

THE PERFORMANCE OF DIFFERENT TYPES OF FLOWER-LIKE ZINC
OXIDE FOR PHOTOCATALYTIC DESULFURIZATION OF SYNTHETIC
THIOPHENE

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A thesis submitted in
fulfillment of the requirement for the award of the
Degree of Master of Engineering Technology

Faculty of Engineering Technology
Universiti Tun Hussein Onn Malaysia

MARCH 2022

For my beloved mother and father



ACKNOWLEDGEMENT

The author would like to express his sincere appreciation to his supervisor, Ts. Dr Nur Hanis Hayati Hairom, Department of Chemical Engineering Technology, Universiti Tun Hussein Onn Malaysia (UTHM) for her superb guidance and support given throughout the duration for this research.

The author also would like to record his gratitude to his project members for helping him at each and every step in conducting this research. Besides, the author would like to take this opportunity to thank his parents, housemates and Japanese friends for constantly supporting and encouraging him during the study. The author wishes to place his deep sense of thanks to all who are directly or indirectly associated with the study for their cooperation and critical suggestions during preparation of this research.



PTTA UTHM
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ABSTRACT

Zinc oxide (ZnO) nanoparticles have received great attention due to their advantages. Several improvements on the morphology of ZnO have been widely studied to solve the problem of agglomeration and surface-active sites. To date, there are limited studies involving the effect of flower-like ZnO in the application of thiophene desulfurization via photocatalysis process. Thus, this study focuses on the performance of different flower-like ZnO for synthetic thiophene desulfurization. Eight ZnO photocatalyst species were synthesised and categorized into two groups, namely flower-like ZnO and non-flower-like ZnO. The physical properties of all the ZnO morphologies were analysed. Moreover, their performances for desulfurization of synthetic thiophene were evaluated. From the findings, flower-like ZnO flakes showed the highest performance in synthetic thiophene desulfurization (30%). Higher pH (pH 11) and turbidity reduction (32%) of the permeate indicated the higher generation of hydroxyl radicals causing higher desulfurization of thiophene. From the kinetic study, all ZnO morphologies were applicable with pseudo-second-order models due to higher linear regression (R^2) values. The highest concentration equilibrium, C_e value for flower-like ZnO flakes (909.09 mg/g) confirmed greater desulfurization of thiophene. Moreover, it was found that pH 7 in the presence of 0.05 g/L flower-like ZnO flakes for 90 minutes of irradiation were the best conditions and yield the highest desulfurization of 300 ppm synthetic thiophene (30%) due to the highest generation of hydroxyl radical. It is expected that this integrated approach could bring forward other initiative methods in overcoming the problems in petroleum industry related to desulfurization of sulphur-containing compounds.

ABSTRAK

Nanozarah zink oksida (ZnO) telah mendapat perhatian tinggi di kalangan penyelidik disebabkan kelebihannya. Beberapa penambahbaikan terhadap morfologi ZnO telah banyak dikaji untuk menyelesaikan masalah penggumpalan dan pertingkatkan tapak aktif permukaan. Sehingga kini, kajian adalah terhad dalam melibatkan keberkesanan ZnO berbentuk bunga dalam penyahsulfuran tiofen melalui pelantar reaktor foto-pemangkin. Maka, kajian ini memfokuskan kepada prestasi pelbagai jenis ZnO berbentuk bunga dalam penyahsulfuran tiofen sintetik. Lapan spesies foto-pemangkin ZnO telah dibentuk dan dikategorikan kepada dua kumpulan, iaitu ZnO berbentuk bunga dan ZnO tidak berbentuk bunga. Sifat fizikal kesemua spesies ZnO telah dianalisis. Tambahan, prestasi ZnO ini telah dinilai dalam penyahsulfuran tiofen sintetik. Daripada penemuan, kepingan ZnO berbentuk bunga telah menunjukkan prestasi tertinggi dalam penyahsulfuran tiofen sintetik (30%). pH yang tertinggi (pH 11) dan pengurangan kekeruhan yang tinggi (32%) menunjukkan penjanaan radikal hidroksil yang sangat besar menyebabkan penyahsulfuran dan menguraikan sebilangan besar sebatian tiofen. Daripada kajian kinetik kesemua morfologi ZnO bersesuaian dengan model pseudo-kedua kerana nilai garisan regresi (R^2) yang tertinggi. Ketinggian nilai keseimbangan kepekatan, C_e untuk kepingan ZnO berbentuk bunga (909.09 mg/g) mengesahkan penyahsulfuran tiofen sintetik yang lebih besar. Tambahan, didapati bahawa pH 7 dengan kehadiran serpihan ZnO berbentuk bunga sebanyak 0.05 g/L selama 90 minit masa penyinaran adalah kondisi terbaik untuk penyahsulfuran 300 ppm tiofen sintetik dan menghasilkan penyahsulfuran tertinggi (30%) disebabkan penjanaan radikal hidroksil yang banyak semasa penyinaran. Pendekatan bersepadu ini diharapkan dapat membawa kemajuan terhadap kaedah inisiatif lain dalam mengatasi masalah dalam industri petroleum berkaitan penyahsulfuran sebatian mengandungi sulfur (SCC).

