DEGRADATION OF METHYLENE BLUE USING MOLECULARLY IMPRINTED IRON (III) OXIDE PREPARED VIA HYDROTHERMAL METHOD

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by

ONG HOAY YEE

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LIST OF ABBREVIATIONS

ADMI	American Dye Manufacturers' Institute
BET	Brunauer Emmett Teller
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DLS	Dynamic Light Scattering
EDX	Energy dispersive X-ray
FTIR	Fourier Transformed Infrared Spectrometry
$FeCl_3.6H_2O$	Iron Chloride
MB	Methylene Blue
$NH_3.H_2O$	Ammonium Hydroxide
NPs	Nanoparticles
pH	Potential Hydrogen
rad	Radian
RPM	Rotation per minutes
SEM	Scanning electron microscope
UV-VIS	Ultraviolet Visible Spectroscopy
WSDA	Without structure Directing Agent
XRD	X-ray diffraction

LIST OF SYMBOL

Symbol	Description	Unit
B_{hkl}	Full-width at half maximumof the X-ray diffraction peak	(rad)
Fe^{3+}/MB	Ferric ion to methylene blue molar ratio	
C_o	Initial concentration of methylene blue	(mg/L)
C_e	Equilibrium concentration of methylene blue	(mg/L)
C_t	Concentration of methylene blue at time t	(mg/L)
D_{BET}	Particle size based on BET data	(nm)
D_{hkl}	Crystallite size in the direction perpendicular to the lattice planes	(nm)
hkl	Miller indices of the planes being analysed	
K	Crystallite-shape factor (0.94)	
q_e	Amount of equilibrium adsorption	(mg/g)
q_t	Amount of adsorption at time t	(mg//g)
S_{BET}	BET surface area for adsorption	(m^2/g)
V_p	Pore Volume	(cm^3/g)
W	Mass of adsorbent	(g)
Θ	Bragg angle	(rad)
ρ	Density	(g/cm^3)
α-Fe_2O_3	Hematite Iron (III) Oxide	
η	Percentage of residual pollutant	(%)
λ	Wavelength	(nm)

DEGRADASI METILENA BIRU MENGGUNAKAN MOLEKULAR 'IMPRINTED' α-Fe$_2$O$_3$ YANG DIHASILKAN MELALUI KAEDAH SINTESIS HIDROTERMA

ABSTRAK

Molekular 'imprinting' nanopartikel oksida ferum hematit (α-Fe$_2$O$_3$) telah dihasilkan melalui kaedah hidroterma. Sintesis ini dilakukan dengan menggunakan 'Ferri Klorida Kontang' (FeCl$_3$.6H$_2$O) dan Ammonium Hidroksida (NH$_3$.H$_2$O) sebagai bahan reaktan dan metilena biru sebagai agen struktur penerus. Pengaruh perbezaan suhu tindakbalas dan kehadiran agen struktur penerus terhadap darjah pengkristalan, morfologi, mikrostruktur dan kumpulan berfungsi permukaan sampel α-Fe$_2$O$_3$ telah dikaji dan dianalisis dengan menggunakan Pembelauan Sinar-X (XRD), Mikroskop Elektron Imbasan (SEM), Luas Permukaan (*Brunauer-Emmett-Teller*) dan Spektrofotometer Inframerah Jelmaan Fourier (FTIR). Berdasarkan hasil pencirian XRD and FTIR, didapati suhu tindakbalas yang tinggi telah menggalakkan pembentukan kristal dan morfologi nanopartikel α-Fe$_2$O$_3$. Aktiviti fotokatalisis bagi α-Fe$_2$O$_3$ ke atas degradasi pewarna metilena biru (MB) dihitung menggunakan spektrofotometer UV-VIS. Aktiviti fotokatalisis α-Fe$_2$O$_3$ yang tertinggi diperoleh pada 160˚ tanpa agen struktur penerus (Fe$_2$O$_3$-WSDA) dengan peratus penyingkiran metilena biru sebanyak 14.22%.

DEGRADATION OF METHYLENE BLUE USING MOLECULARLY IMPRINTED α-Fe$_2$O$_3$ PREPARED VIA HYDROTHERMAL SYNTHESIS METHOD

ABSTRACT

Molecularly imprinted hematite (α-Fe$_2$O$_3$) nanoparticles were synthesized by hydrothermal preparation method. The synthesis was carried out by using iron chloride (FeCl$_3$.6H$_2$O) and ammonium hydroxide (NH$_3$.H$_2$O) as the reactants and methylene blue as a structure-directing agent. The influence of reaction temperature and the presence of the structure-directing agent on the degree of crystallinity, morphology, microstructure and surface functional groups of the α-Fe$_2$O$_3$ samples were studies and analysed by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area and Fourier transform infrared spectrophotometer (FTIR). From XRD and FTIR results, it was found that the reaction temperature increases the formation of crystalline phase and morphology of the α-Fe$_2$O$_3$ nanoparticles. Photocatalytic activity of α-Fe$_2$O$_3$ on degradation of methylene blue (MB) was measured under UV-VIS spectrophotometer. The photocatalytic activity of α-Fe$_2$O$_3$ is the highest when α-Fe$_2$O$_3$ synthesized at 160˚C without structure directing agent (Fe$_2$O$_3$-WSDA) was used with MB removal percentage of 14.22 %.

