

**PHOTODEGRADATION OF NAPHTHALENE BY USING BINARY
TiO₂/CuO AND WO₃/CuO CATALYSTS**

MOHD FIKRI BIN MD ARIFFIN

UNIVERSITI TEKNOLOGI MALAYSIA

**PHOTODEGRADATION OF NAPHTHALENE BY USING BINARY
TiO₂/CuO AND WO₃/CuO CATALYSTS**

MOHD FIKRI BIN MD ARIFFIN

A dissertation submitted in partial fulfillment of the
requirements for the award of the degree of
Master of Science (Chemistry)

**Faculty of Science
Universiti Teknologi Malaysia**

January 2014

Dedicated to my beloved family...

ACKNOWLEDGEMENT

Alhamdulillah praise to Allah S.W.T for His blessing and permission, I have finally completed my project and also for the strength and guidance which accompanied my life.

I would like to thank to my supportive supervisor Assoc. Prof. Dr. Rusmidah Ali for her contribution in finishing this project. Not only she provided me with a workable idea for my project, but also provides supportive instructive comments and evaluation at every stage of the thesis process and allows me to complete this dissertation as scheduled. Last but not least, I would like to express my appreciation to my lab-mates, my parents and friends for their guidance and full supports in carrying out this dissertation. Finally, I would like to express my greatest appreciations to everyone who were involved in helping me to complete this dissertation.

ABSTRACT

Naphthalene is one of polycyclic aromatic hydrocarbons (PAHs) compounds which have been identified as carcinogenic. It is commonly used in industry and domestic. Therefore, it can cause environmental pollution and must be treated. One of the promising methods to remove this pollutant from waste water is by using photocatalyst since it can degrade the pollutant without producing toxic by-products. In this research, two types of photocatalysts namely TiO_2/CuO and WO_3/CuO were prepared with different mass ratio of co-catalyst and it was calcined at various temperatures. TiO_2 was prepared by sol-gel method while WO_3 by aging amorphous peroxy-tungstic acid. The characterizations of the prepared catalysts were done by XRD, FESEM and BET surface area analyzer. XRD patterns revealed that TiO_2/CuO calcined at 450 °C and 650 °C consists of single phase anatase and rutile respectively while TiO_2/CuO calcined at 550 °C consist of a mixture of anatase and rutile. XRD patterns for WO_3/CuO catalyst indicated that the catalyst consist of single phase of WO_3 . FESEM micrographs showed TiO_2/CuO particles were packed loosely compared to WO_3/CuO particles which were small and packed closely. BET analysis discovered that WO_3/CuO catalyst has larger surface area than TiO_2/CuO catalyst. The influence of pH, photocatalyst loading and the uses of different light radiation sources were studied. The reaction was monitored by UV-Vis spectrophotometer. Photocatalytic reaction performed best in neutral medium irradiated with UV light. The optimum mass percent of co-catalyst for both photocatalysts were 10% and the calcination temperature for WO_3/CuO and TiO_2/CuO photocatalysts was 650 °C and 550 °C respectively. The result indicated that the percentage of photodegradation for WO_3/CuO and TiO_2/CuO in neutral environment was 88.60% and 63.55% respectively. TiO_2/CuO removed 11.01% and 33.60% of pollutant in basic and acidic environment respectively. WO_3/CuO degraded 48.03% of pollutant in acidic environment while in basic environment it degraded 46.32% of pollutant. The optimum photocatalyst loading was 0.2 g for both photocatalysts. 0.2 g of WO_3/CuO (90:10 650 °C) degraded 93.23% of pollutant while 0.2 g of TiO_2/CuO (90:10 450 °C) removed 60.9 % of it.

