ORGANIC DYES REMOVAL BY HETEROGENEOUS FENTON AND FENTON-LIKE PROCESSES USING IRON OXIDE MAGNETIC CATALYST

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering

Lee Kong Chian Faculty of Engineering and Science
Universiti Tunku Abdul Rahman

May 2016
DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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Approved by,

Signature : ________________________________

Supervisor : Dr. Pang Yean Ling

Date : ________________________________
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Specially dedicated to
my beloved parents
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In addition, I would also like to express my gratitude to my loving parent and friends who had helped and given me encouragement to complete this project. I would not resolve the problems which I faced during my research without their cooperation.
ORGANICS DYES REMOVAL BY HETEROGENEOUS FENTON AND FENTON-LIKE PROCESSES USING IRON OXIDE MAGNETIC CATALYST

ABSTRACT

Heat-treated iron (II, III) oxides ($\text{Fe}_3\text{O}_4$) were developed and characterized by using XRD and SEM-EDX. Heat treated $\text{Fe}_3\text{O}_4$ at various temperatures ranging from 200 to 800 °C for 2 h could induce phase change to maghemite ($\gamma$-$\text{Fe}_2\text{O}_3$) and further changed to hematite ($\alpha$-$\text{Fe}_2\text{O}_3$) at higher temperature. Majority $\text{Fe}_3\text{O}_4$ particles were spherical shape and composed of iron (Fe) and oxygen (O) atoms only. Mean particle sizes of $\text{Fe}_3\text{O}_4$ were increased with increment of temperature as excessive heat treatment caused the agglomeration of particles. The effect of heat treatment of $\text{Fe}_3\text{O}_4$ for Fenton and Fenton-like processes was identified. Original $\text{Fe}_3\text{O}_4$ showed the highest catalytic activity as it comprised $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ ions to undergo Fenton and Fenton-like processes simultaneously. Several parameters were also investigated including types of organic dyes used, $\text{Fe}_3\text{O}_4$ dosage, hydrogen peroxide ($\text{H}_2\text{O}_2$) dosage, dye concentration, temperature and solution pH in order to determine the optimum condition for the Fenton and Fenton-like processes. Degradation of organic dyes was influenced by their chemical structures. Malachite green exhibited the highest degradation rate as its chemical structure was the most vulnerable to chemical oxidation. The highest degradation efficiency of malachite green (96 %) was achieved in 1 h at the optimum conditions with dye concentration of 20 mg/L, $\text{Fe}_3\text{O}_4$ dosage of 2.5 g/L, $\text{H}_2\text{O}_2$ dosage of 0.20 M, solution pH of 9 and reaction temperature at 30 °C. Reusability of $\text{Fe}_3\text{O}_4$ and kinetic study were studied. Reused $\text{Fe}_3\text{O}_4$ still maintained high catalytic activity. Moreover, $\text{Fe}_3\text{O}_4$ had high stability as leaching of Fe was low. The degradation kinetics of malachite green at different temperatures were fitted well to pseudo first-order model. The activation energy for degradation of malachite green was 36.40 kJ/mol.
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<th>Symbol</th>
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<tr>
<td>Ag</td>
<td>silver</td>
</tr>
<tr>
<td>Al</td>
<td>aluminium</td>
</tr>
<tr>
<td>$A_0$</td>
<td>activation energy, kJ/mol</td>
</tr>
<tr>
<td>C</td>
<td>carbon atom</td>
</tr>
<tr>
<td>Cl</td>
<td>chlorine atom</td>
</tr>
<tr>
<td>$C_{MG}$</td>
<td>concentration of malachite green, mg/L</td>
</tr>
<tr>
<td>$C_{OH}$</td>
<td>concentration of $\cdot OH$</td>
</tr>
<tr>
<td>$C_0$</td>
<td>concentration of dye at time 0, mg/L</td>
</tr>
<tr>
<td>$C_t$</td>
<td>dye concentration at time t, mg/L</td>
</tr>
<tr>
<td>D</td>
<td>crystalline size, nm</td>
</tr>
<tr>
<td>$d$</td>
<td>d-spacing</td>
</tr>
<tr>
<td>Fe</td>
<td>iron atom</td>
</tr>
<tr>
<td>$Fe^{2+}$</td>
<td>ferrous ion</td>
</tr>
<tr>
<td>$Fe^{2+}/H_2O_2$</td>
<td>Fenton process</td>
</tr>
<tr>
<td>$Fe^{3+}/H_2O_2$</td>
<td>Fenton-like process</td>
</tr>
<tr>
<td>FeCl$_3$</td>
<td>iron (III) chloride hexahydrate</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>magnetite</td>
</tr>
<tr>
<td>HCl</td>
<td>hydrogen chloride</td>
</tr>
<tr>
<td>$H^+$</td>
<td>hydrogen ion</td>
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<tr>
<td>$H_2O_2$</td>
<td>hydrogen peroxide</td>
</tr>
<tr>
<td>$H_3O_2^+$</td>
<td>hydroperoxonium ion</td>
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<tr>
<td>K</td>
<td>shape factor</td>
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<tr>
<td>$K_2Cr_2O_7$</td>
<td>potassium dichromate</td>
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<tr>
<td>$k_{app}$</td>
<td>apparent rate constant</td>
</tr>
<tr>
<td>$k_0$</td>
<td>apparent pseudo-zero order rate constant, mg/(L·min)</td>
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<tr>
<td>$k_1$</td>
<td>apparent pseudo-first order rate constant, /min</td>
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\( k_2 \) apparent pseudo-second order rate constant, L/(mg·min)

m reaction order with respect to malachite green

n integer

\( n \) reaction order with respect to \( \cdot OH \)

NaOH sodium hydroxide

O oxygen atom

\( O_2 \) oxygen molecules

\( OH^- \) hydroxyl ion

\( \cdot OH \) hydroxyl radical

R ideal gas constant, 8.314 J/(mol·K)

T absolute temperature, K

t reaction time, min

V volume, ml

\( \rho \) density, g/ml

\( \theta \) half scattering angle, °

\( \beta \) full width at half maximum (FWHM), °

\( \lambda \) wavelength of X-rays, 1.540562 Å

\( \lambda_{max} \) wavelength with highest absorbance

\( \gamma\text{-Fe}_2\text{O}_3 \) maghemite

\( \alpha\text{-Fe}_2\text{O}_3 \) hematite

AOPs advanced oxidation processes

BC before crist

BET Brunauer-Emmett-Teller

BOD biochemical oxygen demand

CCP cubic closed packed

COD chemical oxygen demand

HCP hexagonal closed packed

ICP-OES inductively coupled plasma-optical emission spectroscopy

MNPs ferromagnetic nanoparticles

SEM-EDX scanning electron microscopy coupled with energy dispersive X-ray

TDS total dissolved solid
<table>
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<th>Full Form</th>
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<tr>
<td>TOC</td>
<td>total organic carbon</td>
</tr>
<tr>
<td>UV-vis</td>
<td>ultraviolet-visible-infrared</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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CHAPTER 1

INTRODUCTION

1.1 Water Pollution in Malaysia

Around 71% of the Earth’s surface is covered by water whilst 29% comprises continents and islands (Williams, 2014). Therefore, it can be seen that water is a very essential resource for people and environment. The increasing of population growth, industry processes, agricultural and domestic activities contribute to the water pollution. The main sources of water pollution are point source and non-point source (DOE, 2012). For instance, point sources are industrial and municipal wastewater originating from a specific point such as sewage treatment plants. Non-point sources cannot be simply tracked back to specific location and come from land use activities such as agricultural activities. The water quality degrades as the addition of chemical, physical or biological substances in certain concentrations (Tchobanoglous, Burton and Stensel, 2003).

In 21st century, water pollution has turned into a severe problem around the world including Malaysia. Malaysia is one of the countries which face the issues on the sustainability of water resource. Moreover, plants, living organisms, people’s health and economy are also strongly affected by water pollution. Water pollution is a critical issue in Malaysia with reports representing a decreasing trend annually (Afroz, et al., 2014). Since Malaysia is rapidly turning into an industrial nation, many wastes have been discharged into rivers. Consequently, many rivers have become contaminated. The water and lives revolve around the rivers have been harmed as those rivers have been used as an exit for chemicals to flow out. Total water availability has
reduced as the expense to treat the polluted water is too costly and some polluted water is not suitable to consume although has been treated. Therefore, sufficient water supply to all users cannot be ensured although Malaysia has a substantial amount of water available in catchment (Ling, 2010).

According to environmental quality report 2012, out of 473 rivers, there were 278 (59 %) clean rivers, 161 (34 %) slightly polluted rivers and 34 (7 %) polluted rivers (DOE, 2012). Figure 1.1 demonstrates that throughout 2007 to 2012, the number of clean rivers was continue decreasing except there was a slightly increase in year 2012. On the other hand, the number of polluted river was increased from year 2007 to 2010 and after that slightly decreased in year 2012. Although the number of clean river was increased and polluted river was decreased from year 2011 to 2012, the number of slightly polluted river was increased. This indicates that the rivers in Malaysia are continuously being polluted.

![Figure 1.1: Malaysia River Water Quality Trend from 2005 to 2012 (DOE, 2012)](image_url)
1.2 Dye Production and Environmental Impacts

More than 100 000 commercially available dyes have been reported in the literature. Furthermore, over $7 \times 10^5$ tonnes of dyestuffs are produced annually and 40 000 to 50 000 tonnes of dyes are released to surface water yearly (Rangabhashiyam, Anu and Selvaraju, 2013). China is the largest consumer of synthetic dyes as it has the largest consumption of dyes which is around 40 to 50% in 2013 as shown in Figure 1.2.

![World Consumption of Synthetic Dyes-2013](image)

**Figure 1.2: World Consumption of Synthetic Dyes—2013 (IHS, 2014)**

The industries like textile, dyestuffs, paper and plastics utilize dyes for dyeing their products. Around 67% of the total dyestuff market is used by textile industries. Textile industry ranks the first among all industries in application of dyes for colouration of fibre (Rangabhashiyam, Anu and Selvaraju, 2013). World Bank estimated that approximately 20% of global industrial water pollution originated from treatment and dyeing of textiles (Kant, 2012).

Pang and Abdullah (2013) stated that there is no complete degree of fixation of dyes to fibre. Improper dye uptake and degree of fixation on substrate lead to the
release of dyes which subsequently bring impact to the environment. According to Table 1.1, reactive dyes have the poorest degree of fixation on fibre. However, the percentage of loss of effluent for metal-complex is slight higher than reactive dyes although degree of fixation for metal-complex dye is very high which is from 90 to 98%.

### Table 1.1: Estimated Degree of Fixation for Different Dye/ Fibre Combinations (Joshi, Bansal and Purwar, 2004)

<table>
<thead>
<tr>
<th>Dye Class</th>
<th>Fibre</th>
<th>Loss of effluent (%)</th>
<th>Degree of fixation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Polyamide</td>
<td>5–20</td>
<td>80–95</td>
</tr>
<tr>
<td>Basic</td>
<td>Acrylic</td>
<td>0–5</td>
<td>95–100</td>
</tr>
<tr>
<td>Direct</td>
<td>Cellulose</td>
<td>5–30</td>
<td>70–95</td>
</tr>
<tr>
<td>Disperse</td>
<td>Polyester</td>
<td>0–10</td>
<td>90–100</td>
</tr>
<tr>
<td>Metal-complex</td>
<td>Wool</td>
<td>2–10</td>
<td>90–98</td>
</tr>
<tr>
<td>Reactive</td>
<td>Cellulose</td>
<td>10–50</td>
<td>50–90</td>
</tr>
<tr>
<td>Sulphur</td>
<td>Cellulose</td>
<td>10–40</td>
<td>60–90</td>
</tr>
<tr>
<td>Vat</td>
<td>Cellulose</td>
<td>5–20</td>
<td>80–95</td>
</tr>
</tbody>
</table>

In Malaysia, when the country commenced import-export oriented industrialization and commercialization, textile industry grew rapidly in the early 1970s. Consequently, there was a high demand of dye production. In the East Coast Peninsular Malaysia and Sarawak, homemade textile industry is very popular (Ahmad, et al., 2002). In this industry, effluents comprise of grease, wax, heavy metals, surfactants, suspended solids and dyes are produced. In the process of producing Batik, substantial volume of water has been utilized and thus large volume of wastewater has been discharged.

Wastewater generated from textile industry is more polluted as compared to other industrial sectors by considering the composition of effluent and the volume produced. In the textile effluent, the main pollutants are recalcitrant organic, surfactant, coloured toxicant, salt and chlorinated compounds. Textile effluents are characterized
by great fluctuations in many parameters. For instance, the parameters are pH, salinity, colour, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) (Chequer, et al., 2013). Table 1.2 and Table 1.3 show that large amount of water are consumed as processing water in textile industry. According to Table 1.2, substantial volume of organic load and wastewater are consumed in preparation, dyeing and printing process as compared to other processes.

Table 1.2: Organic Load and Water Consumption in Different Textile Finishing Procedures (Carmen and Daniela, 2012)

<table>
<thead>
<tr>
<th>Operation/Process</th>
<th>Organic load (% from total organic load of textile plant)</th>
<th>Water Consumption (% from total consumption of textile plant)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
</tr>
<tr>
<td>General facilities</td>
<td>0.1</td>
<td>8</td>
</tr>
<tr>
<td>Preparation</td>
<td>45</td>
<td>77</td>
</tr>
<tr>
<td>Dyeing</td>
<td>4</td>
<td>47</td>
</tr>
<tr>
<td>Printing</td>
<td>42</td>
<td>75</td>
</tr>
<tr>
<td>Wetting</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>Fabric washing</td>
<td>1</td>
<td>25</td>
</tr>
<tr>
<td>Finishing</td>
<td>0.1</td>
<td>7</td>
</tr>
</tbody>
</table>

Approximately 2 % of dye generated is estimated to be released in aqueous effluent. Afterwards, 10 % is lost in the colouration procedure. Therefore, approximately 20 % of colourants go into surroundings via effluents from wastewater treatment plants are reasonably to be assumed (Arora, 2014). Low degree of fixation of dye on fibre is an important factor that liable for the release of water-soluble and water-insoluble dyes. Moreover, colour greatly affects the public aesthesis of water quality. In wastewater, colour will be recognized easily even small amount of dyes present in water as it is extremely visible (Wu, et al., 2012). This seriously influences clarity of water bodies and brings harm to aquatic environment.
Table 1.3: Specific Water Consumption in Textile Finishing Processes (Carmen and Daniela, 2012)

<table>
<thead>
<tr>
<th>Type of finishing process</th>
<th>Water Consumption, $10^{-3}$ m$^3$/kg textile product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>Cloth finishing</td>
<td></td>
</tr>
<tr>
<td>• Simplified processing</td>
<td>8.3</td>
</tr>
<tr>
<td>• Complex process</td>
<td>20</td>
</tr>
<tr>
<td>• Panty processing</td>
<td>5.8</td>
</tr>
<tr>
<td>Carpet finishing</td>
<td>8.3</td>
</tr>
<tr>
<td>Fibre finishing</td>
<td>3.3</td>
</tr>
<tr>
<td>Fabric finishing</td>
<td></td>
</tr>
<tr>
<td>• Short process</td>
<td>12.5</td>
</tr>
<tr>
<td>• Complex process</td>
<td>10.8</td>
</tr>
<tr>
<td>Non-fabrics finishing</td>
<td>2.5</td>
</tr>
<tr>
<td>Raw wool washing</td>
<td>4.2</td>
</tr>
<tr>
<td>Wool finishing</td>
<td>110.9</td>
</tr>
<tr>
<td>Yarn finishing</td>
<td>33.4</td>
</tr>
</tbody>
</table>

Furthermore, some dyes maybe toxic to some aquatic life because of the existence of metals and aromatics. The example of dye which is toxic is azo dye as it can form the toxic amines in effluent through the reactive cleavage of azo linkage (Joshi, Bansal and Purwar, 2004). Some dyes are also carcinogenic for example complex dye which is normally chromium based (Yagub, et al., 2014). Dyes also reduce the penetration of light into water subsequently affect photosynthetic activity of aquatic plants and therefore having adverse impact on their growth. Moreover, it causes oxygen deficiency and restricts the benefit uses of downstream for instance drinking water and recreation. The existence of dyes in effluent brings adverse effects to many forms of life as it will cause substantial environmental pollution and adversely affect health of living organisms. Wastewater from textile industry has high colour intensity and high composition variability. Thus, it is difficult to treat satisfactory.
1.3 Problem Statement

Dyes and pigments are extremely visible materials. Incomplete fixation of dyes onto textile fibre is the major source for the release of colour into environment. Colour may appear in water and may be toxic to the aquatic living although only slight amount of it releases into environment. Therefore, it is essential to decrease the quantity of residue dye in textile effluent (Christie, 2015).

Many colour removal techniques have been developed to remove organic dyes from textile wastewater. For instance, the removal techniques are coagulation, aerobic and anaerobic microbial degradation, membrane separation and filtration (Gonawala and Mehta, 2014). However, some conventional techniques for instance coagulation and adsorption are only capable to merely transfer the organic pollutants to another phase such as from wastewater to other media that produce sludge and lead to disposal problems (Inoue, et al., 2006). Conventional treatment process will also become ineffective in degrading and destroying organic pollutants because of the existence of benzene rings in dye structure (Wang, et al., 2007).

Therefore, advanced oxidation processes (AOPs) provide a stunning substitute to the conventional processes because of more efficient in the degradation of any kind of organic pollutants (Swaminathan, Muruganandham and Sillanpaa, 2012). Treatment of wastewater by using AOPs involves \( \cdot \text{OH} \), a strong oxidant that completely degrade and mineralize the organic compound non-selectively into harmless products (Pang, Abdullah and Bhatia, 2010).

Fenton and Fenton-like processes are one of the AOPs. It can be conducted at atmospheric pressure and room temperature. Moreover, the Fenton’s reagents needed for Fenton process are readily obtainable, liable to store and process. Nevertheless, there are two main shortcomings of homogeneous Fenton and Fenton-like processes. Firstly, it refers to the wastage of oxidant because of the radical scavenging effect of \( \text{H}_2\text{O}_2 \) and self-decomposition of it. The second drawback of it is that iron ions are lost continuously and solid sludge is formed (Babuponnusami and Muthukumar, 2014).
Therefore, in order to overcome these drawbacks, heterogeneous Fenton and Fenton-like processes which replace the dissolved iron with solid catalyst need to be further studied. Furthermore, the influence of operating parameters such as Fe$_3$O$_4$ dosage, H$_2$O$_2$ dosage, pH of solution, dye concentration, temperature and different types of organic dye should be identified so as to maximize and optimize the effectiveness of Fenton and Fenton-like processes.