Chapter 1

Introduction

1.1. Research Background

The man made dyes such as methylene blue (MB) are now a threatening source of non-aesthetic pollution, eutrophication and perturbations in the aquatic life (Houas et al., 2001). According to the studies, about 15% of the total production of dyes is lost during dyeing process and is discharged as textile effluent. The presence the volatile organic compound found in wastewater produced from textile, paper and some other industrial processes are usually highly coloured, toxic, carcinogenic or mutagenic which consist of mainly aromatic and aliphatic compounds (Lan et al., 2014, Jan Šíma, 2013). Methylene blue is a heterocyclic aromatic chemical compound which is the most commonly used dyes for dyeing cotton, wood and silk. These aromatic compounds are hard to degrade since they are very stable and complicated. Thus, in order to degrade the aromatic compound of methylene blue, several physical, chemical and biological decolourization methods have been reported during the past three decades. The photocatalysis is found to be an efficient oxidation of the aromatic compound among the advanced oxidation methods. Fe_2O_3 is the common photocatalyst used for methylene degradation due to their narrow forbidden band gap and low cost (Wang, 2013). However, the limitation of the photocatalyst due to difficulties such as low catalytic activity and low selectivity have restricted their electrochemical application under visible sunlight irradiation. Molecularly imprinted method is found to be an alternative method to improve morphology and selectivity of the Fe_2O_3. Thus, this research will focus on the degradation of methylene blue using molecularly imprinted Fe_2O_3 prepared via wet method.

1.2. Problem Statement

The attention on metal oxide nanostructures have increased in the photocatalysis field for degradation of organic compounds found in wastewater. Metal oxides such as iron oxides can be synthesized into different forms such as hematite, maghemite and magnetite. Among all these forms, hematite iron oxides are the most stable at ambient conditions and the most environment friendly n-type functional material and semiconductor. However, this nano-sized hematite iron oxide and their crystal size are hard to synthesize and control due to the nano-sized particles itself tend to agglomerate in the aqueous solution. The low photocatalytic activity and selectivity of the hematite iron oxide photocatalysts have caused the limitation of their development. Thus in this project, it was attempted to establish the degradation pathway of methylene blue by using structure directing agent and different reaction temperature to control the morphology of the iron oxide nanoparticles.

Recent works have shown their focuses to improve the physical and chemical properties of this nanomaterials. There are researchers find their way to improve the selectivity of the photocatalyst to enhance the degradation of certain organic pollutant while maintaining its useful functionality by introducing structure directing agents such as methylene blue and glucine to guide the formation of certain types of pores and channels during the synthesis of iron oxide photocatalyst. This method has advantages such as low cost, easy synthesis, high stability and reusability (Fang et al., 2016). To overcome the agglomeration problem of nanosized particles as mentioned aforesaid, an innovative synthetic approach to synthesize hematite iron oxide must be applied to disperse the catalyst on the organic medium. Hydrothermal synthesis method with advantages such as high yield, low cost, low temperature and formation of uniform particles is chosen in this case. In the previous work done by Fang (Fang et al., 2016),

methylene blue is used as structure directing agent or template molecule which has morphology and microstructure that match the pollutant in order to target aromatic compounds (pollutants). The properties of nanoparticles can also be affected by the reaction temperature. The reaction temperature plays an essential role in the formation of crystalline phase of hematite iron oxide nanopartilces. By using iron chloride and ammonium solution as feedstock and methylene blue and glycine as structure directing agent, the nanoparticles of reaction temperature at 160˚C seems to be better choice compared to 80˚C and 180˚C. The previous works have reported that the mean crystalline sizes of nano-particles increase with the reaction temperature and among them, 160˚C is an optimum reaction temperature for the synthesis of nano-sized hemitate iron oxide particles with template molecules.

1.3. Research Objectives

The aims for this research.

1. To study the physical and chemical changes of Fe_2O_3 towards hydrothermal method at different reaction temperature.
2. To determine the efficiency of methylene blue degradation using fabricated Fe_2O_3.

1.4. Research Scope

The performance of molecularly imprinted nanoparticles has been studied to improve the morphology and selectivity of the nanoparticles. In this research, metal oxide was chosen as nanomaterials and methylene blue as structure directing agent for synthesis of α-Fe_2O_3 nanoparticles. The effect of reaction temperature (80˚C, 160˚C and 180˚C) on the morphology of the synthesized α-Fe_2O_3 nanoparticles has been studied and characterized using XRD, FTIR, SEM & EDX and photocatalytic activity of nanoparticles were investigated using visible light photocatalytic batch reactor.

1.5. Thesis organization

This thesis consists of five main chapters. The following are the contents for each chapter in this study:

Chapter 1 (Introduction) briefly introduces the issues on the current textile wastewater which influences researchers to search for alternative approach remove organic pollutant (dyes) using photocatalyst. A brief introduction on possibility of metal oxide photocatalyst with enhanced properties using structure directing agent to replace conventional catalyst is also addressed in this chapter. Besides that, problem statement and objectives of the research are also presented in this chapter.

Chapter 2 (Literature Review) presents the literature review of this study. The nanotechnology about metal oxide NPs has discussed in detail by comparing different metal oxide NPs which are very popular. Method to synthesize metal oxide NPs is also reviewed in this chapter. Besides that, the growth mechanism of nanostructure using hydrothermal method is also discussed in detailed. The effects of reaction parameter during synthesis of catalyst and during degradation of MB are listed and discussed in this chapter. There are 3 agents that commonly used in synthesis of NPs which are important in controlling morphology of the nanoscaled catalyst are briefly discussed in this part.

