# HETEROGENEOUS PHOTO-FENTON DECOLORIZATION OF ACID GREEN 25 USING LOCAL NATURAL CLAYS AND DOLOMITE BASED

## CATALYSTS

by

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## LIST OF SYMBOLS

λ	Wavelength	-
$\lambda_{max}$	Maximum absorbance wavelength	-
юн	Hydroxyl radical	-
Co	Initial concentration of dye	mg/L
Ct	Concentration of dye at specific reaction time	mg/L
R <sup>2</sup>	Coefficient of determination	-
t	Reaction time	min
Т	Temperature	°C
TOC₀	Initial concentration of TOC	mg/L
TOC	TOC concentration at specific reaction time	mg/L

### Unit

## LIST OF ABBREVIATIONS

AOPs	Advanced Oxidation Process
AG25	Acid Green 25
BET	Brunauer-Emmett-Teller
BOD	Biological oxygen demand
COD	Chemical oxygen demand
DB71	Direct Blue 71
DOE	Department of Environment
EDX	Energy Disperse X-ray
Fe-BBC	Fe-contained Bandar Baru clay
Fe-DOL	Fe-contained Dolomite
Fe-IC	Fe-contained Ipoh clay
FTIR	Fourier Transforms Infrared
НР	Hydrogen Peroxide
IC	Inorganic carbon
KBr	Potassium Bromide
RB4	Reactive Blue 4
SEM	Scanning Electron Microscopy
тос	Total organic carbon
ТС	Total carbon
UV	Ultraviolet
XRD	X-ray Diffraction

# HETEROGEN FOTO-FENTON BAGI PENYAHWARNAAN ASID HIJAU 25 MENGGUNAKAN TANAH LIAT SEMULAJADI DAN DOLOMIT SEBAGAI PEMANGKIN

#### Absrak

Dalam kerja penyelidikan ini, tiga jenis pemangkin telah dihasilkan daripada sumber mineral semulajadi sebagai sokongan pemangkin heterogen untuk penyahwarnaan pewarna Asid Green 25 (AG25) menggunakan proses Foto-Fenton dalam sistem kelompok. Fe-Ipoh tanah liat (Fe-IC), Fe-Bandar Baru tanah liat (Fe-BBC) dan Fe-Dolomit (Fe-DOL) telah berjaya disintesis dengan memegunkan ion besi berasal dari Nonahydrate nitrat ferik (Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O pada sokongan pemangkin, Ipoh tanah liat (IC), Bandar Baru tanah liat (BBC) dan Dolomit (DOL), masing-masing melalui proses peranakan. Kajian awal pada kesan suhu pengkalsinan dan tempoh masa oleh semua pemangkin ke atas penyahwarnaan AG25 telah disiasat. Keadaan terbaik penyahwarnaan AG25 diperhatikan apabila Fe-IC, Fe-BBC dan Fe-DOL dikalsinkan pada suhu 500, 300 dan 400 ° C selama 6, 4 dan 4 jam, dan dilabelkan sebagai Fe-IC500/6, Fe-BBC300/4 dan Fe0-DOL400/4, masing-masing. Ciri-ciri fizikal dan kimia pemangkin telah diuji menggunakan kaedah mikroskopi elektron pengimbas (SEM), penjerapan/penyahjerapan nitrogen dan penyerakan tenaga sinar-X (EDX), serbuk pembelauan sinar-X (XRD) dan spektroskopi inframerah transformasi Fourier (FTIR). Kesan daripada proses pengkalsinan telah menunjukkan peningkatan dalam luas kawasan permukaan pada IC, BBC dan DOL daripada 20.28, 6.96 dan 1.23 m<sup>2</sup>/g kepada 26.42, 35.44 dan 4.75 m<sup>2</sup>/g dalam Fe-IC500/6, Fe-BBC300/4 dan Fe-DOL400/4, masing-masing. Kecekapan pemangkin dalam penyahwarnaan AG25 serta kesan faktor-faktor yang mempengaruhi proses

penyahwarnaan seperti dos bagi mangkin, kepekatan awal AG25, dos bagi hidrogen peroksida (H2O2), pH dan suhu ujikaji dikaji. Dari hasil kajian eksperimen, penyahwarnaan terbaik bagi 50 ppm AG25 telah diperhatikan dalam masa 60 min tindakbalas menggunakan 1.25 g/L bagi setiapFe-IC500/6, Fe-BBC300/4 dan Fe-DOL400/4 pada suhu 30 °C dengan pH larutan 3 bagi Fe-IC500/6 dan Fe-BBC300/4 dan pH 2.5 bagi Fe-DOL400/4. Ia juga diperhatikan bahawa dos bagi H<sub>2</sub>O<sub>2</sub> yang lebih tinggi telah digunakan oleh Fe-DOL400/4 untuk mencapai kecekapan penyahwarnaan yang sama seperti Fe-IC500/6 dan Fe-BBC300/4. Pemangkin yang dihasilkan juga menunjukkan aktiviti sebagai pemangkin yang baik dengan kecekapan penyahwarnaan lebih daripada 98% telah dicapai dalam masa 60 min tindakbalas apabila diuji padapewarna Reaktif Blue 4 (RB4) dan Direct Blue 71 (DB71) di bawah keadaan operasi yang terbaik. Di samping itu, pemineralan AG25 menggunakan kaedah analisis TOC turut dikaji. Penyingkiran TOC bagi 50 ppm AG25 adalah 64%, 59% dan 50% dalam 60 min dan meningkat kepada 86%, 82.3% dan 73.2% selepas 120 min tindakbalas oleh Fe-IC500/6, Fe-BBC300/4 dan Fe-DOL400/4, masing-masing. Keputusan penggunaan semula pemangkin menunjukkan bahawa kesemua pemangkin mempunyai aktiviti sebagai pemangkin yang baik sekurang-kurangnya dalam tiga eksperimen berturut-turut. Keputusan menunjukkan bahawa proses foto-Fenton heterogen adalah satu proses yang berkesan untuk penyahwarnaan AG25 dan juga penyahwarnaan RB4 dan DB71.