Apart from that, conventional filtration and centrifugation can only separate the solid catalyst size at least about 3 $\mu m$ (Xu, et al., 2010). However, magnetic separation is a new promising method to solve the separation of nanocatalyst. Thus, the separation and reusability of Fe$_3$O$_4$ magnetic nanocatalyst are required to be examined as it is expected to be recycled and reused in the process in order to save cost. Last but not least, a reliable reaction kinetic for the degradation of organic dyes by Fenton and Fenton-like processes is required to be determined.

1.4 Research Objectives

The main objective of this study was to investigate the heterogeneous Fenton and Fenton-like processes using iron oxide magnetic catalyst. In order to achieve the main objective of this study, the following sub-objectives were identified:

1. To prepare and characterize heat-treated Fe$_3$O$_4$ catalysts.
2. To identify the effect of various operating parameters such as various organic dyes, Fe$_3$O$_4$ dosage, H$_2$O$_2$ dosage, dye concentration, temperature, and pH of solution for Fenton and Fenton-like processes using Fe$_3$O$_4$ catalyst in order to determine the optimum conditions.
3. To study the reusability of Fe$_3$O$_4$ catalyst on the degradation of organic dyes.
4. To study the reaction kinetics of Fenton and Fenton-like reaction on degradation of organic dyes.
1.5 Scopes of Study

In order to achieve the objectives, the following scopes are studied. Fe$_3$O$_4$ are prepared by heat treating at different temperatures which are 200, 400, 600 and 800 °C. Effect on the characteristics of heat-treated Fe$_3$O$_4$ catalysts and catalytic activity are studied and compared. Characteristics of Fe$_3$O$_4$ are studied by using X-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive X-ray (SEM-EDX).

Then, a series of experiments will be carried out to investigate the effect of process variables which are various types of organic dyes, Fe$_3$O$_4$ dosage, H$_2$O$_2$ dosage, dye concentration, temperature and pH of solution. Fe$_3$O$_4$ catalyst is then reused for the subsequence experiments to evaluate its reusability on the organic dye degradation rate. Furthermore, a suitable kinetics is proposed for a better understanding on the reaction order for Fenton and Fenton-like processes.
CHAPTER 2

LITERATURE REVIEW

2.1 Classification of Dye

Dyes are coloured organic compounds that can be fixed on a substance with more or less permanence in the form of a colour through the sensation of colour is evoked. It is normally used in solution. It also has affinity for one or more textile fibre in the existence of specific auxiliaries under precise circumstances of temperature (Choudhury, 2006). Three methods that have been used to classify dyes are classification based on source of materials, classification based on chemical structure and classification based on application.

According to the sources of origin, dyes can be assorted as natural and synthetic dyes. Natural dyes are extracted from nature via organic and inorganic materials such as roots, leaves, iron buffs, wood and cochineal. It can be categorized into three classes which are natural dyes obtained from plants, animals and minerals. Carmen and Daniela (2012) stated natural dyes were mostly used in textile processing until 1856, commencing in 2600 Before Crist (BC) in China. Tyrian purple yielded from certain kind of crushed sea snails in 15\textsuperscript{th} century BC and indigo dye yielded from indigo plant since 3000 BC were utilized by Phoenicians. In South America, Egyptian mummies clothes and Incas fine textures were wrapped and coloured by utilizing the dyes made from madder plants.

In 1856, the synthetic dye, Mauveneine was first discovered accidentally by William Henry Perkin from United Kingdom who was attempting to produce anti-
malaria drug quinine. Afterward, in 1858, German scientist, O. Gries invented the reaction mechanism diazotization that can produce the azo dyes (Saranraj, 2013). Synthetic dyes rapidly displace natural dyes which are eco-friendly, biodegradable, less allergic and less toxic (Nisar, Ali and Hussian, 2007). This is because synthetic dyes are cheaper and offered an extensive range of new colours and imparted better properties to dyed materials. Nowadays, synthetic dyes have occupied dye market and being utilized by most of the dyeing operation.

Dyes can be classified by their chemical structures. There are two main functional groups that dye molecules have which are chromophores and auxochromes. Chromophores normally are electron withdrawing substituents that principally responsible for colour of dye. The common types of chromophores are azo group \((-N=N-)\), carbon nitrogen group \((-C=N-)\), carbonyl group \((-C=O-)\), nitroso group \((-N=O-)\) and nitro group \((-NO_2)\). Auxochromes normally are electron donating substituents which create or intensify the colour of chromophores. In other words, it does not create colour by itself but deepens the colour of chromogen. The general classes of auxochromes are carboxyl group \((-COOH)\), amine group \((-NH_3)\), sulfonate group \((-SO_3H)\) and hydroxyl group \((-OH)\) (Pang and Abdullah, 2013).

On the other hand, dyes can be classified based on the application. The general classes of dyes based on the application are acid dyes, reactive dyes, basic dyes, direct dyes, mordant dyes, disperse dyes, vat dyes and solvent dye. Different dyes will be used in different application areas. Dyes can also be classified in anionic, non-ionic and cationic dyes by considering only the general structure. Direct, acid and reactive dyes are the major anionic dyes. In addition, highly water soluble reactive and acid dyes are very troublesome because it cannot be get rid of by conventional treatment methods (Choudhury, 2006). Disperse dyes are the major non-ionic dyes that does not ionize in aqueous environment (Carmen and Daniela, 2012). Moreover, azo, basic, anthraquinone disperse and reactive dyes are the major cationic dyes. Classification of dyes and chemical types are shown in Table 2.1
Table 2.1: Classification of Dyes and Types of Chemicals (Beyene, 2014)

<table>
<thead>
<tr>
<th>Class</th>
<th>Principle Substrate</th>
<th>Method of Application</th>
<th>Chemical Types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>Nylon, wool, silk, paper and leather</td>
<td>Usually from neutral to acidic dyebaths</td>
<td>Azo (including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso</td>
</tr>
<tr>
<td>Basic</td>
<td>Paper, Polyacrylonitrile, modified nylon, polyester and inks</td>
<td>Applied from acidic dyebaths</td>
<td>Cyanine, hemicyanine, diazahemicynanine, diphenylmethane, triaryl methane, azo, azine, xanthene, acridine, oxazine, and anthraquinone</td>
</tr>
<tr>
<td>Direct</td>
<td>Cotton, rayon, paper, leather and nylon</td>
<td>Applied from neutral or slightly alkaline baths containing additional electrolyte</td>
<td>Azo, anthraquinone, styryl, nitro and benzodifuranone</td>
</tr>
<tr>
<td>Disperse</td>
<td>Polyester, polyamide, acetate, acrylic and plastics</td>
<td>Fine aqueous dispersions often applied by high temperature/ pressure or lower temperature carried methods; dye may be padded on cloth and baked on thermo fixed</td>
<td>Azo, anthraquinone, styryl, nitro and benzodifuranone</td>
</tr>
<tr>
<td>Reactive</td>
<td>Cotton, wool, silk, and nylon</td>
<td>Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)</td>
<td>Azo, antraquinone, phthalocyanine, formazan, oxazine and basic</td>
</tr>
</tbody>
</table>
Table 2.1: Continued.

<table>
<thead>
<tr>
<th>Class</th>
<th>Principle Substrate</th>
<th>Method of Application</th>
<th>Chemical Types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>Plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils and waxes</td>
<td>Dissolution in the substrate</td>
<td>Azo, triphenylmethane, antraquinone and phthacyanine</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Cotton and rayon</td>
<td>Aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulphur containing products on fiber</td>
<td>Indeterminate structures</td>
</tr>
<tr>
<td>Vat</td>
<td>Cotton, rayon and wool</td>
<td>Water-insoluble dyes solubilized by reducing with sodium hydrogen sulfite, then exhausted on fiber and reoxidized</td>
<td>Antraquinone (including polycyclic quinones) and indigiods</td>
</tr>
</tbody>
</table>

2.2 Colour Removal Methods

Verma, Dash and Buhnia (2012) stated that textile wastewater displayed wide range of pH from 2 to 14, COD from 50 to 18 000 mg/L, total dissolved solid (TDS) from 50 to 6000 mg/L as well as variety of synthetic dyes. These indicate that treatment of textile effluent is rather difficult. Therefore, numerous technologies have been investigated to treat the wastewater effluent as existence of dyes in the effluent is extremely undesirable. There are various types of treatment methods such as physical, chemical and biological methods for the removal of synthetic dyes from wastewater to decrease their impact on environment.

There are various physical methods to treat the wastewater for example adsorption, membrane filtration and ion exchange. Adsorption is used to collect the
soluble substances in the solution on an appropriate interface (Soudani, et al., 2011). Activated carbons have been used as adsorbent as it is able to adsorb various dyes with great adsorption capacity. Nevertheless, activated carbon regeneration is required and it is costly (Cecen and Aktas, 2012). Low cost adsorbent materials have been paid attention in recent years such as wood chips and corn cobs (Pang and Abdullah, 2013). Widespread availability and low cost are their benefit. Although adsorption has been certified that it is efficient to remove multiple solutes, but it still has its limitation in the disposal problem as it will produce waste sludge.

Membrane filtration is applied after coagulation and flocculation or after biological wastewater treatment. This method is able to clarify, concentrate and segregate dye from effluent continuously (Mattioli, Malpei and Bortone, 2002). The common types of filtration are microfiltration, ultrafiltration, nanofiltration and reverse osmosis. This method is effective in removing all types of dyes and has special features for instance resistance to temperature. However, high capital cost is required and clogging is possible to be occurred. Lifetime of membrane is relatively short because of clogging on the pores and it is practically limited to smaller wastewater flow rate only (Pang and Abdulllah, 2013).

Ion exchange is used to remove unwanted anions and cations from wastewater. Wastewater will pass through the ion exchange resin until the available exchange sites are saturated. There is no loss of adsorbent on regeneration, reclamation of solvent after use and the removal of soluble dyes are the merits of this method (Evans and Furlong, 2003). Although ion exchange has these merits, it still has the drawback that it only workable in removing the unwanted anions and cations from wastewater effectively but very poor in removing non-ionic dyes such as disperse dyes. Furthermore, it is quite expensive due to the involvement of expensive organic solvents and cannot accommodate several types of dye.

Generally, biological treatment involves the application of microorganisms to degrade organic dyes either aerobic or anaerobic condition by applying fixed or suspended growth system. Aerobic biological treatment is not an effective method in textile wastewater treatment because azo dyes cannot be removed significantly. Low biodegradability index ($\text{BOD}_5/\text{COD} < 0.1$) of azo dyes is the factor that it is resistant
to conventional biological treatment (Baban, et al., 2010). The other drawbacks of this method are large aerobic tank is required as long hydraulic retention time, production of unknown oxidation compounds that intensify the colour of wastewater as well as the formation of undesirable floc which decreases the efficiency of organic dyes biodegradation.

On the other hand, anaerobic biological treatment method has an advantage that methane gas is produced from process and can be used as a renewable energy. However, degradation of dye by microorganism may lead to the creation of aromatic amines through the azoreductase cleavage of azo bond. Aromatic amines are more toxic as compared to dye itself (You and Teng, 2009). Moreover, it is not adequate as a last step of treatment because process is simply a partial degradation process and it needs a long acclimatization time as the growth rate of microorganisms is slow and it is direct consequent of slow growth of methanogenic bacteria (Pang and Abdullah, 2013).

Chemical treatment involves coagulation/ flocculation and chemical oxidation processes. Coagulation and flocculation method is used in primary treatment of textile effluents for eliminating colloidal and other suspended particles from wastewater by adding coagulant. It is an efficient method that has been widely used in textile industry due to their short detention time and easy to operate. However, this method will generate large quantity of sludge which will lead to disposal problem and hardly get rid of highly water-soluble dyes (Verma, Dash and Bhunia, 2012). On top of that, it is an expensive treatment method as the coagulating or flocculating agent is costly. Capital cost for operation is also high because it is required to handle substantial volume of concentrated sludge. Moreover, Joshi, Bansal and Purwar (2004) stated that it can efficiently remove sulphur and disperse dye while it cannot remove acid, direct, mordant and reactive dye well due to the poor quality flocs which does not settle well. In addition, it cannot remove cationic dyes as coagulation does not happen at all.

Chemical oxidation processes have many types of process to treat textile wastewater such as ozonation, photocatalytic process and Fenton process. It is utilised to degrade organic dyes as it is simple and effective in destructing organic compounds with non-biodegradable property, toxic or inhibitory to microbial growth and even
inorganic compounds. For ozonation of textile wastewater, colour can be removed efficiently, biodegradability is enhanced, phenolic compounds are destructed and COD value is reduced (Kharea and Boseb, 2015). The advantages are the volume of wastewater and production of sludge do not increase because of the use of gaseous ozone. Soluble dyes can be decolourized rapidly by ozone whereas for non-soluble dyes need longer time to oxidise. In order to avoid over consumption of ozone by other organic pollutants, pre-treatment of raw textile wastewater is required before ozone process.

Photocatalytic process uses semiconductor metal oxide as catalyst in the presence of ultraviolet light to degrade organic pollutants in water. It is possible to mineralize organic dyes completely in fairly short time as compared to biological treatment but UV light has low penetration ability in water medium. Therefore, it is limited to low concentration or lightly coloured effluent or as a post-treatment process only. Fenton oxidation encompasses reactions of H₂O₂ with iron ions to generate active oxygen species that oxidize organic or inorganic compounds. Wide range of textile dyes can be completely degraded by Fenton and Fenton-like treatments in rather short reaction times. On top of that, it is able to be carried out at room temperature and atmospheric pressure. Reagents that are needed in this method are easily available and liable to store. They do not bring any damage to environment. Babuponnusami and Muthukumar (2014) states that the drawback of homogeneous Fenton process is the large sludge production via flocculation of reagent and dye molecules and wastage of oxidants because of the radical scavenging effect of H₂O₂ as well as self-decomposition of it. Thus, intensive investigation has been shift towards heterogeneous Fenton and Fenton-like processes to overcome the disadvantages encountered by homogeneous Fenton and Fenton-like processes.

2.3 Oxidation by Fenton and Fenton-like Processes

AOPs are alternative wastewater treatment processes which can be operated near ambient temperature and pressure. It is capable to degrade biorefractory organic compounds with the involvement of the production of highly reactive ∙ OH. ∙ OH is the
strongest oxidants among others except fluorine depending on the substrate to be degraded and it can be shown in Table 2.2. Sufficient quantities of $\cdot OH$ can attack extensive variety of organic compounds due to its high oxidation potential (2.80 V). Fenton ($Fe^{2+}/H_2O_2$) and Fenton-like ($Fe^{3+}/H_2O_2$) processes are probably among the most adopted APOs for the treatment of industrial effluent (Lopez, et al., 2012).

**Table 2.2: Standard Reduction Potential of Common Oxidants (Babuponnusami and Muthukumar, 2014)**

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Oxidation Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorine ($F_2$)</td>
<td>3.03</td>
</tr>
<tr>
<td>Hydroxyl radical ($\cdot OH$)</td>
<td>2.80</td>
</tr>
<tr>
<td>Atomic oxygen ($O$)</td>
<td>2.42</td>
</tr>
<tr>
<td>Ozone ($O_3$)</td>
<td>2.07</td>
</tr>
<tr>
<td>Hydrogen peroxide ($H_2O_2$)</td>
<td>1.77</td>
</tr>
<tr>
<td>Potassium permanganate ($KMnO_4$)</td>
<td>1.67</td>
</tr>
<tr>
<td>Chlorine dioxide ($ClO_2$)</td>
<td>1.50</td>
</tr>
<tr>
<td>Hypochlorous acid ($HClO$)</td>
<td>1.49</td>
</tr>
<tr>
<td>Chlorine ($Cl_2$)</td>
<td>1.36</td>
</tr>
<tr>
<td>Oxygen ($O_2$)</td>
<td>1.23</td>
</tr>
<tr>
<td>Bromine ($Br_2$)</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Fenton process involves the production of highly reactive $\cdot OH$ under acidic conditions via the reaction between $H_2O_2$ and ferrous ions ($Fe^{2+}$) (Bagal and Gogate, 2014). In Fenton-like process, $Fe^{2+}$ ions are replaced by ferric ions ($Fe^{3+}$). Jiang, et al. (2013) stated that there was an inherent relationship between Fenton and Fenton-like processes. $Fe^{2+}$ ions catalyse Fenton reaction, whereas $Fe^{3+}$ ions, which is the product of Fenton reaction, catalyze Fenton-like reaction. Shaobin (2008) reported that the degradation of dye in Fenton process was faster than Fenton-like reaction but the degree of degradation accomplished for two processes was similar after 100 min.

Equations 2.1 to 2.9 show the reactions and rate constants for Fenton and Fenton-like reactions and it is tabulated in Table 2.3 (Babuponnusami and
Muthukumar, 2014). Equation 2.1 is known as Fenton reaction and shows the oxidation of $Fe^{2+}$ ions to $Fe^{3+}$ ions in order to decompose $H_2O_2$ into $\cdot OH$. Equation 2.2 is known as Fenton-like reaction and shows that the generated $Fe^{3+}$ ions can be reduced by reaction with excess $H_2O_2$ to form again $Fe^{2+}$ ions and more radicals. Equations 2.2 to 2.5 are the rate limiting steps as $H_2O_2$ is consumed and $Fe^{2+}$ ions are regenerated from $Fe^{3+}$ ions through these reactions. Equations 2.6 to 2.9 are radical-radical reactions.