Chapter 3 (Materials and Methods) covers the experiment materials and the details of methodology used in the degradation of MB using iron oxide photocatalyst prepared. It addresses the method used for catalyst preparation and characterization in

detail. It also presents the method used for degradation of MB, analysis and quality evaluation.

Chapter 4 (Results and Discussion) presents the results and discussions of the experimental data obtained throughout the research project. The characterization of α-Fe_2O_3 samples synthesized using different reaction temperature and with and without structure directing agent has discussed thoroughly. The photocatalytic performance of α-Fe_2O_3 on degradation of methylene blue is also covered in this chapter.

Chapter 5 (Conclusion and Recommendation) contains the summary of this research project. This chapter also presents recommendations for the future research work based on the content of the research project.

Chapter 2

Literature Review

2.1. Textile Wastewater

Textile industry is one the largest industrial sector in Malaysia that contributes to the growth of Malaysia's economic. However, textile industry also among the industries that consumes a large quantity of water and generates high discharge rate of wastewater which consists of high amount of contaminants in Malaysia. In textile industry, water is mainly used in textile processes such as scouring, bleaching, mercerizing, dyeing and finishing. Among all these processes, dyeing and finishing require the large amount of water for fixing, dyeing and washing (Mudassir, 2017). The wastewater from textile industry is well known to have high level of COD, BOD, oil and grease, suspended solid, high temperature, strong colour, pH, high toxic chemicals and turbidity (Fazal et al., 2018). This is due to the presence of different colouring agents such organic dyes, organic and inorganic matters, tannin, lignin, phosphates, nitrates and other heavy metal which causes significant impact to the environment as well as human beings (Chiang and Lin, 2013, Fazal et al., 2018). Its composition is vary based on the type of chemical and dyes used during the textile processes. Dye is the major source of contamination in textile wastewater (Chiang and Lin, 2013). Approximately 200000 tons which is about 10% of the used dyes are escaped from the wastewater treatment process and discharged as wastewater effluent to the environment every year during dyeing and finishing (Ogugbue, 2011, Pang and Abdullah, 2013). But, the current amount of dyes present in the wastewater annually is still unpredictable as the demand of the textile products is still on the rising trend which substantially causes the increase in the production as long as the increase of the usage of the dyes. This

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scenario has contributed to textile dying processes becoming one of the most environment unfriendly industrial processes that brings severe environmental contamination pollution problems in current times (Verma, 2017, Chequer et al., 2013).

To deal with the environment problem, environment legislation obliges industries to reduce the colour, BOD, COD, pH, and suspended solid of the effluent before disposal. According to the Environment Quality Act 1974, the composition of the discharged effluents must comply the standard as shown in Table 2.1.

Table 2.1   The standard parameter of Discharged Effluent of Textile Industry Wastewater

Composition	Standard	Unit
Colour	200	ADMI
COD	250	ppm
BOD	50	ppm
pH	5.5-9	
Suspended Solid (SS)	100	ppm
Oil and Grease	10	ppm

2.2.   Environmental Impact of Dyes

Dye is a substance that is used to change the colour of a particular material. Dyes have played a main role in current food industry, paint and coating industry, pharmaceutical industry, as well as textile industry in order to increase the sales of the commercial product. Dyes provide desired colour to a substance by altering the crystal structure of the coloured substance. During dyeing, dyes particles attach to the compatible surfaces, forming covalent bond or complexes with salts or metals by mean of physical adsorption or by mechanical entrapment (Kroschwitz, 1993).

There are three types of dyes which includes organic dyes, natural dyes and synthetic dyes. Most of the dyes are organic compounds, it can be either be natural or synthetic. Natural dyes are normally obtained from plants and minerals such as vegetables, fruits, flowers and some insects but they were found to be less cost effective compared to synthetic dyes due to their low colour fastness, limited and dull range of colours produced. Synthetic dyes with wide range of colour fast of wider colour range and brighter shades have discovered by Perkins (1856).

Dyes can be categorized based on their chemical structure and application. Dyes are composed of chromophores, and additional group called auxochrome which is an electron donating or accepting substituent that causes the colour of the chromophores. The common types of chromosome are ethenyl, carbonyl, amino, thiocarbonyl, azo, nitroso, nitro, whereas for auxochromes are amino, carboxylic, sulphonyl and hydroxyl (Verma et al., 2012). The intensity of colour of the dyes vary with the number of the chromophores and auxochromes groups. The function of these groups is to enhance the ionic dissociation property of the dyes such as partitioning the dye molecule into its components and to form salts with acid or alkali. They can also be classified into several classes based on solubility and chemical properties as shown in Table 2.2.

Table 2.2   Classification of Dyes that used in Textile industry (Verma et al., 2012).

