EFFECT OF Fe²⁺ CONCENTRATION ON DEGRADATION OF MALACHITE GREEN OXALATE AND NAPHTHOL BLUE BLACK BY PHOTO-FENTON SYSTEM

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2005

I declare that this thesis is the result of my own research except as citied in references. This thesis has not been accepted for any degree and is not concurrently submitted in candidature of any degree.

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ABSTRACT

The effects of Fe²⁺ concentration on photo-degradation of MGO and NBB by photo-Fenton system (Fe²⁺/H₂O₂/UV) have been investigated. The experiment was conducted in a 400 mL cylindrical photo-reactor and the change in dyes concentration were monitored by measuring absorbance spectrophotometrically at $\lambda = 620$ nm and at $\lambda = 618$ nm, respectively. Results indicate that the degradation increased with Fe²⁺ concentration. Comparatively, the degree of NBB degradation was higher than MGO. The highest degradation degree of NBB was obtained at 85.1% while MGO achieved the highest degree of degradation at 74.8%.



ABSTRAK

Kesan kepekatan Fe²⁺ dalam foto-degradasi MGO dan NBB oleh sistem foto-Fenton (Fe²⁺/H₂O₂/UV) telah dikaji. Experimen dijalankan dengan menggunakan 400 mL reactor-foto berbentuk silinder dan perubahan kepekatan pewarna dianalisis secara spektrofotometri dengan mengukur nilai penyerapan masing-masing pada $\lambda = 620$ nm dan pada $\lambda = 618$ nm. Keputusan kajian menunjukkan degradasi meningkat dengan kepekatan Fe²⁺. Secara perbandingan, NBB dinyahwarnakan dengan lebih berkesan daripada MGO. NBB memperolehi peratus degradasi tertinggi pada 85.1% manakala MGO mencapai peratus degradasi tertinggi pada 74.8%.



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LIST OF SYMBOLS AND ABBREVIATIONS

H_2O_2	Hydrogen peroxide		
MGO	Malachite Green Oxalate		
NBB	Naphthol Blue Black		
Fe ²⁺	Ferrous ion		
Fe ³⁺	Ferric ion		
UV-Vis	Ultraviolet-Visible		
D _{Abs}	Degradation Degree		
λ	Wavelength		
λ_{max}	Maximum wavelength		
3	Molar absorptivity		
R ²	Scatter plot regression coefficient		
k	Rate constant		
v	Frequency		
Т	Transmittance		
Р	Intensity of Light		
с	Velocity of Light $(3.0 \times 10^8 \text{ ms}^{-1})$		
E	Energy		
h	Planck constant (6.63 ×10 ⁻³⁴ Js)		



CHAPTER 1

INTRODUCTION

1.1 An Overview of the Textile Dyes Wastewater Treatment

The textile industry is one of the largest industries in Malaysia which grows drastically from a traditional based to a modern based industry. Yet, it is one of the major polluters to the environment due to the usage of dyes (Azmi *et al.*, 1998). Over 700,000 tons of approximately 10,000 types of dyes and pigments are produced annually worldwide, in which about 20% are assumed to be discharged as industrial effluent during the textile dyeing processes (Azbar *et al.*, 2003).

Effluents from the dyeing and finishing processes are known to contain strong colour; high amounts of surfactants, heavy metals and chlorinated organic; dissolved solids; fluctuating temperature; high and unstable pH; and high chemical oxygen demand (COD) (Arslan and Balcioğlu, 1999; Cisneros *et al.*, 2002). Hence, textile waste effluents are one of the wastewater that is not easily amenable by chemical or biological treatment (Moh *et al.*, 2003). In addition, the problem of coloured effluent has been a major challenge and an integral part of textile effluent treatment as a result



of stricter environmental regulations (Azbar *et al.*, 2003). Conventional wastewater treatment techniques (biological, physical and chemical processes) such as flocculation by chemical reagent and activated carbon adsorption are insufficient and ineffective, for the fact that complete removal of colour, dissolved solids, and refractory chemicals is not possible by this method, unless accompanied by advanced treatment techniques. The development of new treatment process, which is more effective in eliminating the dyes from wastewater, is necessary in term of decolourization as well as mineralization (Ince and Tezcanli, 1999; Moh *et al.*, 2003).