### Table 2.3: Reactions and Rate Constants for Fenton and Fenton-like Reactions (Babuponnusami and Muthukumar, 2014)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Rate Constants $(M^{-1}s^{-1})$</th>
<th>Equation No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH$</td>
<td>$40 - 80$</td>
<td>(2.1)</td>
</tr>
<tr>
<td>$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 \cdot +H^+$</td>
<td>$9.1 \times 10^{-7}$</td>
<td>(2.2)</td>
</tr>
<tr>
<td>$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^-$</td>
<td>$2.5 - 5 \times 10^8$</td>
<td>(2.3)</td>
</tr>
<tr>
<td>$Fe^{2+} + HO_2 \cdot \rightarrow Fe^{3+} + HO_2^-  $</td>
<td>$0.72 - 1.5 \times 10^6$</td>
<td>(2.4)</td>
</tr>
<tr>
<td>$Fe^{3+} + HO_2 \cdot \rightarrow Fe^{2+} + O_2 + H^+$</td>
<td>$0.33 - 2.1 \times 10^6$</td>
<td>(2.5)</td>
</tr>
<tr>
<td>$\cdot OH + \cdot OH \rightarrow H_2O_2$</td>
<td>$5 - 8 \times 10^9$</td>
<td>(2.6)</td>
</tr>
<tr>
<td>$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2 \cdot$</td>
<td>$1.7 - 4.5 \times 10^7$</td>
<td>(2.7)</td>
</tr>
<tr>
<td>$HO_2 \cdot +HO_2 \cdot \rightarrow H_2O_2 + O_2$</td>
<td>$0.8 - 2.2 \times 10^6$</td>
<td>(2.8)</td>
</tr>
<tr>
<td>$\cdot OH + HO_2 \cdot \rightarrow H_2O + O_2$</td>
<td>$1.4 \times 10^{10}$</td>
<td>(2.9)</td>
</tr>
</tbody>
</table>

In both Fenton and Fenton-like processes, iron ions work as catalyst which possess active site which decomposes $H_2O_2$ molecules into $\cdot OH$ (Soon and Hameed, 2011). Iron is considered to function as a catalyst as $Fe^{2+}$ ion is oxidized to $Fe^{3+}$ ion and then reduced back to $Fe^{2+}$ ion during the process (Wang, Liu and Sun, 2012). Catalysis process can be classified according to the phase of catalyst used. Generally, it can be classified as homogeneous and heterogeneous processes.
2.3.1 Homogeneous Process

In homogeneous Fenton process, Fenton reagents such as H$_2$O$_2$ and Fe$^{2+}$ ions are used and only one phase is involved. The source of $\cdot$OH production is the externally added Fe$^{2+}$ or Fe$^{3+}$ ions (Nidheesh, 2015). For instance, it uses iron salts as the catalyst. Moreover, it involves chemical change only and no mass transfer limitation because of its homogeneous catalytic nature (Shaobin, 2008). In other words, chemical change wholly relies on the nature of the interaction between Fenton’s reagents with target compounds (Soon and Hameed, 2011).

The range of pH for the catalytic activity of homogeneous Fenton and Fenton-like processes is very narrow which ranging from 2 to 4 thus strict control of pH is required (Bagal and Gogate, 2014). Its optimum pH is around pH 3 but the pH of wastewater in many cases is either neutral or alkali (Nidheesh, 2015). Gogate and Pandit (2004) state that at lower pH (pH< 2.5), [Fe$^{2+}$($H_2O$)]$^{2+}$ are formed and it reacts more slowly with H$_2$O$_2$. Consequently, less amount of $\cdot$OH is produced thus degradation efficiency also reduced. Moreover, H$^+$ ions will scavenge the $\cdot$OH especially at very low pH and reaction between Fe$^{3+}$ ions with H$_2$O$_2$ is prohibited. At higher pH (pH> 4), free iron species decrease in solution as the production of ferrous complexes with buffer restraining the production of free radicals and precipitation of ferric oxyhydroxide prohibits reformation of Fe$^{2+}$ ions. Thus, decomposition rate decrease. In addition, increment in pH will decrease oxidation potential of $\cdot$OH. Thus, in order to have effective Fenton reaction, large amount of acid is required to add to reaction medium to achieve pH 3 of solution (Garrido-Ramirez, Theng and Mora, 2010).

In homogeneous process, extensive amount of ferric hydroxide sludge will be produced (Garrido-Ramirez, Theng and Mora, 2010). During the process, there is an increment of quantity of Fe$^{3+}$ ions with reaction time but generation rate of Fe$^{2+}$ ions is slow. Insoluble complexes are formed because of the increased concentration of Fe$^{3+}$ ions. In addition, there is also an increment of concentration of hydroxyl ions (OH$^-$) with the reaction and lead to the further production of iron sludge as pH of solution is increased.
The generation of sludge lead to the disposal and other environmental problems (Garrido-Ramirez, Theng and Mora, 2010). Due to the large amount of sludge is produced, additional downstream treatment is required (Nidheesh, 2015). The downstream treatment is required to increase the pH, precipitate and settle ferric hydroxide. However, there is a difficulty to separate it due to the colloidal features of resulting dispersion (Araujo, et al., 2011). Last but not least, catalyst loss in homogeneous process is high as the amount of $Fe^{2+}$ ions spent increases with the increment of reaction time.

Possible mechanism for the homogeneous Fenton and Fenton-like oxidation of organic compounds is shown in Figure 2.1. Babuponnusami and Muthukumar (2014) states that homogeneous Fenton and Fenton-like processes follow a complex mechanism. Desired $\cdot OH$ is produced through the chain initiation reaction (Equation 2.1). However, $Fe^{2+}$ ions (Equation 2.3), $H_2O_2$ (Equation 2.7) and hydroperoxyl radicals ($HO_2^\cdot$) (Equation 2.9) will scavenges $\cdot OH$. $\cdot OH$ may also be auto scavenged (Equation 2.6). Moreover, $H_2O_2$ may act both as radical generator (Equation 2.1) and as scavenger (Equation 2.7).

![Figure 2.1: Possible Mechanism for the Homogeneous Fenton and Fenton-like Oxidation of Organic Compounds (Bouasla, Ismail and Samar, 2012)](image-url)
2.3.2 Heterogeneous Process

Heterogeneous process involves solid and liquid phase where the reaction takes place at or near interface between phases (McNaught and Wilkinson, 1997). The application of heterogeneous catalyst can solve the limitations of homogeneous process. Catalyst consists of surface $Fe^{2+}$ and $Fe^{3+}$ ions which are the source of $\cdot OH$ generation that is different from homogeneous Fenton process (Nidheesh, 2015). The examples of heterogeneous catalysts are iron materials, goethite ($\alpha$-FeOOH), $Fe_3O_4$, $\alpha$-$Fe_2O_3$ and so on.

In heterogeneous process, besides chemical changes, it also depends on the physical steps arise on the catalyst’s surface at the active sites where mass transfer limited adsorption of reactants happens. Products are desorbed from the active sites at the end of the reaction and new reactants can adsorb on the active sites. Therefore, kinetic rate, efficiency and stability of solid catalyst are strongly affected by their surface characteristics and pore structure (Soon and Hameed, 2011).

Garrido-Ramirez, Theng and Mora (2010) stated that heterogeneous solid catalysts were efficient in wide ranges of pH values as iron species was “immobilized” within the structure and in the interlayer of the space. Therefore, $\cdot OH$ can be generated from $H_2O_2$ continuously by catalyst and precipitation of iron hydroxide can be avoided.

Heterogeneous process is able to reduce the formation rate of sludge. Rate of sludge production is affected by catalyst’s metal leaching properties. The production of sludge will increase when there is an increment in leaching rate. In general, there is slight leaching of metal ions from catalyst which lead to insignificant sludge production (Nidheesh, 2015).

No additional sludge treatment is needed for heterogeneous process as leaching of metal ions from catalyst is very limited (Araujo, et al., 2011). Furthermore, amount of iron species is less consumed as compared to homogeneous process. This is because of the very low leaching properties of catalyst. After the process, solid catalyst is easy to be recovered from liquid products.
For a chemical reaction mechanism, it comprises a series of elementary processes which illustrate how the overall reaction proceeds (Palanna, 2009). Possible mechanism for the heterogeneous Fenton and Fenton-like oxidation is shown in Figure 2.2. In analogy to Haber-Weiss mechanism, the activation of H$_2$O$_2$ through iron-surface species is accomplished by a few of steps (Kwan and Voelker, 2003). The surface Fe$^{2+}$ react with H$_2$O$_2$ to form surface Fe$^{3+}$, ·OH and OH$^-$ (Equation 2.10). Meanwhile, surface Fe$^{3+}$ react with H$_2$O$_2$ to form surface Fe$^{2+}$, HO$_2$· and H$^+$ (Equation 2.11) (Shi, et al., 2016). The generated ·OH is able to degrade numerous organic substrates.

\[
\begin{align*}
\text{Fe}_{\text{surface}}^{2+} + \text{H}_2\text{O}_2 & \leftrightarrow \text{Fe}_{\text{surface}}^{3+} + \cdot \text{OH} + \text{OH}^- \\
\text{Fe}_{\text{surface}}^{3+} + \text{H}_2\text{O}_2 & \leftrightarrow \text{Fe}_{\text{surface}}^{2+} + \text{HO}_2\cdot + \text{H}^+
\end{align*}
\] (2.10) (2.11)

![Figure 2.2: Possible Mechanism for the Heterogeneous Fenton and Fenton-like Oxidation of Phenol Degradation (Rusevova, Kopinke and Georgi, 2012)](image)

The comparison of homogeneous and heterogeneous Fenton and Fenton-like processes under different phenomena is concluded in Table 2.4.
Table 2.4: Comparison of Homogeneous and Heterogeneous Fenton and Fenton-like Processes under Different Phenomena

<table>
<thead>
<tr>
<th>Phenomena</th>
<th>Homogeneous Process</th>
<th>Heterogeneous Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>Single phase.</td>
<td>Involves solid and liquid phases.</td>
</tr>
<tr>
<td>Mechanism</td>
<td>Chemical reaction takes place solely.</td>
<td>Chemical reaction and dual processes of physical adsorption and desorption take place.</td>
</tr>
<tr>
<td>pH</td>
<td>Narrow acidic pH range, pH adjustment is required before and after.</td>
<td>Wide pH range.</td>
</tr>
<tr>
<td>Sludge Production</td>
<td>Large amount of solid sludge will be produced</td>
<td>Insignificant sludge production, depends on the metal leaching properties of catalyst</td>
</tr>
<tr>
<td>Downstream Treatment</td>
<td>Required.</td>
<td>Not required.</td>
</tr>
<tr>
<td>Catalyst Loss</td>
<td>High as the amount of $\text{Fe}^{2+}$ ions spent increases with the increment of reaction time</td>
<td>Amount of iron species is less consumed as leaching of metal ions from catalyst is very limited</td>
</tr>
</tbody>
</table>

2.4 Iron Oxide

Iron oxides are present mainly in earth crust. It is applied in many fields extensively such as catalytic reactions, corrosion processes and electromagnetic devices. This is because it is inexpensive and relatively non-toxic as compared to other transition metals such as chromium and copper (Hou, et al., 2014). $\text{Fe}_3\text{O}_4$, $\alpha$-FeOOH, $\gamma$-Fe$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$ are wisely employed in heterogeneous catalysis process (Pouran, Rahman and Daud, 2014). They are attractive options in treating the polluted soil, groundwater and wastewater. Especially, $\text{Fe}_3\text{O}_4$ has been reported as efficient catalyst.
in heterogeneous Fenton (Liang, et al., 2014) and Fenton-like processes (Hou, et al., 2014).

In this study, Fe$_3$O$_4$ has been used as the heterogeneous catalyst. It is found in nature as mineral Fe$_3$O$_4$ and as a black powder in laboratory. It consists of both Fe$^{2+}$ and Fe$^{3+}$ ions and exhibit permanent magnetism. Fe$_3$O$_4$ in bulk is known as natural magnet because of its ferromagnetic behaviour (Morel, Martínez, and Mosquera, 2013). It also consists of the highest iron content among α- Fe$_2$O$_3$, limonite and siderite (Singh, Mukherjee and Dhillon, 2010).

It is also known as Fe$_3$O$_4$ with chemical formula of (Fe$^{3+}$)$_{tet}$[Fe$^{2+}$Fe$^{3+}$]$_{oct}$O$_4$. Crystal structure of Fe$_3$O$_4$ is formed by the inverse spinel with a unit cell comprises thirty-two O atoms in a face-centred cubic structure and a unit cell edge length of 8.3963 Å. Fe$^{2+}$ ions are located in octahedral sites only whereas Fe$^{3+}$ ions are located in both octahedral sites and tetrahedral sites equally (Pouran, Rahman and Daud, 2014). Figure 2.3 and Figure 2.4 shows the crystal structure of Fe$_3$O$_4$ in a unit cell and arrangement of octahedral and tetrahedral respectively.

![Figure 2.3: Crystal Structure of Fe$_3$O$_4$ in a Unit Cell (Cornell and Schwetmann, 2003)](image-url)
Application of Fe₃O₄ as heterogeneous Fenton catalyst is gaining considerable attention nowadays as it displays several features that are crucial for Fenton and Fenton-like processes. Firstly, it contains Fe²⁺ and Fe³⁺ ions which should have a positive effect on catalytic activity. According to Haber-Weiss mechanism, Fe²⁺ ions play significant role as an electron donor to initiate Fenton reaction (Nidheesh, 2015). Secondly, iron species allow reversible oxidation and reduction while structure is unchanged as the octahedral sites are occupied by both Fe²⁺ and Fe³⁺ ions (Liang, et al., 2013). Therefore, Fe₃O₄ could provide high catalytic activity in oxidation processes due to its special structural characters (Munoz, et al., 2015). Thirdly, Fe₃O₄ possesses peroxidase-like activity and can activate H₂O₂ (Hou, et al., 2014). In addition, strong magnetism of Fe₃O₄ is advantageous to the application in wastewater decontamination with facile recycle as separation of it from aqueous medium by means of magnetic separation (Liang, et al., 2013). It is also capable to function steadily without significant loss of mass (Nidheesh, 2015).

### 2.4.1 Heat-treated Fe₃O₄

Phase transition of Fe₃O₄ into γ- Fe₂O₃ and α- Fe₂O₃ can be achieved through heat treatment. γ- Fe₂O₃ is a metastable phase of iron oxide. It is the intermediate form of
Fe$_3$O$_4$ and $\alpha$-Fe$_2$O$_3$. In addition, it can be considered as an entirely oxidised Fe$_3$O$_4$ (Khan, et al., 2015). Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ have different structures although both of it present ferromagnetic behaviour. Fe$_3$O$_4$ consists of $Fe^{2+}$ and $Fe^{3+}$ ions whereas $\gamma$-Fe$_2$O$_3$ only consists of $Fe^{3+}$ ions and vacancies in their sub-lattices (Can, Coskun and Firat, 2012). On the other hand, $\alpha$-Fe$_2$O$_3$ is the most stable phase of iron oxide (Kazeminezhad and Mosivand, 2014) and exhibits the canted antiferromagnetism. It consists of only $Fe^{3+}$ ions like $\gamma$-Fe$_2$O$_3$ but it has no periodic vacancies. Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ have cubic cells while $\alpha$-Fe$_2$O$_3$ has a rhombohedral crystal structure (Can, Coskun and Firat, 2012).

Khan, et al. (2015) reported that Fe$_3$O$_4$ nanoparticles (black in colour) heated in furnace at 300 to 400 °C for 20 min was transformed to $\gamma$-Fe$_2$O$_3$ (reddish brown in colour). Whereas Fe$_3$O$_4$ nanoparticles (black in colour) heated in furnace 600 and 800 °C for 60 min was transformed to $\alpha$-Fe$_2$O$_3$ (dark red in colour). Different colour of the heated Fe$_3$O$_4$ nanoparticles showed different phases of iron oxide. From the results obtained, it can be concluded that Fe$_3$O$_4$ transformed to $\gamma$-Fe$_2$O$_3$ at lower temperature as compared to $\alpha$-Fe$_2$O$_3$. This is due to Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ have cubic closed packed (CCP) anion arrangement but the conversion of Fe$_3$O$_4$ to $\alpha$-Fe$_2$O$_3$ requires change of CCP anion arrangement to hexagonal closed packed (HCP). Therefore, Fe$_3$O$_4$ can only transform to $\alpha$-Fe$_2$O$_3$ at a higher temperature as substantial rearrangement of ions are required.

Kwan and Voelker (2003) reported that heterogeneous Fenton reaction happens at the surface of catalyst and the rate of production of $\cdot$OH depends on the concentration of H$_2$O$_2$ and the surface area of iron oxide. Khan, et al. (2015) had founded that the size of Fe$_3$O$_4$ was the smallest followed by $\gamma$-Fe$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$ when it was synthesised through heat treatment. So, the rate of production of $\cdot$OH of Fe$_3$O$_4$ may be higher than the $\gamma$-Fe$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$ since it has the highest surface area. Furthermore, Kwan and Voelker (2003) also concluded that ferric oxides are catalytically less active than their ferrous counterpart. Moreover, degradation of 2,4,6-trinitrotoluene by using ferric oxide such as $\gamma$-Fe$_2$O$_3$, $\alpha$-Fe$_2$O$_3$ and $\alpha$-FeOOH were less effective than those minerals embodying both $Fe^{2+}$ ions and $Fe^{3+}$ ions, such as
27

Fe₃O₄ (Matta, et al. 2007). As a conclusion, Fe₃O₄ is expected to have higher catalytic activity than γ-Fe₂O₃ and α-Fe₂O₃.

2.4.2 Characterization of Fe₃O₄

Characterization of a heterogeneous catalyst relates to the determination of its physical and chemical characteristics that are liable for its performance in a reaction. The principle purpose of catalyst characterization is to comprehend the relationship among physical, chemical and catalytic properties. Various types of characterization techniques are utilised to identify the physical and chemical properties of catalyst and relate these to its activity. Therefore, in this research, the developed catalysts will be characterized by XRD and SEM-EDX.