Class	Characteristics	Substrate (fibre)	Dye-fibre interaction	Method of application
Acid	Anionic, water soluble	Nylon, wool, silk	Electrostatic, Hydrogen bonding	Applied from neutral to acidic dyebaths
Basic	Cationic, water soluble	Modified nylon, polyester	Electrostatic attraction	Applied from acidic dyebaths
Direct	Anionic, water soluble	Cotton, rayon, leather, nylon	Intermolecular forces	Applied from neutral or slightly alkaline baths containing additional electrolytes
Disperse	Very low water solubility	Polyester, poly-amide, acetate, plastic, acrylic	Hydrophobic-Solid state mechanism	Fine aqueous dispersions often applied by high temperature pressure or lower temperature carrier methods
Reactive	Anionic, water soluble	Cotton, nylon, silk, wool	Covalent bonding	Reactive site on dye reacts with functional group on fibre to bind dye covalently under influence of heat and pH(alkaline)
Sulfur	Colloidal, insoluble	Cotton, rayon	Covalent bonding	Aromatic substrate vatted with sodium sulfide and re-oxidised to insoluble sulfur-containing products on fibre
Vat	Colloidal, insoluble	Cotton, rayon	Impregnation and oxidation	Water insoluble dyes solubilised by reducing with sodium hydrosulfite, then exhausted on fibre and re-oxidised

Among all these dyes, azo dyes are the most commonly used dye type (Verma et al., 2012, Chequer et al., 2013, Jonstrup et al., 2011) due to their cost effectiveness for synthesis high fastness property and excellent structural diversity. Azo dyes such as methylene blue (MB) are aromatic compounds which consists of azo group chromopores and other substituent which they usually attach to radicals (Kamila, 2010). Azo dyes have low fixation yield due to the hydrolysis side reaction occurred in the dyebaths (Jonstrup et al., 2011).

The increased colour intensity of textile wastewater caused by dyes is the current predominant problem in the textile industry. The removal of these dyes by means of cheaper and environmental friendly technologies is still a major challenge. They are also stable under extreme conditions which they are initially designed subsequently to recalcitrant under condition such as exposure to sunlight, washing and microbial attack (Øllgaard, 1998). Some of the azo dyes also exhibit carcinogenic and mutagenic property. According to Pinheiro (2004), the azo dyes will reduce to carcinogenic aromatic amines such as benzidine and methylene under oxygen deficient conditions and some researcher also found that azo dyes is able to produce dangerous by-products via oxidation, hydrolysis and other chemical reaction that happen during wastewater treatment processes (Prevot, 2001). This phenomena will subsequently pose a threat to the agriculture and the health of people.

The disposal of dyes in lake, river and seas not only offer aesthetical displeasure, but it will also cause perturbations in aquatic life as the non-degradable dyes block the sunlight, causing the reduction of oxygen and light penetration in the water which substantially prevent photosynthesis to take place and lead to eutrophication and other damage to the aquatic environment (Chequer et al., 2013, Verma, 2017, Jonstrup et al., 2011).

2.3. Techniques for degradation of organic pollutant

In order to reduce the environment impacts caused by the dyes, one of the method is to perform degradation of dye by introducing nanocatalyst to adsorb the dye particles. An efficient and advanced oxidation of the aromatic compounds have greater potentials in the future as this degradation method can provide high oxidation capacity, complete and fast degradation (Fang et al., 2016). There are four methods in advanced oxidation to generate hydroxyl radicals and treat the waste water which include ozone treatment, electrochemical processes, direct decomposition of water and photocatalysis (Khaki et al., 2017). However, among all these advanced oxidation methods, photocatalysis method has attracted public concerns due to its ability to convert the pollutants into harmless intermediates at ambient temperature and pressure and to produce a strong oxidants which are hydroxyl radicals (Daneshvar et al., 2007). The photocatalysis method uses semiconductor metal oxide as catalyst to absorb radiation energy until it reaches equal to or higher than its band gap energy level which then causes excitation and transfer of electron to generate an electron-hole pair (Andreozzi et al., 1999). The electron-hole pair reacts with water and oxygen which acts as an oxidizing agent to allow formation of highly reactive oxygen species (hydroxyl radicals). These hydroxyl radicals attack the organic components and decompose them via oxidation reaction.

2.4. Method to Synthesize metal oxide nanostructure

The size, morphology and specific surface area of metal oxide photocatalysts are strongly dependent on their preparation methods (Farrouji et al., 2015). There are two common approaches that haven known in preparation of nanoparticles from ancient times which are breakdown (top down) method and build up (bottom-up) method. Breakdown method is the use of external force to a solid to break up the solid into smaller particles while for build-up method, atoms of gas or liquid undergo atomic transformation or molecular condensation to form nanoparticles (Serpone, 2013).

So far, researchers put forward many methods to prepare useful catalyst with different structures (Fang et al., 2016) which include solid precipitation (Ghulam et al., 2013), thermal decomposition method (Mansour et al., 2016) and wet methods such as hydrothermal method (Sonia et al., 2015, Fang et al., 2016), sol-gel method (Hassena, 2016) and sonochemical-assisted method (Mosleh et al., 2018). Among these methods, hydrothermal process has been considered as the most promising and efficient route to synthesize metal oxide nanostructure due to its advantages such simple formation which low temperature is required, potential for large scale production, excellent photocatalytic properties and degradation efficiency (Sonia et al., 2015).

Hydrothermal synthesis is generally defined as crystal synthesis or crystal growth under high temperature and high pressure water conditions from substances which are insoluble in ordinary temperature and pressure ($<100˚C$, $<1atm$) (Hayashi and Hakuta, 2010). According to Fang (2016), hydrothermal process does not impact the crystallization phase of the catalyst when a structure directing agent is used. In hydrothermal synthesis, the morphology and microstructure of the synthesized catalyst and photocatalytic activity can be controlled and enhanced by adding structure-directing agents

The synthetic methods of nanoparticles that are commonly used includes co-precipitation, thermal decomposition and hydrothermal method. The differences between these three methods are compared as shown in Table 2.3.