The chemical limitations of conventional chemical oxidation techniques can be overcome by the advanced oxidation processes (AOPs). AOPs have been successful in degrading most of the organic compounds present in polluted water. In AOP, the hydroxyl radicals (•OH) are generated in solution and responsible for the oxidation and mineralization of the organic pollutants to water and carbon dioxide. Various advanced oxidation processes such as O_3/UV , O_3/H_2O_2 , UV/H_2O_2 and Fenton's reagent (Fe²⁺/H₂O₂) has been applied in wastewater treatment (Ghaly *et al.*, 2000). Among these processes, Fenton's reagent has given a promising and attractive treatment method for the effective decolourization and degradation of dyes (Malik and Saha, 2002). However, the Fenton reaction has two limitations, large production of iron sludge and slow reduction of ferric ions by H₂O₂ in their application (Lee *et al.*, 2002).

The photochemical advanced oxidation processes including photolysis and photocatalysis are gaining increasing importance for degradation of most of the organic pollutants (Ghaly *et al.*, 2000). The photo-Fenton process ($Fe^{2+}/H_2O_2/UV$) involves the hydroxyl radical formation in the reaction mixture through photolysis of



hydrogen peroxide (H₂O₂/UV) and Fenton reaction (Fe²⁺/H₂O₂) (Shyh *et al.*, 1999). This illumination of Fenton system by UV-Vis was suggested to overcome the limitations of Fenton reaction (Lee *et al.*, 2002). Photo-Fenton process represents an efficient and cheap method for wastewater treatment, and produces more hydroxyl radicals in comparison with Fe²⁺/H₂O₂ or UV/H₂O₂ system, thus promoting the rate of degradation of various organic pollutants (Ghaly *et al.*, 2000). The key features of the Fenton system are believed to be its reagent conditions (i.e. concentration of Fe²⁺, Fe³⁺ and H₂O₂) and the reaction characteristics, which are the pH, temperature and the quantity of organic and inorganic constituents. Because these parameters determine the overall reaction efficiency, it is important to understand the mutual relationships between these parameters in terms of hydroxyl radical production and consumption (Neyens and Baeyens, 2002).

1.2 Objectives

The objectives of this study are:

- a. to evaluate the effects of Fe²⁺ towards the degradation of Malachite Green Oxalate and Naphtol Blue Black using photo-Fenton system (Fe²⁺/H₂O₂/UV).
- b. to compare the degradation of Malachite Green Oxalate and Naphtol Blue Black dye using photo-Fenton system.



1.3 Scope of Research

The scope of the research is to examine the effect of Fe^{2+} in the degradation of a basic dye solution and an acid dye solution using photo-Fenton system consists of Fentonreagent method with UV light ($Fe^{2+}/H_2O_2/UV$). This experiment is carried out in labscale using cylindrical photo-reactor (Duran's Pyrex, 400 mL capacity) with the presence of UV irradiation. Two types of simulated textile effluent are prepared from Malachite Green Oxalate salt and Naphtol Blue Black salt, respectively as the organic pollutant. This research has studied three main operational parameters (dye concentration, Fe^{2+} ion concentration and H_2O_2 concentration). The degradation of each dye was obtained by the analysis of samples withdrawn from the reservoir periodically by UV-Visible spectrophotometer. Graphs of Abs against reaction time and also In Abs against reaction time will be plotted to evaluate the degree of degradation and the kinetic rate order of the chemical reactions.



CHAPTER 2

LITERATURE REVIEW

2.1 Colour and Light

The visible region is a small part of the electromagnetic spectrum, and it is the region of wavelengths that can be seen by the human eye, that is, where the electromagnetic radiation (light) appears as a colour. The visible region consists of colours ranging from violet, beginning at around 380 nm, to red, ending at approximately 780 nm (Christian, 2004; Pavia *et al.*, 2001; Shugar and Ballinger, 1996).

When polychromatic light (white light), which contains the whole spectrum of wavelengths in the visible region, is passed through an object, the object will absorb certain wavelengths of the light within that range, leaving the unabsorbed wavelengths to be transmitted. These residual transmitted wavelengths will be seen as a colour. This is complementary to the absorbed colours (Pavia *et al.*, 2001; Christian, 2004; Fritz and Schenk, 1987).

Table 2.1 illustrates the relationship between the wavelength of the light absorbed by a substance and the colour perceived by an observer. These wavelengths



are taken from a study originating at the National Bureau of Standards (Ewing, 1985; Christian, 2004; Fritz and Schenk, 1987).