ABSTRAK

Naftalena adalah salah satu sebatian hidrokarbon polisiklik aromatic (HPA) yang telah dikenal pasti sebagai karsinogen. Ia biasanya digunakan dalam industri dan domestik. Oleh itu ia boleh menyebabkan pencemaran alam sekitar dan mestilah dirawat. Salah satu kaedah yang berkesan untuk menghapuskan bahan cemar ini daripada air kumbahan adalah dengan menggunakan fotomangkin kerana ia boleh menghilangkan bahan cemar tanpa menghasilkan produk sampingan yang bertoksik. Dalam kajian ini, dua jenis fotomangkin iaitu TiO_2/CuO dan WO_3/CuO telah disediakan dengan nisbah peratusan jisim pemangkin bersama yang berbeza dan dikalsin pada pelbagai suhu. TiO_2 telah disediakan dengan kaedah sol-gel manakala WO_3 dengan mematangkan asid amorfus peroxo-tungstic. Pencirian fotomangkin yang disediakan telah dilakukan dengan XRD, FESEM dan analisis luas permukaan BET. Pola XRD mendedahkan bahawa TiO_2/CuO yang dikalsin pada suhu $450\text{ }^\circ\text{C}$ dan $650\text{ }^\circ\text{C}$ masing-masing terdiri daripada fasa anatase dan rutil manakala TiO_2/CuO dikalsin pada suhu $550\text{ }^\circ\text{C}$ terdiri daripada campuran anatase dan rutil. Pola XRD bagi WO_3/CuO pemangkin menunjukkan bahawa pemangkin terdiri daripada fasa tunggal WO_3 . Mikrograf FESEM menunjukkan zarah TiO_2/CuO adalah kurang padat berbanding dengan zarah WO_3/CuO yang kecil dan padat. Analisis BET mendapati bahawa pemangkin WO_3/CuO mempunyai luas permukaan yang lebih besar daripada pemangkin TiO_2/CuO . Pengaruh pH, jisim fotomangkin dan penggunaan sinaran lampu yang berbeza telah dikaji. Tindak balas telah dipantau oleh UV-Vis spektrofotometer. Prestasi fotomangkin terbaik adalah dalam medium neutral dan disinari dengan cahaya UV. Jisim peratus pemangkin bersama yang optimum bagi kedua-dua fotomangkin adalah 10% dan suhu pengkalsinan untuk fotomangkin WO_3/CuO dan TiO_2/CuO masing-masing adalah $650\text{ }^\circ\text{C}$ dan $550\text{ }^\circ\text{C}$. Keputusan eksperimen menunjukkan bahawa fotomangkin WO_3/CuO dan TiO_2/CuO masing-masing menyingkirkan 88.60% dan 63.55% bahan cemar dalam persekitaran neutral. TiO_2/CuO menyingkirkan 11.01% dan 33.60% bahan pencemar dalam persekitaran beralkali dan berasid. WO_3/CuO menyingkirkan 48.03% bahan pencemar dalam persekitaran berasid manakala dalam persekitaran beralkali ia menyingkirkan 46.32% bahan cemar. Muatan fotomangkin yang optimum adalah 0.2 g bagi kedua-dua fotomangkin. 0.2 g fotomangkin WO_3/CuO (90:10 $650\text{ }^\circ\text{C}$) menyingkirkan 93.23% bahan cemar manakala 0.2 g fotomangkin TiO_2/CuO (90:10 $450\text{ }^\circ\text{C}$) menghilangkan 60.93% bahan cemar.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENT	vii
	LIST OF TABLES	x
	LIST OF FIGURES	xi
	LIST OF SYMBOLS AND ABBREVIATIONS	xiv
	LIST OF APPENDICES	xv
1	INTRODUCTION	1
	1.1 Background of the Research	1
	1.1.1 Naphthalene	3
	1.1.2 Mechanism of Photocatalytic Reaction	4
	1.2 Problem Statement	6
	1.3 Significance of the Research	7
	1.4 Scope of the Research	8
	1.5 Objectives of the Research	8
2	LITERATURE REVIEW	9
	2.1 The Application of Photocatalyst in Water Treatment Process	9

2.2	Photodegradation of PAHs in Aqueous Solution	10
2.3	Photocatalysis Reaction Using WO_3/CuO and TiO_2/CuO Photocatalysts	12
2.4	Photodegradation under the Irradiation of Visible Light	15
2.5	Photodegradation under the Irradiation of Sunlight	17
3	EXPERIMENTAL	19
3.1	Chemicals	19
3.2	Instrumentations	19
3.3	Preparation of TiO_2/CuO Photocatalyst	20
3.3.1	Preparation of TiO_2 by Sol Gel Method	20
3.3.2	Preparation of TiO_2/CuO Photocatalyst by Impregnation Method	23
3.4	Preparation of WO_3/CuO Photocatalyst	21
3.4.1	Preparation of WO_3 Powder	21
3.4.2	Preparation of WO_3/CuO Photocatalyst by Impregnation Method	21
3.5	Preparation of Naphthalene Solution	22
3.6	Photocatalysis Reaction	22
3.7	The Effect of pH on Photocatalytic Activity	23
3.8	The Effect of Irradiation Sources on Photocatalytic Activity	24
3.9	Characterization of Photocatalysts	24
3.9.1	X-Ray Diffraction (XRD) Analysis	24
3.9.2	Field Emission Scanning Electron Microscopy (FESEM)/Electron Dispersive X-Ray (EDX) Analysis	25

3.9.3	Brunauer-Emmet-Teller (BET) Surface Analysis	25
4	RESULTS AND DISCUSSION	26
4.1	Field Emission Scanning Electron Microscopy (FESEM) and Electron Dispersive X-Ray (EDX) Analysis	26
4.2	X-Ray Diffraction (XRD) Analysis	32
4.3	Determination of Naphthalene in Aqueous Solution Using UV-Visible Spectrophotometer	35
4.4	Photolysis and Adsorption of Naphthalene	36
4.5	Photocatalytic Performance of TiO ₂ , TiO ₂ /CuO, WO ₃ and WO ₃ /CuO catalysts	38
4.6	Optimization of Calcination Temperature and Amount of Co-Catalyst	39
4.6.1	Influences of Calcination Temperature	39
4.6.2	Optimization of CuO Co-Catalyst	42
4.7	Photocatalyst Loading	44
4.8	The Effect of pH on Photodegradation of Naphthalene	46
4.9	Effect of Radiation Sources	49
5	CONCLUSION AND RECOMMENDATIONS	51
5.1	Conclusion	51
5.2	Recommendations	52
	REFERENCES	53
	APPENDICES	58

LIST OF TABLES

TABLE NO.	TITLE	PAGE
4.1	The atomic composition of elements present on the surface of TiO ₂ /CuO photocatalysts calcined at 550 and 650 °C	28
4.2	Surface area of TiO ₂ /CuO (90:10) calcined at 550 °C and WO ₃ /CuO (90:10) calcined at 650 °C	29
4.3	The atomic composition of elements present on the surface of WO ₃ /CuO photocatalysts prepared at 650 and 750 °C	31