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LIST OF SYMBOLS AND ABBREVIATIONS

<i>BOD</i>	-	Biochemical oxygen demand
<i>CB</i>	-	Conduction band
<i>CBD</i>	-	Chemical bath deposition
<i>CC</i>	-	Cymbopogon citrus
<i>COD</i>	-	Chemical oxygen demand
<i>CP</i>	-	Chlorophenol
<i>CTAB</i>	-	Cetyltrimethyl ammonium bromide
<i>E_g</i>	-	Band gap energy
<i>EQA</i>	-	Environmental quality act
<i>FESEM</i>	-	Field emission scanning electron microscope
<i>FTIR</i>	-	Fourier transform infrared spectrometer
<i>GFD</i>	-	Gallons per square foot per day
<i>HCl</i>	-	Hydrochloric acid
<i>HDS</i>	-	Hydrodesulfurization
<i>HMTA</i>	-	Hexamethylenetetramine
<i>hν</i>	-	Photon energy
<i>KOH</i>	-	Potassium hydroxide
<i>MF</i>	-	Microfiltration
<i>NaOH</i>	-	Sodium hydroxide
<i>NF</i>	-	Nanofiltration
<i>NTU</i>	-	Nephelometric turbidity units
<i>PA</i>	-	Polypiperazine-amide
<i>PEG</i>	-	Polyethylene glycol
<i>PES</i>	-	Polyether sulfone
<i>PL</i>	-	Photoluminescence
<i>PMR</i>	-	Photocatalytic membrane reactor
<i>POMSE</i>	-	Palm oil mill secondary effluent

<i>ppm</i>	-	Parts per million
<i>PVDF</i>	-	Polyvinylidene fluoride
<i>PVP-St</i>	-	Polyvinylpyrrolidone
<i>RhB</i>	-	Rhodamine B
<i>SCCs</i>	-	Sulphur containing compounds
<i>UF</i>	-	Ultrafiltration
<i>UV-Vis</i>	-	Ultra violet - visible
<i>VB</i>	-	Valence band
<i>W</i>	-	Watt
<i>XRD</i>	-	X-ray diffractometer
<i>ZnAc</i>	-	Zinc acetate
<i>ZnNit</i>	-	Zinc nitrate
<i>ZnO</i>	-	Zinc oxide