# HETEROGENEOUS PHOTO-FENTON DECOLORIZATION OF ACID GREEN 25 USING LOCAL NATURAL CLAYS AND DOLOMITE BASED CATALYSTS

#### Abstract

In this research work, three different type of catalysts from natural mineral resources were developed as heterogeneous catalyst support for the decolorization of Acid Green 25 (AG25) dye using photo-Fenton process in a batch system. Fe-Ipoh clay (Fe-IC), Fe-Bandar Baru clay (Fe-BBC) and Fe-Dolomite (Fe-DOL) were successfully synthesized by immobilized iron ions derived from ferric nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O) on the catalyst support, Ipol<sub>1</sub> clav (IC), Bandar Baru clay (BBC) and Dolomite (DOL), respectively through impregnation process. Preliminary studies on effect of calcination temperature and duration of time by all catalysts on decolorization of AG25 were investigated. The best AG25 decolorization was observed when Fe-IC, Fe-BBC and Fe-DOL were calcined at 500, 300 and 400 °C for 6 h, 4 h and 4 h, and labeled as Fe-IC500/6, Fe-BBC300/4 and Fe-DOL400/4, respectively. The developed catalysts were characterized for their physical and chemical properties by scanning electron microscope (SEM), nitrogen adsorption/desorption and energy disperse X-ray (EDX), X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The effect of calcination process increased the surface area from 20.28, 6.96 and 1.23 m<sup>2</sup>/g in IC, BBC and DOL to 26.42, 35.44 and 4.75 m<sup>2</sup>/g in Fe-IC500/6, Fe-BBC300/4 and Fe-DOL400/4, respectively. The effectiveness of these catalysts in AG25 decolorization as well as the effect of factors affecting the decolorization process such as catalyst loading, initial concentration of AG25, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) dosage, pH and

reaction temperature were studied. From the results of experimental studies, the best decolorization of 50 ppm AG25 were observed in 60 min reaction time using 1.25 g/L each of Fe-IC500/6, Fe-BBC300/4 and Fe-DOL400/4 at 30 °C with solution pH of 3 in Fe-IC500/6 and Fe-BBC300/4 and 2.5 for Fe-DOL400/4. it was also observed that higher H<sub>2</sub>O<sub>2</sub> dosage was used by Fe-DOL400/4 to achieve similar decolorization efficiency as Fe-IC500/6 and Fe-BBC300/4. The developed catalysts were also demonstrated the good catalytic activity when tested on other dyes such as Reactive Blue 4 (RB4) and Direct Blue 71 (DB71) with more than 98% decolorization efficiency were achieved under the best operating conditions within 60 min reaction. Besides, the mineralization of AG25 using total organic compound (TOC) analysis was studied. The TOC removal of 50 ppm AG25 was 64%, 59% and 50% in 60 min reaction and increased to 86%, 82.3% and 73.2% after 120 min reaction by Fe-IC500/6, Fe-BBC300/4 and Fe-DOL400/4, respectively. The catalyst reusability results showed that all catalysts have a good catalytic activity at least in three consecutive experiments. The results indicated that the heterogeneous photo-Fenton process was an effective process for AG25 decolorization as well as RB4 and DB71 decolorization using dolomite. by natural clay and

#### CHAPTER ONE

#### INTRODUCTION

#### 1.0 Background

In recent decades, the situation of water for many countries has shifted from one of relative abundance to one of scarcity. Population growth, urbanization, industrialization and the expansion of irrigated agriculture are imposing rapidly growing demands and pressures on the water resources, besides contributing to the rising water pollution. Malaysia is no exception of facing this situation. In fact, water demand is increasing from year to year. From 9,543 million liters per day (MLD) of water demand in 1995 has increased to 15, 285 MLD in 2010. Furthermore, it is estimated that water demand will increase to 20, 338 MLD by the year 2020 (Department of Environment, DOE, 2010). This situation exacerbated by the dumping of wastewater generated from various activities such as commercial and industrial, agricultural activities, domestic waste and hospitals that cause reduction in availability of clean water because these types of effluent are usually discharged before treated and the waste contains numerous toxic and non-biodegradable substances that may cause environmental problems (Tekbas et al., 2008; Borhan and Ahmed, 2012). In addition, the polluted water may cause heart, neurological problem and cancer to human being. One of the manufacturing industries has been identified as an agent of river pollution is the textile industry.

