# Desulfurization of Model Oil using combined Cu/$TiO_2$ Photocatalysis and $BMImCu_2Cl_3$ Ionic Liquid Extraction

by

Tengku Zuhaili binti Tengku Yahya Shah

Dissertation submitted in partial fulfilment of
the requirements for the
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Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

8/12/10

(Assoc Prof Dr Chong Fai Kait)

Assoc. Prof. Dr. Chong Fai Kait
[illegible] Department
[illegible]
[illegible]
[illegible]

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2010

# CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

TENGKU ZUHAILI BINTI TENGKU YAHYA

# ABSTRACT

This final year project is to develop a method for desulfurization from model oil. This sulfur contents is considered a threat to the people and environment. This is because, this sulfur species will be converted to sulfur dioxide ($SO_2$) through the fuel combustion. As we have known, a lot of problems associated with $SO_2$. Conventional process to remove sulfur from crude oil is hydrodesulfurization (HDS). Although this is an efficient method to remove sulfur, but it's required a lot of cost as well as energy. It has come to a conclusion that photocatalysis and ionic liquid extraction can be an alternative solutions that is environmental friendly, non-hydrogen intensive, and can be employed at low temperature. Thus, the idea is to combine both methods for the desulfurization to achieve high efficiency result.In this project, Cu doped $TiO_2$ is used as the photocatalyst. This is because, the limitations of a $TiO_2$ as a photocatalyst for a particular use can be enhanced by modifying the surface of the semiconductor. Plus, BMIMCu2Cl3 is used as the ionic liquid. This project includes the preparation of the photocatalyst, preparation of ionic liquids, preparation of model oil, characterization of the photocatalyst, and the reaction of desulfurization. The experimental results for desulfurization of model oil using $CuTiO_2$ photocatalyst with different percentage of copper loading and calcinations temperature, and $BMImCu_2Cl_3$ ionic liquid show some definite trends. The UV-Vis test also has showed that the photocatalyst active region from UV to visible light. 10 wt% of copper doping shows better performance than 5 wt% of copper doping, and low calcination temperature which is $200^{O}C$ depicted better activity than $300^{O}C$. The sulfur removed for combination of 10CuT200 photocatalyst and $BMImCu_2Cl_3$ ionic liquid is much higher than using photocatalyst alone.

# ACKNOWLEDGEMENT

First of all, I would like to say Alhamdulillah, for giving me the strength and health to complete this project work until it done. Not forgotten to my family for providing everything, such as money, to buy anything that are related to this project work and their advise, which is the most needed for this project. Internet, books, computers and all that as my source to complete this project. They also supported me and encouraged me to complete this task so that I will not procrastinate in doing it.

Then I would like to thank my supervisor, Assoc Prof Dr Chong Fai Kait for guiding me throughout this project. I had some difficulties in doing this task, but she taught me patiently until I knew what to do. She tried and tried to teach me until I understand what I supposed to do with the project work.

I'm also sincerely thank to my project guide Siti Hawatulaila, Research Officer of Ionic Liquid Programme for guidance and encouragement in carrying out this work. Last but not least, my friends who were doing this project with me and sharing our ideas. They were helpful that when we combined and discussed together, we had this task done.

# TABLE OF CONTENTS

## CHAPTER 1: INTRODUCTION

## CHAPTER 2: LITERATURE REVIEW

## CHAPTER 3: METHODOLOGY

## CHAPTER 4: RESULT AND DISCUSSION

## CHAPTER 5: CONCLUSION AND RECOMMENDATION

## LIST OF TABLES

## LIST OF FIGURES

# CHAPTER 1: INTRODUCTION

## 1.1 Background Study

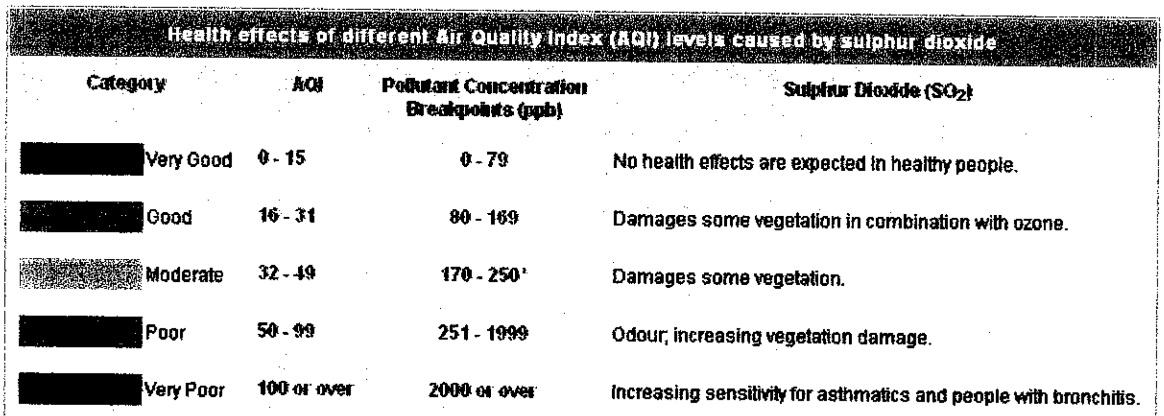
Sulfur contents are considered a threat to the people and environment. This is because; the sulfur species are converted to sulfur dioxide ($SO_2$) through fuel combustion. As we known, a lot of problems are associated with $SO_2$.

Sulfur dioxide ($SO_2$) is one of a group of highly reactive gasses known as "oxides of sulfur." The largest sources of $SO_2$ emissions are from fossil fuel combustion at power plants (73%) and other industrial facilities (20%). Smaller sources of $SO_2$ emissions include industrial processes such as extracting metal from ore, and the burning of high sulfur containing fuels by locomotives, large ships, and non-road equipment. $SO_2$ is linked with a number of adverse effects on the respiratory system. *[www.epa.gov]*

In terms of people's health, the high concentration of sulfur dioxide will result in problems to children and adults who are active in outdoor activities. Short term exposure will cause respiratory problem, chest tightness, and shortness of breath. On the other hand, longer-term exposure to sulfur dioxide will harm the lungs, cause respiratory illness and cardiovascular illness.

The effects of sulfur dioxide associated to the environment, is that it may lead to formation of acid rain. This happens when $SO_2$ can be further oxidized to sulfur trioxide, which could lead to formation of sulfuric acid mist. Acid rains could acidify lakes, streams, and soils, accelerate building corrosion, and reduce visibility. Its also can cause damage to trees and crops. *[www.naturalgas.org]*

The following table shows the health effects of different Air Quality Index levels caused by $SO_2$.



| Health effects of different Air Quality Index (AQI) levels caused by sulphur dioxide | | | |
|---|---|---|---|
| Category | AQI | Pollutant Concentration Breakpoints (ppb) | Sulphur Dioxide ($SO_2$) |
| ■ Very Good | 0 - 15 | 0 - 79 | No health effects are expected in healthy people. |
| ■ Good | 16 - 31 | 80 - 169 | Damages some vegetation in combination with ozone. |
| ▨ Moderate | 32 - 49 | 170 - 250* | Damages some vegetation. |
| ■ Poor | 50 - 99 | 251 - 1999 | Odour; increasing vegetation damage. |
| ■ Very Poor | 100 or over | 2000 or over | Increasing sensitivity for asthmatics and people with bronchitis. |

*[http://www.airqualityontario.com]*

**Table 1.1:** Health effect of different Air Quality Index (AQI) levels caused by $SO_2$

Conventional process to remove sulfur from crude oil is hydrodesulfurization (HDS). HDS is a catalytic chemical process which is operated around 300 to 400 °C and 30 to 130 atm. In HDS process, organic sulfur compounds in the liquid fuels are broken down to $H_2S$ using NiMo-CoMo/$Al_2O_3$.*[Xue M, 2006]* Although this is an efficient method to remove sulfur, it requires a lot of cost as well as energy. Furthermore, it does not work well on the polyaromatic sulfur heterocyclics (PASHs) such as dibenzothiophene (DBT) and its derivatives, especially 4,6-dimethyldibenzothiophene (4,6-DMDBT).*[Mingfang L, 2003]* Thus, deep desulfurization is needed to remove those refractory sulfur compounds in crude oil.

It also doesn't seem right when we are trying to conserve the earth in a way that we consume large amount of energy. We need alternative technology that is environmental friendly, non-hydrogen intensive, and can be applied at low temperature.

Under such circumstances, it has come to a conclusion that photocatalysis can be one of the solutions. In this project, Cu doped $TiO_2$ is used as the photocatalyst. Also, there is another method that is useful for desulphurization of model oil which is extraction from ionic liquid. The idea is to combine these two methods to achieve better efficiency.

## 1.2 Problem Statement

This project is carried out in corresponding to several factors. It is because of the sulfur contents in the crude oil. There are many types of sulfur species present such as thiophene, mercaptans, methyl sulfides, benzothiophene, dibenzothiophene, and many more. These sulfur species will be converted to $SO_2$ through fuel combustion. The emissions of $SO_2$ in the air has resulted serious environmental problems. High sulfur contents are also associated with the poisoning of catalysts in catalytic converters and fuel cells. *[Robertson J, 2006]*

This issue has become a major concern to the public. In order to minimize the negative health and environmental effects, governments are regulating a standard limit of sulfur content in fuels. Currently, a new standard has been set up by the Environmental Protection Agency of the United States and the European Commission to reduce sulfur content to 10-15 ppm by the year 2006. It is expected similar regulations to be implemented in other countries also. *[Colon.G, 2006]* In Malaysia, there are also similar regulations that are states by Environmental Quality Act which is to reduce the sulfur contents in diesel from 0.3% to 0.05%.

With respect to the government regulations, the petroleum industries have to further reduce the sulfur contents in the crude oil end-products. It is expected from time to time, the maximum allowable sulfur contents will be further reduced. Thus, if we depend on the HDS to be the method for desulfurization, the energy consumed will be increased from time to time. From now, we need to identify alternative methods for the betterment of our environment.