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CHAPTER 1

INTRODUCTION

1.1 Background of study

Petroleum industry is one of the largest industries in Malaysia and is a vital part of the national economy. Nevertheless, this largest industry also contributes to major sources of environmental pollutions. Sulphur is the third most abundant element after carbon and hydrogen in petroleum and contributes to air pollutions due to the production of SO₂ species known as toxic gas during combustion (Mousavi-Kamazani, 2020). Thiophene is one of the sulphur pollutants in petroleum and this compound is known as sulphur-containing compounds (SCCs) in petroleum. Previous findings in the literature have defined that thiophene has a simple aromatic compound containing sulphur atom (C₄H₄S). It belongs to heterocyclic compounds as it is structured as five-member rings consisting of one heteroatom, which is Sulphur (Hamdan et al., 2021). Moreover, thiophene is a toxic and flammable aromatic compound where the production of toxic oxides during combustion could lead to negative impact especially on human health such as respiratory problems, wheezing, phlegm and asthma attack meanwhile negative impact on environment such as acid rain (Sadare et al., 2017). Conventional technology, which is hydrodesulfurization, seems not very effective which increases the demand for desulfurization in petroleum. Other observations have indicated that this process requires higher temperatures (>300°C), higher hydrogen pressures (>30 atm) and more active catalysts to achieve deep desulfurization. However, the removal of thiophene through this process is difficult due to its stable aromatic ring structure. Thus, this conventional method is still far from complying with the standard regulations (Rudreshwar et al., 2016).

To date, photocatalysis process has attracted much attention for environmental purification and treatment especially in thiophene desulfurization as it is more environmentally friendly. Previous studies have reported that thiophene was successfully desulfurized more than 95% via photocatalysis process using semiconductor photocatalysts, such as copper-decorated zirconia-silica (ZrO_2-SiO_2), Mn_3O_4 -coupled Ag_2WO_4 , flower-like $BiOI/BiPO_4$, $CdSe/rGO$ and others. However, the preparation of these photocatalysts was very complicated, inducing high level of heavy metal and high cost of chemical reagents when utilized in industrial scale. In addition, the air/oxygen supply to the system over a longer period could affect the capital cost for industrial scale (Sadare et al., 2017). Therefore, the preparation of flower-like zinc oxide (ZnO) via simple route and less hazardous was performed in this study for photo-desulfurization of thiophene.

Khan et al. (2015) stated that photocatalyst should have the desired band gap, suitable morphology, higher surface area, reusability and stability to increase the efficiency of photocatalytic activity. Metal oxides are the best photocatalysts commonly used for photocatalysis process due to their ability to absorb light and generate oxidation of organic pollutants (Kang et al., 2019). ZnO is one of the semiconductor metal oxides that has a direct wide band gap of 3.37 eV and a large excitation binding energy of 60 meV that is widely applied in piezoelectric nano-generators, dye-sensitized solar cells, biodevices, optoelectronic nano-devices and photocatalyst for the degradation and removal of environmental pollutants. Compared to titanium dioxide (TiO_2), ZnO is more stable, economically photosensitive and has higher H_2O_2 generation (Desa et al., 2019). The wurtzite structure of ZnO allows for large excitation binding energy that generates ultraviolet (UV) light efficiency at standard temperature. However, previous studies have emphasized less on improving the morphological structure of ZnO. By improving the morphology and surface area, the efficiency of photocatalytic activity could be increased (Khan et al., 2015).

To date, the control of the shape of ZnO nanostructures has received much attention due to improved morphology, surface area and stability. There are three types of dimensional ZnO structures that have been synthesized: 1-dimensional structure (rod, wires, tubes), 2-dimensional structure (ribbons, sheets) and 3-dimensional structure (flower). Among them, flower-like ZnO structures have shown the best photocatalytic activity due to the improved morphological structure (Fan et al., 2016). Various studies have revealed that the highest degradation of organic compound was

successfully achieved due to greater amount of oxygen vacancies existed on the surface of flower-like ZnO. During the photodegradation, oxygen vacancies act as active centres to inhibit recombination of photoelectrons and photo-holes, thus exhibiting higher photocatalytic activity (Li et al., 2013; Fan et al., 2016). However, studies on photodegradation of thiophene in the presence of flower-like ZnO are still limited. Therefore, this study attempts to discover the performance of different types of flower-like ZnO for desulfurization of thiophene.