XRD is a powerful non-destructive technique which utilizes an X-ray beam to give details on structure, phases, preferred crystal orientations and other structural parameters, for instance grain size, crystallinity, strain and crystal defects (EAG, 2015). Basic principle of XRD is shown in Figure 2.5. The incident beam and diffracted beam are coplanar while the angle between the incident and scattered beam is 2θ. Bragg law is an easy way to describe the diffraction X-rays by a crystal (He, 2009). If the waves represented by 1’ and 2’ are in phase, a reflected beam of maximum intensity will obtain. According to Bragg law (Equation 2.12), the difference in path length between 1 to 1’ and 2 to 2’ must be an integral number of wavelengths.

\[ n\lambda = 2d \sin \theta \]  

(2.12)

where 

\( n = \) integer

\( \lambda = \) wavelength of X-rays

\( d = \) d-spacing

\( \theta = \) half scattering angle

A diffraction pattern which represents the periodic d-spacing present in sample is possible to be obtained by monitoring the reflected intensity versus 2θ. Several
diffraction peaks will be presented depending on the crystal structure of material in the case of polycrystalline material. On the other hand, the diffraction pattern will be formed by a single diffraction peak representing the mean d-spacing in the case of layered materials with a d-spacing (Martucci, 2014). Diffraction peaks for Fe₃O₄ are at 2θ = 18.2, 30.0, 35.4, 43.0, 53.4, 56.9, 62.5 and 74.0 °, marked by (111), (220), (311), (400), (422), (511), (440) and (533) (Wang, Wei and Qu, 2013).

![Figure 2.5: Representation of XRD Process. Angle θ is Made by Two Parallel Incident Rays 1 and 2 with the Diffracting Parallel Planes at a Distance d (Martucci, 2014)](image)

The crystalline size of materials can be calculated from XRD pattern using the Scherrer equation (Abbas, et al., 2015).

\[
D = \frac{K\lambda}{\beta \cos \theta} \tag{2.13}
\]

where

- \( K \) = shape factor, 0.9
- \( \lambda \) = wavelength of X-ray, 1.540562 Å
- \( \beta \) = full width at half maximum (FWHM), °
- \( \theta \) = Bragg angle for the studied peak, °
SEM is one of the most useful instruments for investigating the topography and morphology of samples. Generally, when there is an interaction between electrons and specimen with different mechanisms, signals such as backscattered electrons, secondary electrons, Auger electrons, characteristic X-rays, cathodoluminescince are produced. Any signal that is produced by electron beam can produce an image of the scanned surface region (Carlton, 2011). The samples for SEM must be electrically conductive to avoid a charge build up in sample that influences the incoming primary and emitted secondary electrons, causing in a poor and distorted image that is constantly altering in contrast and location. The sample which is non-electrically conductive must be coated with a thin conductive layer, for instance carbon or metal (ASM International and Lampman, 2003). EDX is complementary to SEM. EDX is utilized to identify the presence and relative abundance of elements that compose the sample surface. When an energetic electron beams reaches the surface of sample, X-ray photon are produced and detected. Energy of X-ray photon depends on which atom they came from (Olea-Mejia, et al., 2014).

2.5 Parameter Studies

2.5.1 Effect of Various organic dyes

Degradation rate was depending on the structure of organic dyes (Abo-Farha, 2010). Hence, different organic dyes will have different degradation rates by Fenton and Fenton-like processes as every organic dye has their own unique structures.

Based on the study of Su, et al. (2011), the degradation rates for reactive black 5, reactive orange 16 and reactive blue 2 were 96.3, 98.1 and 63.6 % respectively after 100 min. In addition, they found that rate of COD removal for reactive black 5, reactive orange 16 and reactive blue 2 were 31.2, 45.7 and 7.8 %, respectively. The degradation rate and COD removal rate for reactive orange 16 was higher than reactive black 5 and reactive blue 2 due to the simple structure and azo bond in reactive orange 16. Colour loss were resulted by the cleavage of the N=N bond of dyes. Reactive black 5 had two
N=N bonds whereas complex Reactive Blue 2 were only slightly cleaved. Thus, degradation rate of Reactive Blue 2 was the lowest.

From the study reported by Tantak and Chaudhari (2006), complete colour removal (>99 %) for 50 mg/L acid orange 7 can be accomplished by Fenton’s reagent rapidly. Arslan-Alaton, Gursoy and Schmidt (2008) also reported that colour removal was practically complete within the first 2 min. Colour removal for azo dyes (acid red 183 and acid orange 51) and for reactive dye reactive blue 4 was 99 and 93 % respectively after 30 min. Generally, the fast colour removal of dyes is due to adequate \( \cdot \text{OH} \) are generated by fast reaction between \( \text{Fe}^{2+} \) ions and \( \text{H}_2\text{O}_2 \) which cleave the dye chromophores promptly. The degradation of dye’s chromophores at high percentage (90 %) can be achieved by the in situ formed oxidants that have enough oxidation capability.

On the other hand, Xu, et al. (2004) also reported the colour removals for acidic, reactive, direct and cationic dyes were range from 87 and 100 % and total organic carbon (TOC) removals were range from 56 to 79 %. Meanwhile, the colour and TOC removals for disperse and vat dyes were range from 30 to 56 % and 21 to 34 % respectively. According to the results, it can be concluded that molecules of disperse and vat dyes are harder to be destroyed by Fenton process. Moreover, the TOC removal of dyes is difficult as compared to colour removal. This indicates that the chromophoric groups are damaged and are partly mineralized to carbon dioxide and water during the degradation of dyes. Some colourless degradation intermediate compounds for instance adjacent aromatic ring structure are formed during reaction even though the chromophoric structures of dye molecules are damaged by \( \cdot \text{OH} \).

2.5.2 Effect of \( \text{Fe}_3\text{O}_4 \) Dosage

The loading of \( \text{Fe}_3\text{O}_4 \) is a considerable parameter in determining the efficiency of Fenton and Fenton-like processes. Generation of \( \cdot \text{OH} \) is depends on \( \text{Fe}_3\text{O}_4 \) dosage dependence and it can be seen from Equation 2.1 that discussed in Section 2.3.1. \( \cdot \text{OH} \) are generated by the catalytic decomposition of \( \text{H}_2\text{O}_2 \) by \( \text{Fe}^{2+} \) ions.
The increase in the Fe$_3$O$_4$ dosage will increase the efficiency of degradation. Yaman and Gündüz (2015) have reported colour removal slightly increased from 97 to 100 % after 2 h of reaction by doubling the amount of catalyst. The increment of amount of catalyst also increased the COD reduction from 52 to 81 %. The increment in COD removal may be enhanced by the production of more $\cdot \text{OH}$. In addition, degradation is enhanced as more active catalytic site of $Fe^{2+}/Fe^{3+}$ species is provided by the increase of amount of catalyst.

However, degradation rate will decrease when there is an overdose of Fe$_3$O$_4$. This is because $\cdot \text{OH}$ will be scavenged by excessive $Fe^{2+}$ which resulting in reduced degradation efficiency (Bagal and Gogate, 2014). It can be shown in Equations 2.3 and 2.4. Ali, Gad-Allah and Badawy (2013) had reported that the degradation rate was increased with the increment of catalyst concentration until reaching the highest value. After that, there was a slight decrease in the degradation rate due to the further increase of catalyst. Eventually, treatment cost will increase because amount of sludge increases due to the usage of excessive amount of iron salts (Bagal and Gogate, 2014).

### 2.5.3 Effect of H$_2$O$_2$ Dosage

H$_2$O$_2$ is a strong oxidizing agent and its dosage plays an important role in determining the overall degradation rate. When H$_2$O$_2$ dosage increases, degradation percentage of degradation of pollutants will increase (Babuponnusami and Muthukumar, 2014). However, excess amount of H$_2$O$_2$ should be avoided as unused portion of H$_2$O$_2$ during the process will contribute to COD. Excess H$_2$O$_2$ will affect the degradation efficiency as well as harmful to many organisms. According to Bagal and Gogate (2014), an optimum H$_2$O$_2$ dosage exists where maximum degradation of organic pollutants is obtained and excessive H$_2$O$_2$ dosage could decrease the degradation rate.

Yaman and Gündüz (2015) reported the initial rate of colour removal was positively affected when there was an increment of H$_2$O$_2$ concentration from 0.007 to 0.033 M. This is because the increase in the amount of H$_2$O$_2$ increases the formation
rate of $\cdot \text{OH}$. It can be shown in Equation 2.1. However, the initial degradation is slowed down when increasing the $\text{H}_2\text{O}_2$ concentration from 0.033 to 0.07 and to 0.267 M. This is due to $\text{H}_2\text{O}_2$ also acts as the scavenger to produce free radicals when there are large quantities of $\text{H}_2\text{O}_2$ and it can be seen in Equation 2.7 (Bagal and Gogate, 2014).

Furthermore, Yaman and Gündüz (2015) also reported that COD removal at all $\text{H}_2\text{O}_2$ dosage is significantly lower than colour removal. Precedence of the $\cdot \text{OH}$ attack on the $\text{N} = \text{N}$ bonds and the slower devastation of the aromatic or olefinic carbons in dye is signified by the results. The increase in concentration of $\text{H}_2\text{O}_2$ will increase the treatment cost as the use of $\text{H}_2\text{O}_2$ (Bagal and Gogate, 2014). Therefore, it is crucial to optimise the $\text{H}_2\text{O}_2$ dosage in such a way that entire amount is used up.

### 2.5.4 Effect of Dye Concentration

Another significant parameter that will affect the degradation rate is the initial concentration of organic dye. On the basis of collision theory of chemical reactions, concentration of reactant is an important parameter in reactions. Hashemian (2013) reported the rate of degradation increased when there was an increment of initial dye concentration. This is because the frequency of collision between reactants increases when concentration of reactants increases. Moreover, the frequency of effective collision that causes a reaction to happen will also be high (Hassan and Hameed, 2011). Life time of $\cdot \text{OH}$ is very short such as only a few nanoseconds and can only react where they are formed. Thus, the increment of the quantity of dye molecules per volume unit enhances the probability of collision between dyes and $\cdot \text{OH}$. Eventually, degradation rate is increased.

On the other hand, Bouasla, Ismail and Samar (2012) observed that degradation of dye decreased from 97.5 to 67.26 % within 25 min when concentration of dyes increased from 0.03 to 0.15 mmol/L. In addition, according to the study that had been done by Ali, Gad-Allah and Badawy (2013), methyl orange took longer time to be degraded when its concentration was high. For example, for the 10, 20 and 40 mg/L
of methyl orange concentration, concentration of methyl orange was below the detectable level after 30 min whereas for 60 and 80 mg/L methyl orange concentration, 120 min was required for degradation rate of 99 and 97 % respectively. This is due to the increment of initial concentration cause an increase of the number of dye molecules but not the concentration of $\cdot \text{OH}$. Eventually, the number of $\cdot \text{OH}$ available for the complete destruction of organic compounds is insufficient (Bagal and Gogate, 2014). On top of that, excessive dye molecules are adsorbed onto the surface of catalyst at higher concentration of dyes. Consequently, the efficiency of catalyst to degrade dye molecules is limited (Abdullah and Pang, 2010).

2.5.5 Effect of Temperature

Temperature has a crucial role to increase the extent of degradation of dye with the production of $\cdot \text{OH}$ as it is a thermodynamic state function that increases the feasibility of a chemical process. As per Arrhenius law, the rate of $\cdot \text{OH}$ formation increases in a higher temperature. However, at higher temperature, the decomposition of $\text{H}_2\text{O}_2$ into oxygen and water will be accelerated (Velichkova, et al., 2013). This is because the decomposition of $\text{H}_2\text{O}_2$ to oxygen and water is affected by the evolution of heat. The rate of decomposition of $\text{H}_2\text{O}_2$ will be increased with temperature at about 2.3 times per 10 °C rise (Jones, 1999). A beneficial effect was shown in the study of Velichkova, et al. (2013) when there was an increment of temperature from 30 to 60 °C.

Based on the study of Medien and Khalil (2010), an increment in the extent of dye degradation was observed during the reaction temperature raised from 298 to 328 K. The rate and extent of degradation of reaction were practically no difference in temperature between 323 and 328 K. The rates of degradation were decreased at higher reaction temperature more than 328 K. The decrease in rate of degradation might due to the thermal decomposition $\text{H}_2\text{O}_2$. Consequently, effective concentration of $\text{H}_2\text{O}_2$ for producing $\cdot \text{OH}$ was decreased. Thus, lower conversion of dye is happened at higher temperature.
Yaman and Gündüz (2015) reported when the temperature increased from 298 to 333 K, the degradation rate was increased clearly. Degradation and mineralization will increase with the increase of the reaction temperature on the basis of Arrhenius law (Queirós, 2015). This is because there is an increase in the collision frequency of the molecules at catalyst surface and the fraction of molecules that possess energy in surplus of the activation.

2.5.6 Effect of pH

In Fenton and Fenton-like processes, pH of wastewater is very crucial. It has been reported that the activity of catalyst, the activity of oxidant, the dominant iron species, and the stability of H$_2$O$_2$ will be controlled by pH of solution (Xu and Wang, 2011). In classic Fenton process, the optimum pH was found to be around 3 regardless of target substrate. However, in heterogeneous Fenton process, catalysts still can work efficiently in a wide pH range (Nidheesh, 2015). Garrido-Ramirez, Theng and Mora (2010) reported that iron oxide catalyst did not require strict control of pH that was similar to homogeneous Fenton process as Fe/H$_2$O$_2$ heterogeneous system can catalyse oxidation of pollutants through Fenton-like reaction at pH values between 3 and 7.

At acid conditions, degradation rate is higher as Fe$^{2+}$ ions and H$_2$O$_2$ are more stable when pH ranges from pH 3 to 4. At very acidic pH values such as below 2, reaction between Fe$^{2+}$ ions and H$_2$O$_2$ slows down as H$_2$O$_2$ can keep stable to form an oxonium ion (H$_3$O$_2^+$) by proton solvation as presented by Equation 2.14. H$_3$O$_2^+$ ions will reduce the reactivity of H$_2$O$_2$ with Fe$^{2+}$ ions by making H$_2$O$_2$ to be electrophilic and enhancing its stability (Kwon, et al., 1999). Meanwhile, the existed complex species such as [Fe(H$_2$O)$_6$]$^{2+}$ and [Fe(H$_2$O)$_6$]$^{3+}$ also react with H$_2$O$_2$ more slowly. Moreover, scavenging effect of H$^+$ ions could consume O$_2^-$ which will limit the degradation rate and it is presented by Equation 2.15 (Hassan and Hameed, 2011).

$$H_2O_2 + H^+ \rightarrow H_3O_2^+$$ (2.14)
\[ \cdot OH + H^+ + e^- \rightarrow H_2O \] (2.15)

In contrast, at higher pH values such as greater than 3, efficiency of oxidation decreases speedily as \( \text{H}_2\text{O}_2 \) becomes unstable. \( \text{H}_2\text{O}_2 \) begins to decompose rapidly into oxygen and substantial amounts of \( \cdot \text{OH} \) do not formed. The formed oxygen is not able to oxidise the organics efficiently in mild operating conditions used (Hassan and Hameed, 2011). Lee, Oh and Park (2005) reported that modified iron oxide could degrade phenol efficiently up to neutral pH (pH = 7) as it was virtually insoluble and ferric hydroxide was not formed. However, it could not degrade phenol above pH 7 as \( \cdot \text{OH} \) reacted with \( \text{OH}^- \) or \( \text{H}_2\text{O}_2 \) faster than organic compounds above pH 7. In addition, Zhuang, et al. (2015) reported that heterogeneous Fenton process with FeOx/SBAC catalyst could remove refractory pollutants efficiently over a wide range of pH as the catalyst possessed large specific surface area and high point of zero charge (7.6). These promoted the exposure of iron oxide to \( \text{H}_2\text{O}_2 \) at high pH and improved the \( \cdot \text{OH} \) generation rate, further weakening the pH effect of solution.

2.6 Reusability Study

Reusability of catalyst is very important and it is necessary to be studied for economic and environmental reasons. The cost of wastewater treatment can be reduced by the reusability of catalyst. The advantage of heterogeneous process over homogeneous process is that catalyst can be reused. In homogeneous process, the iron content in solution decreases with longer reaction time due to sludge formation (Nidheesh, 2015). The remaining \( \text{Fe}^{2+} \) ions are hard to be separated from solution as it is homogeneously dissolved in water. However, in heterogeneous process, catalysts are solid thus it is not difficult to be separated from solution.

Zhang, et al. (2008) examined reusability of ferromagnetic nanoparticles by repeating phenol removal experiment for five times utilizing same ferromagnetic nanoparticles reproduced easily by sonication and rinsing by deionized water. The ferromagnetic nanoparticles’ catalytic activity still remained almost 100% after 5 rounds of catalytic cycle. In addition, magnetic recovery of ferromagnetic
nanoparticles can prevent secondary pollution such as generation of sludge. This was further reduced the cost per treatment. On the other hand, Nidheesh (2015) also reported Fe$_3$O$_4$ displayed higher stability even after five cycles. In addition, the reusability of Fe$_3$O$_4$ was studied by Zhuang, et al. (2008). It was found that catalytic activity of Fe$_3$O$_4$ was almost remains unchanged after three catalytic cycles.

Khataee (2015) evaluated the catalytic stability of plasma treated Fe$_3$O$_4$ in degradation of basic blue 3 dye by performing four continuous experiments at similar conditions. Catalyst was then separated from treated solution by an external magnetic field. After that, it was rinsed with distilled water and dried. Next, it was used for next test. The results showed that after four degradation cycles, the degradation efficiency of plasma treated Fe$_3$O$_4$ was still high. Thus, nanostructured Fe$_3$O$_4$ can be reused effectively without great activity loss.

2.7 Kinetic Study

Fundamental understanding of reaction kinetic is useful information for up-scale of catalytic chemical processes. Generally, chemical kinetics involves the experimental determination and analysis of quantity of a substance as a function of time. Rate of change in mass of chemicals per unit of time is described in terms of concentration rather than amount in kinetic process as the free concentration of a chemical is the driving force for its kinetics (Roberts, James and Williams, 2015). The “order” of the process is the power to which concentration is increased in the kinetic equation.

Kinetics of pollutant degradation by Fenton and Fenton-like oxidation processes follow the pseudo first or pseudo second reaction order. Liang, et al. (2014) reported that the degradation of acid orange II by Mn substituted magnetite was well fitted with pseudo first-order kinetic equation. Similar result was obtained by Sun and Lemley (2011) that the degradation rate of p-Nitrophenol followed the pseudo first-order degradation kinetics. On the other hand, He, et al. (2014) reported that the degradation of catechol and 4-chlorocatechol were best fitted with pseudo second-order kinetic equation.
CHAPTER 3

METHODOLOGY

3.1 Materials and Chemicals

Chemical reagents that will be used in this experiment and their specifications are listed in Table 3.1. pH of solution will be adjusted by hydrogen chloride (HCl) and sodium hydroxide (NaOH).