Photocatalysis is a simple, safe, and cost effective way for desulfurization. It has been discovered that $TiO_2$ has the potential to be an efficient photocatalyst. This project involves in developing a potential carried out to develop the potential of $Cu/TiO_2$ photocatalyst to remove sulfur from model oil. An ionic liquid system of 1-butyl-3-methylimidazolium copper chloride ($BMImCu_2Cl_3$) has been investigated and shows remarkable ability for sulfur removal too. Considering these two alternatives, this project intends to develop method for desulfurization of model oil using $Cu/TiO_2$ photocatalysis and $BMImCu_2Cl_3$ extraction.

### 1.3 Objective

This project has been carried out with the objective to develop a potential $Cu/TiO_2$ photocatalyst with $BMImCu_2Cl_3$ ionic liquid extraction to remove sulfur from model oil and to study the efficiency for the combined photocatalysis-extractive approach using $BMImCu_2Cl_3$ as the ionic liquid extractant.

### 1.4 Scope of Study

This project will study on the potential of combining photocatalysis and ionic liquid extraction. For the photocatalyst, the project will be studying the potential of transition metal doping on $TiO_2$ photocatalyst which is copper in the effort for remove sulfur from crude oil. $TiO_2$ is only active in the ultraviolet region. In order to utilize the abundant solar energy which consists of higher visible light component, modification to $TiO_2$ need to be carried out to shift the active region from ultraviolet to visible region. For the extraction method, the ionic liquid that will be used is $BMIMCu_2Cl_3$.

Sulfur compound (dibenzothiophene) also is added into dodecane to produce model oil. There are also characterization processes being carried out to determine the chemical and physical properties of the photocatalyst. Those are Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), UV-Vis Diffuse Reflectance Spectra (UV-vis DRS), Field Emission Scanning Electron Microscopy (FE-SEM), and Temperature Programmed Reduction (TPR).Desulfurization is carried out using model oil. The experiment will be carried out in the presence of $Cu/TiO_2$ photocatalyst and of ionic liquid. Therefore, oxidation and extraction processes are happening simultaneously.

# CHAPTER 2: LITERATURE REVIEW

## 2.1 What is photocatalyst?

Photocatalyst is a substance that can produce surface oxidation or reduction in the presence of light. There are various sources of light that is necessary for the process such as the sun, incandescent lamps, fluorescent lamps, light traps, disinfectant lights and so on. Those sources emit lights with different wavelengths necessary for their specific purposes.

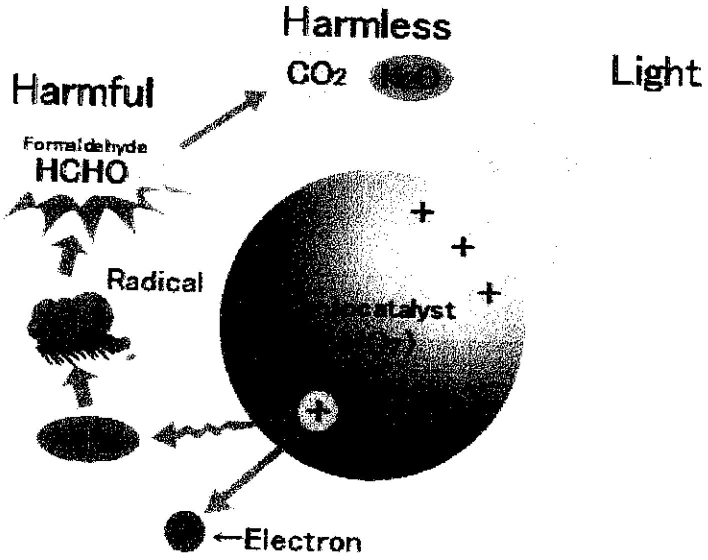


**Figure 2.1**: Photooxidation process

Figure 2.1 is an example of photooxidation by $TiO_2$ photocatayst. Oxidation is a process where an atom or molecule or compound loses an electron. When the process occurs in the presence of light, it will be called photooxidation. It has been discovered by Fujishima and Honda in the early seventies *[Abdel Wahab,1998]* that $TiO_2$ has the potential to be an efficient photocatalyst.

## 2.2 $TiO_2$ photocatalyst

$TiO_2$ is a harmless substance widely employed in various products such as cosmetics, toothpaste, extenders for medicine, and coating. The strong oxidizing power of the photogenerated holes, the chemical inertness, and resistance to both photocorrosion and decomposition reactions, low cost, and wide availability and non toxicity has made $TiO_2$ as a superior photocatalyst. *[Abdel Wahab,1998]*

$TiO_2$ is a semiconductor which turns to a high-energy state by receiving light energy, and releases electrons from its illuminated surface. If the energy received at this stage is high enough, electrons that were initially located in the so-called 'valence band' will move up to the conduction band. Thus, the energy that makes electrons jump up is provided by light, and this light energy is believed to be the energy of the light's wavelengths. Therefore, calculating from the height that the electrons have to jump up, this light should have the same wavelengths as the ultraviolet light.

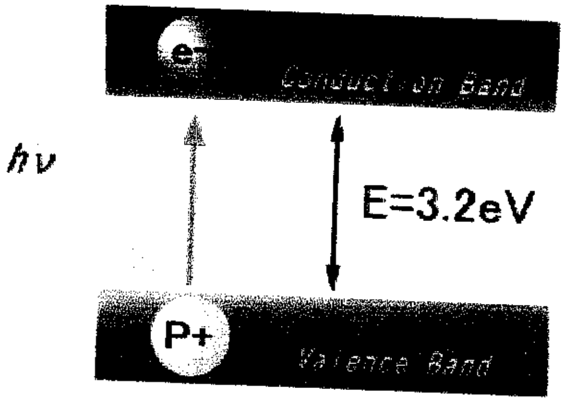


**Figure 2.2**: Energy for $TiO_2$ semiconductor

**$E = h\nu$** **E** : Energy **h** : Plank's constant $\nu$: frequency

**$\nu = c/\lambda$** **c** : light speed **$\lambda$** : wavelengths

Here the band gap energy, E for titanium oxide is 3.2eV. After substitute the values, the necessary wavelengths is approximately 380nm, which is the light needed to activate this photocatalyst is ultraviolet light. *[Linsebigler, 1995]* Meaning that, $TiO_2$ is a quite stable photocatalyst, but since the band gap is large, it is only active in the ultraviolet region which is <10% of the overall solar intensity as shown in Figure 2.3.

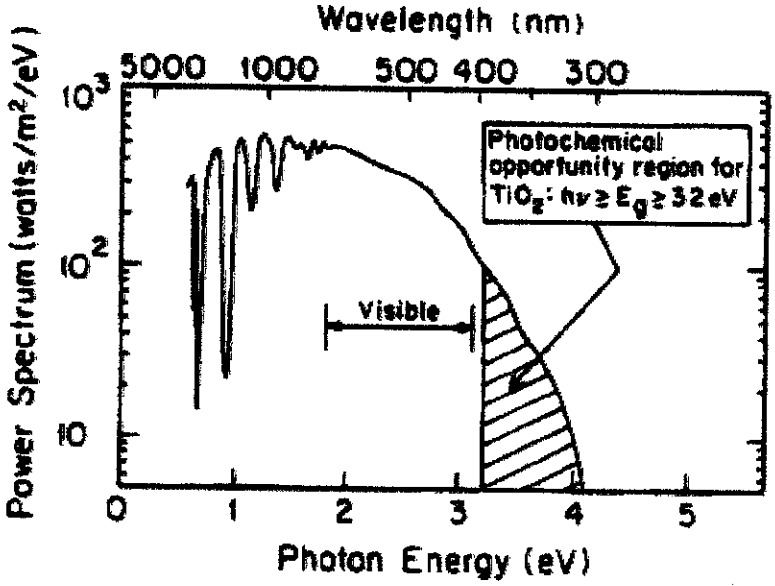


**Figure 2.3**: Solar spectrum at sea level with the sun

## 2.3 Transition metal doping on $TiO_2$ photocatalyst

The limitations of a $TiO_2$ as a photocatalyst for a particular use can be enhanced by modifying the surface of the semiconductor. There are three benefits of the modifications which are;

- Inhibiting recombination by increasing the charge separations and therefore the efficiency of the photocatalytic process.
- Increasing the wavelengths response range (excitation of wide band gap semiconductors by visible light)
- Changing the selectivity or yield of a particular product.

In photocatalysis, the addition of noble metals to a semiconductor ($TiO_2$ ) can change the photocatalytic process by changing the semiconductor surface properties. The enhancement in reactivity was first observed for the photoconversion of $H_2O$ to $H_2$ and $O_2$ using Pt/ $TiO_2$ system. After excitation, the electron migrates to the metal where it becomes trapped and electron-hole recombination is suppressed. The migration of electrons to the metal particles was confirmed by studies showing the reduction in the photoconductance of the semiconductor for the Pt deposited $TiO_2$ compared to $TiO_2$ alone. The hole is then free to diffuse to the semiconductor surface where oxidation of organic species can occur. *[Linsebigler, 1995]* Starting from these, researchers has been studied the same principle to photooxidation as well. They are also trying to use the other metal such as Al, Mn, Fe, and others. In this project, we'll studied Cu doping on $TiO_2$.