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	Molecular structure of naphthalene	3
1.2	Schematic diagram of photocatalyst and the reactions that occur on its surface	4
3.1	The pictures of (a) photocatalytic reaction box (b) apparatus set up for photocatalytic reaction process	23
4.1	FESEM micrographs of TiO ₂ /CuO (90:10) photocatalyst calcined at a) 550 °C b) 650 °C with magnification of 10,000 x	26
4.2	EDX of a) TiO ₂ /CuO (90:10) calcined at (a) 550 °C and b) 650 °C	27
4.3	FESEM/EDX mapping of TiO ₂ /CuO (90:10) calcined at a) 550 °C and b) 650 °C	28
4.4	FESEM micrographs of WO ₃ /CuO (90:10) catalyst prepared at a) 650 °C and b) 750 °C with magnification of 10,000 x	29
4.5	EDX analysis of WO ₃ /CuO catalysts synthesized at a) 650 °C and b) 750 °C	30
4.6	FESEM/EDX mapping of WO ₃ /CuO (90:10) calcined at a) 650 °C and b) 750 °C	31
4.7	XRD patterns of TiO ₂ /CuO (90:10) photocatalyst prepared at (a) 650 °C (b) 550 °C and (c) 450 °C	32

4.8	The XRD patterns of prepared WO ₃ /CuO (90:10) photocatalyst calcined at (a) 750 °C, (b) 650 °C and (c) 550 °C	34
4.9	UV spectra of naphthalene at various concentrations of (a) 3 x 10 ⁻⁴ M, (b) 2 x 10 ⁻⁴ M (c), 1 x 10 ⁻⁴ M (d), 9 x 10 ⁻⁵ M and (e) 8 x 10 ⁻⁵ M	35
4.10	The percentage degradation of naphthalene by photolysis, photocatalysis and adsorption on TiO ₂ /CuO (90:10) photocatalyst calcined at 550 °C	36
4.11	The percentage degradation of naphthalene by photolysis, photocatalysis and adsorption on WO ₃ /CuO (90:10) photocatalyst calcined at 650 °C	37
4.12	Photocatalytic performance of (A) TiO ₂ calcined at 450 °C, (B) WO ₃ calcined at 450 °C, (C) TiO ₂ /CuO (90:10) calcined at 550 °C and (D) WO ₃ /CuO photocatalysts calcined at 650 °C after 240 minutes of photocatalytic reaction	38
4.13	The effect of calcination temperature on photocatalytic activity of TiO ₂ /CuO (90:10) catalyst calcined at 450, 550 and 650 °C	40
4.14	The effect of calcination temperature on photocatalytic activity of WO ₃ /CuO (90:10) catalysts calcined at 550, 650 and 750 °C	41
4.15	The effect of CuO co-catalyst amount on the photocatalytic activity TiO ₂ /CuO catalysts calcined at 550 °C	42
4.16	The effect of CuO co-catalyst amount on photocatalytic activity of WO ₃ /CuO catalyst calcined at 650 °C	43
4.17	The effect of catalyst loading on photocatalysis reaction of naphthalene by using TiO ₂ /CuO (90:10) calcined at 450 °C	45
4.18	The effect of catalyst loading on photocatalysis	

	reaction of naphthalene by using WO_3/CuO (90:10) calcined at 650 °C	45
4.19	The effect of pH on photocatalysis reaction of TiO_2/CuO (90:10) photocatalysts calcined at 550 °C	47
4.20	The effect of pH on photocatalysis reaction of WO_3/CuO (90:10) photocatalysts calcined at 650 °C	48
4.21	Photocatalytic activity of TiO_2/CuO (90:10) photocatalyst synthesized at 650 °C under irradiation of UV and visible light	49
4.22	Photocatalytic activity of WO_3/CuO (90:10) calcined at 450 °C photocatalyst under irradiation of UV and visible light	50

LIST OF SYMBOLS AND ABBREVIATIONS

AOP	Advanced oxidation process
BET	Brunauer-Emmet-Teller
CuO	Copper oxide
h^+	Proton hole
FESEM	Field emission scanning electron microscopy
PAH	Polycyclic aromatic hydrocarbon
TiO ₂ /CuO	Titanium oxide with CuO co-catalyst
UV	Ultraviolet
UV-Vis	Ultraviolet/visible
WO ₃ /CuO	Wolfram oxide with CuO co-catalyst
XRD	X-ray diffraction

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Amount of WO_3 and TiO_2 used in the preparation of 3 g WO_3/CuO and TiO_2/CuO photocatalysts	58
B	The change of UV absorbance spectra for photocatalytic degradation of naphthalene using TiO_2/CuO photocatalyst (90:10) calcined at 550 °C	59
C	The change of UV absorbance spectra for photocatalytic degradation of naphthalene using WO_3/CuO photocatalyst (90:10) calcined at 650 °C	60

CHAPTER 1

INTRODUCTION

1.1 Background of the Research

Polycyclic aromatic hydrocarbons (PAHs), refers to a large group of organic chemicals that consist of two or more fused aromatic rings and do not carry substituents and contain heteroatoms. PAHs usually exist in solid form and range in appearance from colorless to white or pale yellow green. PAHs can be found naturally in the environment and also can be formed from human activity. They are formed during the incomplete combustion of fossil fuel or other organic materials, forest fire, volcanic eruption, industrial incineration, industrial and domestic waste and smoke from vehicles (Sanches *et al.*, 2011). PAHs are used to make dyes, plastics and pesticides and some are even used in medicine (US EPA, 2003).