<table>
<thead>
<tr>
<th>Chemical Reagent</th>
<th>Purity (%)</th>
<th>Brand</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid orange G</td>
<td>80</td>
<td>Sigma-Aldrich</td>
<td>Model pollutant</td>
</tr>
<tr>
<td>Congo red</td>
<td>40</td>
<td>R &amp; M</td>
<td>Model pollutant</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ nanopowder, 50-100 nm</td>
<td>97</td>
<td>Sigma-Aldrich</td>
<td>Catalyst</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>30</td>
<td>Sigma-Aldrich</td>
<td>Source of ·OH</td>
</tr>
<tr>
<td>HCl</td>
<td>37</td>
<td>Sigma-Aldrich</td>
<td>pH adjustment</td>
</tr>
<tr>
<td>Iron (III) chloride hexahydrate</td>
<td>100</td>
<td>Friendemann Schmidt</td>
<td>Standard solution for ICP-OES</td>
</tr>
<tr>
<td>Malachite green</td>
<td>99</td>
<td>Fisher Scientific</td>
<td>Model pollutant</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>85</td>
<td>R &amp; M</td>
<td>Model pollutant</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>82</td>
<td>R &amp; M</td>
<td>Model pollutant</td>
</tr>
<tr>
<td>NaOH powder</td>
<td>97</td>
<td>Sigma-Aldrich</td>
<td>pH adjustment</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td>95</td>
<td>Sigma-Aldrich</td>
<td>Model pollutant</td>
</tr>
</tbody>
</table>
The model pollutants used in this study are acid orange G, congo red, malachite green, methylene blue, methyl orange and rhodamine B. Chemical structures and classifications of model pollutants are listed in Table 3.2.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Chemical Structure</th>
<th>Classification</th>
<th>Molecular Weight (g/mol)</th>
<th>Maximum absorption wavelength, λ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid orange G</td>
<td><img src="image" alt="Acid orange G" /></td>
<td>Anionic</td>
<td>452.37</td>
<td>479</td>
</tr>
<tr>
<td></td>
<td></td>
<td>acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>azo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Congo red</td>
<td><img src="image" alt="Congo red" /></td>
<td>Anionic</td>
<td>696.67</td>
<td>498</td>
</tr>
<tr>
<td></td>
<td></td>
<td>direct</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>diazo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Malachite green</td>
<td><img src="image" alt="Malachite green" /></td>
<td>Cationic</td>
<td>364.911</td>
<td>619</td>
</tr>
<tr>
<td></td>
<td></td>
<td>basic</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>triarylmethane</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 3.2: Continued.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Chemical Structure</th>
<th>Classification</th>
<th>Molecular Weight (g/mol)</th>
<th>Maximum absorption wavelength, λ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene blue</td>
<td><img src="image" alt="Methylene blue" /></td>
<td>Cationic</td>
<td>373.88</td>
<td>665</td>
</tr>
<tr>
<td></td>
<td></td>
<td>basic</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>thiazine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl orange</td>
<td><img src="image" alt="Methyl orange" /></td>
<td>Anionic</td>
<td>327.33</td>
<td>464</td>
</tr>
<tr>
<td></td>
<td></td>
<td>acid</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>azo</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhodamine B</td>
<td><img src="image" alt="Rhodamine B" /></td>
<td>Cationic</td>
<td>479.02</td>
<td>555</td>
</tr>
<tr>
<td></td>
<td></td>
<td>basic</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>xanthene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.2 Equipments

The instruments needed for this study are presented in Table 3.3 together with their model. Furnace is used for heat treatment of Fe₃O₄. XRD and SEM-EDX are used for characterization of heat-treated Fe₃O₄. COD reactor was used to heat sample with COD digestion reagent vials. Analysis of liquid samples will be done by using ultraviolet-visible-infrared (UV-vis) spectrophotometer, spectrophotometer and inductively coupled plasma-optical emission spectroscopy (ICP-OES). pH meter is utilized to measure the pH of solution whereas incubator shaker is used to ensure uniform mixing of Fe₃O₄ and solution.

Table 3.3: Model of Apparatus

<table>
<thead>
<tr>
<th>Apparatus</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbolite furnace</td>
<td>Carbolite RHF 1500</td>
</tr>
<tr>
<td>COD reactor</td>
<td>DRB200</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Optima 7000 DV</td>
</tr>
<tr>
<td>Incubator shaker</td>
<td>Labtech LSI-2016A</td>
</tr>
<tr>
<td>pH Meter</td>
<td>Eutech PC300</td>
</tr>
<tr>
<td>SEM-EDX</td>
<td>Hitachi SEM Model S-3400N</td>
</tr>
<tr>
<td>Spectrophotometer</td>
<td>DR3900</td>
</tr>
<tr>
<td>UV-vis spectrophotometer</td>
<td>Jenway 6320D</td>
</tr>
<tr>
<td>XRD</td>
<td>Shimadzu XRD-6000</td>
</tr>
</tbody>
</table>

3.3 Overall Experiment Flowchart

Figure 3.1 shows the flow chart for overall research activities. Fe₃O₄ catalysts are heat-treated in furnace at different temperature. The heat-treated Fe₃O₄ catalysts are then characterized through XRD and SEM-EDX. After that, the various parameters studies are done by varying type of organic dyes, Fe₃O₄ dosage, H₂O₂ dosage, concentration of organic dye, temperature and pH of solution. The liquid samples are then analysed through UV-vis spectrophotometer, COD analysis and ICP-OES. The reusability of Fe₃O₄ is studied. Lastly, the kinetic of organic dye degradation is also studied.
Heat Treatment of Fe$_3$O$_4$ Catalyst

Characterization
- XRD
- SEM-EDX

Parameter Studies
- Types of Organic Dyes (Acid orange G, congo red, malachite green, methylene blue, methyl orange, rhodamine B)
- Fe$_3$O$_4$ Dosage (0, 0.5, 1.0, 1.5, 2.0, 2.5 g/L)
- H$_2$O$_2$ Dosage (0, 0.05, 0.10, 0.15, 0.20, 0.25 M)
- Concentration of Organic Dye (20, 30, 40, 50, 60 mg/L)
- Temperature (30, 60, 70, 80 °C)
- pH of Solution (pH 3, 5, 7, 9, 11)

Reusability Study

Kinetic Study

Liquid Sample Analysis
- UV-vis Spectrophotometer
- COD Analysis
- ICP-OES

Figure 3.1: Flow Chart of Overall Research Activities
3.4 Experimental Setup

The experiment setup is shown in Figure 3.2. Incubator shaker was used to ensure uniform mixing of Fe₃O₄ in dye solution in the conical flask. Speed of agitation, time duration for mixing and temperature of the reaction can be controlled.

![Figure 3.2: Schematic Diagram of Fenton and Fenton-like Processes using Incubator Shaker](image)

3.5 Experiment Procedures

3.5.1 Preparation of Fe₃O₄

Fe₃O₄ was purchased from Chemolab Supplier. Five samples of original and heat-treated Fe₃O₄ were prepared. 1.5 g of Fe₃O₄ was weighted for each set. One set of Fe₃O₄ was not heat-treated and another four sets were heat-treated at temperatures of 200, 400, 600 and 800 °C in a furnace for 2 h to induce phase transformation. Original and heat-treated Fe₃O₄ at 200, 400, 600 and 800 °C were defined as Fe₃O₄-0, Fe₃O₄-200, Fe₃O₄-400, Fe₃O₄-600 and Fe₃O₄-800 respectively. Afterwards, the heat-treated Fe₃O₄ were characterized by using XRD and SEM-EDX.
3.5.2 Characterizations of Catalysts

3.5.2.1 XRD

The crystallization phase analysis was performed by XRD to study the crystalline structure of Fe₃O₄. The Cu-Kα (λ = 1.540562 Å) radiation source was manipulated at 40 kV/30 mA. Interference peak was removed by using K-beta filter. Divergence slit and scattering slit 1 ° together with 0.3 mm of receiving slit were applied. The sample was placed into a sample holder by smear uniformly onto a glass slide. The intensity of diffracted X-rays was recorded continuously by monitoring the diffraction pattern emerging in the 2θ ranging from 10 to 80 ° with a scan rate 2 °/min and a scan step 0.02 °. A peak in intensity happened when the mineral had lattice planes with d-spacing adequate to diffract X-rays at the value of θ.

3.5.2.2 SEM-EDX

SEM analysis was done with a scanning electron microscope in order to examine the morphological structure and measure particle size of heat-treated Fe₃O₄ catalysts. The catalysts were adhered on specimen holder by using the double-sided adhesive tape prior to observation under SEM. During sample preparation and transfer, gloves must be worn all the time to prevent contamination to SEM system. The scanning electron images were acquired by utilizing the acceleration voltage of 20 kV and magnification of 10, 20 and 40 kX. By using EDX coupled to SEM, the element composition of the catalysts was identified.
3.5.3 Parameter Studies

Varies operating parameters such as various organic dyes (Acid orange G, congo red, malachite green, methylene blue, methyl orange and rhodamine B), Fe$_3$O$_4$ dosage (0 to 2.5 g/L), H$_2$O$_2$ dosage (0 to 0.25 M), dye concentration (20 to 60 mg/L), pH (pH 3 to 11) and temperature (30 to 80 °C) were studied for the purpose of investigating the efficiency of Fenton and Fenton-like processes.

3.5.3.1 Effect of Various Organic Dyes

Effect of various organic dyes on the rate of degradation was investigated. Six organic dyes used were acid orange G, congo red, malachite green, methylene blue, methyl orange and rhodamine B. 100 ml of organic dye solution with concentration of 20 mg/L was filled into conical flask. pH of solution was adjusted to pH 7 by utilizing 0.1 M HCl or 0.1 M NaOH. The dosages of Fe$_3$O$_4$ and H$_2$O$_2$ used were 1 g/L and 0.2 M respectively. Reaction temperature was maintained at 30 °C in incubator shaker with agitation at 130 rpm. The sample was withdrawn from the flask every 10 min in duration of 1 h for analysis. The experiments were carried out in six sets by using different types of organic dye solution. Malachite green was used for subsequent experiment due to its high degradation efficiency by Fe$_3$O$_4$.

3.5.3.2 Effect of Fe$_3$O$_4$ Dosage

The effect of Fe$_3$O$_4$ dosage on the rate of degradation was investigated by changing the dosage of Fe$_3$O$_4$ to 0, 0.5, 1.0, 1.5, 2.0 and 2.5 g/L. 100 ml of malachite green solution with concentration of 20 mg/L was filled into conical flask. pH of solution was adjusted to pH 7. After that, no Fe$_3$O$_4$ was added into the solution for 0 g/L. Reaction was initiated by adding H$_2$O$_2$ with dosage of 0.2 M. Then, the solution was placed into incubator shaker and agitated at 130 rpm. The experiment was conducted at room temperature of 30 °C. The sample was withdrawn from the flask every 10 min
in duration of 1 h for analysis. The other five set was repeated by adding Fe₃O₄ and other parameters kept constant in the experiment. Fe₃O₄ with optimum dosage of 2.5 g/L was used for the subsequent experiment which varying the H₂O₂ dosage.

### 3.5.3.3 Effect of H₂O₂ Dosage

The dosage of H₂O₂ in 0, 0.05, 0.10, 0.15, 0.20 and 0.25 M was varied to investigate the effect of H₂O₂ dosage on the rate of degradation. Similarly, 100 ml of malachite green solution with concentration of 20 mg/L was filled into conical flask and adjusted to pH 7. After that, Fe₃O₄ with dosage of 2.5 g/L was added into the solution and no H₂O₂ was added. Next, the solution was placed into incubator shaker at 30 ℃ and agitation was provided at 130 rpm. The sample was withdrawn from the flask every 10 min in duration of 1 h for analysis. The other five set was repeated by adding H₂O₂ and other parameters kept constant in the experiment. H₂O₂ with optimum dosage of 0.20 M was used for the subsequent experiment which varying concentration of dye.

### 3.5.3.4 Effect of Dye Concentration

The effect of concentration of dyes was also studied by varying the concentration of malachite green solution to 20, 30, 40, 50 and 60 mg/L. 100 ml of malachite green solution with concentration of 20 mg/L was filled into conical flask. pH of solution was adjusted to pH 7. Fe₃O₄ with dosage of 2.5 g/L and H₂O₂ with dosage of 0.2 M was added into the solution. After that, the solution was placed into incubator shaker at 30 ℃ and agitated at 130 rpm. The sample was withdrawn from the flask every 10 min in duration of 1 h for analysis. The other four set of different concentration of malachite green solution were repeated by displacing the concentration 30 mg/L and other parameters kept constant in the experiment. Solution of malachite green of 20 mg/L was used for the subsequent experiment which varying the reaction temperature.
3.5.3.5 Effect of Temperature

The temperature of reaction was varied to 30, 60, 70 and 80 °C in the experiment thus the effect of temperature on the rate of degradation could be studied. In this experiment, 100 ml of malachite green solution with concentration of 20 mg/L was filled into conical flask and adjusted to pH 7. Fe₃O₄ with dosage of 2.5 g/L and H₂O₂ with dosage of 0.2 M was added into the solution. Then, the solution was placed into incubator shaker at 30 °C and agitated at 130 rpm. The sample was withdrawn from the flask every 10 min in duration of 1 h for analysis. The other three different temperatures were repeated by displacing the temperature of 30 °C and other parameters kept constant in the experiment. Reaction temperature of 30 °C was used for the subsequent experiment which varying the pH of solution.

3.5.3.6 Effect of pH

The effect of pH on the rate of degradation was also be studied by varying the pH to pH 3, 5, 7, 9 and 11. The pH of solution was adjusted by using 0.1 M HCl or 0.1 M NaOH. Similar to previous experiment, Fe₃O₄ with dosage of 2.5 g/L and H₂O₂ with dosage of 0.2 M was put into 100 ml of malachite green solution with concentration of 20 mg/L. In this case, initially pH 3 was set in this experiment. Then, the solution was placed into incubator shaker at 30 °C and agitated at 130 rpm. The sample was withdrawn from the flask every 10 min in duration of 1 h for analysis. The other four value of pH was repeated by replacing the pH 3 and other parameters remain unchanged in the experiment. Optimum solution pH was pH 9.

3.5.4 Reusability Study

The reusability of Fe₃O₄ catalyst was also studied. 2.5 g/L of Fe₃O₄ was placed in contact with 100 ml of malachite green solution with concentration of 20 mg/L at
pH 9. The dosage of H$_2$O$_2$ used was 0.2 M. Then, the solution was placed into incubator shaker with agitation at 130 rpm and temperature at 30 °C for 1 h. The sample was withdrawn from the flask every 10 min in duration of 1 h for analysis. The used Fe$_3$O$_4$ was then recovered by magnet. After that, it was rinsed with distilled water and dried. The Fe$_3$O$_4$ was subsequently used in another cycle keeping the same standard conditions and ratio of catalyst/dye.

3.5.5 Kinetic Study

Kinetic analysis was done in this experiment. Pseudo zero-order, first-order and second-order reaction kinetics were applied to investigate the degradation kinetics of dyes by Fenton and Fenton-like processes using Fe$_3$O$_4$ catalyst. The individual expression was shown as equations given below:

Apparent zero order reaction kinetics:

$$C_t = C_0 - k_0 t$$  \hspace{1cm} (3.1)

Apparent first order reaction kinetics:

$$\ln C_t = \ln C_0 - k_1 t$$  \hspace{1cm} (3.2)

Apparent second order reaction kinetics:

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t$$  \hspace{1cm} (3.3)

where

- $C_t =$ dye concentration at any time, $\frac{mg}{L}$
- $k_0 =$ apparent pseudo-zero order rate constant, $\frac{mg}{L \cdot min}$
- $k_1 =$ apparent pseudo-first order rate constant, $/min$
\( k_2 \) = apparent pseudo-second order rate constant, \( \frac{L}{mg \ min} \)

\( t \) = the reaction time, \( min \)

The regression analysis based on pseudo zero-order, pseudo first-order and pseudo second-order reaction kinetics for the colour of dye was conducted. A linear plot was obtained only if using correct order of reaction kinetics.

### 3.6 Liquid Sample Analysis

The residual concentration of organic dyes in the solution at different times of sampling was measured in order to study the course of degradation reactions. The absorbance of organic dyes was measured by using UV-vis spectrophotometer at the wavelength with highest absorbance, \( \lambda_{max} \). The \( \lambda_{max} \) for different organic dyes is shown in Table 3.2. According to Lambert-Beer law, the organic dye concentration was quantified via a calibration curve. The degree of degradation of organic dye was computed by using Equation 3.4.

\[
\text{Degradation efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \ \% 
\]

where

\( C_0 \) = dye concentration at time 0, mg/L

\( C_t \) = concentration of dye at time \( t \), mg/L

COD is applied to identify the quantity of organic compounds. It is a useful measurement indicator of water quality. For COD test, its basis is almost all organic compounds can be completely oxidised by a strong oxidizing agent to carbon dioxide under acidic conditions. In order to study the extent of mineralization, COD of sample was determined by Colorimetric Determination Method 8000. In this study, sample was heated for 2 h with COD digestion reagent vials. After that, low range test was taken place.
ICP-OES is a powerful and popular analytical tool in determining trace elements in infinite sample types. This apparatus is based upon the spontaneous emission of photon from ions and atoms that have been stimulated in a radiofrequency discharge. Liquid samples may be injected directly into the instruments but solid samples need extraction or acid digestion so analytes will be existed in solution. The stability of Fe₃O₄ was studied by evaluating leaching of iron from Fe₃O₄. The concentration of leaded iron was determined by using an ICP-OES. Iron (III) chloride hexahydrate (FeCl₃) was used as the iron source to prepare the standard solution for the analysis. The concentration of standard solution was 10, 20, 30, 40 and 50 mg/L. The liquid samples without pH control and the liquid samples with pH control (pH 9) were tested. The other parameters used for the liquid samples was as followed: Fe₃O₄ dosage was 2.5 g/L, H₂O₂ dosage was 0.2 M, dye concentration was 20 mg/L, temperature was 30 °C and reaction time was 1 h.
CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterizations of Fe$_3$O$_4$

4.1.1 XRD Results

The crystal structures of original Fe$_3$O$_4$ and various heat-treated Fe$_3$O$_4$ at different temperatures were observed by using XRD measurement. The XRD patterns are shown in Figure 4.1. Fe$_3$O$_4$-0 had the same patterns with standard Fe$_3$O$_4$ where the characteristic peaks were at 2$\theta$ = 18.2, 30.0, 35.4, 43.0, 53.4, 56.9, 62.5 and 74.0 ° (Wang, Wei and Qu, 2013). Moreover, it was black in colour which black was the characteristic colour of Fe$_3$O$_4$ (Legodi and Waal, 2007). Therefore, it verified that it was Fe$_3$O$_4$ nanoparticles.