Textile industry is one of the most chemically intensive industries in the world as well as the largest consumer of colorants. Almost 2,000 different chemicals

are used in the textile industry from dyes to transfer agents and it requires a great amount (Panda et al., 2011). Water used at every stage of processes, for instance to deliver the chemicals into the fabric and for washing has becomes very contaminated with chemical additive, dyes and salts which in turn pollute the environment. Furthermore, according to Han et al. (2011), over 15% especially dyes are lost in wastewater without treatment during synthesis and dyeing processes. In addition, nowadays, dyeing process uses both organic and inorganic synthetic dye that available in variety of colors and it is estimated around 10<sup>6</sup> tonne and more than 10,000 different synthetic dyes are known to be toxic and carcinogenic to aquatic animals and plants. Besides, the presence of dyes in water matric can interfere with the growth of microorganism and prevent photosynthesis in aquatic plants by absorb and reflect sunlight from entering the water which eventually led in destruction of aquatic life; indirectly threaten human life (Bouasla et al., 2010). Therefore, removal of dyes from aqueous effluent is an important environmental issue.

The challenge of dye removal from wastewater is well known because the synthetic dyes used are stable compounds and difficult to destroy by common treatments (Ramirez et al., 2007b). The common wastewater treatment processes that have been used either separately or combined with other processes to enhance the are overall treatment efficiency are biological (El-Sheikh et al., 2011), physical (Auta and Hameed, 2011) and chemical. However, these conventional wastewater treatment processes are inefficient to handle these stubborn dyes, for instance, physical methods such as liquid–liquid extraction, ion-exchange, adsorption, air or steam stripping, are ineffective on pollutants which are not readily adsorbable or

volatile, and have further disadvantages because they simply transfer the pollutants to another phase rather than destroying them (Benkli et al., 2005; Duarte et al., 2009). Other methods that are available but costly is chemical treatment and electrochemical. These high-technology processes have significant disadvantages, including incomplete metal removal, highly cost due to expensive equipment and monitoring systems, high reagent, energy and generation of toxic sludge or other waste products that require disposal. Similarly, in biological treatment methods, the treatment units tend to become large due to the slowness of the reaction. Besides, the effluent containing dyes are toxic and non-biodegradable and difficult to treat by biological processes (Daneshvar et al., 2003; Herney-Ramirez et al., 2010; Babuponnusami and Muthukumar, 2011).

Advanced Oxidation Processes (AOPs), have been attracted much attention as an alternative method most suitable for wastewater treatment. This is due to its ability to treat recalcitrant organic pollutants from different sources of wastewater and generated low or non-waste after the treatment (Bouasla et al., 2010). Besides, the advantages presented by AOPs transcend beyond just only chemical transformation of the pollutants, it also presents very attractive features such as the complete mineralization of some compounds at room temperature and pressure (Soon and Hameed, 2010). Furthermore, the generation of environmentally benign byproducts, easy to operate and low operating cost made these processes are preferred (Herney-Ramirez et al., 2010). AOPs are based on the generation of free hydroxyl radicals (HO') which are known as strong and non-selective oxidizers of the organic molecules in wastewater. In many AOPs, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) had been used as the main oxidizing agent due to its environmental friendly decomposition products of water and oxygen and easy to handle.

Among these AOPS, Fenton's reagent is particularly interesting since the reagents (Fe(II) and  $H_2O_2$ ) used are low toxicity and the chemicals are readily available at moderate cost and there is no need for special equipment. Besides, Fenton reaction is an attractive oxidation process due to simplicity of its technology (Agustina and Ang, 2012). The process involves in the reaction of ferrous ion as catalyst in acidic solution with  $H_2O_2$  to generate highly reactive 'OH as shown in Equation 1.1, which will further attack organic compounds present in the solution (Fenton, 1894; Li et al., 2006; Wu et al., 2010). The ferrous ions can be regenerated according to Equation 1.2-1.3 to keep producing HO' radicals in the system.

$$Fe^{2^+} + H_2O_2 \rightarrow Fe^{3^+} + OH + OH$$
 (1.1)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH + H^+$$
(1.2)

$$Fe-OOH^{2+} \rightarrow Fe^{2+} + HO_2^{-}$$
(1.3)

From literature pool, degradation of organic compounds using Fenton reaction was significantly increased with presence of UV light irradiation. The effectiveness of this process is attributed to the photolysis of hydrated  $Fe^{3+}$  to yield  $Fe^{2+}$  (Equation 1.4), which is faster compared to Equation 1.2-1.3. In addition, the used of UV light can help in generation of HO' since H<sub>2</sub>O<sub>2</sub> itself can undergoes photolysis to form HO' according to Equation 1.5 (Aleksic et al., 2010).

$$Fe(OH)^{2^+} + hv \rightarrow Fe^{3^+} + HO^{*}$$
(1.4)

$$H_2O_2 + hv \to 2HO' \tag{1.5}$$

Unfortunately, the homogeneous Fenton and photo-Fenton processes have shown a number of limitations such as generation of iron hydroxide sludge as the result of Fe<sup>2+</sup> precipitation which makes the process to require additional treatment steps to separate the sludge in the final effluent to be expensive to treat, labories and time consuming in order to comply with the environmental regulations Herney-Ramirez, 2010; Navalon et al., 2010). In addition, the process is only work within a narrow range of pH (pH  $\leq$ 3) which requires strong conditioning before and after treatment. Therefore, a wide range of heterogeneous catalysts was proposed as an alternative way by many researchers such as immobilized of iron ions into porous support like pillared clays (Chen and Zhu, 2007; Ayodele et al., 2012), zeolite (Hassan and Hameed, 2011b), activated carbon (Zazo et al., 2006) or iron oxide (Xue et al., 2009) to overcome the deficiencies in the homogeneous Fenton process. Among the catalyst supports that had been reported in the literature, natural clay have showed a good candidate as catalyst support due to it's low cost, abundant and non-toxic to environment as well as other natural resources such as dolomite which has shown a good catalyst in the wastewater treatment in previous literatures.