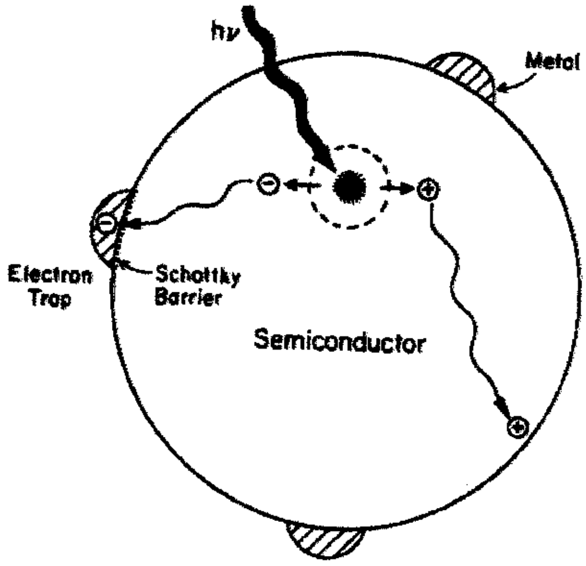
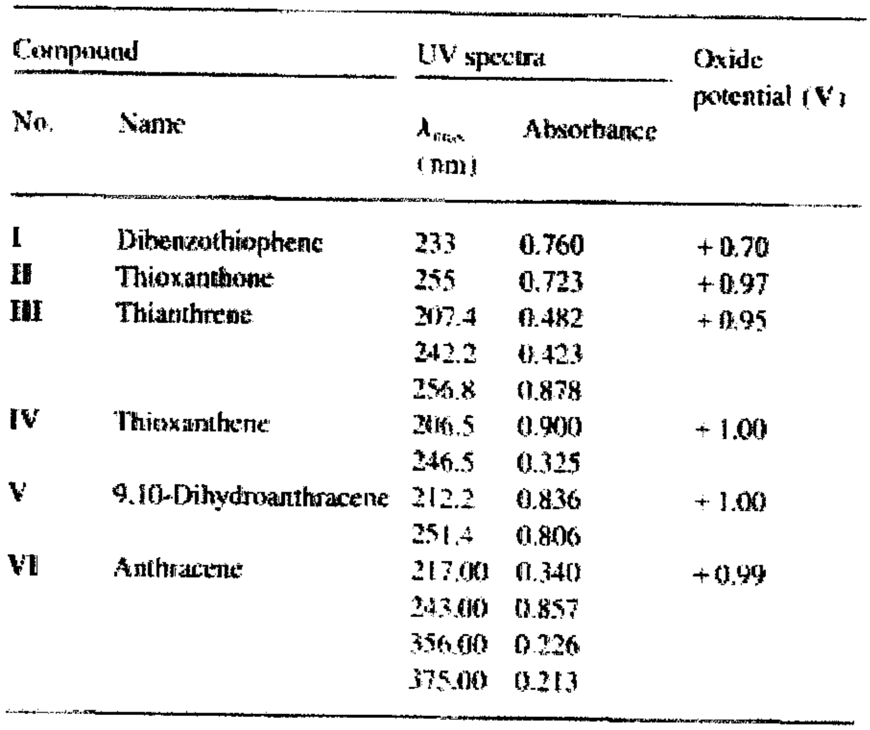


**Figure 2.4**: Metal-modified semiconductor photocatalyst

The use of copper doped $TiO_2$ for photo-oxidation process is less explored. However, there have been reported that the photocatalytic activity values clearly indicate that surface Cu may act as the photoactive species, leading to improved photoactivities with respect to undoped $TiO_2$. *[Colon G, 2006]* However, there are also report proposing that Cu has strong π-complexation interaction with thiophene. So, in this project we'll study more on the potential of Cu/$TiO_2$ photocatalyst for desulfurization.

## 2.4 $TiO_2$ photocatalytic oxidation of sulfur compounds

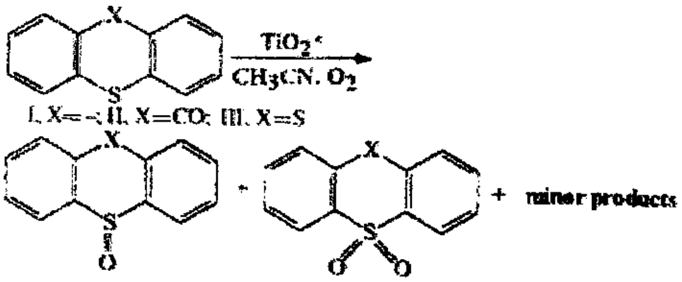
In previous work, it embraces band gap irradiation of titanium oxide suspension. The results shows the oxidation potential of various types of sulfur compounds as shown in Table 1.2;



| Compound | | UV spectra | | Oxide potential (V) |
|---|---|---|---|---|
| No. | Name | $\lambda_{max}$ (nm) | Absorbance | |
| I | Dibenzothiophene | 233 | 0.760 | + 0.70 |
| II | Thioxanthone | 255 | 0.723 | + 0.97 |
| III | Thianthrene | 207.4 | 0.482 | + 0.95 |
| | | 242.2 | 0.423 | |
| | | 256.8 | 0.878 | |
| IV | Thioxanthene | 206.5 | 0.900 | + 1.00 |
| | | 246.5 | 0.325 | |
| V | 9,10-Dihydroanthracene | 212.2 | 0.836 | + 1.00 |
| | | 251.4 | 0.806 | |
| VI | Anthracene | 217.00 | 0.340 | + 0.99 |
| | | 243.00 | 0.857 | |
| | | 356.00 | 0.226 | |
| | | 375.00 | 0.213 | |

**Table 2.1**: UV spectra and oxidation potential *[Abdel Wahab, 1998]*

The photocatalytic oxidation of sulfur compounds gave mainy the correspondingsulfoxide and sulfon described in the route below; *[Abdel Wahab, 1998]*



## 2.5 Desulfurization of model oil by extraction of ionic liquid

Excellent sorbents often contain Cu(I) or Ag(I), because of their stronger π-complexation interaction with thiophene, which is sulfur component in oil. However, the problem involved with preparation of Cu(I) sorbents is the sensitivity of Cu(I) to air and moisture. There is another way to prepare an adsorbent with a stable Cu(I) which is using a mixture of CuCl and dialkylimidazolium chlorides which is liquid at room temperature. This is called ionic liquid.

Excelled desulfurization results have been observed for $AlCl_3$- based ionic liquid. However, because of the sensitivity of $AlCl_3$- based ionic liquid to moisture and air and side reaction such as polymerization of olefin in gasoline induced by the strong Lewis acidity, the use of $AlCl_3$ based ionic liquid has been disregard as one of the promising approach. *[Chongpin Huang, 2004]*

In this paper, we investigate the potential of CuCl-based ionic liquid in extractive desulfurization of model oil. Based on study of the structure of CuCl-based ionic liquids, $Cu_2Cl_3^-$ is more stable to moisture and air than the $AlCl_3$ based ionic liquids.

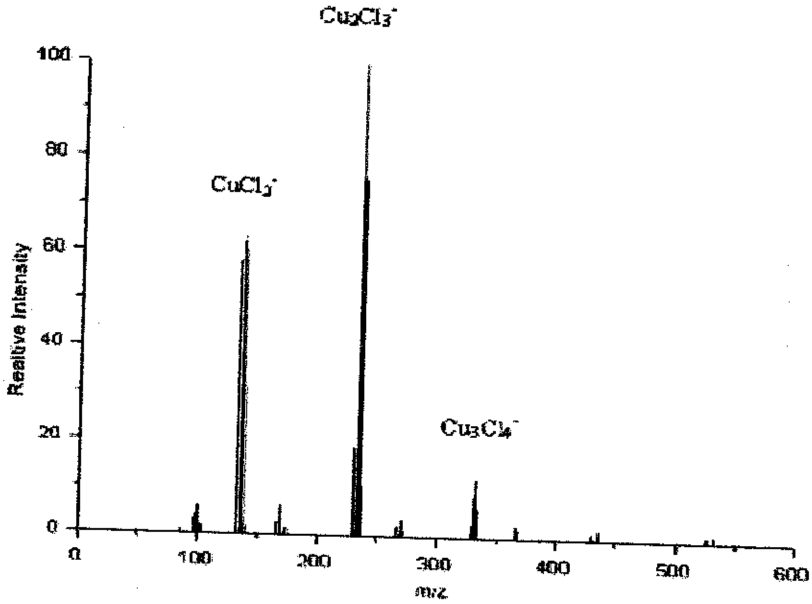
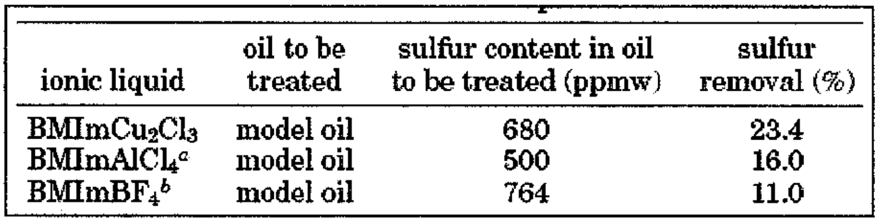


**Figure 2.5:** Intensive peaks of $BMImCu_2Cl_3$ ionic liquid *[Chongpin Huang, 2004]*

It has been reported that up to 23.4 % of sulfur removal can be achieved by using ionic liquid. Cu(I) anionic species existed in the ionic liquid, which was synthesized by mixing 1-butyl-3methylimidazolium chloride and purified anhydrous CuCl. These Cu(I) anionic species are moisture insensitive and stable in air. CuCl-based ionic liquid exhibits remarkable extraction desulfurization ability fro model oil (gasoline in this example), which may attributed to the π-complexation interaction of thiophene and Cu(I). In addition, the extraction desulfurization of gasoline with CuCl-based ionic liquid has the advantage of no polymerization reaction of the olefins in the gasoline. *[Yi Nie, 2006]*



| ionic liquid | oil to be treated | sulfur content in oil to be treated (ppmw) | sulfur removal (%) |
|---|---|---|---|
| $BMImCu_2Cl_3$ | model oil | 680 | 23.4 |
| $BMImAlCl_4$[a] | model oil | 500 | 16.0 |
| $BMImBF_4$[b] | model oil | 764 | 11.0 |

**Table 2.2**: Desulfurization of model oil by extraction with ionic liquids *[Chongpin Huang, 2004]*

# CHAPTER 3: METHODOLOGY

This project includes a few steps that will be describes briefly by figure 3.1.