Absorbed Colour	Wavelength of Light Absorbed (nm)	Observed Colour
Violet	400-465	Yellow-green
Blue	465-482	Yellow
Greenish Blue	482-487	Orange
Blue-Green	487-493	Red-Orange
Bluish Green	493-498	Red
Green	498-530	Red-Purple
Yellowish Green	530-559	Reddish Purple
Yellow-Green	559-571	Purple
Greenish Yellow	571-576	Violet
Yellow	576-580	Blue
Yellowish Orange	580-587	Blue
Orange	587-597	Greenish Blue
Reddish Orange	597-617	Blue-Green
Red	617-780	Blue-Green

Table 2.1 Colours in Different Wavelength Regions

2.1.1 UV-Visible Absorption Spectroscopy

The ultraviolet, UV and visible light region extends from 200 nm to 780 nm. Beer's Law explains the relationship between the absorption of UV-Visible radiation and the concentration of the analyte in a solution (Harvey, 2000). The following equation is the common form of Beer's Law, where Absorbance, A of the solution can be obtained:

$$A = \log (P_0 / P)$$
$$= \varepsilon b l$$

(2.1)



Where,

 P_0 = Intensity of incident light (at a particular wavelength)

P = Intensity of transmitted light through a sample

b = molar concentration of absorbing species (mol/L)

l =layer thickness or length of the sample cell (cm)

The absorbance is directly proportional to the concentration. The constant, ε is called the absorptivity and is dependent on the wavelength and the nature of the absorbing species (Pavia *et al.*, 2001; Fritz and Schenk, 1987; Ewing, 1985; Christian, 2004). Beer's law valid only for low concentration of analyte. At higher concentration, individual particles of analyte no longer behave independently with each other (Harvey, 2000). The ratio P / P_0 is equivalent to transmittance, *T*, where as;

$$\log T = -A \tag{2.2}$$

Thus, the absorbance can be measured experimentally by determining the ratio of the incident to emergent intensities taking the logarithm.

2.1.2 Photon Absorption by Molecules

As a result of energy absorption in UV-Visible regions, atoms and molecules will involve in the promotion of electrons in σ , π , and n orbital, which transit from a state of low energy (ground state) to a state of higher energy (excited state) (Pavia *et al.*, 2001). The increase in energy is equal to the energy of the absorbed radiation (*hv*). The energy



of a quantum of radiation, called the photon, is related to the frequency or wavelength where:

$$\Delta E = E_{(excited)} - E_{(ground)}$$

= hv
= h(c / \lambda) (2.3)

E is the energy of the photon in ergs and *h* is Planck's constant, 6.62 X 10^{-34} joulesecond (J-s). λ is the wavelength (cm), *v* is the frequency (s⁻¹ or Hz), and *c* is the velocity of light (3 X 10^{10} cm/s). It is apparent that the shorter the wavelength or the greater the frequency, the greater the energy (Hollas, 2002; Christian, 2004; Fritz and Schenk, 1987).

The internal energy of a molecule, E_i (excluding translation energy) can be written as:

$$E_i = E_{\text{rotation}} + E_{\text{vibration}} + E_{\text{electron}}$$
(2.4)

The colour appearance of dyes and pigments are basically explainable by the theory of photon absorption in UV-Visible regions, which is a field of quantum chemistry study. The transitions that result in the photon absorption in UV-Visible region are transitions between electronic energy levels (Pavia *et al.*, 2001; Abrahart, 1977).

When an atom or molecule absorbs UV-Visible radiation, it undergoes a change in valence electron configuration. The valence electron in organic molecules and inorganic anions occupied quantized sigma bonding (σ), pi bonding (π) and non-



bonding (n) molecular orbital. There are 4 types of transitions between quantized energy levels account for molecular UV-Visible regions, as shown in Table 2.2 (Harvey, 2000):

Transition	Wavelength range (nm)	Examples
$\sigma \to \sigma^{\star}$	< 200	С–С, С–Н
$n \to \sigma^*$	160-260	H ₂ O, CH ₃ OH, CH ₃ Cl
$\pi ightarrow \pi^*$	200-500	$C=C, C=O, C=N, C\equiv C$
$n ightarrow \pi^{\star}$	250-600	C=O, C=N, N=N, N=O

Table 2.2 Types of electronic transitions, wavelength range and examples

All coloured organic compounds contain carbon-carbon double bond, which are formed by σ bond and π bond. According to Pauli Exclusion Principle, these bonds are molecular orbitals. Each orbital occupied two electrons and have opposite spin (Pavia *et al.*, 2001; Moh, 2002). As UV-Visible radiation is absorbed, σ , π or n electron (in ground state) is promoted to occupy an empty anti-bonding orbital, σ^* or π^* which occur at higher energy level. Electrons are positioned in non-bonding orbitals (n) when molecule contains lone-paired electrons of nitrogen or oxygen atom. Each of these orbitals has specific energy level. Figure 2.1 below shows the energy level diagram according to the type of molecular orbital (Moh, 2002; Suppan, 1994; Atkins, 2001):



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