Generally, in heterogeneous Fenton process, the reactions can occur either at the surface or in the pores of the support which is slower than homogeneous catalyst as a result of diffusion resistance between the  $H_2O_2$  into the pore and 'OH radicals out of the support pores. Many researchers have been adding sodium carbonate in the preparation of the catalyst to reduce or minimize the diffusion resistance in the pore catalysts by opening the pores and increasing the surface area (Feng et al., 2006; Gaigneaux et al, 2010). Besides, an important point in the preparation of heterogeneous catalyst is the resistance of meta! species to be leached from support catalyst under the acidic and oxidant conditions in which Fenton reactions usually head. From the previous studies, impregnation method was used in the catalyst preparation and showed a good catalytic activity with the leaching of Fe ion from solid support was very low or negligible (Feng et al., 2003b; Daud et al., 2010). In addition, the catalyst also exhibited high stability and can be reused for several times without extremely decreases in the catalytic activities (Hassan and Hameed, 2011a; Wei et al., 2012). Furthermore, this method was found to be convenient and less toxic compared to other methods (Zhou, 2011).

#### 1.1 Problem Statement

The need to keep to the national water quality standard and to ensure a sustainable environment, the organic pollutants must be treated before being discharged into the environment. Thereby, the homogeneous Fenton process has been proposed and applied in the treatment of wide range of organic pollutants by many researchers. However, the process has a number of disadvantages such as difficulty of catalyst recovery due to the number of complementary steps such as sedimentation and coagulation, generation of sludge and requirement to be operated in a narrow pH range, consequently increased the cost of the homogeneous process. The usage of heterogeneous catalysts to replace the classical Fenton process has proven to be successful, especially in the areas of facilitating catalyst recovery. However, several studies have reported instability of the catalyst due to the Fe leaching from support catalyst in the course of reaction as well as the sensitivity of

the catalyst to the solution pH. Therefore, there is need to develop a heterogeneous catalyst that can be used at a wide range of pH and temperature and have high resistance of metal leaching from the catalyst support apart from a reasonable cost in terms of manufacturing and the materials used are not give a negative impact to the environment.

In the present work, Fe-Ipoh Clay (Fe-IC), Fe-Bandar Baru Clay (Fe-BBC) and Fe-Dolomite (Fe-DOL) were developed by incorporation of Fe ions into the support, Ipoh clay (IC), Bandar Baru clay (BBC) and Dolomite (DOL), respectively using impregnation process as new heterogeneous catalyst in photo-Fenton process for decolorization of non-biodegradable dye, Acid Green 25 (AG25) as a model pollutant. The influences of operating conditions on the decolorization efficiency were studied. Besides, the catalytic activity of developed catalysts were also tested on different dye pollutants such as Reactive Blue 4 (RB4) and Direct Blue 71 (DB71) under the best experimental conditions to study the catalyst ability towards different pollutants. Furthermore, the reusability of the catalyst, mineralization of the dye and the concentration of iron ions in the bulk after the treatment were evaluated.

#### 1.2 Research Objectives

In this study, the heterogeneous Fenton process is used on decolorization of AG25 using photo-Fenton reaction. The main objectives of this research are to:

- a) Synthesis of catalysts for decolorization and mineralization of AG25 under photo-Fenton oxidation process.
- b) Characterize the prepared catalyst for their physical and chemical properties.

- c) Study the effect of calcination temperature and duration of time by all catalysts against decolorization of AG25.
- d) Study the influence of operating conditions such as catalyst loading, initial concentration of dye and H<sub>2</sub>O<sub>2</sub>, initial pH and reaction temperature for the decolorization of AG25 in batch system.
- e) Study the leaching and reusability of the developed catalysts.

#### 1.3 Scope of study

The scope of this research study covered the synthesis of catalysts by incorporation of iron into support catalysts by impregnation method and screening of the best calcination temperature and duration of time, catalyst characterization and testing of activity on decolorization of AG25. The synthesized catalyst at the best calcination temperature and duration of time was characterized using surface area analyzer, energy dispersive x-ray (EDX), x-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). After the preliminary studies of the contributory role of UV light, catalyst support, catalyst and hydrogen peroxide, the effect of experimental conditions such as pH, catalyst loading, initial concentration of AG25 and H<sub>2</sub>O<sub>2</sub>, and temperature on decolorization of AG25 were studied using photo-Fenton process. Mineralization studies also were carried out on AG25 decolorization at the best operating conditions by using total organic compound (TOC) measurement to investigate the activity of the developed catalysts in mineralizing AG25. Besides, the catalytic activity of all catalysts was tested on different dye pollutants to study the catalyst capability against other pollutants. Finally, catalyst reusability and Fe leaching test were carried out to evaluate the catalyst stability.

#### 1.4 Organization of Thesis

Chapter one focuses on brief introduction of the polluted water and its negative impact to the living things. It also presents general introduction to homogeneous and heterogeneous Fenton reaction as well as the challenges encountered in the past studies. Others include the problem statement, research objectives and the organization of the thesis.