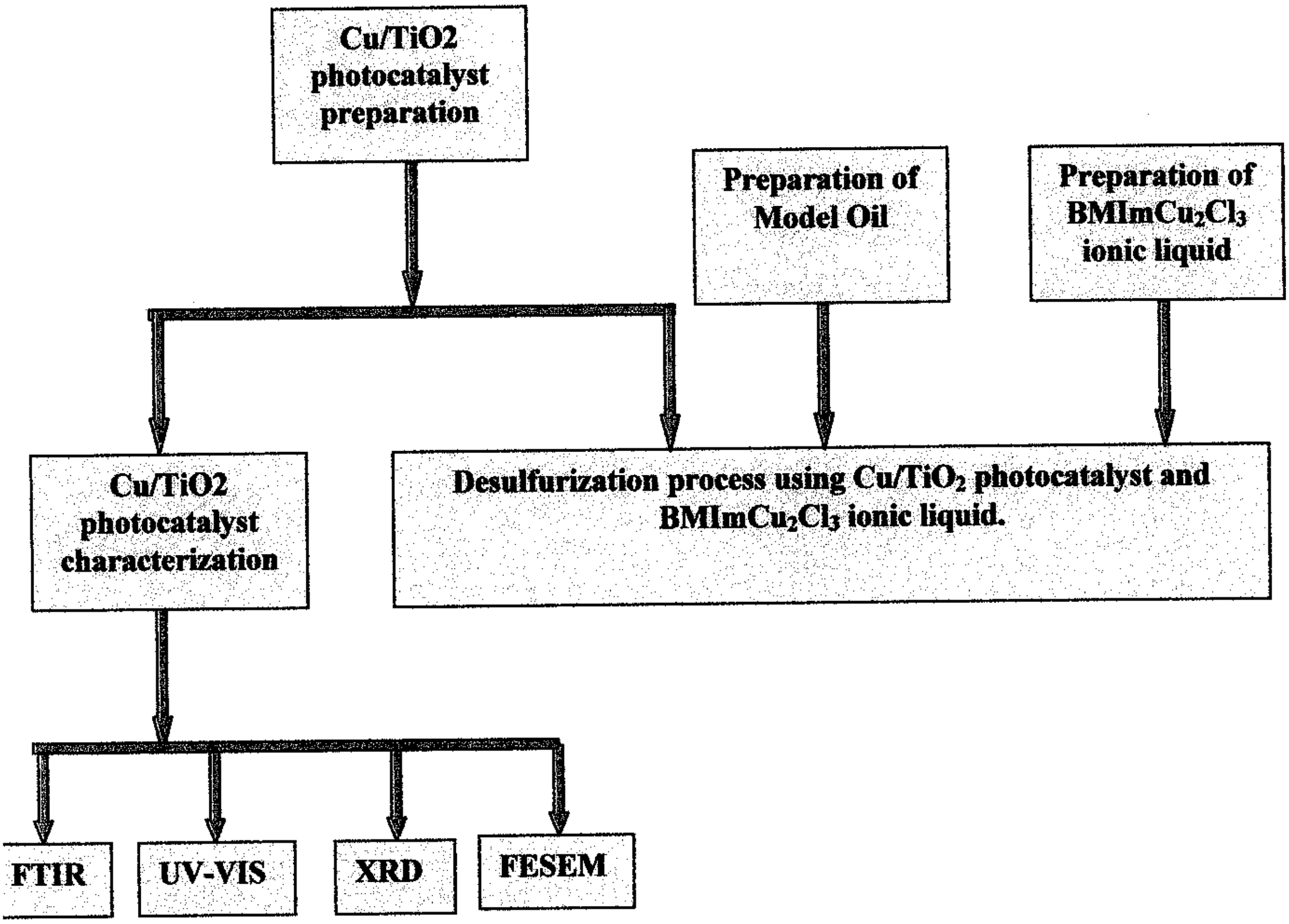


**Figure 3.1**: Flowchart for methodology

## 3.1 Cu/TiO$_2$ photocatalyst

### 3.1.1Preparation of Cu/TiO$_2$ photocatalyst

The preparation method for photocatalyst is very important because we use transition metal doped into the TiO$_2$. In order to use the photocatalyst effectively, it has to be ensured that the copper is dispersed into the TiO$_2$. There are several techniques to prepare the photocatalyst such as wet impregnation method, complex precipitation method, sol-gel method, and many more. In this project, wet impregnation method has been selected to prepare the photocatalyst because of its simplicity and versatile technique which can be controlled to give a good dispersion and better distribution of the metal on the TiO$_2$.

The CuTiO$_2$ photocatalyst has been prepared using wet impregnation method. The percentage of copper (Cu) doped into TiO$_2$ is 5 wt% and 10 wt%. A calculated amount of copper nitrate in distilled water being stirred for 1 hour with TiO$_2$ added to it. (Calculation in Appendix A) The solvent has been evaporated slowly in water bath at 80$^{O}$C until the solvent has transform into super-saturated solvent. The solvent being oven-dried at 120$^{O}$C for 18 hours. The dried solution being grinded to get the photocatalyst in powder form. This is to ensure that the photocatalyst get the maximum surface area contact during calcinations. Finally, calcination process which is to remove NO3- substance been conducted at 200$^{O}$C and 300$^{O}$C for 12 hour.

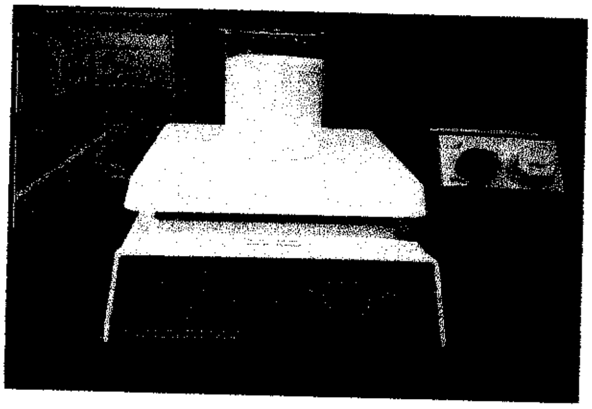


**Figure 3.2:** Stirring Process

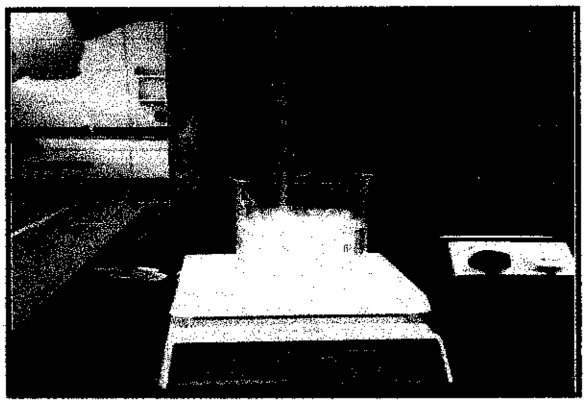


**Figure 3.3:** Evaporating Process

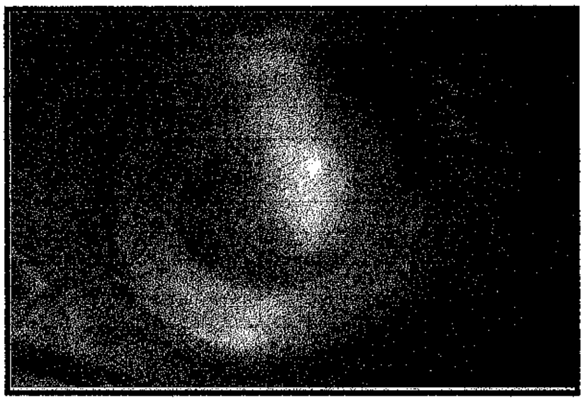


**Figure 3.4:** Super-saturated Solution

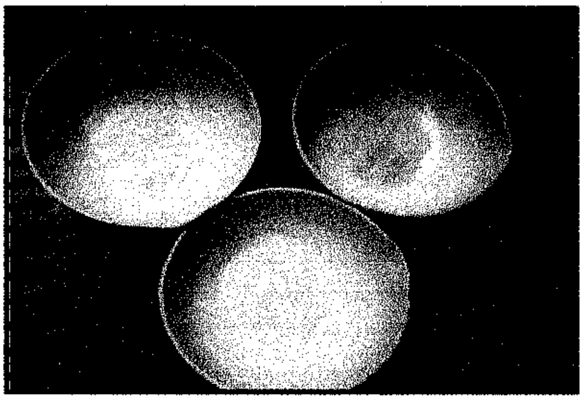


**Figure 3.5:** Oven-dried photocatalyst

The amount of copper loading is differs with 5 wt%, and 10 wt%. This parameter is important to determine the performance of the photocatalyst in a different amount of doping. The experiment also been carried out in three different calcinations temperature which are 200$^oC$ and 300$^oC$. This is to determine the suitable calcinations temperature for the photocatalyst. The details of the photocatalyst prepared are explained in the Table 3.1. The photocatalyst prepared are designated as mCuT; where m is the percentage of copper loading, and T is the calcinations temperature.

| Metal Loading, wt% | Calcination Temperature | |
|---|---|---|
| | 200degC | 300degC |
| 5 | 5CuT200 | 5CuT300 |
| 10 | 10CuT200 | 10CuT300 |

**Table 3.1:** Details of the photocatalyst prepared

### 3.1.2 Characterization of photocatalyst

Characterization of the photocatalyst is important to determine the chemical and physical properties of the photocatalyst before and after calcinations, and to relate the properties to the performance of the photocatalyst. The characterization used in this project are;

- **Fourier Transform Infrared Spectroscopy (FTIR)**
  This test is done to determine the functional group(s) present in the photocatalyst before and after calcinations process. The functional groups are identified by characteristics peaks in the spectrum.

- **X-ray Diffraction (XRD)**

  This test is carried out to determine the phases and crystal structure of the modified TiO2 photocatalyst. The phases are either anatase and rutile. It is performed using X-ray diffractometer at room temperature.

- **UV-vis Diffuse Reflectance Spectra (UV-Vis DRS)**

  This test is carried out to determine the absorption region and band gap of the modified TiO2 photocatalyst. This is to see whether the photocatalyst can be activated by visible light or not.

- **Field Emission Scanning Electron Microscopy (FE-SEM)**

  This test is carried out to show how well the dopant is dispersed into TiO2. It wil be determined by the morphologies of the photocatalyst.

- **Temperature Programmed Reduction (TPR)**

  This test is carried out to determine different types and amount of different reducible species in the catalyst and aso helps to identify of characteristics reduction peaks of these species. It is also determine the temperature where the oxidation reduction takes place.

