ENHANCING PHOTOCATALYTIC ABILITY OF TITANIUM DIOXIDE THROUGH INCORPORATION OF MIL-53(Fe) TOWARDS DEGRADATION OF METHYL ORANGE AND METHYLENE BLUE

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DECLARATION

I hereby declare that the material in this thesis is my own except for quotations, excepts, equations, summaries and references, which have been duly acknowledged.

1st November 2016

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ABSTRACT

MIL-53(Fe) is an iron(III) carboxylate compound fall under the subclass of metal-organic frameworks (MOFs). This compound was incorporated to TiO_2, a non-toxic and highly efficient semiconductor for photocatalysis application. MIL-53(Fe) was synthesized by reflux method for 3 hours. The obtained MIL-53(Fe) powder was dispersed in ethanol and water mixture, sonicated and injected with a titanium(IV) butoxide. The mixture was then further heated in Teflon-lined autoclave to produce MIL-53(Fe)/TiO_2. To produce MIL-53(Fe) derived Fe_2O_3/TiO_2 composite, the powder was calcined at 500 °C. XRD pattern confirmed the obtained powder corresponds to the MIL-53(Fe)/TiO_2 with characteristic feature of an anatase and MIL-53(Fe), while the XRD pattern of the calcined MIL-53(Fe)/TiO_2 powder suggested that the derived material were Fe_2O_3/TiO_2 composite. EDX data proved that there was MIL-53(Fe) material incorporated to the TiO_2. Scanning Electron Microscope (SEM) image of MIL-53(Fe) showed a triangular prism-shaped with particle size in the range of 0.2 to 0.25 µm. A spherical morphology were observed on MIL-53(Fe)/TiO_2 and MIL-53(Fe) derived Fe_2O_3/TiO_2 composites with the particle size in the range of 0.73 to 0.94 µm and 0.61 to 0.81 µm respectively. The photocatalytic activity of photocatalyst MIL-53(Fe)/TiO_2, MIL-53(Fe) derived Fe_2O_3/TiO_2 and a control sample of TiO_2 nano powder were evaluated towards methyl orange (MO) and methylene blue (MB) dye in water under UV-vis light irradiation at different time interval for 6 hours time. The results revealed that both MIL-53(Fe)/TiO_2 and MIL-53(Fe) derived Fe_2O_3/TiO_2 materials exhibit better photocatalytic activity compared to the bare TiO_2. MIL-53(Fe)/TiO_2 has slightly increased the photocatalytic performance of TiO_2 for about 6% towards MO and 11% towards MB while MIL-53(Fe) derived Fe_2O_3/TiO_2 has successfully increased the photocatalytic performance of bare TiO_2 for about 75% in MO and 30% in MB dye. The results obtained show that, the MIL-53(Fe) derived Fe_2O_3/TiO_2 has good photocatalytic degradation efficiency compared to MIL-53(Fe)/TiO_2. This implies that MIL-53(Fe) derived Fe_2O_3/TiO_2 is a potential material for environmental remediation such as water purification and air purification.

ABSTRAK

PENINGKATAN KEUPAYAAN FOTOPEMANGKINAN TITANIUM DIOKSIDA MELALUI PERGABUNGAN MIL-53(Fe) KE ARAH DEGRADASI METIL JINGGA DAN METILEN BIRU