Table 2.3   Summary comparison of synthetic method of nanoparticles

Method	Synthesis	Temperature (˚C)	Period	Solvent	Size distribution	Shape control	Yield
Co-precipitation	Very simple, ambient conditions	20-90	Minutes	Water	Relatively narrow	Not good	High
Thermal decomposition	Complicated, inert atmosphere	100-320	Hours-days	Organic compound	Very narrow	Very good	High
Hydrothermal	Simple, high pressure	100-220	Hours-days	Water, ethanol	Very narrow	Very good	Medium

2.4.1. Growth Mechanism of Nanostructure (Hydrothermal Method)

As shown in Figure 2.1, in the primary stage from synthesis of α-Fe_2O_3 nanosheets, the dissolution of iron chloride (Fe^{3+}) and ammonium hydroxide (OH^-) in water at room temperature promotes the hydrolysis reaction to form $Fe(OH)_3$. Solution which is homogeneous with the directing agent. The nucleation of α-Fe_2OOH starts during the second stage of synthesis. The directing agent is adsorbed on the nucleus surface to allow the growth of α-Fe_2OOH. The formed α-Fe_2OOH with trapped directing agent undergo dehydration in the third stage. In this stage, the interplanar H-bonds are broken due to the heating which eventually speed up the dehydration rate. This mechanism increases the transformation rate of orthorhombic structure, α-Fe_2OOH to monoclinic structure, α-Fe_2O_3. The heating effect also able to promote a growth process of crystallographic planes as the result of effective collision and the aggregation

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of plates surface takes place under van der Waals forces. The last stage of synthesis of metal oxide nanoparticles is calcinations where directing agents are decomposed under high temperature and its molecular imprinting is left inside the α-Fe_2O_3 catalyst (Fang et al., 2016, Jiang, 2014).
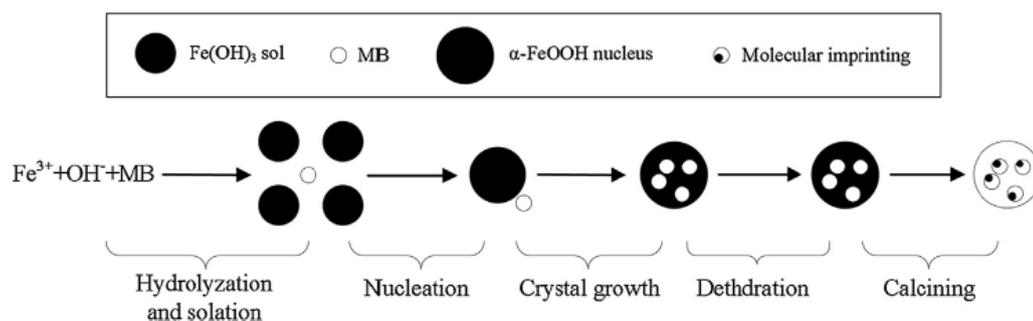
Figure 2.1   *Metal oxide (α-Fe_2O_3) formation mechanism (Fang et al., 2016)*

2.5. Metal oxide Nanoparticles

Nanotechnology has contributed in different fields including the development of analytical devices, alternative and innovative approaches to synthesize high quality shaped nanoscaled particles and development of new method based upon molecular self-assembly (Huang et al., 2010).

Nanomaterials refers to nanoscale materials that have a size range of 1-100nm in all dimensions. They have enhanced properties such as catalytic activity, thermal conductivity, non-linear optical performance and chemical steadiness which lead them to have large surface area to volume ratio (Tabrez, 2016). There are seven main classes of manufactured nanomaterials which includes carbonaceous nanomaterials, semiconductors, metal oxides, nanopolymers, nanoclays, emulsions and metals (Batley et al., 2013). These nanomaterials have different shapes, coatings, and surface

functionality and can exist in many forms such as single, aggregated, or agglomerated forms.

Among them, metal oxides nanoparticles are popular because they have improved physical and chemical properties such as lower melting points, higher specific surface areas, specific optical properties, mechanical strengths and specific magnetization as compared to bulk metal (Serpone, 2013). Metal oxide nanoparticles have wide applications mainly in the technology field, including their use as a semiconductor, electroluminescent or thermoelectric material. At the same time, they are also used in biomedical applications as drug delivery systems for treatment and diagnosis and in environmental decontamination applications (Corr, 2013, Haddad, 2012).

2.5.1. Comparison of Various Metal Oxide Performance

Among different nano sized semiconductors, metal oxide such as titanium dioxide (TiO_2) and zinc oxide (ZnO) are the most successful and popular photocatalyst. Titanium dioxide (TiO_2) has properties such as wide band gap semiconductor, high redox potential, low cost, non-toxicity and high chemical stability which made it as the most investigated material as photocatalyst (Khaki et al., 2017, Andreozzi et al., 1999, Atout et al., 2017). However, the low quantum efficiency of photocatalytic hydrogen evaluation which caused by the high recombination ability of photo-generated electron-hole pairs has made poor photcatalytic activity of this catalyst (Zhang et al., 2012). Thus, another alternative material for environmental application and waste water treatment is investigated.

Copper oxide (CuO) is another metal oxide which is a p-type semiconductor with 1.21-1.51 eV energy band gap. Its properties such as low cost, non-toxic, easily

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obtainable constituents and high specific surface area have made it used as an efficient adsorbent for adsorption of Methylene blue cationic dye (Abhishek, 2014).