PAHs are persistent organic pollutant which can resist to environmental degradation through chemical, biological and photolytic processes, due to the complexity and high stability of its molecule (Sanches *et al.*, 2011). Due to their persistent in the environment, PAHs can be bioaccumulated in human and animal tissue and can have significant effects to human health and environment. PAHs are well known carcinogenic and mutagenic chemicals which can cause cancer. Some of these chemicals can increase the risk of stomach, skin, lung, gastrointestinal, bladder

and liver cancer (Wu *et al.*, 2011). Studies reveal that the exposure of PAHs during pregnancy is associated with lower IQ and childhood asthma, adverse birth outcomes including low birth weight, premature delivery, and heart defects (US EPA, 2008). The studies also show that the cord blood of exposed babies shows DNA damage that has been linked to cancer, slow development at age three, lower scores on IQ tests and increased behavioral problems at ages six and eight (US EPA, 2008).

PAHs pollutant can enter river and lake which are the source of drinking water. Drinking water is treated by conventional surface water treatment which involves coagulation, flocculation, sedimentation, filtration and disinfection. Disinfection involves the use of chlorine which can reacts with natural organic matters present in the water and produces harmful by-product that can causes different types of cancer and adverse reproductive outcomes (Sanches *et al.*, 2011).

Due to these problems, an alternative method is needed to treat the waste water effectively and efficiently. One of the potential method is advanced oxidation process (AOP), a process in which a powerful oxidizing agent (hydroxyl radical, $\bullet\text{OH}$) is generated and oxidizes organic molecules to smaller and harmless molecules like carbon dioxide (CO_2) and water (H_2O) (Chan *et al.*, 2012). This process involves the irradiation of photocatalyst like titanium oxide (TiO_2), zinc oxide (ZnO) or tungsten oxide (WO_3) with UV light to generate the radical. The energy from the light will displace the electrons from the valence band to the conduction band of the catalyst, creating an h^+ hole in the valence band (Robert and Malato, 2002). $\bullet\text{OH}$ radical is produced by the reaction of h^+ holes with hydroxyl species (OH) in water on the surface of photocatalyst and by the reaction of electrons or oxygen ions with hydrogen peroxide (H_2O_2) (Tryba *et al.*, 2004).

Photocatalyst is only active under the irradiation of UV light due to its large band gap energy. Many studies have been done to decrease the band gap and to inhibit the recombination process by doping it with transition and/or noble, non metal or other semiconductors (Tran *et al.*, 2012). In this research, TiO_2 and WO_3 photocatalysts impregnated with copper oxide (CuO) as co-catalyst was used to

degrade naphthalene, which is the simplest chemical in PAH group and it is listed in US EPA priority controlled PAHs.

1.1.1 Naphthalene

Naphthalene is polycyclic aromatic hydrocarbon characterized by its white crystal and has distinct mothball odor. The molecular structure is shown in Figure 1.1. It consists of two benzene rings fused together. Among the PAHs chemicals, it is the most water soluble chemical with solubility of 25-30 mgL⁻¹ at ambient temperature, making it the most dominant PAHs found in water.

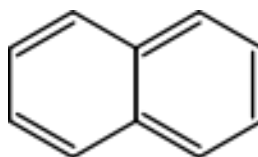


Figure 1.1 Molecular structure of naphthalene

Naphthalene is used as a household fumigant and it is the main ingredient in the production of mothball. In agricultural chemistry and textile industry, it is used as a wetting agent. It is also used in the production of phthalic anhydride, which is an intermediate in the manufacturing of resins, dyes, pharmaceuticals and other products (US EPA, 2003). In addition, naphthalene is used to make the insecticide carbaryl, leather tanning agents and surface active agents (US EPA, 2003). Crystalline naphthalene is used as deodorizer for diaper pails and in toilets.

According to US EPA (2003), naphthalene can causes hemolytic anemia, nausea, abdominal pain, diarrhea, headache, confusion, agitation leading to convulsion and coma, damage to the liver and neurological damage if it is inhaled or ingested. Haemoglobinuria and haemolysis can occur after 3 to 5 days leading to

acute renal failure. The patient's urine turns to dark brown or black due to haemoglobinuria and the presence of naphthalene metabolites. Dermal contact can cause irritation and dermatitis and exposure to eye can cause irritation and possible injury to the eye. It has been reported that long term exposure to naphthalene causes cataracts and damage to the retina. EPA has classified naphthalene as possible human carcinogen, which can causes cancer to human.

1.1.2 Mechanism of Photocatalytic Reaction

Heterogeneous photocatalysts activity consist of five steps which are diffusion of reactants to the surface, adsorption of reactants onto the surface, reaction on the surface, desorption of products off the surface, and diffusion of products from the surface (Pirkanniemi and Sillanpaa, 2002). When photocatalyst is irradiated with light which has energy equal to or more than the band gap energy, the electrons from the valence band will be excited and move to the conduction band. This will generate redox environment in the system. Figure 1.2 shows the schematic diagram of photocatalyst and redox reactions that occur on the surface of the photocatalyst.