MIL-53(Fe) adalah merupakan sebatian karboksilat besi(III) di bawah pengkelasan rangka logam organik. Sebatian ini telah digabungkan ke dalam titanium dioksida, semikonduktor yang tidak toksik dan cekap dalam aplikasi fotopemangkinan. MIL-53(Fe) disintesis menggunakan kaedah refluks selama 3 jam. Serbuk MIL-53(Fe) yang diperoleh di suraikan, di sonikasi, dan disuntik dengan titanium(IV) butoksida. Campuran tersebut kemudiannya dipanaskan di dalam autoklaf Teflon untuk menghasilkan MIL-53(Fe)/TiO_2. Manakala untuk menghasilkan komposit Fe_2O_3/TiO_2 terbitan MIL-53(Fe), serbuk tersebut telah dikalsinasi pada suhu 500 °C. Corak XRD membuktikan serbuk yang diperoleh merupakan MIL-53(Fe)/TiO_2 dengan ciri anatasa manakala corak XRD MIL-53(Fe)/TiO_2 yang dikalsinasi menunjukkan bahawa bahan terbitan tersebut merupakan komposit Fe_2O_3/TiO_2. Data dari spektroskopi tenaga serakan sinar-x membuktikan bahawa MIL-53(Fe) bergabung pada TiO_2. Gambar SEM MIL-53(Fe) menunjukkan bentuk prisma segi tiga dengan saiz zarah pada kadar 0.2 kepada 0.25 µm. Morfologi sfera dapat dilihat pada komposit MIL-53(Fe)/TiO_2 dan Fe_2O_3/TiO_2 terbitan MIL-53(Fe) masing-masing dengan kadar saiz antara 0.73 kepada 0.94 µm dan 0.61 kepada 0.81 µm. Aktiviti pemangkinanfoto MIL-53(Fe)/TiO_2, Fe_2O_3/TiO_2 terbitan MIL-53(Fe) dan sampel serbuk TiO_2 telah dinilai ke atas larutan pewarna metil jingga dan metilen biru dibawah pancaran cahaya UV pada selang masa yang berbeza selama 6 jam. Keputusan tersebut menunjukkan bahawa kedua-dua pemangkin foto MIL-53(Fe)/TiO_2 dan Fe_2O_3/TiO_2 terbitan MIL-53(Fe) mempamerkan aktiviti pemangkinan foto yang lebih baik jika dibandingkan dengan TiO_2. MIL-53(Fe)/TiO_2 telah meningkatkan prestasi fotopemangkinan TiO_2 pada kadar 6% di dalam MO dan 11% pada MB manakala Fe_2O_3/TiO_2 terbitan MIL-53(Fe) telah berjaya menigkatkan prestasi fotopemangkinan TiO_2 pada kadar 75% di dalam MO dan 30% pada MB. Daripada keputusan yang diperoleh, Fe_2O_3/TiO_2 terbitan MIL-53(Fe) menunjukkan keberkesanan degradasi fotopemangkinan yang lebih baik berbanding MIL-53(Fe)/TiO_2. Ini menunjukkan bahawa Fe_2O_3/TiO_2 terbitan MIL-53(Fe) adalah bahan yang berpotensi untuk pe/mulihan alam sekitar seperti pembersihan air dan udara.

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LIST OF SYMBOLS AND ABBREVIATIONS

AOP	-	Advance oxidation process
D_{abs}	-	Photodegradation efficiency
EDX	-	Energy-dispersive X-ray
eV	-	Electronvolt
h^+	-	Photogenerated holes
MB	-	Methylene blue
MIL	-	Materials of Institute Lavoisier
MO	-	Methyl orange
MOFs	-	Metal-organic frameworks
SEM	-	Scanning electron microscopy
TGA	-	Thermogravimetric analysis
UV-A	-	Ultraviolet A
UV-Vis	-	Ultraviolet-visible
XRD	-	X-ray diffractometer
wt %	-	Weight percentage
λ_{max}	-	Maximum wavelength

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CHAPTER 1

INTRODUCTION

1.1 Photocatalytic Degradation of Organic Pollutants by Titanium Dioxide

Photocatalytic degradation has been considered as an efficient way to solve the environmental pollution worldwide due to its ability to convert solar energy into chemical energy (Akple *et al.*, 2015; Xiang *et al.*, 2015). In water treatment field, advanced oxidation processes (AOPs) were proven to be very effective for the degradation of organic pollutant in the wastewater (Arslan *et al.*, 1999; Bergamini *et al.*, 2009). AOP in wastewater treatment generates sufficient quantity of hydroxyl radicals (•OH) with very high oxidizing power which capable to degrade recalcitrant organic pollutants (Banerjee *et al.*, 2007; Da Silva *et al.*, 2011) to CO_2 and H_2O (Rathi *et al.*, 2003). Moreover, the removal and degradation of pollutants are very difficult using conventional treatment methods. Conventional water treatment methods such as adsorption on activated carbon, coagulation, and membrane separation has several disadvantages such as high operating costs and generate secondary pollutants resulting from transferring pollutants towards a new medium process (Damardji *et al.*, 2009).