Besides copper dioxide, iron (III) oxide (Fe_2O_3) nonmaterial also exhibits promising photocatalytic activities due to their properties such as environmental compatibility, low cost, high specific area, narrow forbidden band gap, no toxicity, high photocatalytic activity under visible light and prevention of electron-hole complex with grapheme regulation (Hassena, 2016, Fang et al., 2016). Iron (III) oxide can be exist in three typical forms which are hematite, maghemite and magnetite. Among them, hematite (α-Fe_2O_3) is the most stable and environment friendly n-type semiconductor under ambient condition. However, it is unstable in aqueous solutions which will undergo corrosion by water (Bak et al., 2002).

Fe_2O_3 exhibits good photocatalytic properties and has potential to effectively treat waste water but due to their photo corrosion (rapid recombination of the photogenerated electron-hole pair, these narrow band gap photocatalysts are unstable. For that reason, various methods such as surface modification, doping and co-doping with different components have been explored to achieve efficient visible light photocatalysis with these oxides (Siuleiman et al., 2014). Recent researches focus on the microstructure and morphologies of the material in enhancement of photodegadation of these photoctalysts to work efficiently under visible light irradiation.

2.5.2. Control of Morphology of Nanoparticles

Recent researchers focus on how to improve selectivity of the photocatalytic degradation to decompose certain compound in the aromatic mixtures while retaining the functionality of other useful one (Fang et al., 2016). The molecular imprinting is

considered as one of the processes to improve photocatalytic selectivities by introducing methylene blue as a structure-directing agent or template molecule to gain catalyst with morphology and microstructures which matches the pollutants one. The definitions of dispersing agent, structure directing agent and reducing agent are shown below.

a. *Dispersing Agents*

The optical characteristic of nanoparticles will change significantly base on the size distribution of nanoparticles. Thus, fabricating single target size or monodispersed nanoparticles is significant during synthesis of nanoparticles (Serpone, 2013). To achieve this aim, the addition of dispersing agent is necessary once the desired growth size is achieved. The use of dispersing agent is to stabilize the surface of particulate to avoid aggregation due to the increase in surface energy of the particulate. To maintain a high dispersivity of nanoparticles, an optimum concentration of nanoparticles should be chosen. The selection of suitable dispersing agent can refer to the hard and soft acid and bases (HSAB) rule.

b. *Structure Directing Agent*

The shape of nanoparticles is important to determine the nature of the surface plasmon resonance band. The increase of size ratio of a crystal face can shift the maximal absorption band to longer wavelength by adding template consisting of surfactant (Serpone, 2013). During the growth mechanism as discussed in 2.4.1, the template molecule is adsorbed onto the crystal faces of the nanoparticles. The shape and forms of nanoparticles is depend on the adsorption characteristic of template molecule used.

c. *Reducing/ Precipitating Agent*

The nanoparticles can be synthesized through reduction of a metal ion solution which surrounded by the reducing agent. This method is found to be a great success in

controlling the size of nanoparticles. The famous reducing agent that commonly used to prepare base metal is ethylene glycol due to its polar nature which is useful to be a reaction solvent to dissolve metal salt and can act as a dispersing agent at the same time since it has a high boiling point of 198˚C. The boiling of the reducing agent must not be too high as it will make the removal of the solvent becomes difficult.

2.5.3. Effect of Reaction Parameter on the Surface Morphology

There are several parameters that will affect the morphology and crystallinity of the nanoparticles. These parameters are reaction time, molar ratio of metal ion to directing agent, and reaction temperature.

The influence of reaction time and temperature on morphology and photocatalytic performance of α-Fe_2O_3 is reported in many research works. The research has shown that the performance of the α-Fe_2O_3 improves when both of the reaction time and temperature used are increased. When the longer reaction time is given for reaction to occur, there is more time available for the due crystallite sizes of α-Fe_2O_3 nanoparticles to grow. At reaction higher temperature, the interplanar H-bonds break and speed up the dehydration rate. Thus, more α-Fe_2O_3 particles is formed from floccules. The result from Wang 2013 has shown that the crystalline phase of the products has little dependence on the reaction time compared to reaction temperature (Wang et al., 2013).

Molar ratio of metal ion to directing agent (Fe^{3+}/MB) is also very important in synthesis of higher performance of α-Fe_2O_3 catalyst. According to Fang (2016), as the amount of directing agent is changed specific area, pore volume and pore size of the α-Fe_2O_3 samples also alter significantly (Fang et al., 2016). The increase of the structure

directing agent also increase the clarity of the crystal matrix. The molar ratio that shows the best result is 200.

2.5.4. Photocatalytic Activity of α-Fe$_2$O$_3$ NPs

α-Fe$_2$O$_3$ is an n type semiconductor. Its main mechanism of photocatalytic reaction is to generate electron-hole pairs under photon-excitation at certain range of wavelength. A good photocatalyst should have strong oxidation potentials on the surface hole of particles in order to react with water which adsorb on the particle surface to produce OH radicals for degradation of organic pollutant on the catalyst. The O^{2-} radicals produced from the binding of free electrons and oxygen that adsorbed on the particle surface can further degrade the organic compounds (Fang et al., 2016). The operational parameters of the conducted phototcatalytic processes on the quality and effectiveness of degradation of MB is the amount of catalyst loading, pH of solution, and initial concentration of MB. According to Bubacz (2010), the photocatalytic reaction increased with a rise of the amount of catalyst used and then remained almost constant above certain level. Regarding the effect of initial concentration of MB on the photocatalytic reaction, Chiou (2014) indicated that photocatalytic oxidation shows better performance when low MB concentration is used.