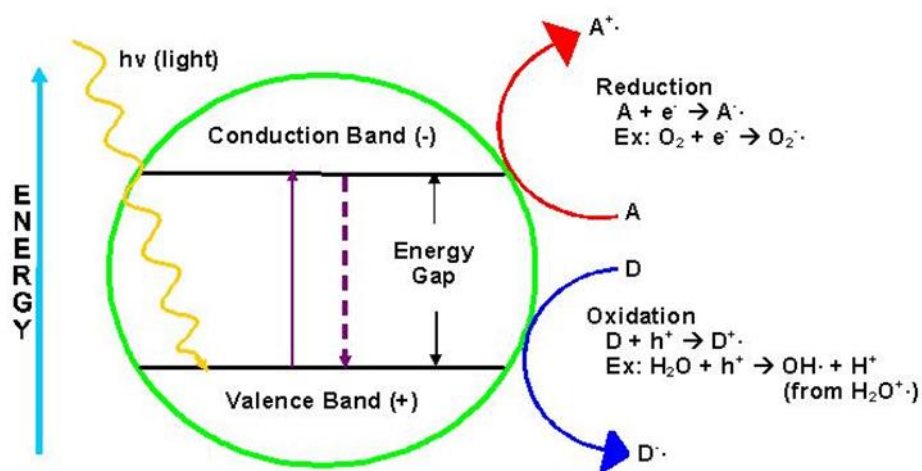
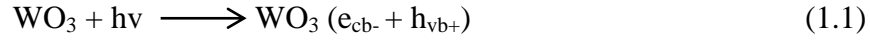
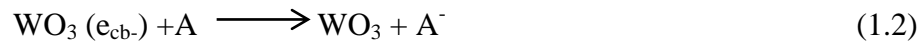


Figure 1.2 Schematic diagram of photocatalyst and the reactions that occur on its surface

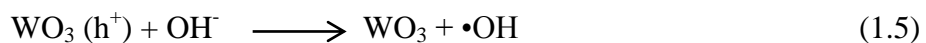
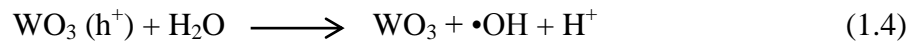
The excitation of electrons creates a h^+ holes in the valence band (h_{vb+}) and electron pairs in the conduction band (e_{cb-}) of the photocatalyst as shown in Equation 1.1 (Puma *et al.*, 2008).



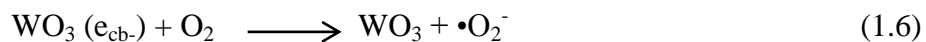
Photocatalyst particle will reduce and oxidize the surrounding molecules such as water, pollutant, hydroxide ion (OH^-) and oxygen. Generally, acceptor molecule (A) such as oxygen will react with the e_{cb-} and donor molecule (D) like water will react with the h_{vb+} (Herrmann, 1999) as shown in the Equation 1.2 and 1.3.



The reaction with water molecule is likely to happen than the reaction with the pollutant molecule due to the abundance of water molecules in the system. The oxidation of OH^- ion or water molecule by the h_{vb+} hole produces $OH\cdot$ radical, a powerful oxidant as shown in Equation 1.4 and 1.5.



The e_{cb-} will reduce the oxygen molecule (O_2) to produce superoxide radical ($\cdot O_2^-$). The reduction process is shown in Equation 1.6. This reaction is important to the photocatalyst as it prevent the electrons from recombining with the hole (Al-Rasheed, 2005).



$\cdot OH$ and $\cdot O_2^-$ radicals will attack pollutant molecules and degrading it to CO_2 and H_2O as shown in Equation 1.7 and 1.8.



1.2 Problem Statement

As a developing country, Malaysia is experiencing rapid economic development and urbanization together with population growth. This can increase the use of fossil fuel including petroleum and coal and thus increases the emission of PAHs. In addition, Malaysia is oil producing country and its strategic location surrounded by the Straits of Melaka makes it one the busiest shipping route in the world to transport petroleum from the Middle East to the Far East (Sakari *et al.*, 2010). The presence of PAHs from petroleum in the environment can be caused by the introduction of crude oil and oil derivatives via atmospheric transportation, urban runoff, oil spills, tanker incident and many other possible ways (Sakari *et al.*, 2010). In addition, the heavy usage of petroleum products in domestic and industrial such as factories, power plants, transportation and residential areas can release the significant amount of PAHs to the environment (Sakari *et al.*, 2010). The emitted PAHs can enter the surface water such as lake, river and sea by precipitation and runoff on the ground surface (Wu *et al.*, 2011). PAHs can enter the food chain by depositing in the fatty acid of aquatic lives, hence harm the aquatic animals and human (Retnam *et al.*, 2013). Research done by Sakari *et al.* (2010) showed that the concentration of PAHs coastal region such as Melaka Coast, Tebrau Strait offshore Klang were 700 ng/g, 900 ng/g and 500 ng/g respectively.