- **Temperature Programmed Reduction (TGA)**

  This test is carried out to determine different types and amount of different reducible species in the catalyst and aso helps to identify of characteristics reduction peaks of these species. It is also determine the temperature where the oxidation reduction takes place.

### 3.2 Preparation of model oil

In this project, the use of model oil is because of the crude oil is a complicated sample. Thus, to study on the sulfur removal we have to start with the simple one. Model oil used in this project is dodecane. Dibenzothiophene which is the sulfur species has been added into the model oil to make it more clearly on the performance of sulfur removal in model oil.

The preparation of the model oil involved simple mixing process in a volumetric flask. 500ml of dodecane is mixed together with a calculated amount of dibenzothiophene to get 0.1 wt% of sulfur content. (Calculation in Appendix B) The solution is being shake slowly to ensure that the sulfur species distributed uniformly in dodecane.

### 3.3 Preparation of $BMImCu_2Cl_3$ Ionic Liquid

The ionic liquid that is going to be prepared is $BMImCu_2Cl_3$. The method is that to mix 1-methyl-3-butylimidazolium (BMIC) with CuCl. A Calculated amount of CuCl is added to 30g of 1-butyl-3-methylimidazolium chloride (BMIC) with a molar ratio of 2:1. (Calculation in Appendix C) The solution is stirred for 24 hours in room temperature to ensure proper mixing between the two substances. $BMImCu_2Cl_3$ ionic liquid is obtained in one phase of thick liquid form. It's colour is chocolate brown.

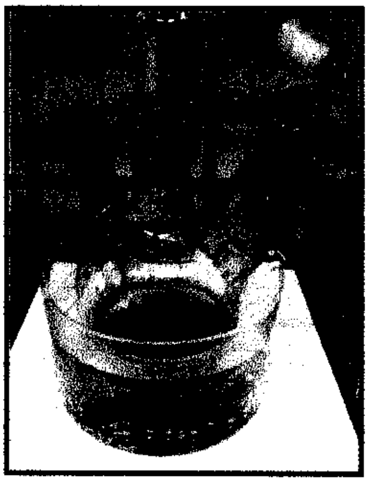


**Figure 3.6**: Preparation of BMImCu$_2$Cl$_3$ Ionic Liquid

### 3.4 Desulfurization process using Cu/TiO$_2$ photocatalyst with and without BMIMCu$_2$Cl$_3$ (ionic liquid).

The reaction of the photolysis is been carried out to study on the ability of the Cu/TiO$_2$ photocatalysis and BMIMCu$_2$Cl$_3$ extraction for sulfur removal in model oil. The experiment is prepared by adding 0.1g 5CuT200 in 20ml of model oil. The solution is being stirred for 30 minutes (without irradiation of light) to ensure well mixing of photocatalyst in model oil. Then, the mixture is subjected to irradiation with a visible light source. The reactions were carried out for 5 hours. The sample of model oil is being taken after every hour. The sample is subjected to centrifugal force to separate the oil phase and photocatalyst. The oil phase of the samples were taken and sent to Gas Chromatograph analysis (GC) to determine the amount of sulfur left in the oil phase. The procedure is repeated for 5CuT300, 10CuT200, and 10CuT300. The result is studied and the best Cu/TiO$_2$ photocatalyst is determined.

The experiment followed for ionic liquid extraction. Model oil is added to $BMIMCu_2Cl_3$ with a ratio of 20:1 weight percent. 0.1g of the best $Cu/TiO_2$ photocatalyst is added to the solution to determine the ability of sulfur removal by photocatalysis and ionic liquid extraction at the same time. The reactions were carried out for 5 hours and sample is taken for every hour. The samples is centrifuged to separate the oil phase with the ionic liquid phase. The oil phase of the samples was sent to Gas Chromatograph analysis (GC) to determine the amount of sulfur left in the oil phase.

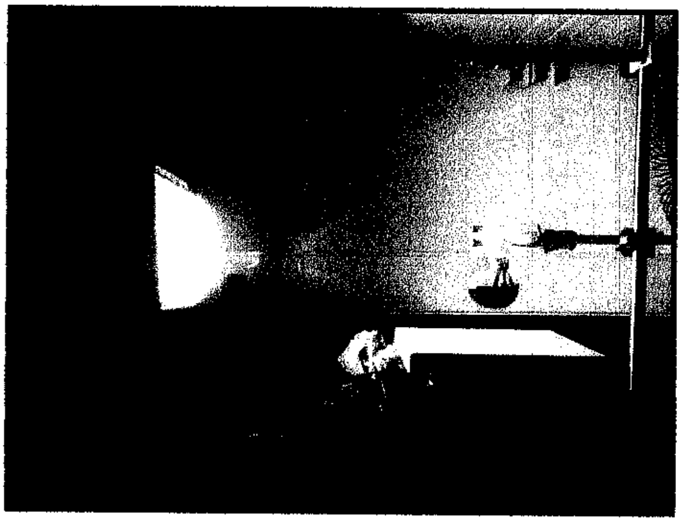


**Figure 3.7:** Desulfurization Procedure

## 3.5 Data Analysis

After the experiment, the oil phase will be analyzed to determine the degree of success of the $Cu/TiO_2$ photocatalyst and $BMIMCu_2Cl_3$ extraction for sulfur removal in model oil. The GC analysis has been chosen to do the qualitative analysis and determination of those. Percentage of sulphur contents in model oil phase were analyzed by GC and identified by comparing their retention time with those of standard. Standard samples of 0.01% S, 0.03% S, 0.07% S, and 0.1% S are prepared for calibration purposes.

# CHAPTER 4: RESULT & DISCUSSION

## 4.1 Characterization of $Cu/TiO_2$ photocatalyst

### 4.1.1 Field Emission Scanning Electron Microscopy (FE-SEM)

The morphologies of the photocatalyst were determined using FESEM. The samples were coated with a layer of platinum-palladium prior to scanning at 100 K magnification. Under vacuum, electrons generated by a Field Emission Source are accelerated in a field gradient. *[L.S.Yoong, 2009]* The beam passes through Electromagnetic Lenses, focussing onto the specimen. As result of this bombardment different types of electrons are emitted from the specimen. A detector catches the secondary electrons and an image of the sample surface is constructed by comparing the intensity of these secondary electrons to the scanning primary electron beam. Finally the image is displayed on a monitor. An FESEM picture is also expected to show how well the dopant material which is copper (Cu) is dispersed on the base material, pure titania ($TiO_2$).

FESEM of the catalyst samples depict the particle structures like irregular spherical. The displayed particles ranging from 20-100nm. Figure 4.1, 4.2, 4.3, and 4.4 show morphologies of 5 wt% and 10 wt% copper doped on $TiO_2$ calcined at $200^OC$ and $300^OC$. However, the magnification is not enough to determine morphological structure of the catalyst. We can see no detectable Cu particles were observed. However, the catalyst were evenly dispersed and incorporated into the $TiO_2$ support.