The pH value of a mixture of catalyst and MB is the most important controlling parameters having an effect on MB degradation. The result from Jiabin Zhou (Zhou, 2012), the removal of MB increase when the pH value increases from 3 to 7 due to the surface charge behaviour of the α-Fe$_2$O$_3$ and the dissociation chemistry of the solute. Since methylene blue is cationic dye, when the pH value is below 7, the α-Fe$_2$O$_3$ will have positive surface charge density which causes difficulty for adsorption of MB onto adsorbent. While at pH above 7, the α-Fe$_2$O$_3$ surface will have negatively charged,

converting the molecular MB to anions in a system due to dissociation. The optimum pH in this case is 7.

2.5.5. Agglomeration and Aggregation of NPs

The small particle size of nanoparticles tend to colloid together to form larger cluster. When the NPs are stored in the dry state, there high tendency for NPs to undergo agglomeration and aggregation. Agglomerates refer to particles bonded by weak physical forces whereas aggregates are particles bonded by strong chemical. The differences between agglomeration and aggregation are as shown in Table 2.4. Since at room temperature, the Brownian motion in nanoparticles is sufficient enough to cause solid bridging between the nanoparticles in close contact due to van der Waal attraction. The small aggregates will eventually from micron-sized aggregates after experiencing relative stability (Rawle, 2007, Lim et al., 2013). It is extremely difficult to disperse the hard aggregates which will probably reduce the surface area for adsorption due to increased cluster size. Thus, the nanoparticles contains both micron sized and larger agglomerates and aggregates and exhibits both of their properties in dry and wet system.

Table 2.4   Difference between agglomeration and aggregation (Rawle, 2007)

Agglomeration	Aggregation
Soft agglomerates	Hard agglomerates
Van Der Waals forces due to adsorbed moisture and capillary-condensed liquids	Solid bridging caused by sintering, phase transformation and solid state reactions.
Viscous binders	Strong glassy binders

Chapter 3

Materials and Methods

3.1. Introduction

This chapter describes the methodology used in this study for the entire research work. The contents of this chapter includes the materials and chemicals used, equipment procedures and overall experiment flow chart. The experiment was divided into three stages: synthesis of catalyst, characterization test and performance test. Synthesis of hematite iron (III) oxide (α-Fe_2O_3) using hydrothermal method was done with varying reaction temperature with specific ferric ion to MB molar ratio, Fe^{3+}/MB of 200. Photocatalytic performance of the synthesized photocatalyst α-Fe_2O_3 was taken place by first stirring the α-Fe_2O_3 sample and organic pollutant (MB) in the dark to reach the equilibrium of adsorption. Then, the mixture was exposed under visible light irradiation for the degradation of MB to take place via oxidation reaction. The characterization of α-Fe_2O_3 samples was done to study the morphology, physical and chemical properties of the photocatalysts.

3.2.   Materials and Chemicals

In this study, $FeCl_3.6H_2O$ and $NH_3.H_2O$ were used as feedstock to produce iron oxides. The structure directing agents used in this study were glycine and methylene blue. All the materials and chemicals used are listed in Table 3.1.

Table 3.1   List of materials and chemicals used

Materials	Chemical formula	Supplier	Purpose of use
Iron (III) Chloride 6-Hydrate	$FeCl_3 \cdot 6H_2O$	Ever Gainful Enterprise	Reactant
Ammonium Solution (25%)	$NH_3 \cdot H_2O$	Ever Gainful Enterprise	Reactant
Glycine	$C_2H_5NO_2$	MERCK Sdn Bhd	Structure of Photocatalyst (Surfactant)
Methylene Blue	$C_{16}H_{18}ClN_3S \cdot 3H_2O$	Mallinckrodt PLC	Synthesis of Photocatalyst (Structure directing Agent)
Ethyl Alcohol (95% v/v)	C_2H_5OH	Ever Gainful Enterprise	Solvent to wash sample
Sodium Hydroxide (1N)	NaOH	Ever Gainful Enterprise	To prepare 0.1 N NaOH to adjust pH of iron oxide solution
Hydrochloric acid (37%)	HCl	Ever Gainful Enterprise	To prepare 0.1 N HCl to adjust pH of iron oxide solution
Deionized water	H_2O	Laboratory	Preparation of α-Fe_2O_3 samples

3.3. Equipment

There are several equipments were used in this study which includes the equipments required for preparation of photocatalyst, photocatalystic degradation, photocatalyst characterization and analysis. The equipments are listed in Table 3.2.

Table 3.2   List of equipment used

Equipment	Brand	Purpose of use
UV-Vis Spectrophotometer	Shimadzu UV-1700 PharmaSpec	Product Analysis
X-ray diffractometer (XRD)	Siemens D5000	Catalyst characterization (Crystallinity)
Scanning electron microscopy (SEM)	Leo Supra 50 VP equipped with Oxford INCA 400 EDX (Germany)	Catalyst characterization (Structure and surface morphology, chemical composition)
Fourier transform infrared spectrophotometer (FTIR)	Shimadzu IR Prestige-21	Catalyst characterization (Surface functional species)
Nitrogen adsorption-desorption isotherm	Micromerities ASAP 2020 V3.02	Catalyst characterization (Surface area)
Dynamic Light Scattering (DLS)	Malvern Zetasizer Nano series, (Malvern Instruments, Westborough, MA, USA)	Catalyst characterization (Hydrodynamic diameter)
Visible Light Photocatalytic Batch Reactor	Peltier Cooling unit for water baths (CDP 115) and Shaking device (SV 22)	Photocatalytic degradation of photocatalyst samples
Teflon Lined Stainless Autoclave	Techinstro TI010 (10ml)	Hydrothermal synthesis reaction
Oven	Memmert UN30	Removal of moisture of the catalyst sample
Furnace	Carbolite CWF 1300	Calcination of the catalyst sample
Analytical balance	Mettler Toledo AY220	Weighing
Magnetic Heater Stirrer	Heidolph MR Hei-Tec P/N 505-30000-00	Stirring during Catalyst Preparation

The below Figure 3.1 shows the experimental activities and tasks were carried out in this study.

