. The positive effect of UV irradiation on the degradation rate include the photolysis of Fe^{3+} that leading to the production of $\cdot\text{OH}$ and Fe^{2+} (Arslan-Alaton and Gurses, 2004).

1.2 Objective

Fenton-like system can treat the effluents from textile industry with effectively. Hence the objectives of my study are:

- a. To evaluate the effect of Fe^{3+} towards the degradation of Malachite Green Oxalate (MGO) of Fenton-like and Photo-Fenton-like systems.
- b. To compare the effect of UV towards the degradation of Malachite Green Oxalate (MGO) between Fenton-like and Photo-Fenton-like systems.



1.3 Scope of Research

The scope of my research is to examine the effect of Fe^{3+} in Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$) and Photo-Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$) systems over Malachite Green Oxalate solution (MGO), a basic dye solution. The experiment was carried out in lab-scale using a cylindrical photo-reactor (Duran's Pyrex, 400ml in capacity) with and without the presence of UV irradiation. Malachite Green Oxalate M6880/Sigma solution was used as a simulated textile dyeing effluent. The performances of the oxidative system in various Fe^{3+} concentration were evaluated by UV-Visible analysis of the samples withdrawn from the reservoir periodically. Graphs of the degradation degree against reaction time and also \ln Absorption against reaction time will be plotted to evaluate the degree of the degradation and order of the chemical reactions.



CHAPTER 2

LITERATURE REVIEW

2.1 Colour

White light can be separated into its various colour using a glass prism by the reflection process. Light of different colours travels at different speeds through the prism. Violet light travels most slowly and has the largest angle of deviation relative to the beam incident on the prism face, whereas red light travels the faster and has the smaller angle of deviation (Hollas, 2002).

The electromagnetic spectrum extends far beyond both the red and violet, and the various regions of the spectrum are characterized by their wavelength. The visible region constitutes only a relatively minor portion of the electromagnetic spectrum. The extent of the visible region of the electromagnetic spectrum is approximately 350 nm (violet) to 750 nm (red). The reason why the visible region assumes such great importance is because the human eyes is uniquely sensitive to it (Hollas, 2002).

Gases, liquids or solids can completely, partly, or not at all absorb or reflect the light. When a coloured object is illuminated by white light (which constituted by violet, indigo, blue, green, yellow, orange and red lights), certain lights with the particular wavelengths will be absorbed and the reflected lights that represent the colour of the object will reach the retina of a normal eye and finally observed by human as a coloured object. *White object* referred to the object that reflect all visible light in a diffuse way and with complete reflectance. Contrary, if the object absorbs all visible light, also known as white light, we recognize it as *black object* (Moh, 2002).

Collier and Helen (1999) stated that the Munsell Colour System categorizes colour on the basis of three attributes, there are *hue, value, and chroma*. Hue is the quality distinguishes one colour from another, such as red from blue or yellow from green. The terms red, blue, green, yellow, and so forth are hue names. Value is the lightness and darkness of a coloured surface. The value designation ranges from one (very dark) to nine (very light), while the nonexistent absolute black and absolute white are zero and ten, respectively. Chroma is the strength of the colour. It is also designated by number. A high chroma colour is usually referred to as a bright colour, and a low chroma may be described as dull.

2.1.1 Photon Absorption By Molecules

A qualitative picture of the absorption of radiation can be obtained by considering the absorption of light in the visible region. We “See” things because they transmit or reflect only a portion of the light in the visible region. When white light, which contains the whole spectrum of wavelengths in the visible region is passed through an



object, the object will absorb certain of the wavelengths, leaving the unabsorbed wavelengths to be transmitted. These transmitted wavelengths will be seen as a colour (Christian, 1994)

A molecule can absorb light energy whether in rotational transition, electronic transition or vibrational transition. Rotational and vibrational transitions are associated with a polyatomic molecule with covalent bonds. The overall energy associated with a molecule is given by (Christine, 1994):

$$\text{Internal energy, } E = E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{electronic}} \quad (2.1)$$

Definite amounts of these three types of energies are absorbed by a molecule. This is called quantized energy. By absorption of energy, the molecule move from ground state (E_0) to excited state (E_1) (Christian, 1994). Figure 2.1 shows the excitation process of a molecule from ground state to excited state.