The structure of flower-like ZnO composed of 2-dimensional structure of ZnO nanorods. These nanorods are assembled and intersect with each other to form a flower-like structure. To date, there are many techniques for preparing flower-like ZnO including thermal evaporation, chemical vapor deposition, hydrothermal and electro-deposition (Liang et al., 2019). However, most of the reported techniques require special conditions, high temperatures, longer preparation time, and difficulty in tailing ZnO microstructure. Therefore, this study synthesized flower-like ZnO using a simpler and low-temperature preparation method. Recently, hydrothermal method has been used to prepare flower-like ZnO structure as it offers many advantages to produce products that are homogenous in composition, and control morphology, purity, composition, size and crystallinity of nanomaterial. Previously, Rayerfrancis et al. (2015) synthesized flower-like ZnO using hydrothermal method under basic conditions. They claimed that the synthesized flower-like ZnO has pure composition and greater wurtzite structure.

Another simpler method is the chemical bath deposition (CBD) method which promises a great commercial value, better replicability, large area scaling, simplicity and convenience (Dubal et al., 2014). On another note, Zhang et al. (2015) synthesized branch-like ZnO nanorods which were similar to that of flower-like via CBD technique at low temperatures and times without the surfactant addition and pH modification. They have found that the branch-like ZnO nanorods combined with copper oxide/copper sulphate (CuO/CuS) core-shell structures exhibited good performance under visible light for photocatalytic degradation of RhB solution (Cao et al., 2019). However, there is little discussion on the preparation of flower-like ZnO via CBD and hydrothermal method including its application in desulfurization of thiophene. Therefore, this study has been conducted through hydrothermal and CBD method due to its promising replicability, simple route and less harmful, which is proven the improvement of morphology, surface area, stability, less poisonous and band gap of

flower-like ZnO photocatalyst. Besides, their performances in desulfurization of thiophene via photocatalytic reactor were evaluated.

1.2 Problem statement

Petroleum is the largest industry that contributes to major hazardous air and water pollutants which could adversely affect the environment and human. Thiophene is one of the sulphur-containing compounds (SCCs) in petroleum known as an aromatic compound with toxic and flammable behaviour. This compound could cause air pollutions due to toxic gases produced during combusting and also cause severe corrosion of reactors and equipment during oil processing. In conventional technology, hydrodesulfurization (HDS) is still ineffective for removing thiophene due to stable aromatic compound. This technology also requires high cost to implement due to its high demand. Therefore, advanced desulfurization technology is required to reduce problems such as photocatalytic desulfurization.

Recently, ZnO nanoparticles have showed great performance for desulfurization of thiophene and produced high quality of permeate. However, previous studies have focused less on the improvement of the morphological and surface structure of ZnO. By improving ZnO morphology, the efficiency of the photocatalytic activity could be increased. Previously, precipitation method of ZnO nanoparticles has a major problem in controlling the morphologic, size distribution and surface area of ZnO nanoparticles.

Morphology of flower-like ZnO have shown the best photocatalytic activity due to improved morphology, surface area and light absorption thus, increase the degradation efficiency of organic compound. However, the challenging is most of the reported preparation methods require special conditions, high temperatures, longer preparation time, and difficulty in tailing ZnO microstructure. Besides, studies on photo-desulfurization of thiophene in the presence of flower-like ZnO are still limited. Therefore, this study evaluated the performance of different types of flower-like ZnO for desulfurization of thiophene via photocatalytic reactor rig.

1.3 Objectives of study

The objectives of this study are:

- (i) To synthesis flower-like ZnO via hydrothermal and chemical bath deposition (CBD) methods.
- (ii) To characterize the physicochemical properties of flower-like ZnO.
- (iii) To elucidate the performance of flower-like ZnO for synthetic thiophene desulfurization in terms of desulfurization efficiency, kinetic study and optimum condition.