Based on the Figure 4.1, it could be observed that the XRD patterns for Fe$_3$O$_4$-0 and Fe$_3$O$_4$-200 had same characteristic peaks. It was reported that Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ had same XRD characteristic peaks (Abbas, et al., 2015). The diffraction peaks of Fe$_3$O$_4$-200 were in consistent with the standard $\gamma$-Fe$_2$O$_3$ where 2$\theta$ = 18.3, 30.2, 35.6, 43.2, 53.7, 57.2 and 62.9 ° (Gatabi, Moghaddam and Ghorbani, 2016). In addition, Fe$_3$O$_4$-200 was in brown which was same as the characteristic colour for $\gamma$-Fe$_2$O$_3$ (Legodi and Waal, 2007) and it was considered as evidence for the formation of $\gamma$-Fe$_2$O$_3$ phase. Occurrence of phase transformation from Fe$_3$O$_4$ to $\gamma$-Fe$_2$O$_3$ was caused by the heat treatment of Fe$_3$O$_4$ at lower temperature and in the presence of air (oxygen). This was due to the unstable Fe$_3$O$_4$ sensitive to oxidation (Khan, et al., 2015).
Figure 4.1: XRD Patterns for (a) Fe₃O₄-0, (b) Fe₃O₄-200, (c) Fe₃O₄-400, (d) Fe₃O₄-600 and (e) Fe₃O₄-800

The XRD pattern of Fe₃O₄-400 was slightly different from Fe₃O₄, γ-Fe₂O₃ and α-Fe₂O₃. Its XRD pattern showed the presence of both γ-Fe₂O₃ and α-Fe₂O₃ phases. At θ = 30.2 °, it contained the peak which represented γ-Fe₂O₃ phase. Meanwhile, it also comprised the peak which represent α-Fe₂O₃ phase at θ = 33.1 and 49.5 °. Thus, Fe₃O₄-400 might contain both γ-Fe₂O₃ and α-Fe₂O₃ phases. Besides, the colour of Fe₃O₄-400 was similar to brown of γ-Fe₂O₃ and red of α-Fe₂O₃ which could be considered as the evidence that it might consist both phases. At temperature of 400 °C, the incomplete phase changed from metastable γ-Fe₂O₃ to stable α-Fe₂O₃ might take place. Islam, et al. (2012) observed that γ-Fe₂O₃ could be obtained when oxidizing Fe₃O₄ at 250 °C for 8 h in the presence of oxygen and α-Fe₂O₃ could be obtained when sintering γ-Fe₂O₃ at 500 °C for 3 h in the presence of argon. In addition, Khan, et al. (2015) also reported that γ-Fe₂O₃ could be obtained when sintering iron oxide nanoparticles at 350 °C via dry oxidation for 30 min and α-Fe₂O₃ could be obtained at 600 °C via dry oxidation for 60 min. Therefore, 400 °C might be the phase transition temperature for γ-Fe₂O₃ transforming to α-Fe₂O₃.

Fe₃O₄-600 and Fe₃O₄-800 had the same patterns with standard α-Fe₂O₃ where the characteristic peaks were at 2θ = 24.1, 33.2, 35.8, 40.7, 49.5, 54.2, 57.6 and 62.5 ° (Ramasami, et al., 2016). Moreover, both samples were in red colour which red was
the characteristic colour of α-Fe₂O₃ (Legodi and Waal, 2007). Therefore, it was suggested that both samples mainly composed of α-Fe₂O₃ phase. As increasing the temperature from 400 until 600 and 800 °C, the remaining of γ-Fe₂O₃ phase transformed completely to α-Fe₂O₃ (Bora, et al., 2012). Cudennec and Lecerf (2006) claimed that the formation of α-Fe₂O₃ is favoured at higher temperature. This was due to the substantial rearrangement of ions was required to transform from CCP anion arrangement of γ-Fe₂O₃ to HCP of α-Fe₂O₃ (Khan, et al., 2015).

The crystalline size of the samples was calculated from XRD pattern using the Scherrer equation (Equation 2.13) (Abbas, et al., 2015). The calculated values of crystalline size for original Fe₃O₄ and various heat-treated Fe₃O₄ are represented in Table 4.1. According to Table 4.1, crystalline size of sample decreased when temperature increased to 400°C. Similar result was obtained by Múquiz-Ramos, et al. (2015). They found out that the crystalline size of γ-Fe₂O₃ obtained at different temperature was decreased when temperature increased from 200 to 300 °C. This was due to the crystallization of γ- phase, whose particles were generally ultrafine (Cava, et al., 2007). However, crystalline size of sample increased when temperature increased from 400 to 800 °C. The increase in crystalline size was due to the acquirement of a stable phase by minimizing surface energy (Bora, et al., 2012). In addition, crystallite growth or aggregation of Fe₃O₄ particles would be promoted by high temperatures (Abdullah and Pang, 2010).

Table 4.1: Crystalline Sizes for Original Fe₃O₄ and Various Heat-treated Fe₃O₄

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>Crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>47.39</td>
</tr>
<tr>
<td>200</td>
<td>44.53</td>
</tr>
<tr>
<td>400</td>
<td>39.51</td>
</tr>
<tr>
<td>600</td>
<td>40.37</td>
</tr>
<tr>
<td>800</td>
<td>50.51</td>
</tr>
</tbody>
</table>
4.1.2 SEM-EDX Results

The particle morphology of the original and various heat-treated Fe$_3$O$_4$ particles was studied using SEM as shown in Figure 4.2. The morphology of the majority particles was spherical in shape (Khan, et al., 2015). In addition, the size of particles in Fe$_3$O$_4$-0 was in the range of 150 to 180 nm whereas the size of particles in Fe$_3$O$_4$-800 was in the range of 220 to 250 nm. It could be seen that the increment of the sintering temperature up to 800 °C increased the mean particle size. There was an obvious particle agglomeration could be observed in Figure 4.2 (d) and (e) and it might be caused by the heating of Fe$_3$O$_4$ particles and magnetic dipole interaction of Fe$_3$O$_4$ magnetic particles (Kazeminezhad and Mosivand, 2014).

![SEM Images of (a) Fe$_3$O$_4$-0, (b) Fe$_3$O$_4$-200, (c) Fe$_3$O$_4$-400, (d) Fe$_3$O$_4$-600 and (e) Fe$_3$O$_4$-800](image)

Figure 4.2: SEM Images of (a) Fe$_3$O$_4$-0, (b) Fe$_3$O$_4$-200, (c) Fe$_3$O$_4$-400, (d) Fe$_3$O$_4$-600 and (e) Fe$_3$O$_4$-800
Hu, et al. (2011) reported that agglomeration of Fe₃O₄ nanoparticles after heating at 650 and 700 °C. Besides, Kazeminezhad and Mosivand (2014) observed that the size of electrooxidized Fe₃O₄ nanoparticles was in nano range and they agglomerated into clusters after heating at 650, 800 and 1000 °C. Thus, the result in this research works was consistent with the reported results.

The EDX analysis of the samples is shown in Figure 4.3. It illustrated that all samples composed of Fe and O atoms only and no other elements presented. The theoretical atomic Fe/O ratio for Fe₃O₄ was 0.75 whereas for Fe₂O₃ was 0.667 (Wu and Wang, 2013). The atomic Fe/O ratio for the samples were calculated and summarized in Table 4.2. According to Table 4.2, the atomic ratio for Fe₃O₄-0 was closer to the theoretical atomic ratio of Fe₃O₄ as compared to Fe₂O₃. Thus, Fe₃O₄-0 was confirmed as Fe₃O₄. The rest of the samples possess the closer atomic ratio to theoretical value of Fe₂O₃ as compared to value of Fe₃O₄. Thus, it is anticipated that the samples had the molecular compound of Fe₂O₃. Even though the atomic ratio of Fe₃O₄-800 was quite closer to the value for both Fe₃O₄ and Fe₂O₃ the colour of the sample was red colour instead of black colour. Thus, there was a high possibility that Fe₃O₄-800 contains Fe₂O₃ instead of Fe₃O₄. γ- Fe₂O₃ and α- Fe₂O₃ possessed same atomic and weight ratio but it could be easily differentiated with the help of their colour (Legodi and Waal, 2007). By differentiating their colour, Fe₃O₄-200 was γ- Fe₂O₃ (brown) whereas Fe₃O₄-600 and Fe₃O₄-800 were α- Fe₂O₃ (red). In addition, sample Fe₃O₄-400 might contain both γ- Fe₂O₃ and α- Fe₂O₃ as its colour was similar to brown as well as red.

<table>
<thead>
<tr>
<th>Samples No.</th>
<th>Fe (%)</th>
<th>O (%)</th>
<th>Fe/O (Atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>44.40</td>
<td>55.60</td>
<td>0.80</td>
</tr>
<tr>
<td>b</td>
<td>41.42</td>
<td>58.58</td>
<td>0.70</td>
</tr>
<tr>
<td>c</td>
<td>38.47</td>
<td>61.43</td>
<td>0.63</td>
</tr>
<tr>
<td>d</td>
<td>41.23</td>
<td>58.77</td>
<td>0.70</td>
</tr>
<tr>
<td>e</td>
<td>41.83</td>
<td>58.17</td>
<td>0.71</td>
</tr>
</tbody>
</table>
Figure 4.3: EDX Analysis of (a) Fe$_3$O$_4$-0, (b) Fe$_3$O$_4$-200, (c) Fe$_3$O$_4$-400, (d) Fe$_3$O$_4$-600 and (e) Fe$_3$O$_4$-800

4.2 Effect of Heat Treatment

The effect of various heat treatment of Fe$_3$O$_4$ (200, 400, 600 and 800 °C) on the degradation of malachite green by Fenton and Fenton-like reactions was investigated. As noted in Figure 4.4, the highest degradation efficiency of malachite green was achieved by the original Fe$_3$O$_4$ without heat treatment. This observation demonstrated that Fe$_3$O$_4$ without any heat treatment already possessed the highest catalytic activity.
Figure 4.4: Degradation Efficiency of Malachite Green during Fenton and Fenton-like Processes by Different Heat-treated Fe₃O₄ Catalysts (Fe₃O₄ dosage = 1 g/L, initial dye concentration = 20 mg/L, H₂O₂ dosage = 0.2 M, reaction temperature = 30°C, pH = 7, reaction time)

Original Fe₃O₄ possessed the highest degradation efficiency in degradation of malachite green due to its unique characteristics. Fe₃O₄ without heat treatment had Fe²⁺ and Fe³⁺ ions in its structure whereas the heat-treated Fe₃O₄ contained predominantly Fe³⁺ ions only. Fe₃O₄ was the only most plentiful iron oxide with Fe²⁺ ions in its structure that enhanced the production of ·OH (Pouran, Raman, and Daud, 2014). Xue, Hanna and Deng (2009) claimed that the structural Fe²⁺ content was influential in Fenton oxidation system as the rate constant of Equation 2.1 was much higher than Equation 2.2 (40 − 80 vs 9.1 × 10⁻⁷ /M · s). Moreover, Matta, et al. (2008) reported that degradation efficiency was positively correlated with the Fe²⁺ content in the structure of mineral in Fenton oxidation of 2,4,6-trinitrotoluene. In addition, the octahedral structure of Fe₃O₄ could simply accommodate both Fe²⁺ and Fe³⁺ ions and allowed iron species to be reversibly oxidized and reduced while maintaining the same structure (Munoz, et al., 2015). Thus, Fe₃O₄ presented higher potential for degradation of dyes than γ-Fe₂O₃ and α-Fe₂O₃.
The particle size of catalyst was one of the significant parameter in the degradation of dye. From the SEM image, the mean particle size of Fe₃O₄ increased with the high temperature of heat treatment could be noted. Excessive heat treatment caused the agglomeration of particles. Particle agglomeration was a problem as it could reduce the surface area and active sites for adsorption or reaction (Wei and Viadero Jr, 2007). Consequently, the degradation efficiency of malachite green became lower. Therefore, Fe₃O₄ without heat treatment possessed higher degradation efficiency of malachite green than other heat-treated Fe₃O₄. In short, due to its high degradation efficiency, original Fe₃O₄ had been chosen to be used in the rest of experiment in order to study the organic dyes removal by heterogeneous Fenton and Fenton-like processes.

4.3 Parameter Studies

4.3.1 Effect of Various Organic Dyes

The effect of various organic dyes on the Fenton and Fenton-like degradation was investigated. Six organic dyes used were acid orange G, congo red, malachite green, methylene blue, methyl orange and rhodamine B. The results are shown in Figure 4.5. Based on the result, the degradation of malachite green was significantly increased as compared to other organic dyes. The organic dye degradation efficiency generally followed the order as below:

Malachite green > acid orange G > congo red > methylene blue > rhodamine B > methyl orange
Figure 4.5: Degradation Efficiency of Various Organic Dyes during Fenton and Fenton-like Processes by Fe₃O₄ Catalyst (Fe₃O₄ dosage = 1 g/L, H₂O₂ dosage = 0.2 M, initial dye concentration = 20 mg/L, reaction temperature = 30 °C, reaction time = 1 h, initial pH = 7)

The degradation process was mainly influenced by the molecular structures of organic molecules (Rao and Venkatarangaiah, 2014). Malachite green had the highest degradation efficiency compared to other organic dyes might due to the triphenyl methane structure of malachite green was the most vulnerable to electrochemical oxidation (Rao and Venkatarangaiah, 2014). Moreover, the structure of malachite green was considered simpler as compared to other organic dyes. Lavanya, et al. (2014) reported that organic dyes with simpler structure displayed higher rate of colour removal. The other five organic dyes could not be highly degraded might because of their complex chemical structures. For instances, the low degradation efficiency of acid orange G, congo red and methyl orange might due to the presence of azo (-N=N-) groups bound to aromatic ring. Methylene blue which was a thiazine dye had the heterocyclic aromatic structure which was resistant to degradation (Rao and Venkatarangaiah, 2014). Rhodamine B which was a xanthene dye had a comparatively high resistance to oxidation degradation (Xue, Hanna and Deng, 2009). In addition, the high degradation efficiency of malachite green might also partially due to the
decolourization by $OH^-$. This is because the basic hydrolysis of malachite green causes the formation of triphenylcarbinol structure and leads to the loss of conjugation in its structure (Rao and Venkatarangaiah, 2014). This further lead to the mineralization of dye. Process of hydrolysis is shown in Figure 4.6. Therefore, due to the high degradation efficiency of malachite green by Fe$_3$O$_4$ as compared to other organic dyes, it had been chosen to be used in the rest of experiment.

![Figure 4.6: Basic Hydrolysis of Malachite Green (Rao and Venkatarangaiah, 2014)](image)

4.3.2 Effect of Fe$_3$O$_4$ Dosage

The effect of Fe$_3$O$_4$ dosages (0, 0.5, 1.0, 1.5, 2.0 and 2.5 g/L) was investigated on the Fenton and Fenton-like degradation of malachite green. The result is shown in Figure 4.7. The result indicated that the degradation of dye solution was positively influenced by the Fe$_3$O$_4$ dosage. In other words, the increase of Fe$_3$O$_4$ dosage increased the degradation rate of dye solution. The degradation efficiency for catalyst dosage of 0, 0.5, 1.0, 1.5, 2.0 and 2.5 g/L was 2.46, 5.47, 13.27, 18.94, 29.25 and 40.09 % respectively. The degradation efficiency for catalyst dosage of 2.5 g/L was the highest among the other catalyst dosages.

The increment of Fe$_3$O$_4$ dosage increased the surface area available for the reaction. This indicated more active catalytic sites for $Fe^{2+}/Fe^{3+}$ species to
accelerate the decomposition of H$_2$O$_2$ to highly reactive $\cdot$ OH. This was in agreement with the result observed by Kwan and Voelker (2003) where the decomposition rate of H$_2$O$_2$ was favoured by increasing the Fe$_3$O$_4$ dosage in a heterogeneous Fenton-like reaction. Moreover, Kong, et al. (1998) reported that for Fenton reaction, the decomposition of the compounds was promoted by the increase of the concentration of the mineral suspension as the increment of available area or amount of available iron promoted the generation of $\cdot$OH. A similar trend where α- Fe$_2$O$_3$ dosage influenced the reactive dye degradation was also reported by Yaman and Gündüz (2015).

Figure 4.7: Effect of Fe$_3$O$_4$ Dosages on the Fenton and Fenton-like Degradation of Malachite Green (H$_2$O$_2$ dosage = 0.2 M, initial dye concentration = 20 mg/L, reaction temperature = 30 °C, pH = 7, reaction time = 1 h)

In short, the higher the Fe$_3$O$_4$ dosage, the higher the degradation rate of dye solution as decomposition of H$_2$O$_2$ to $\cdot$OH was accelerated. The optimal dosage of Fe$_3$O$_4$ catalyst was 2.5 g/L as it had the highest degradation efficiency.
4.3.3 Effect of H$_2$O$_2$ Dosage

The effect of H$_2$O$_2$ dosages (0, 0.05, 0.10, 0.15, 0.20 and 0.25 M) was investigated on the Fenton and Fenton-like degradation of malachite green. The result is represented in Figure 4.8. As noted in Figure 4.8, no significant degradation of malachite green was observed without H$_2$O$_2$ as only 5.10 % of degradation efficiency was achieved in 60 min. By adding the H$_2$O$_2$ dosage from 0.05 to 0.20 M, the degradation efficiency of malachite green was increased from 10.47 to 40.09 % in 60 min. However, when the H$_2$O$_2$ dosage was further increased to 0.25 M, it was observed that the degradation efficiency of malachite green decreased to 27.54 %.