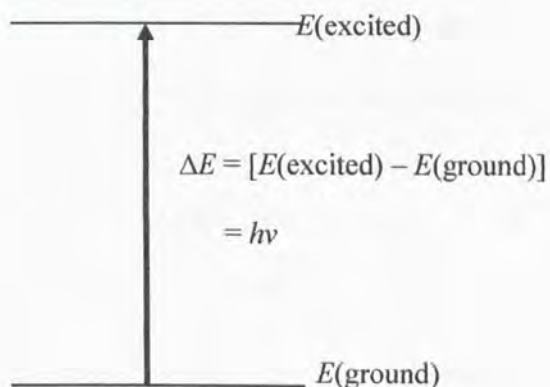


Figure 2.1 The excitation process

The colour appearance of dyes and pigments are basically explainable by the theory of photon absorption in the visible and ultraviolet region, which is a field of quantum chemistry study. A molecule in its ground (unexcited) state will absorb a quantum of light energy known as photon, and transferred to a higher energy state so called the excited state (Suppan, 1994; Harvey, 2000). Generally, the most probable transition is from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The energy differences between electronic levels in most molecules vary from 125 to 650 kJ/mole (Pavia *et al.*, 1996).

Pavia *et al.*, (1996) stated that for most molecules, the lowest-energy occupied molecular orbitals are the σ bonds. The π orbitals lie at somewhat higher energy levels, and orbitals that hold unshared pairs, the nonbonding (n) orbitals, lie at even higher energies. The occupied, or anti-bonding orbitals (π^* and σ^*), are the orbitals of highest energy. Figure 2.2 shows a typical progression of electronic energy levels.

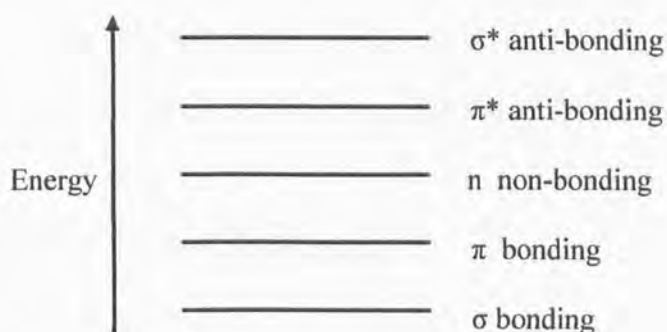


Figure 2.2 Electronic energy levels and transitions

In general, colourless organic substances absorb radiation in the ultraviolet, relatively high energies being required to raise the molecule from the ground state E_0

to the excited state E_1 . When ultraviolet or visible radiation is absorbed, an n, σ or π electron is (in ground state) promoted to occupy an empty π^* and σ^* anti-bonding orbital (in excited state), the wavelength of the absorbed energy is equal to the energy difference, ΔE (Moh, 2002).

According to Quantum theory, light is composed of discrete particles called quanta or photons that carry amount of energy E . The relationship between wavelength and frequency can be depicted by the following formula (Atkins, 2001; Anderson, 1994):

$$\lambda\nu = c \text{ (In vacuum)} \quad (2.2)$$

Let energy transformation, $\Delta E = E_1 - E_0$, then,

$$= h\nu \quad (2.3)$$

$$= hc / \lambda \quad (2.4)$$

Where E_1 is the energy of the higher state and E_0 the energy of the lower state. λ resembles the wavelength of the absorbed radiation, c is the velocity of light ($3.0 \times 10^8 \text{ ms}^{-1}$), ν is the frequency and h represented the Plank's constant ($6.63 \times 10^{-34} \text{ Js}$).

2.1.2 Spectroscopy: UV-visible Absorption

The spectroscopy of UV-visible absorptions of an organic compound is related with the chemical bond and substituent. Interpretation of the information provided by UV-visible spectra, Infrared spectra (IR) and Nucleus Magnetic Resonance spectra



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