1.4 Scopes of study

The scopes of this study are:

- (i) Synthesis of flower-like ZnO via hydrothermal and chemical bath deposition (CBD) method under different chemical precursors (ZnAc-NaOH, ZnAc-HMTA and ZnNit-HMTA), pH (6-12), temperature (90-150°C), operating time (1-10 hours) to study and differentiate the effects of different conditions on ZnO morphology.
- (ii) Characterization of flower-like ZnO using X-ray diffractometer (XRD), field emission scanning electron microscope (FESEM) and Fourier transform infrared (FTIR) spectrometer to investigate crystallinity, purity, morphology, particle size and functional group, respectively.
- (iii) Elucidation of flower-like ZnO performance in desulfurization of synthetic thiophene via photocatalysis process under different initial pH (6, 7, 8) and types of flower-like ZnO photocatalyst to determine the best and higher performance among the synthesized photocatalyst.
- (iv) Analysis of permeate quality in terms of concentration, pH and turbidity to study the effectiveness of synthesized ZnO photocatalysts in desulfurization of synthetic thiophene.
- (v) Elucidation of kinetic studies on photocatalytic desulfurization of synthetic thiophene through pseudo-first-order and second-order kinetic reaction to evaluate the efficiency of synthesized ZnO photocatalysts in synthetic thiophene desulfurization
- (vi) Determination of the optimum conditions for flower-like ZnO photocatalyst in

desulfurization of synthetic thiophene in terms of photocatalyst loading (0.04, 0.05, 0.06 g/L) and time contact (5 hours).

1.5 Significance of the study

This study focuses on the long-term benefits of photocatalytic degradation for treating crude petroleum oil from sulphur-containing compounds (SCCs) by increasing the desulfurization efficiency of thiophene to enhance petroleum refining plant technology. Higher demand in the petroleum industry confirms that more effective sulphur-treatment approach is necessary. Thus, this study applied the recommended treatment approach that is technically and economically significance to the industry to produce less harmful and environmentally friendly petroleum oils. It is important to save energy as well as to reduce capital cost and installation size due to higher temperature, higher hydrogen pressure and greater amount of active catalyst are not required for this photocatalytic system. Moreover, this preliminary study is important and could serve as a reference for future applications in the pilot scale of treatment plant. Therefore, this study provides an elucidation of the performance of different types of flower-like ZnO in desulfurization of synthetic thiophene to develop advanced sulphur treatment systems that have the potential to comply with the permissible limit of sulphur-containing compounds worldwide.



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CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Currently, the petroleum industry is one of the largest industries in Malaysia and is a vital part of the national economy. Towards achieving developing country status, the industry is growing day by day to support the development of advanced technology. Apart from the positive impacts on the industry, adverse impacts also need to be considered. It is known that this largest industry is also major sources of hazardous, toxic, air and water pollutants which can adversely affect the environment and human (Kan et al., 2010). Therefore, petroleum refining is the most importance sector to separate and treat crude oil into safe and environmentally friendly petroleum products (petroleum gas, diesel fuel, motor oil and others) through a series of physical and chemical separation and treatment techniques. There are five major processes involved in crude oil refining, namely conversion, treatment, blending or combination and auxiliary processes. Among these processes, petroleum refining needs to be emphasized more to separate and reduce impurities, undesired and potentially harmful components from the products.

Speight (1980) reported that in petroleum, sulphur is the third most abundant element after carbon and hydrogen. About 0.05 to 5% present in crude oils. The sulphur content in petroleum could contribute to air pollution as it produces SO₂ species known as toxic gas during combustion (Alhaddad & Shawky, 2020). Severe corrosion of reactors and equipment could also occur during oil processing steps due the presence of sulphur compound (Rudreshwar et al., 2016). Due to this serious environmental issue, new regulation has been gazette to lower the sulphur content

(S-content) in fuel oils. Hence, the permissible limit of sulphur-containing compounds in fuels is 10-15 ppm worldwide (Amiri et al., 2020). Refining plays an important role especially during the petroleum refining process as this process could reduce sulphur content from the petroleum products. Hydrodesulfurization (HDS) is a conventional desulfurization technology applied during petroleum refining. This technology promotes the removal of sulphur compounds such as thiols, sulphides and disulphides by converting them into hydrogen sulphide (Shafi et al., 2000). However, HDS could lead to high capital cost as this process requires high temperatures ($>300^{\circ}\text{C}$), high hydrogen pressures (>30 atm) and more active catalysts to achieve deep desulfurization (Shawky et al., 2020). Moreover, some sulphur compounds in fuels, such as thiophene, are difficult to remove by typical HDS due to its stable aromatic ring structure (Di-shun et al., 2008). HDS technology can be burdensome to the petroleum industry owing to high capital cost and the sulphur content in fuels is still far from complying with standard regulations.