Chapter two presents the current situation related to water pollution caused by industrial effluent such as textile industry as well as its characteristics. The different type of dyes commonly used in industrial and the historical background of this study which included the successes and failures recorded in the literature. The review on different types of catalyst supports was also discussed. Finally, the factors that affect the reaction process were well discussed.

Chapter three is overview of the research experimental work in this study. This includes the list of chemicals and their suppliers, basic information on the catalyst supports and methods used including the synthesis of catalysts and the experimental procedures to study the catalytic activities of the catalysts. Different catalyst characterization techniques were also listed as well as the range value of process parameters affecting the rate of decolorization.

Chapter four presents the results and discussion of the preliminary studies, characterization of catalyst either on physical or chemical properties, and effect of factors affecting the decolorization of AG25. The evaluation of reusability and leaching of iron ions from the supported catalyst are also discussed in this chapter.

Chapter five features the conclusions derived from this research and recommendations based on the observation in this research study.

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#### **CHAPTER TWO**

#### LITERATURE REVIEW

#### 2.1 Water Pollution

Water is a basic human need. However, water increasingly polluted and is becoming a serious issue today. Despite all the efforts the government has done such as 'Love Our Rivers' campaign for almost nine year from 1993-2002, but continued widespread pollution in most states in Malaysia (Department of Irrigation and Drainage Malaysia, DIDM). It can be seen the number of clean rivers in 2010 was decreased from 306 rivers in 2009 to 293, slightly polluted rivers decreased from 217 in 2009 to 203 while the number of polluted rivers increased to 74 from 54 (2009), as shown in Table 2.1 (Department of Environment (DOE), 2010). Water pollution occurs when there are changes in content, condition, color and quality of water itself is not appropriate to give effect when used. This situation occurs as a result of industrial activities and human activities that lack of awareness about the importance of clean water for life.

Vaar		Number of rivers	5
Y ear	Clean	Slightly Polluted	Polluted
2005	338	166	90
2006	335	180	58
2007	368	164	48
2008	334	197	48
2009	306	217	54
2010	293	203	74

Table 2.1Malaysia: River Water Quality Trend (2005-2010) (DOE)

Industrial wastewater is produced by all industries, which use water in different technologies processes. The waste materials presented either in solid, semisolid (sludge) and liquid for with one or more of the following characteristics; reactive, corrosive, toxic, ignitable, radioactive, carcinogenic, infectious, mutagenic and teratogenic and much of the waste produced directly discharged into natural water bodies (Anjaneyulu et al., 2005; Fang et al., 2011; Unuabonah et al., 2010). Industrial is the biggest water consumer with 50 to 80 % of total demand in developed countries which in turn discharge large amount of effluents. The effluents of industrial typically contain organic and inorganic constituents and toxicants depending upon on nature of industries and difficult to biodegrade (Ho et al., 2005; Tekbas et al., 2008). Chemical process industries such as dye and intermediates industries, leather industries, textile industries, food processing industries, among others, are typical industries that discharge toxic and amongst them, textile industries and dye and intermediates industries prominent as they produce a large amount of effluents contain colored compounds which cause problems to the environment (Timofeeva et al., 2005; Berberidou et al., 2007; Daud et al., 2010).

In Malaysia, there are about 1500 textile factories and mostly operate as backyard or cottage industries producing the local "batik" which is lack of water treatment system. Under the Environment Quality (Industrial Effluents) Regulation, 2009, color is included in the water quality standard for the industrial effluents discharge and the limits according to standard A and B are 100 and 200 Platinum-Cobalt (PtCo) units, respectively (DOE). Textile wastewater contains a large variety of dyes, salts, and chemical additions that make the environment challenge for textile industry not only as liquid waste but also in its chemical compositions (Al-Kdasi et al., 2005). The direct release of these wastewaters is detrimental to both human and aquatic life due to their mutagenic, toxic and carcinogenic tendencies (Weisburger, 2002; El-Shafei et al., 2010; Oller et al., 2011). The characteristic of textile wastewater in most cases contains high BOD/COD ratio which reflect the large amount of non-biodegradable organic matter. This resulted the biological treatment is not suitable due to the toxicity of the wastewater matric to biological life (Azbar et al., 2004; Daud et al., 2010).

The effluents from textile industries are generally high in organic contents and have strong color as well as contain surfactants and additives which make them non-biodegradable. Application of traditional methods as disposal ways may result in activated sludge treatment at the end of process which causes the serious environmental contamination (Shu et al., 2005; Tekbas et al., 2008). Nowadays, the dye treatments from the wastewater become one of the major thrust areas of scientific research. In view of this, there will be need to research more into cheaper and sustainable treatment methods.

#### 2.2 Dyes

At present most of the dyes used in textile industries consist of synthetic dyes because of its low production cost, brighter colors, better resistance to environmental factors, and easy-to-apply factor (Ngah et al., 2011). Compared to natural dyes, synthetic dyes however are often highly toxic and carcinogenic as they are made from known carcinogens, such as naphthalene, benzidine, dioxins and dioxin-like compounds and other aromatic compounds (Anjaneyulu et al., 2005). Dyes consist of two main groups of compounds, the chromophores and auxochromes. The

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chromophores are responsible for color of the dye while the auxochromes cause the dye molecule soluble in water and give enhanced affinity toward the fibers as well as determine the intensity of the color (Christie, 2007; Moussavi and Mahmoudi, 2009; Ngah et al., 2011).