Generally, PAHs level in river water is at the permitted level except for some region in Terengganu, Kedah, Penang, Kelantan, Johor and Negeri Sembilan, where the PAHs level is very high (Tran *et al.*, 2012). The high concentration of PAHs can harm the human health. The pollutant can enter the river water from oil spills, car workshop, sewage discharge, industrial activities and city surface run-off (Sakari *et al.*, 2010). Waste water released from power plant also contains high level of PAHs since all power plants in Malaysia are burning fossil fuels.

At the moment, the removing of naphthalene and other PAHs are done by biofiltrations, bioreactors, membrane bioreactors, ozonolysis and pulse radiolysis (Lair *et al.*, 2008). However, these water treatment techniques have many drawbacks.

For example, ozonolysis and pulse radiolysis are expensive and bioreactors treatment is too slow. The conventional water treatment also can causes new problem since the degradation of naphthalene can introduce new carcinogenic by-product into the water. Due to these problems, photocatalyst is used because the treatment is effective, easier and cheaper to operate. The process will convert the pollutant to harmless substances such as CO₂ and H₂O.

Two types of photocatalysts TiO₂/CuO and WO₃/CuO were prepared. They were used to degrade naphthalene as a model sample to CO₂ and H₂O. These catalysts perform better than the single by delaying the recombination of positive holes and electrons. Therefore, the photocatalytic activity is increase. To the date, no research was conducted to degrade naphthalene using these catalysts.

1.3 Significance of the Research

This research is done to find the best method to degrade the naphthalene in waste water effectively and efficiently. WO₃/CuO and TiO₂/CuO photocatalysts which expected to have high photocatalytic activity are used. The photodegradation is conducted under the radiation of UV light, visible light and sun light. The use of solar light for water treatment is important to reduce the operation cost on the future water treatment plant since it is free and clean energy. The use of photocatalyst will also reduce the possibility of the occurrence of highly toxic by-products because it can degrade the naphthalene completely into CO₂ and H₂O (Lair *et al.*, 2008).

1.4 Scope of the Research

The research work covers the preparation of WO_3/CuO and TiO_2/CuO photocatalysts with different ratio of CuO co-catalyst and different calcination temperature. The prepared photocatalysts were tested by photodegrading the naphthalene. This research was also conducted for effect of pH of naphthalene solution and the use of different amount of photocatalyst loading on photocatalytic activity. The photoreaction was conducted under the UV, visible and sun light radiation. The characterization of the photocatalyst was conducted by using X-ray diffractometer (XRD), Brunauer–Emmett–Teller surface analysis (BET) and field emission scanning electron microscope (FESEM).

1.5 Objectives of the Research

The objectives of this research are:

1. To prepare the WO_3/CuO and TiO_2/CuO photocatalysts.
2. To find the optimum calcination temperature and the amount of CuO for both WO_3/CuO and TiO_2/CuO photocatalysts.
3. To characterize the photocatalysts by using XRD and FESEM and BET.
4. To find the optimum conditions for the photocatalytic degradation of naphthalene using the prepared catalysts.

REFERENCES

- Adlan, Z.M.H. (2013). *Ternary Semiconductor Photocatalysts for the Degradation of Benzene-Toluene-Xylene in Aqueous Phase*. Master of Science. University Technology Malaysia.
- Al-Rasheed, R.A. (2005). Water Treatment by Heterogeneous Photocatalysis an Overview. *4th SWCC Acquired Experience Symposium*. 19 March 2005. Jeddah, 1-14.
- Altomare, M., Chiarello, G.L., Costa, A., Guarino, M. and Selli, E. (2012). Photocatalytic Abatement of Ammonia in Nitrogen-Containing Effluents. *Chemical Engineering Journal*, 191, 394-401.
- An, T., Chen, J., Li, G., Ding, X., Sheng, G., Fu, J., Mai, B. and O'Shea, K.E. (2008). Characterization and the Photocatalytic Activity of TiO₂ Immobilized Hydrophobic Montmorillonite Photocatalysts degradation of Decabromodiphenyl Ether (BDE 209). *Catalysis Today*, 139, 69-76.
- Arai, T., Yanagida, M., Konishi, Y., Iwasaki, Y., Sugihara, H., and Sayama, K. (2008). Promotion Effect of CuO Co-Catalyst on WO₃-Catalyzed Photodegradation of Organic Substances. *Catalysis Communications*, 9, 1254-1259.
- Bouzaida, I., Ferronato, C., Chovelon, J.M., Rammah, M.E. and Herrmann, J.M. (2004). Heterogeneous Photocatalytic Degradation of the Anthraquinonic Dye, Acid Blue 25 (AB25): A Kinetic Approach. *Journal of Photochemistry and Photobiology A: Chemistry*, 168, 23-30.
- Byrne, H.E. and Mazyck, D.W. (2009). Removal of Trace Level Aqueous Mercury by Adsorption and Photocatalysis on Silica-Titania Composites. *Journal of Hazardous Materials*, 170, 915-919.