Thiophene is found as a contaminant in benzene as it has the simplest aromatic compound but contains sulphur atom and it has similar chemical properties similar to benzene (Mishra et al., 2011). In addition, thiophene is known as a sulphur pollutant as it is categorized as sulphur-containing compounds (SCCs) in petroleum. The sulphur content could lead to negative impact on the environment due to its toxic behaviour (Sadare et al., 2017). This compound is also difficult to oxidise and degrade as it has stable aromatic ring structure (Otsuki et al., 2000). Since conventional HDS is not effective, other alternative to deep desulfurization of petroleum oil was examined in this study to improve the cost-effectiveness of the process.

2.2 Thiophene

Before implementing the thiophene desulfurization technique, the properties and behaviour of thiophene need to be studied. Thiophene is defined as the simplest aromatic compound containing sulphur atom with the formula $\text{C}_4\text{H}_4\text{S}$ and belongs to heterocyclic compounds as it is structured as five-member ring consisting of one heteroatom, which is sulphur (Shah & Verma, 2018). Thiophene and its derivatives are usually present in petroleum oil or coal. Previous literature has described the physical behaviour of thiophene as a colourless liquid which has a mild pleasant odour reminiscent of benzene as it shares some chemical properties similar to benzene.

Thiophene also has high reactivity to sulphonation which is difficult to separate from benzene by distillation due to its similar boiling points (4°C at ambient pressure) (Mishra et al., 2011).

Table 2.1: Toxicological data for thiophene and its derivatives (Canada National Energy Board, 2006)

	<i>Thiophene</i>	<i>2-Methylthiophene</i>	<i>2-Acetylthiophene</i>	<i>2-Bromothiophene</i>
Acute Toxicity				
<i>Oral LD₅₀</i>	1400 mg/kg (rat)	3200 mg/kg (mouse)	50 mg/kg (mouse)	200-250 mg/kg (rat)
<i>Dermal LD₅₀</i>	830 mg/kg (rabbit)	No data	370 mg/kg (rat)	134 mg/kg (rat)
<i>Inhalation LC₅₀</i>	9500 mg/kg (mouse)	No data	1460 mg/m ³ , 1h (rat)	1.04 mg/L, 4h (rat)
Irritation				
<i>Skin</i>	Yes	Expected	Not reported	Yes
<i>Eye</i>	Yes	Expected	Predicted	Yes
Eco toxicity	- Caused acid rain that harm aquatic organism -Inflammation and irritation to respiratory system - Contribute to air pollution	- Caused acid rain that harm aquatic organism -Inflammation and irritation to respiratory system - Contribute to air pollution	- Caused acid rain that harm aquatic organism -Inflammation and irritation to respiratory system - Contribute to air pollution	- Caused acid rain that harm aquatic organism -Inflammation and irritation to respiratory system - Contribute to air pollution
Occupational exposure limits	None specified	None specified	2ppm (provisional)	1 ppm (provisional)
Persistence	Expect ultimate biodegradability	Expect ultimate biodegradability	Expect ultimate biodegradability	Expect very slow biodegradability
Materials to avoid	Strong oxidizers	Strong oxidizers	Strong oxidizers	Strong oxidizers
Conditions	Stable under normal conditions	stable under normal conditions	stable under normal conditions	slow decomposition unless cool/dark
Combustion products	Toxic oxides of S+CO, CO ₂	Toxic oxides of S+CO, CO ₂	Toxic oxides of S+CO, CO ₂	HBr during storage, CO, CO ₂

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