**Figure 4.1**: FESEM micrographs of 5CuT200 photocatalyst

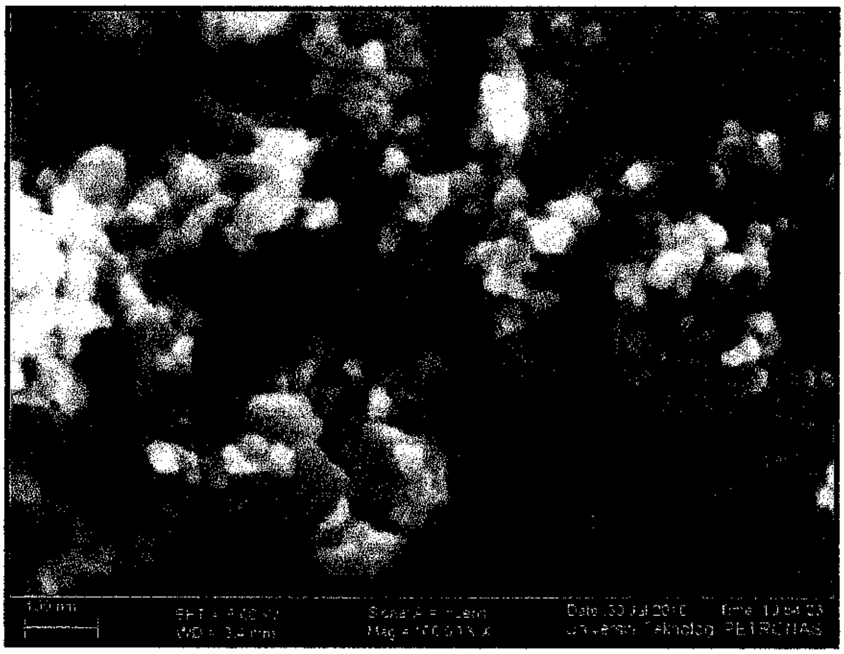


**Figure 4.2**: FESEM micrographs of 5CuT300 photocatalyst

Figure 4.3: FESEM micrographs of 10CuT200 photocatalyst

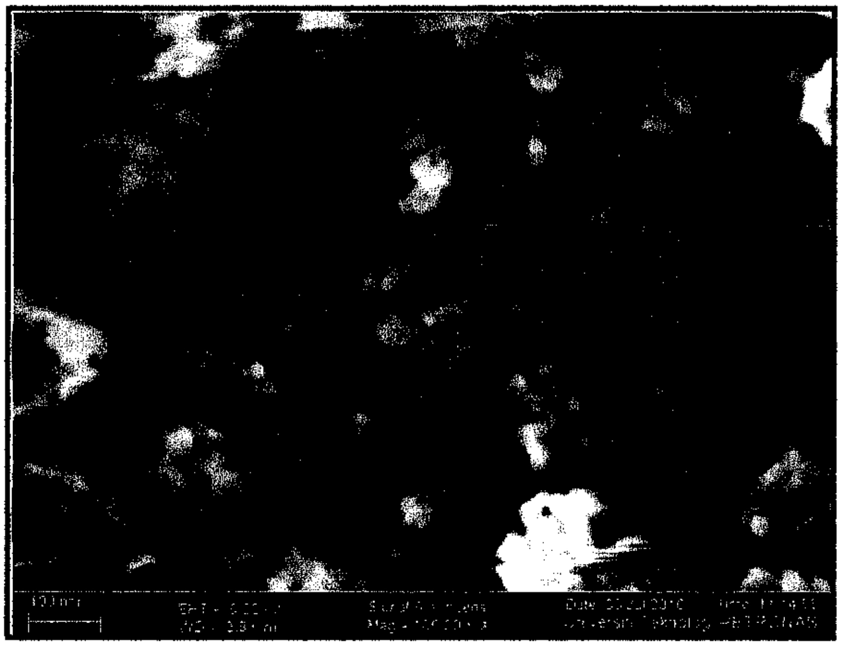


Figure 4.4: FESEM micrographs of 10CuT300 photocatalyst

### 4.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.

This test is done to determine the functional group(s) present in the photocatalyst before and after calcinations process. The functional groups are identified by characteristics peaks in the spectrum. Infrared spectra of the catalyst samples were obtained using Perkin-Elmer *Spectrum One* spectrometer. A sample of FTIR analysis was prepared by grinding and mixing 1 mg of the catalyst with 200 mg of IR-grade KBr and then the sample was pressed into a pellet using a hydraulic press. The FTIR spectrum of the pellet,taken over a wavenumber range of 450 $cm^{-1}$ – 4000 $cm^{-1}$, wa recorded as the percentage of transmittance (%T) versus wavenumber. FTIR spectra are used for determination of the functional groups $NO_3^-$ present in the catalyst before and after the calcinations process. The functional group is identified by characteristics peaks in the spectrum. *[L.S.Yoong, 2009]*

Figure 4.5 and 4.6 show the FTIR transmission spectra of the catalyst samples before and after calcinations process. In the spectra, the absorption peaks around 1600 $cm^{-1}$ and 3400 $cm^{-1}$ depicted the O-H bending and stretching. While the IR band around 400 $cm^{-1}$ to 900 $cm^{-1}$ attributed by the Ti-O stretching vibrations. The absorption band at 1384 $cm^{-1}$ is attributed by the presence of nitrate ($NO_3^-$). When the raw photocatalyst was calcined at 200$^{O}$C the intensity of the peak attributed $NO_3^-$ species decreased. At higher calcinations temperature (300$^{O}$C) the peak attributed to $NO_3^-$ species disappeared. It shows that $NO_3^-$ functional group is able to be removed at temperature of 300$^{O}$C.

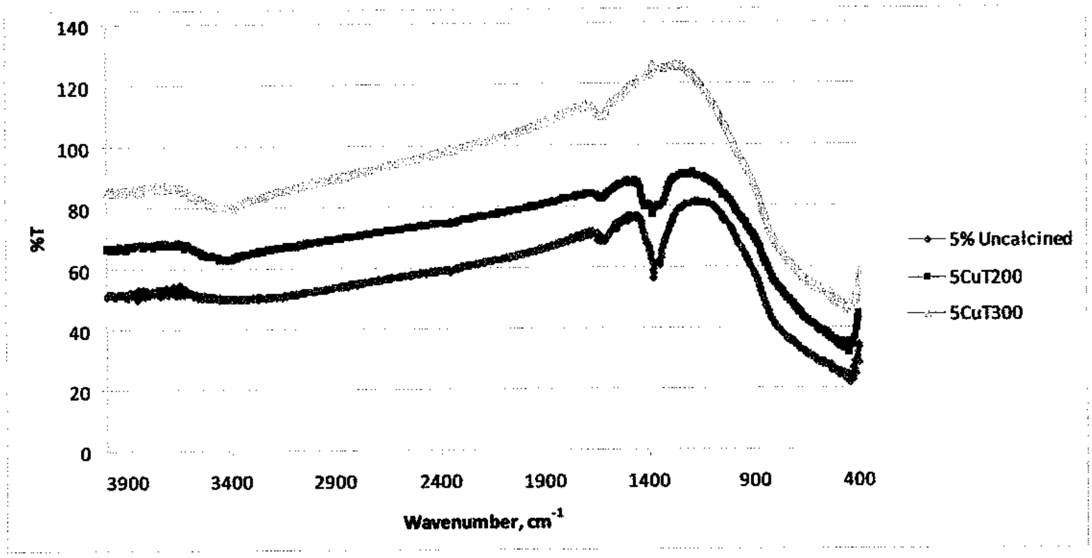


Figure 4.5: The FTIR spectra of 5wt% copper

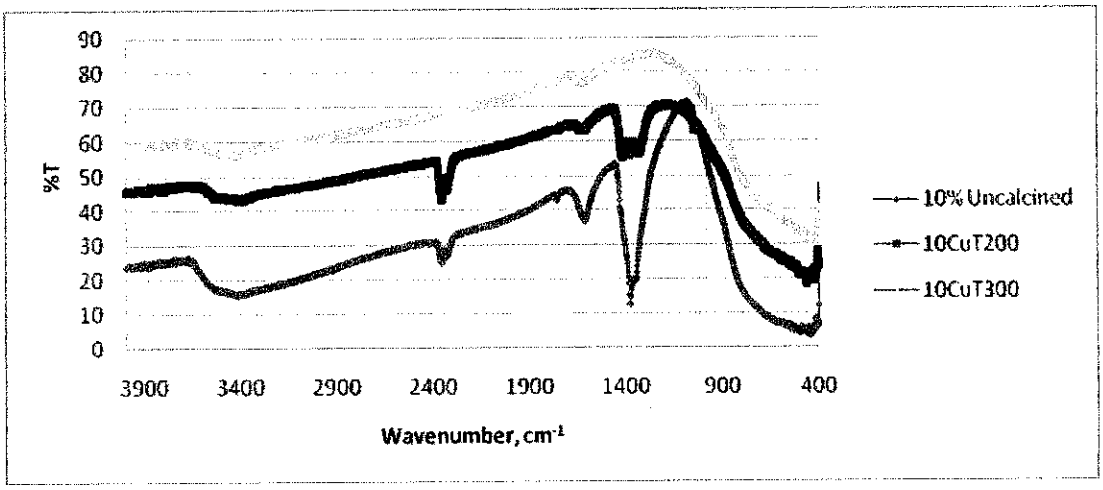


Figure 4.6: The FTIR spectra of 10wt% copper

### 4.1.3 UV-vis Diffuse Reflectance Spectra (UV-Vis DRS)

This test is carried out to determine the absorption region and band gap of the modified TiO2 photocatalyst. This is to see whether the photocatalyst can be activated by visible light or not. Diffuse reflectance UV-Vis spectra were recorded on Perkin-Elmer Lambda 900 instrument with an integrating sphere attachment using $BaSO_4$ powder as an internal reference. The layer of powder sample was made sufficiently thick such that all incidents light was absorbed or scattered before reaching the back surface of the sample holder. Typically a thickness 1-3 mm is required.

The diffuse reflectance spectra were plotted as the Kubelka-Munk function or remission, F(R), versus wavelength. Based on the Kubelka–Munk equation, $F(R)=(1-R)^2/2R$, where reflectance, R = Rsample/Rreference. The relative position of the catalysts absorption edge compared to TiO2 in the diffuse reflectance spectra is an important indication whether the absorption edge has been successfully shifted to the visible region. Since the major objective of this work is to modify anatase TiO2 by doping with appropriate metals so as to enhance absorption of visible light, DR-UV-Vis spectra of the catalyst material are very important for its characterization. The band gaps (Eg) for all the catalysts were determined from the extrapolation of the linear fit for the Tauc plot onto the photon energy axis. *[L.S.Yoong, 2009]*

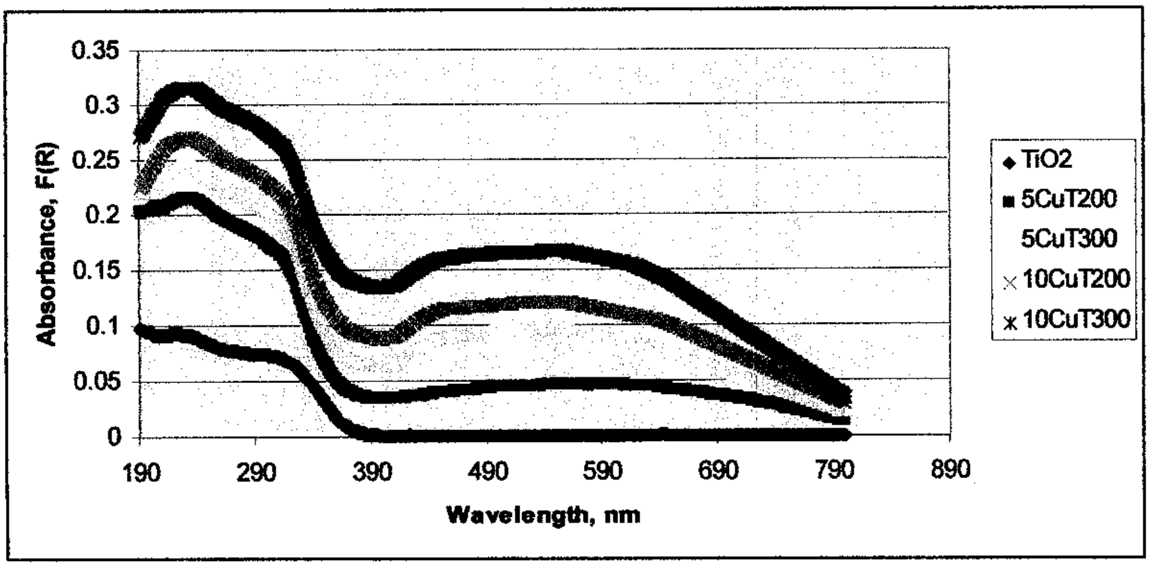


**Figure 4.7**: UV-Vis spectra of the catalyst samples

Figure 4.7 shows the DR-UV-Vis spectra of the catalyst samples and the pure $TiO_2$. The spectra of $TiO_2$ showed an absorption peak at 388nm in the UV region. When pure $TiO_2$ has been doped with 5 wt% copper and 10 wt% copper, the peak has been shifted towards visible range at around 400-800 nm. The band at 210–270 nm would indicate the $O^{2-}$ (2p) → $Cu^{2+}$ (3d) ligand to metal charge transfer transition, where the Cu ions occupy isolated sites over the support. A broad band between 400 and 600 nm is attributed to the presence of $Cu^{1+}$ clusters in partially reduced CuO matrix as well as $(Cu–O–Cu)^{2+}$ clusters. The absorption band at 600–800 nm indicates the crystalline and bulk CuO in octahedral symmetry *[Colon G, 2006]*.