Preparation of catalysts
- Hydrothermal method
- Effect of reaction temperature
- Fe^{3+}/MB molar ratio (200:1)

Characterization of catalysts
- Specific surface area
- Pore volume
- Particle size
- Crystalline phase
- Morphology
- Distribution of pore sizes

Photocatalystic activity of catalysts
- Reaction time
- Reaction temperature
- Initial MB concentration
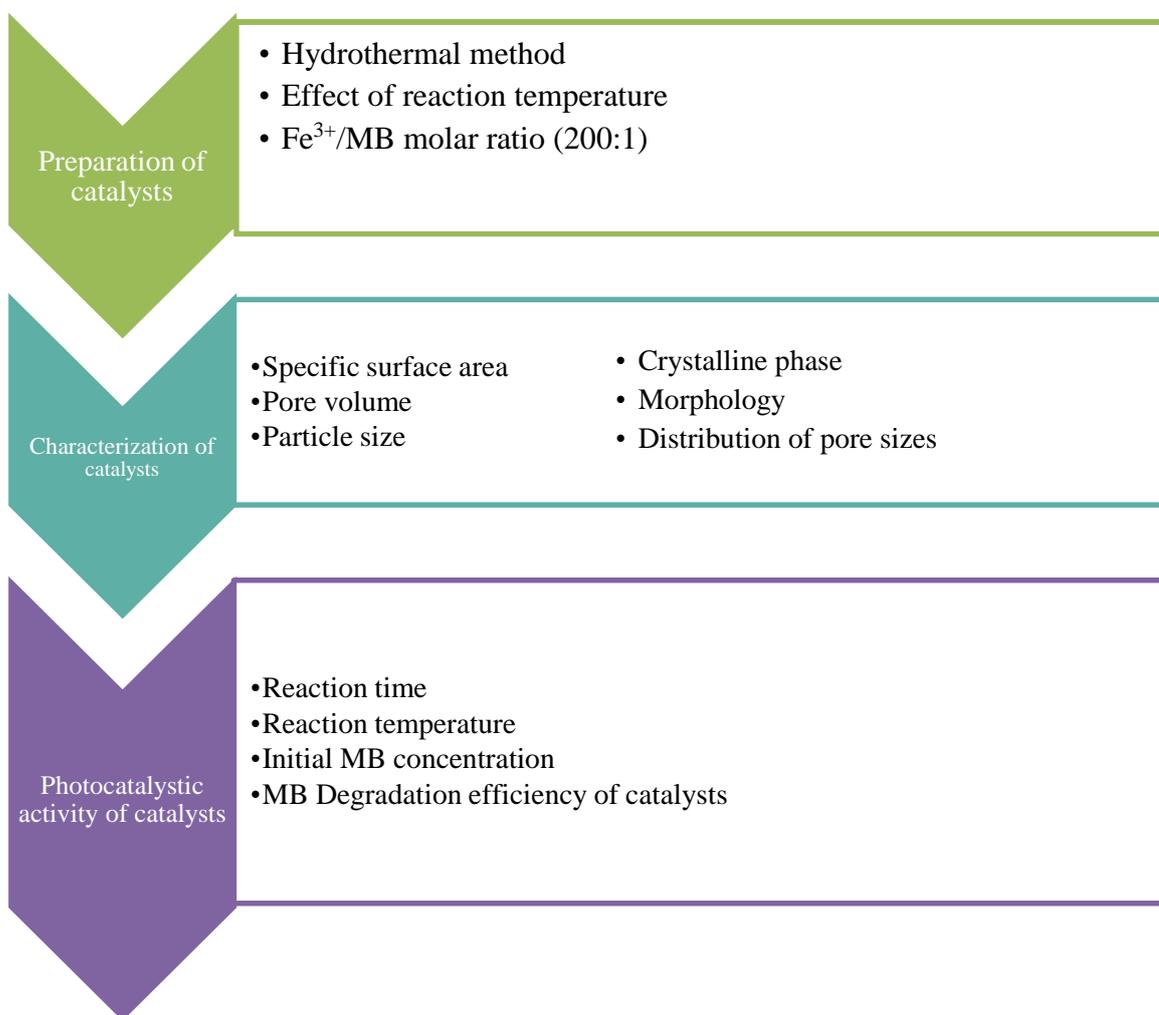- MB Degradation efficiency of catalysts

Figure 3.1   The activities of the research

3.4.   Preparation of α-Fe₂O₃ Photocatalyst

Iron(II) oxide was synthesized by using hydrothermal method in which the preparation procedure was adapted from Fang (Fang et al., 2016). First, 5g of Iron chloride, $FeCl_3.6H_2O$ was dissolved in 50ml of deionized water to which desired amount of glycine (2g) and methylene blue (0.0493g) were added as structure directing agents. The desired Fe^{3+}/MB molar ratio is fixed to 200:1. Then, the solution was stirred