Anthraquinone and azo dyes have become the largest classes of dyes with 15% and 70% of total dyes produced are made from these type of dyes, respectively. Anthraquinone based dyes are the most resistant to degradation due to their fused aromatic structure and may cause mutagenic effects or even acute toxicity on exposed to living things (Novotny et al., 2006). Moreover, the anthraquinone based dyes remain colored for long period of time (Anjaneyulu et al., 2005). On another hand, azo dyes have complex molecular structures make them resistant to biological or even chemical degradation while basic dyes have high brilliance, thus higher color intensity, causing them more difficult to decolorize (Baughman and Perenich, 1988; Gupta and Suhas, 2009).

Among the different classes of dye, reactive dyes are believed to have the highest worldwide market share due to their characteristics. They contain the reactive groups which enable them to react chemically with the fiber substrate and formed a covalent bond (Zollinger, 2003). In addition, compared to other classes, reactive dyes have very low degree of fixation on fabric causing about 10-50% of dyes discharged as wastewater (Lau and Ismail, 2009).

Besides, acid dyes which are the largest and most important class of synthetic dyes are used in dyeing wool, silk, nylon, leather and also to some extent for paper,

food, cosmetic and ink-jet printing. These type of dyes are formed from chemical classes such as anthraquinone, azo, nitro, azine, nitroso and xanthene which make them chemically stabil and versatility, (Mall et al., 2005; Orozco et al., 2008; Gupta and Suhas, 2009: Daud et al., 2010). Moreover, these two types of dye are very problematic as the color fastness and stable, consequently recalcitrant to conventional wastewater treatment (Willmott et al., 1998; Anjaneyulu et al., 2005; Hassan and Hameed, 2011a).

As the result, the wastewaters from industrial are increasingly major concern in worldwide and need to be treated before being discharged into the environment. Moreover, government legislation is becoming more stringent; especially in developed countries to ensure the effluent from industries meet the required standard. Dyes have become one of the main sources of severe water pollution as a result of the rapid development of the textile industries. The release of the colorant effluent has triggered a major concern on the human health as well as marine lives.

#### 2.3 Environmental Quality (Industrial Effluents) Regulations 2009

In Malaysia, there are limitation of discharge wastewater from industrial effluent and treatment plant as has been stipulated in the Fifth Schedule of Environmental Quality (Industrial Effluent) Regulation 2009. This regulation is under the Environmental Quality Act 1974 for Standard A and B to control pollution and enhance the environment. Table 2.2 shows the safety limits stated by Malaysian Government. Department of Environment (DOE), 2010.

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Parameter	Unit	Sta	Standard	
		A	В	
Cemperature	°C	40	40	
pH vaue	-	6.0-9.0	5.5-9.0	
BOD <sub>s</sub> at 20 °C	mg/L	20	50	
Suspended solids	mg/L	50	100	
Mercury	mg/L	0.01	0.01	
Cadmium	mg/L	0.01	0.02	
Chromium, Hexavalent	mg/L	0.05	0.05	
Chromium, Trivalent	mg/L	0.2	1	
Arsenic	mg/L	0.05	0.1	
Cvanide	mg/L	0.05	0.1	
Lead	mg/L	0.1	0.5	
Copper	mg/L	0.2	1	
Manganese	mg/L	0.2	1	
Nickel	mg/L	0.2	1	
Tin	mg/L	0.2	1	
Zinc	mg/L	2	2	
Boron	mg/L	1	4	
Iron (Fe)	mg/L	1	5	
Silver	mg/L	0.1	1	
Aluminium	mg/L	10	15	
Selenium	mg/L	0.02	0.5	
Phenol	mg/L	0.001	1	
Free chlorine	mg/L	1	2	
Sulphide	mg/L	0.5	0.5	
Oil and grease	mg/L	1	10	
Color	Platinum-Cobalt (PtCo)	100	200	

Table 2.2:Parameters Limits of Effluents of Standard A and B (Environmental<br/>Quality (Industrial Effluents) Regulations 2009 under Environment<br/>Quality Act 1974) (DOE (Department of Environment), 2010)

## 2.4 Commercial Wastewater Treatment Technology

The typical processes used to treat wastewater are physical, chemical and biological process. These processes can be used separately or combined with other

processes to increase the overall treatment efficiency (Inglezakis and Poulopoulos, 2006; Iurascu et al., 2009). Many researchers have studied these processes with different conditions to remove contaminants in wastewater and have shown good performance. However, since the effluents from the industries commonly contain high concentration of organic compounds which are toxic and strong color, the typical processes exhibit some disadvantages as shown in Table 2.3.