Photocatalyst such as TiO_2 is one of the materials (Kangwansupamonkon *et al.*, 2010) which were mostly applied in AOPs process. TiO_2 penetrated by UV light give rise to hydroxyl radicals (•OH) that is important for the degradation of organic pollutants. This process is called AOP. In AOP, TiO_2 can be photo-excited by radiation with a wavelength below 380 nm producing positive hole (h^+) at the valence band and electron at the conduction band of TiO_2 which will then react with water molecules or hydroxide ions (OH^-) to produce hydroxyl radical (•OH). The •OH has high oxidizing properties that capable of degrading and eventually mineralizing organic contaminants into CO_2 and H_2O (Rathi *et al.*, 2003).

Nowadays, modification of TiO_2 has been extensively investigated aiming for more unique properties and functionality of the photocatalyst. Various approaches have been implemented such as impurity doping, noble metal deposition, coupling with narrow gap materials and modification with nanostructures (Qi *et al.*, 2016). The main objectives of the TiO_2 modifications are to improve the charge carrier separation yielding more •OH species that enhance the photocatalytic performances and to overcome wide band gap of the photocatalyst (Qi *et al.*, 2016; Kumar and Rao, 2017).

Beside TiO_2, other metal oxides photocatalyst such as ZnO and WO_3 are also studied and been modified due to their stability, non-toxicity, ease of preparation, biocompatibility and their structure-electronic properties. These metal oxides are widely applied in heterogeneous photocatalysis owing to their valence band (VB) ability to generate •OH radicals and their identical band gap excitation mechanism (Kumar and Rao, 2017). However, among these metal oxides photocatalyst, TiO_2 is proven to generate the highest amount of hydroxyl radicals and has the highest activity compared to other semiconductor photocatalyst which contribute to more efficient photocatalytic activity (Xiang *et al.*, 2011; Kumar and Devi, 2011).

1.2 Problems of TiO_2 as Photocatalyst

TiO_2 is one of the most used semiconductor materials owing to its non-toxicity, chemical stability, inexpensive and high efficiency in photocatalysis applications. However, TiO_2 photocatalyst facing several problems that limit its photocatalytic performance such as rapid electron-hole recombination, fast desorption of organic pollutants which can slow down the photocatalytic degradation and wide band gap energy of 3.2 eV where ultraviolet (UV) light is needed as an excitation source (Ganesh *et al.*, 2012; Kokila *et al.*, 2011). However, the high recombination rate which limits its catalytic performance is the major problem.

Recombination of electron and holes takes place either on the surface or in the bulk of the TiO_2 which are caused by impurities or defects resulting in the imperfection of the crystals surface or bulk (Choi *et al.*, 1994; Serpone, 1997).

Once the recombination occur, the excited electron will return back to the valence band without reacting with the adsorbed species (Sclafani and Herrmann, 1996).

Thus, the design of highly efficient photocatalyst with the ability to decrease the recombination rate semiconductor along with high mobility of electron and hole including having a numerous active sites is focused in this research. The photocatalytic activity will increase accordingly as the density of the surface •OH increases due to its high oxidizing power capable to degrade organic pollutants into harmless materials such as CO_2 and H_2O. Sufficient amount of •OH are crucial to enhance the photocatalytic degradation efficiency of the TiO_2 (Banerjee *et al.*, 2007; Rathi *et al.*, 2003). Therefore, modifying the TiO_2 surface is rationale to study the its effect and eventually increase the concentration of •OH in enhancing the photocatalytic efficiency.

1.3 Modification of TiO_2 with Metal-Organic Frameworks (MOFs)

Numerous study and efforts in modifying TiO_2 photocatalyst has been devoted aiming to improve and overcome the critical problems of unmodified TiO_2 such as fast electron hole recombination and low efficiency in visible light absorption (Nasirian and Mehrvar, 2016; Qi *et al.*, 2016). To date, there has been a growing number of publications on the modification of TiO_2 photocatalyst such as integrating with metal and non metal, impurity doping, noble metal deposition, coupling with narrow gap materials and modification with nanostructures (Qi *et al.*, 2016; Kumar *et al.*, 2014; Sun *et al.*, 2013). In this research, we aim to enhance the photocatalytic property of TiO_2 by reducing the electron-hole recombination and increasing the active sites of photocatalyst through incorporation of metal-organic frameworks.