The incorporation of copper ion shifts the absorption band to the visible or even near-infrared range and this promotes the photocatalytic activity . Thus, it can be inferred that doping with a transition metal such as copper was effective for visible light response *[Akihiko K, 2007]* and can play a significant role in enhancing the hydrogen evolution *[Sadhana, R]* using solar energy economically. The UV-Vis absorption edge and band gap energies of the samples have been determined from the reflectance [F(R)] spectra using the KM (Kubelka–Munk) formalism and the Tauc plot.

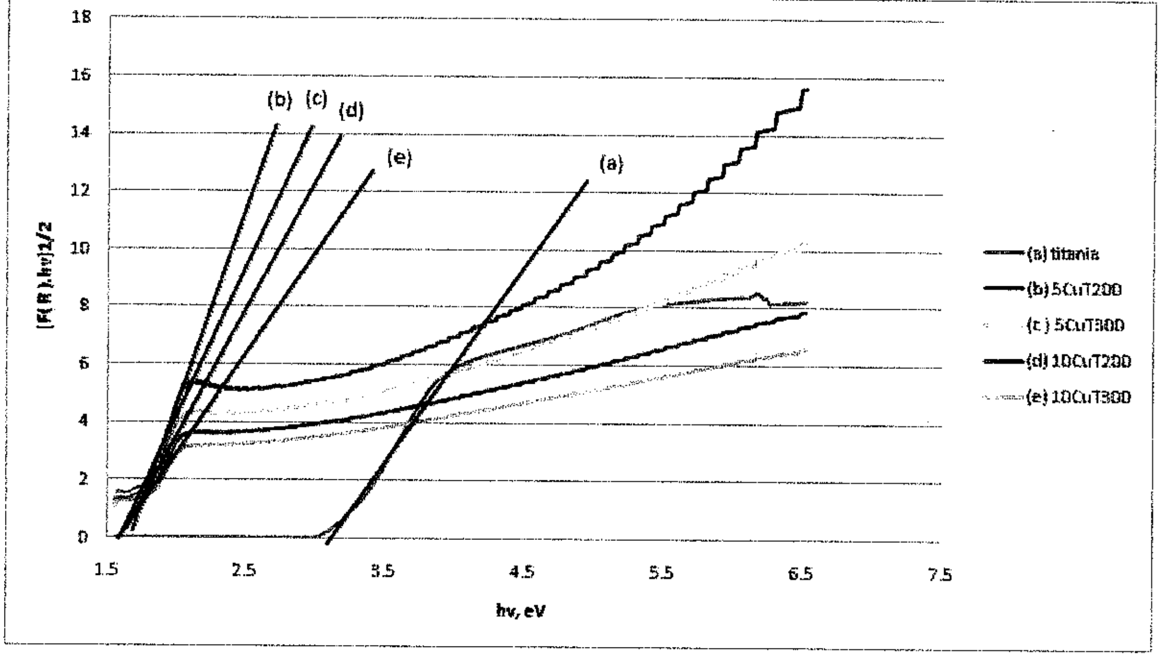


**Figure 4.8:** Plots of transformed Kubelka-Munk functions

The extrapolation lines in Figure been used to determine the bad gaps for the catalyst samples. The calculated values of the band gap energy are given in Table . All the catalysts showed reduction in their band gaps compare to pure titania. The largest reduction in band gap is observed for 10CuT200.

| **Photocatalyst** | **Band gap energy** |
|---|---|
| **$TiO_2$** | **3.27** |
| **5Cu2** | **2.85** |
| **5Cu3** | **2.75** |
| **10Cu2** | **2.38** |
| **10Cu3** | **2.51** |

**Figure 4.9**: Band gap energies

## 4.14 X-ray Diffraction (XRD)

This test is carried out to determine the phases and crystal structure of the modified $TiO_2$ photocatalyst. The phases are either anatase and rutile. It is performed using X-ray diffractometer at room temperature. X-ray Diffraction (XRD) is one of the primary techniques used by mineralogists and solid state chemists to examine the physico-chemical make-up of unknown solids. This data is represented in a collection of single-phase X-ray powder diffraction patterns for the three most intense D values in the form of tables of interplanar spacings (D), relative intensities ($I/I_0$), and mineral name.

The XRD technique takes a sample of the material and places a powdered sample in a holder, then the sample is illuminated with x-rays of a fixed wave-length and the intensity of the reflected radiation is recorded using a goniometer. This data is then analyzed for the reflection angle to calculate the inter-atomic spacing (D value in Angstrom units - $10^{-8}$ cm). The intensity(I) is measured to discriminate (using I ratios) the various D spacings and the results are to identify possible matches.

Figure shows the XRD patterns for all the catalyst samples. The peaks at $2\theta=25.34^O$ and $2\theta=27.42^O$ appear in all samples. These correspond to the main peak of anatase and rutile, respectively. CuO diffraction peaks appeared at $2\theta=35.6^O$ and $38.73^O$ for all the samples. It is also observed that the CuO peak intensities for higher calcinations temperature.

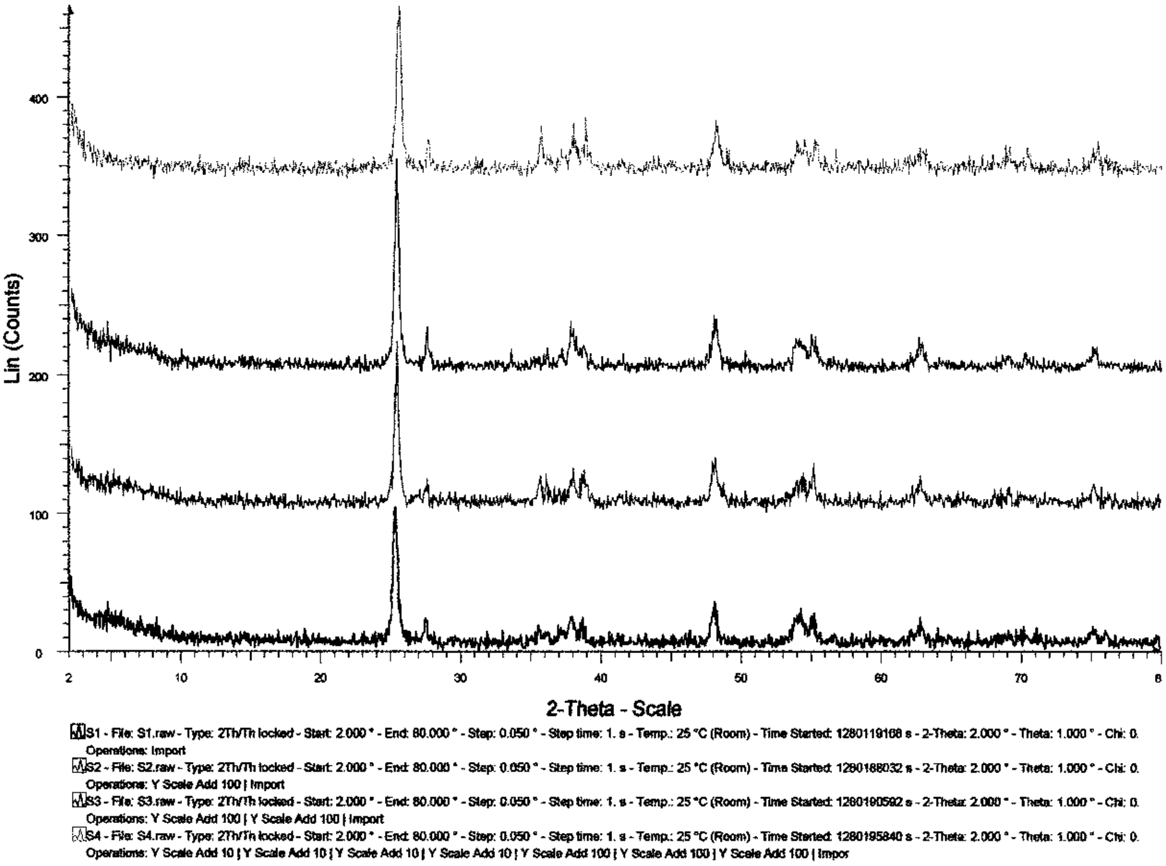


**Figure 4.10**: XRD Diffractograms

## 4.2 Desulfurization Reaction

Desulfurization reaction has been done to five different catalysts which are 5CuT200, 5CuT300, 10CuT200, 10CuT300, pure Titania and $BMImCu_2Cl_3$ ionic liquid. The reaction has been carried out for 5 hours under visible light for 5 hours. The sample of the model oil was taken for every hour and been tested using GC to determine the amount of the sulfur left. Catalyst that showed the best performance will be combined with $BMImCu_2Cl_3$ ionic liquid in model oil. The reaction is to investigate the performance of $Cu/TiO_2$ photocatalysis and ionic liquid extraction at the same time.

The desulfurization results were listed in Table. From the result, it shows that 10CuT200 has the best performance of desulfurization with 14.00% of sulfur removal and 5CuT300 has the least performance with 3.43% of sulphur removal. With the reaction of $BMImCu_2Cl_3$ alone the efficiency is up to 27.00% of sulphur removal. By combining the photocatalysis of 10CuT200 and $BMImCu_2Cl_3$ ionic liquid , the results was achieved to 57.00%.