Advantages and limitations of various degradation methods for industrial effluents (Anjaneyulu, 2005; Herney-Ramirez Ineffective for light resistant huge quantities are required Cost intensive regeneration Surface area is lower than Larger contact times and Post treatment disposal requirement is high. Specific application Dissolved oxygen activated carbon Limitations colorants process Effective removal for a wide Waste to treat another waste Regeneration with low loss Effective adsorbent due to Good sorption for specific range of colorants at low Good removal efficiency Economically attractive. cellular structure. No activation required of adsorbents Advantages colorants volumes Kraftmill/Tannery/distillary/ Any industries as post or Any industries as post or Textile/tannery/brewery Type of industry Sugar/brewary pulp and paper Any industry pretreatment pretreatment Main treatment Pre-treatment Pre-treatment Pre-treatment Pre-treatment treatment treatment et al., 2010). Stage of Pre/post I. Adsorption 2. Irradiation methodology a. Activated b. Bagasse I. Physical Treatment Available exchange methods methods Table 2.3: d. Wood carbon c. Peat 3. lonchips

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Treatment methodology	Stage of treatment	Type of industry	Advantages	Limitations
II. Chemical methods				
1. Oxidation			Effective for both soluble and insoluble colorants	Problem with sludge disposal
b. Ozonation	Main treatment	Textile/tannery/brewery/ distillery	Effective for azo dye removal	Not suitable for dispersed dyes. Releases aromatic amines
c. Sodium hypochlorite	Post treatment	Brewery/distillery	Low temperature requirement.	Cost intensive process
d. Electrochemical oxidation	Pre treatment	Kraft mill/distillery	No additional chemicals required and end products are non-hazardous	Cost intensive process
2. Coagulation and precipitation	Pre/main treatment	Any industry	Short detention time and low capital costs. Good removal efficiencies	High cost of chemicals for pH adjustment. Dewatering and sludge handling problems
3. Cucurbituril	Post treatment	Sugar/pulp and paper/ kraftmill	Complete decolorization for all class of dyes	Expensive
III. Biological methods				
1. Aerobic process	Main treatment	Textile/tannery/kraftmill/ distillery	Colour removal is facilitated along with COD removal	Longer detention times and substrate specific removal. Less resistant to recalcitrant

Treatment methodology	Stage of treatment	Type of industry	Advantages	Limitations
2. Anaerobic process	Main Treatment	Distillary/brewary/ pulp and paper/sugar	Resistant to wide variety of complex colorants. Bio gas produced is used for steam generation	Longer acclimatization phase
<ol> <li>Single cell</li> <li>(Fungal. Algal &amp; Bacterial)</li> </ol>	Post Treatment	Any industry as Post- treatment	Good removal efficiency for low volumes and concentrations. Very effective for specific colorant removal	Culture maintenance is cost intensive. Cannot cope up with large volumes of colored effluents

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#### 2.5 Advanced Oxidation Processes (AOPs)

Advanced Oxidation Processes (AOPs) have emerged as outstanding alternative for the removal of organic compounds in industrial wastewater and are very useful in the case of substances resistant to typical treatments. AOPs are used since the early 1970s to remove both high and low concentration of organic from wastewater sources like municipal and industrial wastewater. Specials about these processes, there are viable to treat effluents containing toxic, non-biodegradable and refractory materials besides the process requires low energy consumption in comparison with other treatment methods (Herney-Ramirez et al., 2010; Navalon et al., 2010). These processes are characterized by production of hydroxyl radicals ('OH) as strong oxidant, very reactive, attack most organic molecules, and nonselective to mineralize virtually all organic compounds to carbon dioxide and water which are environmentally benign byproducts as shown in Equation 2.1 (Skoumal et al., 2006; Ayodele et al., 2012).

$$AOPs \rightarrow OH + organic compound \rightarrow CO_2 + H_2O + inorganic ions$$
 (2.1)

Compared to others oxidizing agent, 'OH is the second most powerful oxidizing agent after fluorine (F) and higher than other oxidants such as ozone, hydrogen peroxide ( $H_2O_2$ ) and oxygen as shown in Table 2.4. Besides oxidation products of 'OH are less toxic (Zhou and Smith, 2002; Li et al., 2010; Babuponnusami and Muthukumar, 2011). Moreover, 'OH can be generated *in situ* in reaction environment by different possible ways.

Name of oxidant	Oxidation potential (eV	
Fluorine	3.0	
Hydroxyl radical	2.8	
Ozone	2.1	
Hydrogen peroxide	1.8	
Potassium permanganate	1.7	
Chlorine dioxide	1.5	
Chlorine	1.4	

Table 2.4:Oxidation Potential of Different Oxidant (Zhou and Smith, 2002; Li et<br/>al., 2010).

In treatment method, AOPs used different combination methods or different reagent systems in order to produce extremely reactive 'OH radicals such as (a) chemical oxidation processes (Fenton's reagent,  $H_2O_2$ , ozone (O<sub>3</sub>), (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) (Zhang et al., 2010; Kusvuran et al., 2011), (b) photocatalysis (titanium dioxide (TiO<sub>2</sub>)/UV, photo-Fenton reaction) (Tong et al., 2011) and (c) photochemical reaction (UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>) (Khatee et al., 2009). Among these AOPs, Fenton's reagent is particularly interesting due to its cost effective, non-toxic reagent (Fe(11) and H<sub>2</sub>O<sub>2</sub>), reliable, no residue generated and the simplicity of the process made the Fenton process a valuable to industrial wastewater treatment (Farre et al., 2007; Bouasla et al., 2010; Wu et al., 2010). Many studies have been conducted and showed that the reaction of Fenton's reagent is effective in degradation of organic compounds (Daud et al., 2010; Mahmoud et al., 2010; Hassan and Hameed, 2011b; Tian et al., 2011).