Metal-organic frameworks (MOFs) are new generation of inorganic-organic porous solids. They are hybridized materials constructed by metal nodes coordinated with organic linkers as bridging molecules to give three-dimensional (3D) structures (Zhou *et al.*, 2012). The variability of organic and inorganic components, highly crystalline and porous properties makes MOFs as promising

materials for versatile applications such as energy storage, molecules adsorption and separation, catalysis and drugs delivery (Czaja *et al.*, 2009).

Due to the MOFs unique characteristics such as high surface areas ranging from 1000 to 10,000 m_2/g and high adsorption affinities (for example by Zn-based metal-organic frameworks, TMU-5 and TMU-6 which adsorb 96.2% and 92.8% of 100 ppm rhodamine B dye respectively), it can be considered as a good support for materials with photocatalytic properties which favor the diffusion of foreign species from water (Li *et al.,* 2009; Furukawa *et al.*, 2013; Masoomi *et al.*, 2016). MOFs have been reported as potential photocatalysts for the photocaatlytic degradation of organic pollutants (Wang *et al.*, 2014). Owing to the significant properties of MOFs such as high density of active sites and high tunable properties, MOFs can serve as the potential candidate in photocatalysis (Corma *et al.,* 2010; Stock and Biswas, 2012). The combination of MOFs and TiO_2 might therefore improve the performance of TiO_2 in photocatalysis.

MIL-53(Fe) is a subclass of MOFs which were built up from chains of Fe(III) octahedra and 1,4-benzenedicarboxylic acid. This iron-based MOF has been selected to be incorporated into TiO_2 since it contain high iron oxoclusters and has been proof to be effective for common application in both catalysis and photocatalysis process (Liang *et al.*, 2015; Wang and Wang, 2015; Sciortino, *et al.*, 2015). Apart from that, low recombination rate are expected due to the small size of the Fe(III)-oxide cluster thus contributes to the enhancement of the photocatalytic degradation efficiency (Liang *et al.*, 2015). Moreover, the MIL-53(Fe) consisting of Fe(III) as the metal nodes where the empty *d* orbitals will form conduction band when mix with the organic ligands. This property was similar to the TiO_2 where its conduction band was built by empty Ti 3*d* orbitals (Gascon *et al.*, 2008). It is believed that the incorporation of MIL-53(Fe) in TiO_2 through hydrothermal and calcinations which produce MIL-53(Fe)/TiO_2 and MIL-53(Fe) derived Fe_2O_3/TiO_2 respectively favours the appearance of many active sites for photocatalytic degradation.

1.4 Objectives

The objectives of this study are to:

(i) Prepare and characterize MIL-53(Fe)/TiO_2 and MIL-53(Fe) derived Fe_2O_3/TiO_2 composite,

(ii) Evaluate the photocatalytic activity of MIL-53(Fe)/TiO_2 and MIL-53(Fe) derived Fe_2O_3/TiO_2 towards the degradation methyl orange (MO) and methylene blue (MB) dye in water,

(iii) Determine the reaction kinetics of the MIL-53(Fe)/TiO_2 photocatalyst towards MO and MB.

(iv) Evaluate the effect of H_2O_2 towards the reaction kinetics of the MIL-53(Fe)/TiO_2 photocatalyst towards MO and MB.

1.5 Scope of Study

MIL-53(Fe) powder was synthesized by solvothermal-reflux method reported by Munn *et al.* (2013) while TiO_2 was prepared under hydrothermal synthesis according to Yang *et al.*, (2015). The product were further used to synthesis MIL-53(Fe)/TiO_2 by hydrothermal annealing and MIL-53(Fe) derived Fe_2O_3/TiO_2 photocatalyst by calcination using furnace. In this study, the optimum conditions for preparing MIL-53(Fe)/TiO_2 composites/nanoparticles were investigated. Four parameters/conditions were optimized consisted of: (i) amount of MIL-53(Fe) incorporated into TiO_2; (ii) effect of photocatalyst amount; (iii) effect towards the degradation of MO and MB dyes; (iv) effect of initial concentration of H_2O_2 towards the photocatalytic degradation of MO and MB dyes. All the synthesized samples were then characterized by X-ray diffractometer (XRD) to confirm the crystal structure of the samples and energy dispersive x-ray spectroscopy (EDX) to provide the elemental concentrations in the samples. The morphology of all samples was observed under scanning electron microscope (SEM). The photocatalytic activity of photocatalysts MIL-53(Fe)/TiO_2, MIL-53(Fe) derived Fe_2O_3/TiO_2 and a control sample of TiO_2 were evaluated towards the degradation of methyl orange (MO) and