- Chan, P.Y., El-Din, M.G. and Bolton, J.R. (2012). A Solar-Driven UV/Chlorine Advanced Oxidation Process. *Water Research*, 46, 5672-5682.
- Chu, W., Choy, W.K. and So, T.Y. (2007). The Effect of Solution pH and Peroxide in The TiO₂-Induced Photocatalysis of Chlorinated Aniline. *Journal of Hazardous Materials*, 141, 86–91.
- Fang, Y., Wang, R., Jiang, G., Jin, H., Wang, Y., Sun, X., Wang, S. and Wang, T. (2012). CuO/TiO₂ Nanocrystals Grown On Graphene as Visible-Light Responsive Photocatalytic Hybrid Materials. *Bulletin of Material Science*, 4, 495-499.
- Harraz, F.A., Abdel-Salam, O.E., Mostafa, A.A., Mohamed, R.M. and Hanafy, M. (2012). Rapid Synthesis of Titania–Silica Nanoparticles Photocatalyst by a Modified Sol–Gel Method for Cyanide Degradation and Heavy Metals Removal. *Journal of Alloys and Compounds*, 551, 1-7.
- Herrmann, J.M. (1999). Heterogeneous Photocatalysis: Fundamentals and Applications to the Removal of Various Types of Aqueous Pollutants, *Catalysis Today*. 53,115-129.
- Kohtani, S., Tomohiro, M., Tokumura, M. and Nagaki, R. (2005). Photooxidation Reactions of Polycyclic Aromatic Hydrocarbons over Pure and Ag-Loaded BiVO₄ Photocatalysts. *Applied Catalysis B: Environmental*, 58, 265-272.
- Lair, A., Ferronato, C., Chovelon, J.M. and Herrmann, J.M. (2008). Naphthalene Degradation in Water by Heterogeneous Photocatalysis: An Investigation of the Influence of Inorganic Anions. *Journal of Photochemistry and Photobiology A: Chemistry*, 193, 193-203.
- Lalitha, K., Sadanandam, G., Kumari, V.D., Subrahmanyam, M., Sreedhar, B. and Hebalkar, N.Y. (2010). Highly Stabilized and Finely Dispersed Cu₂O/TiO₂: A Promising Visible Sensitive Photocatalyst for Continuous Production of Hydrogen from Glycerol: Water Mixtures. *Journal of Physical Chemistry*, 114, 22181-22189.
- Lee, S.S., Bai, H., Liu, Z. and Sun, D.D. (2013). Novel-Structured Electrospun TiO₂/CuO Composite Nanofibers for High Efficient Photocatalytic Cogeneration of Clean Water and Energy from Dye Wastewater. *Water Research*, 47, 4059-4073.

- Lin, H.F. and Valsaraj, K.T. (2003). A Titania Thin Film Annular Photocatalytic Reactor for the Degradation of Polycyclic Aromatic Hydrocarbons in Dilute Water Streams. *Journal of Hazardous Materials*, B99, 203-219.
- Lo, S.C., Lin, C.F., Wu, C.H., and Hsieh, P.H. (2004). Capability of Coupled CdSe/TiO₂ for Photocatalytic Degradation of 4-chlorophenol. *Journal of Hazardous Materials B*, 114, 183-190.
- Lydakakis, S.N., Riga, D., Katsivela, E., Mantzavinos, D. and Xekoukoulotakis, N.P. (2010). Disinfection of Spring Water and Secondary Treated Municipal Wastewater by TiO₂ Photocatalysis. *Desalination*, 250, 351-355.
- Martinez, M.J.G., Canoira, L., Blaquez, G., Riva, I.D., Alcantara, R. and Llamas, J.F. (2005). Continuous Photodegradation of Naphthalene in Water Catalyzed by TiO₂ Supported On Glass Raschig Rings. *Chemical Engineering Journal*, 110, 123-128.
- Martinez, M.J.G., Riva, I.D., Canoira, L., Llamas, J.F., Alcantara, R. and Gallego, J.L.R. (2006). Photodegradation of Polycyclic Aromatic Hydrocarbons in Fossil Fuels Catalyzed by Supported TiO₂. *Applied Catalysis B: Environmental*, 67, 279-289.
- Ohno, T., Tokieda, K., Higashida, S. and Matsumura, M. (2003). Synergism between Rutile and Anatase TiO₂ Particles in Photocatalytic Oxidation of Naphthalene. *Applied Catalysis A: General*, 244, 383-391.
- Pirkanniemi, K. and Sillanpaa, M. (2002). Heterogeneous Water Phase Catalysis as an Environmental Application: A Review. *Chemosphere*, 48, 1047-1060.
- Puma, G.L., Bono, A., Krishnaiah D. and Collin, J.G. (2008). Preparation of Titanium Dioxide Photocatalyst Loaded Onto Activated Carbon Support Using Chemical Vapor Deposition: A Review Paper. *Journal of Hazardous Materials*, 157, 209-219.
- Retnam, A., Zakaria, M.P., Juahir, H., Aris, A.H., Zali, M.A. and Kasim, M.D. (2013). Chemometric Techniques in Distribution, Characterization and Source Apportionment of Polycyclic Aromatic Hydrocarbons (PAHs) in Aquaculture Sediments in Malaysia. *Marine Pollution Bulletin*, 69, 55-66.
- Robert, D. and Malato, S. (2002). Solar Photocatalysis: A Clean Process for Water Detoxification. *The Science of the Total Environment*, 291, 85-97.
- Sakari, M., Zakaria, M.Z., Mohamed, C.A.B., Lajis, N.H., Chandru, K., Bahry, P.S., Shafiee, M.M. and Anita, S. (2010). The History of Petroleum Pollution in