#### 2.6 Fenton and photo-Fenton process (Homogeneous Process)

Fenton's reagent consists of ferrous ion (Fe<sup>2+</sup>) as homogeneous catalyst and  $H_2O_2$  to generate 'OH for degradation and mineralization of organic compounds under strong acidic medium. The 'OH generated can oxidize virtually all known organic pollutants by abstraction of protons producing highly reactive organic radicals (R') which can be further oxidized and degraded (Stapleton et al., 2009; Sun et al., 2009; Herney-Ramirez et al., 2010; Navalon et al., 2010). The easiest ways for Fenton process can be performed by reacting Fe salts such as FeSO<sub>4</sub> with  $H_2O_2$  in aqueous sulphuric acid solution.

This reaction was first discovered by Fenton in 1894 (Sun et al., 2007) and has been continuously used by many researchers to remove recalcitrant compounds because of its simplicity and easy to handle (Poyatos et al., 2009). In addition, the  $H_2O_2$  used is cheaper compared to other oxidants while the iron is abundant on earth (Ricciardi, 2006). Table 2.5 shows the different organic compounds that can be removed or mineralized by means of hydroxyl radicals. This process has been proven to treat wide ranges of wastewater without generating toxic products at the end of the treatment by many researchers (Sun et al., 2009). For example, Gutowska et al., 2007 used this process for decolorization of Reactive Orange 113. The results showed that 80% color removal was achieved in 120 min reaction in the presence of 5 to10 mg/L  $Fe^{2+}$  ions. The best decolorization conditions were found at 0.4 mg of  $H_2O_2$  per mg of dye and 10 mg/L  $Fe^{2+}$  ions at pH 3 with 100% dye removal. After 5 h reaction time, COD reduction value was 70% and increased to 90% after 20 h under these conditions.

	Compounds
Acids	Formic, gluconic, lactic, malic, tartaric, propionic
Alcohols	Benzyl, <i>tert</i> -butyl, ethanol, ethylene glycol, glycerol, isopropanol, methanol, propenediol
Aldehydes	Acetaldehyde, benzaldehyde, formaldehyde, glyoxal
Aromatics	Benzene, chlorobenzene, chlorophenol, creosote, dichlorophenol, hydroquinone, p-nitrophenol, phenol, toluene, xylene, trinitrotoluene
Amines	Aniline. Cyclic amines, diethylamine, dimethylfoemamide, EDTA, propanediamine, n- propylamine
Dyes	Anthraquinone, diazo, monoazo
Ethers	Tetrahydrofuran
Ketones	Dihydroxyacetone, methyl ethyl ketone

 Table 2.5:
 Oxidizable compounds by hydroxyl radicals (Bigda, 1995)

It was reported that the classical homogeneous Fenton process required a number of complementary steps such as coagulation and neutralization, sedimentation and precipitation to recover the iron catalyst for reuse and to prevent contamination (Xing and Sun, 2009: Wu et al., 2010). Therefore, the efficiency of homogeneous Fenton process become questionable because the process needs a large amount of chemicals, labor intensive to operate throughout the processes, power, and other service requirements.

In the homogeneous Fenton process, basically  $Fe^{2+}$  will be oxidized to  $Fe^{3+}$  by  $H_2O_2$  as oxidant generates 'OH and hydroxide anions (Equation 2.2). Parallel to this Fenton reaction, other processes can also simultaneously take place as shown in Equation 2.3-2.8. These parallel processes are essentially considered an undesirable since  $H_2O_2$  is consumed without generating the needed HO' (Navalon et al., 2010).

Compared to the Equation 2.2 and 2.3, the reaction rate of Equation 2.2 (k = 70 M<sup>-1</sup> s<sup>-1</sup>) is much higher than that in the Equation 2.3 (k = 0.001-0.01 M<sup>-1</sup> s<sup>-1</sup>) (Pignatelo et al., 1999; Wu et al., 2010). Consequently, the accumulation of the ferric ions slows down the degradation process as ferric ions will react with the hydroperoxyl radical and oxidize it to ferrous ion as shown by Equation 2.7 and subsequently reacts further with HO<sup>•</sup> according to Equation 2.8. These reactions resulted in the retarded of hydroxyl radical geration and led to decrease in degradation efficiency. In addition, the generated ferric ion scavenges on the H<sub>2</sub>O<sub>2</sub> resulted starving the process of sufficient H<sub>2</sub>O<sub>2</sub> required to generate the HO<sup>•</sup>. Moreover, the Fe<sup>2+</sup> reproduction is slow causing the HO<sup>•</sup> generation is slow, thus may slow down the Fenton reaction. Because of this defiance, Fenton process had in the recent past improve through the use of ultra violet (UV) irradiation.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{-} + HO^{-}$$
 (2.2)

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe-OOH^{2+} + H^+$$
 (2.3)

$$\text{Fe-OOH}^{2+} \rightarrow \text{HOO}^{*} + \text{Fe}^{2+}$$
 (2.4)

$$Fe^{2^{+}} + HO^{\cdot} \rightarrow Fe^{3^{+}} + HO^{\cdot}$$
(2.5)

$$H_2O_2 + HO' \rightarrow H_2O + HOO'$$
(2.6)

$$Fe^{3+} + HOO' \rightarrow Fe^{2+} + O_2 + H^+$$
 (2.7)

$$Fe^{2+} + HOO^{\bullet} \rightarrow Fe^{3+} + HOO^{\bullet}$$
 (2.8)

Many studies have indicated that the degradation rate of organic compounds is strongly increased with presence of UV irradiation in the system and it called