methylene blue (MB) dyes in aqueous solution under UV-vis light irradiation at different time interval. Due to their toxicity, it is very crucial to remove them from water. For that reason, throughout this research, MO and MB were selected as the representative acidic (anionic) dye and basic (cationic) dye respectively. The absorbances were recorded by ultraviolet-visible (UV-Vis) spectroscopy. Langmuir-Hinshelwood model and pseudo-second order were studied for the degradation kinetics of the photocatalysts.

CHAPTER 2

LITERATURE REVIEW

2.1 Advanced Oxidation Processes (AOP)

Oxidation is a chemical reaction which involves the transfer of one or more electrons from an electron donor to an electron acceptor. A chemical transformation of both the oxidant and reactant occurred due to the electron transfer process which in some cases producing chemical species with an odd number of valence electrons known as radicals. Radical species is an unpaired electron which is highly unstable and reactive. It will undergo additional oxidation with organic or inorganic reactants to form stable oxidation products (Carey, 1992).

Over the past three decades, advanced oxidation processes (AOPs) have earned a significant level of interest for the treatment of drinking water and wastewater industry. Advanced oxidation processes (AOPs) are technologies which involved the generation of highly reactive and non-selective oxidant, hydroxyl radicals, primarily used to destroy a wide range of toxic organic compound that cannot be oxidized by conventional oxidant present in wastewater, soil and air (Glaze *et al.*, 1987). The toxic pollutants will eventually oxidized into mineral end-products which will yield CO_2 and inorganic ions. Table 2.1 shows the comparison of relative oxidation power of several oxidizing species. Hydroxyl radicals which are one of the strongest oxidants in an aqueous medium able to oxidize a wide range of recalcitrant pollutants into harmless compound such as mineral salts, carbon dioxide and water through mineralization process (Chen *et al.,* 2000). Figure 2.1 shows some interesting characteristics of hydroxyl radical that brings AOPs as a powerful chemical treatment procedure to remove organic contaminants. A common reaction for the initial attack once the hydroxyl radicals generated is the abstraction of hydrogen atom from water to initiate a radical chain oxidation (Munter, 2001). The reactions were shown in Equation 2.1 to 2.5.

Table 2.1: Comparison of relative oxidation power of some oxidizing species

Oxidizing species	Relative oxidation power
Chlorine, C_2	1.00
Hypochlorous acid, HOCL	1.10
Permanganate, MnO_4	1.24
Hydrogen peroxide, H_2O_2	1.31
Ozone, O_3	1.52
Atomic oxygen, O	1.78
Hydroxyl radical (•OH)	2.05
Fluorine, F_2	2.25
Positively-charged hole on titanium dioxide, TiO_2^+	2.35

Source: Carey (1992); Zhou and Smith (2002)

$$RH + \bullet OH \rightarrow H_2O + R\bullet \quad (2.1)$$

$$2\bullet OH \rightarrow H_2O_2 \quad (2.2)$$

$$\bullet R + H_2O_2 \rightarrow ROH + OH\bullet \quad (2.3)$$

$$\bullet R + O_2 \rightarrow ROO\bullet \quad (2.4)$$

$$ROO\bullet + RH \rightarrow ROOH + R\bullet \quad (2.5)$$

AOP can be classified into two classes which are homogeneous and heterogeneous (Huang *et al.*, 1993). Table 2.2 shows a classification of AOP. Heterogeneous photocatalysis applying the usage of semiconductor such as zinc oxide (ZnO), tin dioxide (SnO_2) and TiO_2 in the presence of UV irradiation and hydrogen peroxide (H_2O_2). The main advantages of these methods are high rates of pollutant oxidation, flexibility concerning water quality variations, and small dimension of the equipment.