- Malaysia: Urgent Need for Integrated Prevention Approach. *Environment Asia*, 3, 131-142.
- Sanches, S., Leitao, C., Penetra, A., Cardoso, V.V., Ferreira E., Benoliel, M.J., M.T, Crespo, M.T.B and Pereira, V.J. (2011). Direct Photolysis of Polycyclic Aromatic Hydrocarbons in Drinking Water Sources. *Journal of Hazardous Materials*, 192, 1458– 1465.
- Saravanan, R., Karthikeyan, S., Gupta, V.K., Sekaran, G., Narayanan, V. and Stephen, A. (2013). Enhanced Photocatalytic Activity of ZnO/CuO Nanocomposite for the Degradation of Textile Dye on Visible Light Illumination. *Materials Science and Engineering C*, 33, 91-98.
- Sayama, K., Hayashi, H., Arai, T., Yanagida, M., Gunji, T. and Sugihara, H. (2010). Highly Active WO_3 Semiconductor Photocatalyst Prepared From Amorphous Peroxo-Tungstic Acid for the Degradation of Various Organic Compounds. *Applied Catalysis B: Environmental*, 94, 150-157.
- Sharifuddin, M.A. (2011). *Photocatalytic Degradation of N-Methyldiethanolamine and Benzene- Toluene-Xylene in Aqueous System Assisted with Ozonation and Sonication Processes*. Master of Science. University Technology Malaysia.
- Shavisi, Y, Sharifnia, S., Zندهzaban, M., Mirghavami, M.L. and Kakehazar, S. (2013). Application of Solar Light for Degradation of Ammonia in Petrochemical Waste Water by a Floating TiO_2/LECA Photocatalyst. *Journal of Industrial and Engineering Chemistry*, 19, 67149-67246.
- Soltani, T. and Entezari, M.H. (2013). Photolysis and Photocatalysis of Methylene Blue by Ferrite Bismuth Nanoparticles under Sunlight Irradiation. *Journal of Molecular Catalysis A: Chemical*, 377, 197-203.
- Sridharan, K., Jang, E. and Park, T.J. (2013). Novel Visible Light Active Graphitic $\text{C}_3\text{N}_4\text{-TiO}_2$ Composite Photocatalyst: Synergistic Synthesis, Growth and Photocatalytic treatment of Hazardous Pollutants. *Applied Catalysis B: Environmental*, 142-143, 718-728.
- Tran, D., Kamaria, A.A. and Zakaria, M.P. (2012). Pollution Status of PAHs in the Malaysian Aquatic Environment for the Past Two Decades. *LIPi - JSPS Asian Core Program Joint International Seminar on Coastal Ecosystems in Southeast Asia (COMSEA)*. 12-14, November 2012. Jakarta, Indonesia. 115-136.

- Tran, T.T., Seng, P., Huang, C., Li, J., Chen, L., Yuan, L., Grimes, C.A. and Cai, Q. (2012). Synthesis and Photocatalytic Application of Ternary Cu–Zn–S Nanoparticle-Sensitized TiO₂ Nanotube Arrays. *Chemical Engineering Journal*, 210, 425-431.
- Tryba, B., Tsumura, T., Janus, M., Morawski, A.W. and Inagaki, M. (2004). Carbon-Coated Anatase: Adsorption and Decomposition of Phenol in Water. *Applied Catalysis B: Environmental*, 50, 177-183.
- United States Environmental Protection Agency (US EPA) (2003). *Health Effects Support Document for Naphthalene*. Washington DC: Office of Water Health and Ecological Criteria Division.
- United States Environmental Protection Agency (US EPA) (2008). *Polycyclic Aromatic Hydrocarbons (PAHs)*. Washington DC: Office of Solid Waste Environmental Protection Agency.
- Vela, N., Menchon, M.M., Navarro, G., Lucas, G.P., and Navarro, S. (2012). Removal of Polycyclic Aromatic Hydrocarbons (PAHs) From Groundwater by Heterogeneous Photocatalysis under Natural Sunlight. *Journal of Photochemistry and Photobiology A: Chemistry*, 232, 32-40.
- Wang, S. and Zhou, S. (2011). Photodegradation of Methyl Orange by Photocatalyst of CNTs/P-TiO₂ under UV and Visible-Light Irradiation. *Journal of Hazardous Materials*, 185, 77-85.
- Wu, B., Zhang, Y., Zhang, X.X. and Cheng, S.P. (2011). Health Risk Assessment of Polycyclic Aromatic Hydrocarbons in the Source Water and Drinking Water of China: Quantitative Analysis Based On Published Monitoring Data. *Science of the Total Environment*, 410-411, 112–118.
- Yousef, A., Barakat, N.A.M., Amna, T., Unnithan, A.R., Deyab, S.S.A and Kim, H.Y (2012). Influence of CdO-Doping On the Photoluminescence Properties of ZnO Nanofibers: Effective Visible Light Photocatalyst for Wastewater Treatment. *Journal of Luminescence*, 132, 1668-1677.
- Zhao, K., Lu, Y., Lu, N., Zhao, Y., Yuan, X., Zhang, H., Teng, L. and Li, F. (2013). Design of H₃PW₁₂O₄₀/TiO₂ Nano-Photocatalyst for Efficient Photocatalysis under Simulated Sunlight Irradiation. *Applied Surface Science*, 285P, 616– 624.