We can see that higher doping of copper has increase the efficiency for sulphur removal. While, lower calcinations temperature shows better performance of desulfurization. The addition of metals on the $TiO_2$ semiconductor changes the photocatalysis process by changing the surface properties. The metal enhance the yield of a particular rate of the photocatalytic reaction. With a dose of 5wt% and 10wt% of copper, only small area of the semiconductor surface area covered. A large surface area of the semiconductor is still exposed. The metal actually modifies the photocatalytic properties by changing the distribution of electrons. *[Amy L, 1994]* It shows that higher doping of copper on the semiconductor shows better performance. However, there is an optimum loading of Cu to achieve a maximum photocatalytic rate of desulfurization from model oil. An optimum content affects the distribution of electrons in the system. Above the optimum metal content the efficiency of the photocatalytic process actually decreases.

| Sample\Time | 30 min | 1hr | 2hr | 3hr | 4hr | 5hr |
|---|---|---|---|---|---|---|
| $TiO_2$ | 1.10% | 1.15% | 2.13% | 2.55% | 2.57% | 3.10% |
| 5CuT200 | 1.11% | 3.46% | 4.11% | 4.66% | 5.01% | 5.22% |
| 5CuT300 | 1.33% | 1.87% | 2.31% | 2.87% | 3.23% | 3.43% |
| 10CuT200 | 1.43% | 5.45% | 7.89% | 9.33% | 12.13% | 14.00% |
| 10CuT300 | 1.45% | 6.78% | 7.81% | 9.87% | 10.78% | 11.80% |
| $BMImCu_2Cl_3$ | 5.76% | 7.87% | 13.74% | 19.87% | 25.43% | 27.00% |
| 10CuT200 + BMImCu2Cl3 | 6.89% | 9.45% | 15.45% | 35.46% | 46.66% | 57.00% |

**Table 4.2:** Desulfurization results hourly

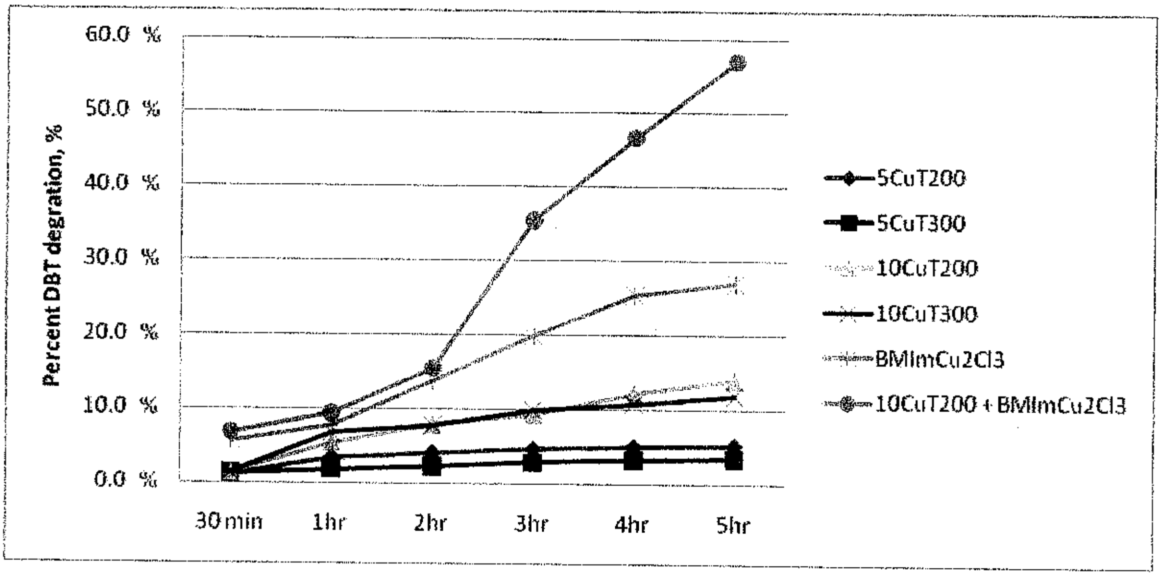


**Figure 4.11**: Graph of desulfurization results

By observing the results above, it can be noticed that high photocatalytic rate behavior displayed by photocatalysis calcined at lower temperature. The difference rate has been related to protonated precursor in the formation of oxygen vacancies and structural stabilization. *[Colon G, 2006]*. As calcinations temperature increases, the photocatalytic rates were decreases. This worst photocatalytic behavior could be related with an important sintering process, in which surface area values decreases and rapid rutilization would take place probably induced by unstabilized oxygen vacancies. Thus, we can say that 200°C calcinations temperature exhibit well crystallized anatase structure with higher surface area.

The desulfurization of model oil using combination of 10CuT200 photocatalysis and $BMImCu_2Cl_3$ extraction exhibits high performance. The obtained results revealed that the 10CuT200 photocatalytic oxidation of sulfur contents gain a good yield. With the combination of $BMImCu_2Cl_3$ extraction, it contributed to $\pi$-complexing interaction of sulfur and Cu (I). With this method, the desulfurization process is been equipped with two desulfurization systems. Thus, the efficiency of desulfurization increases as well.

# CHAPTER 5: CONCLUSION AND RECOMMENDATION

## 5.1 Conclusion

The experimental results for desulfurization of model oil using $CuTiO_2$ photocatalyst with different percentage of copper loading and calcinations temperature, and $BMImCu_2Cl_3$ ionic liquid show some definite trends. Percentage of sulphur removed by $TiO_2$ alone is 3.10% while using $BMImCu_2Cl_3$ ionic liquid alone is 27.00%. $Cu/TiO_2$ photocatalyst showed best performance up to 14.00% by 10CuT200. The combination of 10CuT200 with $BMImCu_2Cl_3$ ionic liquid yield performance of desulfurization up to 57.00%.

10CuT200 photocatalyst which is prepared using wet impregnation method, doped with 10% of copper and calcined at $200^{O}C$ showed better activity than the other photocatalyst. The sulfur removed for combination of 10CuT200 photocatalyst and $BMImCu_2Cl_3$ ionic liquid is much higher than using photocatalyst alone. 10 wt% of copper doping shows better performance than 5 wt% of copper doping, and low calcination temperature which is $200^{O}C$ depicted better activity than $300^{O}C$.

The size range of the dopant particles varied between 20-110 nm. The uniformity dispersion of Cu on pure titania indicated by FESEM images. XRD analysis also confirmed the full crystallinity which is one of the factors that contributed to high photocatalytic efficiency. The UV-Vis test also has showed that the photocatalyst active region from UV to visible light.

## 5.2 Recommendation

A study should be carried out for the systhesis of photocatalyst using complex precipitation method. This is because this method proposed better dispersion of metal on the semiconductor. Percentage of copper doping onto $TiO_2$ is increased to determine the optimum of copper content that will provide high photocatalytic efficiency. Calcination temperature and duration can be best determined using TGA analysis. By implying this analysis beforehand, we can increase the efficiency of photocatalyst. Another type of metal transition doping also should be studied for the desulfurization process such as Fe, Mn, Ni, Zn, Pt, Ag, and etc. Studied should be implied for another type of ionic liquid such as $BMImAlCl_4$, $BMImBF_4$, and others. Instead of using model oil, the reaction should be continued by using the crude oil. We can observe real efficiency of the deufurization.

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# APPENDICES

## **Appendix A:** Mass Balance Calculation for Cu Metal Doping

Molecular weight for the chemical used in Cu/$TiO_2$ photocatalyst

- Copper (III) Nitrate, $Cu(NO_3)_2.3H_2O$ = 241.6 g/mol
- Iron metal = 63.546 g/mol
- Titanium Dioxide, $TiO_2$ = 79.87 g/mol

Sample calculation (for 5 wt% Cu metal doping):

100 g of Cu/$TiO_2$ photocatalyst → 5 g Fe metal needed
20 g of Fe/$TiO_2$ photocatalyst → 1.00 g Fe metal needed

1 mole of $Cu(NO_3)_2.3H_2O$ → 63.546 g Fe metal
Therefore, 0.08 g of Fe metal,

= (1g/63.546 g)*241.6 g/mol
= 3.8020 of salt, 19g of $TiO_2$

Table: Summary of $Fe(NO_3)_3.9H_2O$ mass needed for respective loading

| Description | Cu loading (wt%) | |
|---|---|---|
| | 5 | 10 |
| Amount of catalyst (g) | 20 | 20 |
| Mass of Fe (g) | 3.80 | 7.60 |
| Mass of $TiO_2$ (g) | 19.00 | 18.00 |

**Appendix B**: Mass Balance Calculation for Ionic Liquid Preparation

**Molecular weight:**

| | |
|---|---|
| • [BMIM]Cl | = 174.67 g/mol |
| • CuCl | = 99.00 g/mol |

From the methodology of Ionic Liquid Preparation, a ration of 1:2 amount of both [BMIM]Cl and CuCl are needed. So, to prepare in 30g of [BMIM]Cl , 0.1717 mole of [BMIM]Cl is prepared. The Calculation for the right amount of reactants to be mixed is as below:

1 of [BMIM]Cl → 2 of CuCl
0.1717 mole of [BMIM]Cl → x mole of CuCl
X = 0.3435 mole

= (99 g/mol x 0.3435 mole)
= 34.01 g

So, 30.00 g of [BMIM]Cl is mixed with 34.01 g of CuCl.

## **Appendix C:** Mass Balance Calculation for Model Oil

**Dodecane + Dibenzothiophene (0.1wt %)**

0.1 wt% → 1000ppm → 1000 mg/L S

$1\ L = 1000\ mg\ S$

$100\ mL = 100\ mg\ S$

$1\ mol\ S = 32.06\ g\ S$

$1\ mol\ DBT = 32.06g\ S$

$1\ mol\ DBT = 32060\ mg\ S$

$x\ mol\ DBT = 100\ mg\ S$

$$x\ mol\ DBT = \frac{100\ mg\ S}{32060\ mg/mol\ S}$$

$x\ = 0.003119\ mol\ DBT$

$$0.003119\ mol\ DBT = \frac{mass}{184.26\ g/mol\ DBT}$$

$mass\ = 0.5747\ g\ DBT$

$y(purity) = 99\%$

$mass\ = 0.5747\ \div 0.99$

$mass\ = 0.5805\ g\ DBT$