![Figure 4.8: Effect of H$_2$O$_2$ Dosages on the Fenton and Fenton-like Degradation of Malachite Green (Fe$_3$O$_4$ dosage = 2.5 g/L, initial dye concentration = 20 mg/L, reaction temperature = 30 °C, pH = 7, reaction time = 1 h)](image)

Without adding H$_2$O$_2$, the degradation efficiency of malachite green was very low as the adsorption of dye on the catalyst did not contribute to significant removal. However, it did not imply that dye molecules did not adsorb on the surface of catalyst. A positive contribution of H$_2$O$_2$ addition on the degradation of malachite green was expected. It could be explained by the fact that the oxidation power of Fenton and Fenton-like process was enhanced. At low H$_2$O$_2$ concentration, insufficient $\cdot OH$ in
solution was produced to degrade the dye molecules as H$_2$O$_2$ could be easily consumed. Therefore, when increasing the H$_2$O$_2$ dosage, quantity of ·OH was increased from the decomposition of increasing H$_2$O$_2$ and the degradation efficiency could be enhanced (Hassan and Hameed, 2011; Wu, et al., 2015).

Beyond critical concentrations, the degradation efficiency of malachite green was decreased with increasing H$_2$O$_2$ dosage. This might be caused by two factors. Firstly, the concentration of dyes on the surface of catalyst was limited by the competition of the excessive H$_2$O$_2$ for adsorption on the surface of catalyst (Zhuang, et al., 2015). Secondly, it might be caused by the scavenging effect of H$_2$O$_2$ and the recombination of ·OH (Bouasla, Ismail and Samar, 2012). ·OH that had been produced were scavenged by H$_2$O$_2$ itself to form ·HO$_2$ with a lower oxidizing power (Equation 2.7). Meanwhile, produced ·HO$_2$ could also scavenge ·OH to form H$_2$O and O$_2$ (Equation 2.9). ·OH itself could also recombined to form H$_2$O$_2$ back (Equation 2.6). Moreover, H$_2$O$_2$ might auto decomposed to water and oxygen instead of being selectively converted to ·OH. These reactions lowered the likelihood of attack of dye molecules by ·OH and resulted a decrease in the degradation rate.

Similar results have been reported by Sun, et al. (2007) and Sun, et al. (2009), in the Fenton oxidation of amido black 10B and orange G, respectively. Excessive H$_2$O$_2$ dosage would detrimental to the degradation of dye and increase the cost of the wastewater treatment, thus it is crucial to control the dosage. Therefore, a concentration 0.2 M appeared as an optimal H$_2$O$_2$ dosage.

### 4.3.4 Effect of Dye Concentration

The effect of malachite green concentration (20, 30, 40, 50 and 60 mg/L) was investigated on the Fenton and Fenton-like degradation. The result is depicted in Figure 4.9. It was observed that the degradation efficiency was decreased from 40.09 to 5.19 % when increasing the concentration of malachite green from 20 to 60 mg/L. It could be said that an increase of concentration of organic dye led to a decreasing degradation efficiency (Daneshvar, et al., 2008).
Figure 4.9: Effect of Malachite Green Concentration on the Fenton and Fenton-like Degradation of Malachite Green (Fe$_3$O$_4$ dosage = 2.5 g/L, H$_2$O$_2$ dosage = 0.2 M, reaction temperature = 30 °C, pH = 7, reaction time = 1 h)

The lower degradation efficiency at high concentration could be explained by the fact that the increase of the concentration of organic dye led to an increment of the number of dye molecules. This indicated that more dye molecules were adsorbed and reacted on the surface of catalyst when increasing the concentration of organic dye. Thus, the generation of $\cdot$OH was reduced as active sites were occupied by dye ions (Ali, Gad-Allah and Badawy, 2013). This result was in agreement with those found in the literature (Bouasla, Ismail and Samar, 2012; Zhang, Fu and Zhang, 2009).

For the concentration of 60 mg/L, dye was degraded more in 40 min as compared to the concentration of 50 mg/L might due to the fact that the interaction between dye and $\cdot$OH was enhanced by the increase of the dye concentration. It could be explained by the collision theory of chemical reaction. The increase of dye concentration increased the frequency of collision between dye and $\cdot$OH. Thus, the frequency of effective collisions that caused the reaction to occur would also be high. Eventually, the degradation efficiency was increased (Hassan and Hameed, 2011). The degradation efficiency for 60 mg/L was slightly lower than 50 mg/L as it might due to the reason that with constant H$_2$O$_2$ dosage and Fe$_3$O$_4$ dosage, more H$_2$O$_2$ was
consumed in first 40 min. After 40 min, amount of H₂O₂ was lesser and so the degradation of dye slowed down (Sun, et al., 2007).

In short, the higher the concentrations of malachite green, the lower the degradation efficiency of dye solution. The optimal concentration of malachite green was 20 mg/L as it had the highest degradation efficiency.

### 4.3.5 Effect of Temperature

The effect of temperature (30, 60, 70 and 80 °C) was investigated on the Fenton and Fenton-like degradation of malachite green. The result is represented in Figure 4.10. As noted in Figure 4.10, raising the temperature had a positive impact on the degradation of malachite green. The degradation efficiency of malachite green was increased from 40.09 to 98.99 % within 60 min as temperature of solution increased from 30 to 80 °C. Nevertheless, the degradation efficiency after 60 min was very similar at 60, 70 and 80 °C. Moreover, the period of time required for the degradation of malachite green was also much shorter at higher temperature. In 10 min, the degradation efficiency of malachite green for 80 °C already reached 53.89 % as compared to the degradation efficiency for 30 °C which only reached 17.65 %.

A positive contribution of the increasing temperature on the degradation of malachite green was expected. It could be explained according to the Arrhenius kinetics. Fenton’s reaction could be accelerated by increasing temperature as higher temperature could supply more energy to conquer the activation energy of reaction and then quicken the reaction rate between H₂O₂ and iron species on the surface of catalyst (Wang, et al., 2016). This enhanced the production rate of ·OH and hence degradation of malachite green was raised (Sun, et al., 2009). In literature, similar enhancement results had been reported in Fenton-like oxidation of orange II solutions using heterogeneous catalysts of saponite clay (Ramirez, et al., 2007) and iron-based nanoparticles (Wu, et al., 2015).
Figure 4.10: Effect of Temperature on the Fenton and Fenton-like Degradation of Malachite Green ($\text{Fe}_3\text{O}_4$ dosage = 2.5 g/L, $\text{H}_2\text{O}_2$ dosage = 0.2 M, initial dye concentration = 20 mg/L, pH = 7, reaction time = 1 h)

In conclusion, the degradation efficiency of malachite green was increased with the increasing of the reaction temperature. Although the degradation efficiency for temperature at 30 °C is lower than those obtained at higher temperature (60, 70 and 80 °C), 30 °C was chosen as an ideal temperature to conduct the following experiment as its degradation of dye might be considered satisfactory and lower temperature might lower the process cost.

4.3.6 Effect of solution pH

The effect of solution pH (pH 3, 5, 7, 9 and 11) was observed on the Fenton and Fenton-like degradation of malachite green. The pH was adjusted from pH 3 to 11 by using 0.1 M HCl and 0.1 M NaOH. The result is represented in Figure 4.11. Figure 4.11 illustrated that the increment of pH from pH 3 to 11 positively affected the degradation efficiency of malachite green. It clearly showed that the heterogeneous
Fenton and Fenton-like process with Fe$_3$O$_4$ can efficiently remove malachite green in pH range from 7 to 11.

![Figure 4.11: Effect of pH on the Fenton and Fenton-like Degradation of Malachite Green (Fe$_3$O$_4$ dosage = 2.5 g/L, H$_2$O$_2$ dosage = 0.2 M, initial dye concentration = 20 mg/L, reaction temperature = 30 °C, reaction time = 1 h)](image)

It was well known that the homogeneous Fenton and Fenton-like processes were efficient in the acidic range from pH 3 to 4 (Bagal and Gogate, 2014). However, in this research works, it was observed that there was an increase in malachite green degradation through heterogeneous Fenton and Fenton-like processes at alkaline pH range. The degradation of malachite green by Fe$_3$O$_4$ was partially accomplished when surface of catalyst was negative charge. In alkaline solution (> pH 7), the surface of Fe$_3$O$_4$ contained abundant hydroxyl groups (−OH) that supplied a negatively charge to the catalyst surface as the pH was greater than the point of zero charge of Fe$_3$O$_4$ surface (pH$_{pzc}$ = 6.9) (Iram, et al., 2010). On the other hand, malachite green could present in two ionic forms: cationic form of the dye and colourless carbinol form in aqueous solution (Mitrowska, Posyniak and Zmudzki, 2008). The negative charge on the surface of Fe$_3$O$_4$ would cause electrostatic attraction between Fe$_3$O$_4$ and cationic malachite green molecules. Consequently, malachite green was adsorbed and degraded (Dahri, Kooh and Lim, 2014).
In acidic solution, the degradation efficiency of malachite green was low and it might due to the $\cdot OH$ was consumed by the scavenging effect of $H^+$ ions and $H_2O_2$ was solvated to form stable oxonium ion when $H^+$ and $[H_3O_2]^+$ ions were highly concentrated (Wu, et al., 2015). Moreover, it might be also caused by the electrostatic repulsion and poor interaction between $Fe_3O_4$ and cationic malachite green molecules as $Fe_3O_4$ surface became positively charge (Iram, et al., 2010).

In conclusion, the degradation efficiency of malachite green by $Fe_3O_4$ increased with increment of pH. The optimum pH of this experiment was pH 9 instead of pH 11 as the degradation efficiencies of pH 9 and 11 were similar and it saved money from the economic point of view.

4.4 Reusability Study

The degradation efficiency of malachite green by used $Fe_3O_4$ catalyst was studied. The used catalyst was regenerated through washing by distilled water. According to Figure 4.12, the degradation efficiency for fresh $Fe_3O_4$ and reused $Fe_3O_4$ were 95.70 and 96.43 % respectively. It was noted that reused $Fe_3O_4$ still maintained high catalytic activity and this indicated that $Fe_3O_4$ was reusable under this experimental conditions.

Similar results were reported by other researchers. Chen, et al. (2016) reported that $Fe_3O_4$ magnetic nanoparticles remained the high catalytic activity after continuously running for 12 h in total as degradation efficiency of rhodamine B in 2 h was more than 98 % in each run. In addition, Zhang, et al. (2008) claimed that the catalytic activity of ferromagnetic nanoparticles still maintained almost 100 % for the degradation of phenol after 5 rounds of recycle. Baldrian, et al. (2006) also reported that $Fe_3O_4$ had remarkable stability of performance and no decrease in degradation efficiency was observed during five 72 h cycles of degradation of chicago sky blue 6B using 25 mg/L of catalyst. Therefore, it could be concluded $Fe_3O_4$ was reusable and represented a promising alternative to other conventional catalyst because of their reusability as well as easy recovery by using magnet.
Figure 4.12: Degradation of Malachite Green by Fresh and Reused Fe$_3$O$_4$ Catalyst (Fe$_3$O$_4$ dosage = 2.5 g/L, H$_2$O$_2$ dosage = 0.2 M, initial malachite green concentration = 20 mg/L, pH = 9, temperature = 30 °C, reaction time = 1 h)

4.5 Kinetic Study

Kinetic studies were performed on the basis of the rate of disappearance of malachite green in order to determine the order of the reaction for Fenton and Fenton-like degradation of the dye. Zero, first and second orders graph were studied for the experimental data acquired using malachite green at an initial concentration of 20 mg/L with different temperature.

Since ·OH is the main oxidants responsible to attack organic matter in Fenton and Fenton-like reactions, the kinetics of the reaction on the degradation of malachite green can be presented as follows:

$$-\frac{dC_{MG}}{dt} = kC_{MG}^m C_{OH}^n$$ (4.1)

where $C_{MG}$ is concentration of malachite green (mg/L) at time $t$, $C_{OH}$ is the concentration of ·OH at time $t$, $m$ is the reaction order with respect to malachite green,
$n$ is the reaction order with respect to $\cdot OH$, $t$ is the reaction time (min) and $k$ is the reaction rate constant. It is difficult to measure and consider $\cdot OH$ as constant at specific time as its life time is relatively short (Momani, 2008). Therefore, Equation 4.1 can be simplified in the form:

$$-\frac{dc_{MG}}{dt} = k_{app}c_{MG}^m$$

(4.2)

where $k_{app}$ is an apparent reaction rate constant. In this experiment, pseudo first-order was satisfactory fitted all the data. It was consistent with the result of Elhami, Karimi and Aghbolaghy (2015) in the study of decolourization of malachite green. In addition, Shi, et al. (2016) reported that the degradation of methylene blue by Fe$_2$SiS$_4$ Fenton system was fitted to the pseudo-first order rate law. Since the reaction is well-fitted to pseudo first-order, $m$ is equal to 1. By integrating Equation 4.2, the equation relating the concentration of malachite green to the reaction time can be acquired and it is shown in Equation 4.3.

$$ln\frac{c_0}{c_t} = k_{app}t$$

(4.3)

where $c_0$ and $c_t$ are the concentration of malachite green (mg/L) at time 0 and $t$ respectively. Plot of $ln\frac{c_0}{c_t}$ versus time ($t$) for the four cases of different temperatures considered can be approximately as straight lines. Figure 4.13 suggested that the degradation of malachite green satisfactory fitted the pseudo first-order kinetics because of high determination of coefficient ($r^2 > 0.91$). Therefore, the slope of the straight lines should be equal to the apparent first-order rate constant ($k_{app}$). The values of $k_{app}$ and $r^2$ are shown in Table 4.3. It was noted that the rate constant significantly increased from 0.0093 to 0.0694/min as the temperature increased from 30 to 80 °C. It could be explained that more energy was supplied at higher temperature to conquer energy of reaction (Wang, et al., 2016). Kuang et al. (2013) claimed that the increment of rate constant was due to faster catalysis of $H_2O_2$ at a higher temperature. The number of $\cdot OH$ was increased and eventually the oxidation of malachite green was accelerated. Similar trend was obtained by Aygun, et al. (2012).
Figure 4.13: Pseudo First-order Reaction Kinetics Plot for Fenton and Fenton-like Degradation of Malachite Green

Table 4.3: Rate Coefficients for Degradation of Malachite Green by Fe₃O₄ under Different Temperature

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pseudo zero-order model</th>
<th>Pseudo first-order model</th>
<th>Pseudo second-order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r^2$</td>
<td>$k_{app}$</td>
<td>$r^2$</td>
</tr>
<tr>
<td></td>
<td>($\frac{mg}{L \cdot min}$)</td>
<td>(/min)</td>
<td>($\frac{L}{mg \cdot min}$)</td>
</tr>
<tr>
<td>30</td>
<td>0.9243</td>
<td>-0.1191</td>
<td>0.9165</td>
</tr>
<tr>
<td>60</td>
<td>0.8122</td>
<td>-0.2693</td>
<td>0.9833</td>
</tr>
<tr>
<td>70</td>
<td>0.7933</td>
<td>-0.2595</td>
<td>0.9878</td>
</tr>
<tr>
<td>80</td>
<td>0.7410</td>
<td>-0.2596</td>
<td>0.9658</td>
</tr>
</tbody>
</table>

$k_{app}$ values obtained can be correlated by an Arrhenius-type expression for the experiment conducted at different temperatures. The graphical representation of $\ln k_{app}$ on the basis of $1/T$ permits the calculation of the parameters of Arrhenius equation:
\[
\ln k_{\text{app}} = \ln A_0 - \frac{E_a}{RT} \tag{4.4}
\]

where \(E_a\) is the activation energy (kJ/mol) and \(A_0\) is the pre-exponential factor (/min), \(R\) is ideal gas constant (8.314 J/mol·K) and \(T\) is absolute temperature (K). Based on Figure 4.14, good linear relationships exist between the plots of \(\ln k\) and \(1/T\) as \(r^2\) was higher than 0.97. The Arrhenius relationship can be shown in Equation 4.5.

\[
\ln k_{\text{app}} = -4377.7 \left(\frac{1}{T}\right) + 9.8323 \quad r^2 = 0.9756 \tag{4.5}
\]

\(E_a\) and \(A\) in Arrhenius form were determined according to the slope \((-E_a/R)\) and intercepts (\(\ln A\)). \(E_a\) and \(A\) for degradation of malachite green under different temperature were 36.40 kJ/mol and 1.86 \(\times\) 10\(^3\) /min respectively. The \(E_a\) value was very close to the \(E_a\) (35.90 kJ/mol) obtained in the study for heterogeneous Fenton-like oxidation of reactive red 141 (Yaman, Gündüz and Dükkancı, 2013). Moreover, it was lower than the \(E_a\) (43.00 kJ/mol) gained in the study for heterogeneous Fenton-like oxidation of monochlorobenzene (Kuang, et al., 2013). The degradation of malachite green by \(\text{Fe}_3\text{O}_4\) was a process of surface-controlled reaction as \(E_a\) value for surface was more than 29 kJ/mol while for diffusion-controlled reaction ranged from 8 to 21 kJ/mol (Shi, et al., 2011).

![Arrhenius Plot of ln k_{app} against 1/T](image)

**Figure 4.14: Arrhenius Plot of ln \(k_{\text{app}}\) against 1/T**
4.6  

**Liquid Sample Analysis**

4.6.1  

**COD Results**

The COD removal by the heterogeneous Fenton and Fenton-like reactions was investigated. COD of the solution with the optimum condition (Fe$_3$O$_4$ dosage = 2.5 g/L, H$_2$O$_2$ dosage = 0.2 M, initial malachite green concentration = 20 mg/L, pH 9, 30 °C, time = 1 h) for the case before reaction and after reaction had been determined by Colorimetric Determination Method 80000. 32 % of the COD had been removed by the reaction after 1 h. At the end of reaction, only partial COD removal was attained as reaction decelerated due to the cleavage of dye chromophores and this led to partially degradation of highly complex-structured dye molecules into comparatively small organic fragments (Arslan-Alaton, Gursoy and Schmidt, 2008). It should be noted that the intermediate products of malachite green are hard to be oxidized by AOP and the complete oxidation might continue in a longer time.

Similar observation had been reported by other researchers. Alaton and Teksoy (2007) observed that the overall COD removal efficiency of synthetic acid effluent by Fenton oxidation after 30 min was only 23 % although the colour removal efficiency can be achieved to 92 %. Arslan-Alaton, Gursoy and Schmidt, 2008 also reported that only partial COD had been removed during Fenton treatment of acid red 183, acid orange 51 and reactive blue 4. Therefore, a complete oxidation of malachite green would require more than 1 h oxidation process.

4.6.2  

**ICP-OES Results**

Stability of catalyst is one of the important properties for its practical applications. From the environmental point of view, the leaching of transition metals such as iron should be limited in order to avoid their toxic effects on living organisms (Pouran, et al., 2015). The amount of iron loss from Fe$_3$O$_4$ catalyst was determined with ICP-OES.
by determining iron concentration in the solution after 1 h reaction. Two liquid samples had been tested, which were the liquid samples without pH control and the liquid samples with pH control (pH 9).

According to the ICP results, the concentration of leached iron concentration for liquid samples without pH control and the liquid samples with pH control (pH 9) were 0.793 and 0.673 mg/L respectively. The concentration of leached iron for both samples could be considered as quite low as the value was within the acceptance condition for discharge of iron (below 1 mg/L) according to Environmental Quality (Industrial Effluent) Regulations 2009 (DOE, 2009). However, more iron ions leached from Fe$_3$O$_4$ for liquid sample without pH control. It might due to the solution was originally in acidic condition. Matei, et al. (2011) reported that iron dissolution tended to be higher for acidic conditions as compared with neutral and basic media. Baba, et al. (2007) also reported that the rate of iron ore dissolution is directly proportional to the concentration of $H^+$.
CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this study, the characteristics of heat-treated Fe₃O₄ catalyst were investigated. Heat-treated Fe₃O₄ was prepared by heating in a furnace at temperatures of 200, 400, 600 and 800 °C for 2 h. The heat-treated Fe₃O₄ were then characterized by XRD and SEM-EDX. XRD patterns indicated that the transformation of Fe₃O₄ into γ-Fe₂O₃ occurred at temperature of 200 °C and further transformed into α-Fe₂O₃ completely at temperature 800 °C. SEM showed that majority Fe₃O₄ particles were spherical shape and the mean particle sizes of Fe₃O₄ increased when increasing temperature up to 800 °C. EDX illustrated all the original and heat-treated Fe₃O₄ samples composed of Fe and O atoms only. Original Fe₃O₄ showed better catalytic activity than other heat-treated Fe₃O₄. This was due to the available Fe²⁺ and Fe³⁺ ions where Fe²⁺ ions had the higher oxidation rate constant to produce \( \cdot OH \).

The effect of various parameters such as various organic dyes, Fe₃O₄ dosage, H₂O₂ dosage, malachite green dye concentration, pH of solution and temperature for Fenton and Fenton-like processes were identified in order to determine the optimum conditions. The degradation of organic dyes (acid orange G, congo red, malachite green, methylene blue, methyl orange and rhodamine B) depended on the chemical structures of organic dyes. Triphenyl methane structure of malachite green was the most vulnerable to chemical oxidation compared to other structures such as azo, thiazine and xanthene structures. Malachite green could be degraded the most among other organic dyes by Fe₃O₄ catalyst during Fenton and Fenton-like processes. The
optimum conditions for degradation efficiency of malachite green were obtained at an initial dye concentration of 20 mg/L, Fe$_3$O$_4$ dosage of 2.5 g/L, H$_2$O$_2$ dosage of 0.2 M, reaction temperature at 30 ℃ and pH 9 in 1 h to achieve to 96 %. However, only partial COD removal (32 %) was achieved. This was due to the intermediate products were more difficult to be oxidized.

On the other hand, the reusability of Fe$_3$O$_4$ catalyst on the degradation of dye was studied. The reused Fe$_3$O$_4$ which regenerated through washing by distilled water still maintained high catalytic activity. ICP-OES results illustrated that Fe$_3$O$_4$ had high stability as the concentration of leached iron in water samples could be considered as quite low. The reaction kinetics of Fenton and Fenton-like reaction on degradation of organic dyes was also studied. The degradation process of malachite green at different temperatures (30, 60, 70 and 80 ℃) were followed pseudo first-order kinetics. The $E_a$ and $A$ for degradation of malachite green were 36.40 kJ/mol and $1.86 \times 10^3$ /min respectively.

5.2 Recommendation for Future Work

Original and heat-treated Fe$_3$O$_4$ should be characterized by using Brunauer-Emmett-Teller (BET) surface analysis in order to study the effect of heat treatment on the specific surface area and porosity of Fe$_3$O$_4$. Specific surface area was a significant property for Fe$_3$O$_4$ as it determines the catalytic reaction of Fenton and Fenton-like processes. Catalytic activity of Fe$_3$O$_4$ could be higher if possessing larger specific surface area. This was due to high surface area of catalyst potentially provided more active sites for the generation of ·OH. Therefore, it was important to study specific surface area and porosity of heat-treated Fe$_3$O$_4$.

FTIR analysis can be carried out for malachite green, fresh and used Fe$_3$O$_4$ for the degradation of malachite green. FTIR was powerful in identifying the types of chemical bonds in a molecule by generating an infrared absorption spectrum. By using FTIR, the functional groups and chemical bonds of malachite green and Fe$_3$O$_4$ catalyst could be identified. Adsorption of malachite green and its degraded products on the
surface of Fe$_3$O$_4$ might also be observed by comparing the FTIR spectrum of Fe$_3$O$_4$ before and after the degradation of malachite green.


APPENDICES

APPENDIX A: Preparation of Various Concentrations of Organic Dyes

In order to obtain the concentration of organic dye that required for experiment from a stock solution, dilution is needed. By knowing the concentration of stock solution, desired concentration and volume of organic dye, the volume from stock solution that is required can be computed by using

\[ C_1V_1 = C_2V_2 \]

where

\( C_1 \) = Stock solution’s concentration, g/L

\( V_1 \) = Stock solution’s volume, L

\( C_2 \) = Diluted solution’s final concentration, g/L

\( V_2 \) = Diluted solution’s final volume, L

After the value of \( V_1 \) is computed, \( V_1 \) of stock solution is pipetted and then it is diluted by adding distilled water until the volume reach \( V_2 \) value.

To prepare the stock solution of 80 % Acid Orange G with concentration of 500 mg/L in 1 L, the mass of Acid Orange G required is calculated as below:

\[
\text{mass of Acid Orange G} = \frac{1}{0.80} \times \frac{500 \text{ mg}}{L} \times 1 \text{ L} \\
= 625 \text{ mg} \\
= 0.625 \text{ g}
\]
Therefore, 0.625 g of Acid Orange G is dissolved in 1 L distilled water to get the stock solution with concentration of 500 mg/L in 1 L.

Volume of 80 % Acid orange G stock solution with 500 mg/L required to prepare different concentration of organic dyes in 100 ml solution is shown in Table A.1. The volume of 80 % Acid Orange G stock solution with concentration 500 mg/L required to prepare 100 ml of diluted Acid Orange G solution with concentration 50 mg/L is calculated as below:

\[
(500 \text{ mg/L})(V_1) = (50 \text{ mg/L})(100 \text{ ml})
\]

\[
V_1 = 10 \text{ ml}
\]

Hence, 10 ml of Acid Orange G stock solution is pipetted and then it is diluted by adding distilled water until the volume reach 100 ml.

<table>
<thead>
<tr>
<th>Concentration of Acid Orange G (mg/L)</th>
<th>Volume of 80 % Acid orange G Stock Solution with 500 mg/L Required (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>150</td>
<td>30</td>
</tr>
<tr>
<td>200</td>
<td>40</td>
</tr>
<tr>
<td>250</td>
<td>50</td>
</tr>
</tbody>
</table>
APPENDIX B: Preparation 0.1 M HCl from a 37 % HCl

Molarity of 37 % HCl is determined first.

\[ \text{HCl – 37% v/v} = \frac{37 \text{ ml}}{100\text{ ml}} \]

Specific gravity of 37 % HCl = 1.19 g/ml
Molecular weight of HCl = 36.46 g/mol

Concentration of HCl in g/L = \( \frac{37 \text{ ml}}{100 \text{ ml}} \times \frac{1.19 \text{ g}}{\text{ml}} \)
\[ = \frac{0.4403 \text{ g}}{\text{ml}} \times \frac{1000 \text{ ml}}{1 \text{ L}} \]
\[ = 440.3 \text{ g/L} \]

Molarity of HCl = \( \frac{440.3 \text{ g}}{L} \times \frac{\text{mol}}{36.46 \text{ g}} \)
\[ = 12.07 \text{ mol/L} \]

Volume of 0.37 % HCl required can be computed in order to get 0.1 M by using equation

\[ M_1V_1 = M_2V_2 \]

Where
\( M_1 = \) Concentration of 37 % HCl solution, mol/L
\( V_1 = \) Volume from 37 % HCl solution, L
\( M_2 = \) Final concentration of diluted HCl solution, mol/L
\( V_2 = \) Final volume of diluted HCl solution, L
$M_1 = 12.07 \text{ M}, M_2 = 0.1 \text{ M}, V_2 = 500 \text{ ml}$

\[
V_1 = \frac{M_2 V_2}{M_1} = \frac{0.1 \text{ M} \times 500 \text{ ml}}{12.07 \text{ M}} = 4.14 \text{ ml}
\]

Therefore, 4.14 ml of 37 % HCl is pipetted and then it is diluted by adding distilled water until the volume reach 500 ml.
APPENDIX C: Preparation of 0.1 M NaOH from a 97 % NaOH

To prepare 0.1 M of NaOH in 500 ml, the mass of NaOH powder required is computed.

$$Number\ of\ moles\ of\ NaOH = \text{Molarity} \times \frac{\text{Volume (L)}}{\text{Moles of NaOH (mol/L)}} \times \text{purity}$$

$$= \frac{0.1 \text{ mol}}{L} \times 500 \text{ ml} \times \frac{1 \text{ L}}{1000 \text{ ml}} \times \frac{100}{97}$$

$$= 0.052 \text{ moles}$$

NaOH’s Molecular weight = 40 g/mol,

$$\text{Mass of NaOH} = \text{No. of moles of NaOH (moles)} \times \frac{\text{Molecular weight (g/mol)}}{\text{moles}}$$

$$= 0.052 \text{ moles} \times 40 \frac{\text{g}}{\text{mol}}$$

$$= 2.08\ g$$

Therefore, 0.1 M of NaOH can be obtained by adding 2.08 g of NaOH to 500 ml of distilled water.
APPENDIX D: Preparation of H₂O₂ from 30 % H₂O₂

Concentration of H₂O₂ used in this experiment is 30 % H₂O₂ (w/w) in H₂O which indicates that 30 g of H₂O₂ is present in 100 g of solution. Density of 30 % H₂O₂ is 1.11 g/ml. Volume of 100 g of 30 % H₂O₂ solution is calculated by using

\[ \rho = \frac{m}{V} \]

Where
\( \rho \) = Density, g/ml
\( m \) = Mass, g
\( V \) = Volume, ml

\[ V = \frac{m}{\rho} = \frac{100 \, g}{1.11 \, g/ml} = 90.09 \, ml \]

Next, the percentage concentration (w/v) of H₂O₂ solution is computed by

\[ \text{Percent Concentration} \left( \frac{w}{v} \right) = 100 \times \frac{\text{Amount of solute (g)}}{\text{Amount of solution (ml)}} \]

\[ = 100 \times \frac{30 \, g}{90.09 \, ml} \]

\[ = 33.30 \, g/ml \]

Mole of H₂O₂ present in 33.30 g of H₂O₂ is calculated.
Moles = \( \frac{\text{Mass of substance (g)}}{\text{Atomic Weight (g/mol)}} \)

\[ = \frac{33.30 \, g}{34.01 \, g/mol} \]

\[ = 0.98 \, \text{moles of } H_2O_2 \]

It means that 0.98 moles of $H_2O_2$ is present in 100 ml solution.

Now, the molarity of $H_2O_2$ solution is calculated by

\[ Molarity = \frac{\text{Number of moles of solute (moles)}}{\text{Volume of solution (L)}} \]

\[ = \frac{0.98 \, \text{moles}}{0.1 \, L} \]

\[ = 9.80 \, M \]

Volume of 0.30 % $H_2O_2$ required can be computed in order to get the desired concentration of $H_2O_2$ by using equation

\[ M_1V_1 = M_2V_2 \]

where

$M_1$ = Concentration of 30 % $H_2O_2$ solution, mol/L

$V_1$ = Volume of 30 % $H_2O_2$ solution, L

$M_2$ = Final concentration of diluted $H_2O_2$ solution, mol/L

$V_2$ = Final volume of diluted $H_2O_2$ solution, L

After value of $V_1$ is computed, $V_1$ of stock solution is pipetted and then it is diluted by adding distilled water until the volume reach $V_2$ value.

Volume of 30 % $H_2O_2$ required to prepare different dosage in 100 ml solution is shown in Table D.1. The volume of $H_2O_2$ required is calculated as below:

\[ (9.80 \, M)(V_1) = (0.1 \, M)(100 \, ml) \]

\[ V_1 = 1.0204 \, ml \]
Table D.1: Volume of H\textsubscript{2}O\textsubscript{2} Required to Prepare Different Dosage in 100 ml Solution

<table>
<thead>
<tr>
<th>H\textsubscript{2}O\textsubscript{2} Dosage (M)</th>
<th>Volume of 30 % H\textsubscript{2}O\textsubscript{2} solution Required (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.0204</td>
</tr>
<tr>
<td>0.2</td>
<td>2.0408</td>
</tr>
<tr>
<td>0.3</td>
<td>3.0612</td>
</tr>
<tr>
<td>0.4</td>
<td>4.0816</td>
</tr>
<tr>
<td>0.5</td>
<td>5.1020</td>
</tr>
</tbody>
</table>
APPENDIX E: Preparation of Standard Solution for ICP-OES Analysis

In order to obtain the concentration of FeCl₃ that required from a stock solution, dilution is needed. By knowing the concentration of stock solution, desired concentration and volume of FeCl₃, the volume from stock solution that is required can be computed by using

\[
C_1V_1 = C_2V_2
\]

where

\( C_1 = \) Stock solution’s concentration, g/L
\( V_1 = \) Stock solution’s volume, L
\( C_2 = \) Diluted solution’s final concentration, g/L
\( V_2 = \) Diluted solution’s final volume, L

After the value of \( V_1 \) is computed, \( V_1 \) of stock solution is pipetted and then it is diluted by adding distilled water until the volume reach \( V_2 \) value.

To prepare the stock solution of FeCl₃ with concentration of 1000 ppm (1000 mg/L) in 100 ml, the mass of FeCl₃ required is calculated as below:

\[
\text{mass of FeCl}_3 = 1000 \frac{mg}{L} \times \frac{1 L}{1000 ml} \times 100 ml \\
= 100 \ mg
\]

Therefore, 100 mg of FeCl₃ is dissolved in 100 ml distilled water to get the stock solution with concentration of 1000 ppm in 100 ml.
Volume of FeCl₃ stock solution with 1000 ppm required to prepare different concentration of FeCl₃ in 100 ml solution is shown in Table E.1. The volume of FeCl₃ stock solution with concentration 1000 ppm required to prepare 100 ml of FeCl₃ solution with concentration 10 ppm is calculated as below:

\[
(1000 \text{ ppm}) (V_1) = (10 \text{ ppm})(100 \text{ ml})
\]

\[
V_1 = 1 \text{ ml}
\]

Hence, 1 ml of FeCl₃ stock solution is pipetted and then it is diluted by adding distilled water until the volume reach 100 ml.

Table E.1: Volume of FeCl₃ Stock Solution with 1000 ppm Required to Prepare Different Concentration of FeCl₃ in 100 ml Solution

<table>
<thead>
<tr>
<th>Concentration of FeCl₃ (ppm)</th>
<th>Volume of FeCl₃ Stock Solution with 1000 ppm Required (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>40</td>
<td>4</td>
</tr>
<tr>
<td>50</td>
<td>5</td>
</tr>
</tbody>
</table>
APPENDIX F: Calibration Curve of Organic Dyes

Calibration curves for each organic dye are shown in Figure below.

**Figure F.1: Calibration Curve of Acid Orange G**

**Figure F.2: Calibration Curve of Congo Red**
Figure F.3: Calibration Curve of Malachite Green

Figure F.4: Calibration Curve of Methylene Blue
Figure F.5: Calibration Curve of Methyl Orange

Figure F.6: Calibration Curve of Rhodamine B
APPENDIX G: Calibration Curve of Standard Solution for ICP-OES Analysis

Figure G.1: Calibration Curve of Standard Solution for ICP-OES Analysis
APPENDIX H: Calculation of Crystalline Size

The crystalline size of materials can be calculated from XRD pattern using the Scherrer equation (Abbas, et al., 2015)

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

where
K = shape factor, 0.9
λ = wavelength of X-ray, 1.540562 Å
β = width at half maximum (FWHM), °
θ = Bragg angle for the studied peak, °

Peak data for Fe₃O₄-0:
β = 0.17600 °
θ = 35.4723 °

Crystalline size of Fe₃O₄-0 is calculated as below:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]
\[ = \frac{0.90 \times 1.540562}{(0.17600 \times \frac{\pi}{180}) \cos \left(\frac{35.4723}{2}\right)} \]
\[ = 473.9 \, \text{Å} \]
\[ = 47.39 \, \text{nm} \]
APPENDIX I: Reaction Kinetics Plot

The kinetics of the Fenton and Fenton-like reaction on the degradation of malachite green can be described as:

\[
- \frac{dC_{MG}}{dt} = k_{app}C_{MG}^m
\]

where

\(C_{MG}\) = concentration of malachite green at time \(t\), mg/L

\(m\) = reaction order with respect to malachite green

\(t\) = reaction time, min

\(k_{app}\) = reaction rate constant

For pseudo zero-order reaction, the above equation after integration becomes:

\[C_t = C_0 - k_0 t\]

A plot of \(C_t\) against \(t\) is shown in Figure I.1.

For pseudo second-order reaction, the integrated equation becomes:

\[
\frac{1}{C_t} = \frac{1}{C_0} + k_2 t
\]

A plot of \(\frac{1}{C_t}\) against \(t\) is shown in Figure I.2.
Figure I.1: Pseudo Zero-order Reaction Kinetics Plot for Fenton and Fenton-like Degradation of Malachite Green

Figure I.2: Pseudo Second-order Reaction Kinetics Plot for Fenton and Fenton-like Degradation of Malachite Green
APPENDIX J: MSDS