ADSORPTIVE DESULPHURIZATION OF DIBENZOTHIOPHENE BY USING BENTONITE-BASED ADSORBENT

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by

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LIST OF SYMBOLS

Symbol	Description	Unit
T	Operating temperature	°C
W	Weight of the adsorbent	g
V	Volume of the model oil	L
Ni	Nickel	-
Mg	Magnesium	-
Na	Sodium	-

LIST OF ABBREVIATIONS

DBT	Dibenzothiophene
ADS	Adsorptive desulphurization
HDS	Hydrodesulphurization
SO_x	Sulphur oxide gaseous
AC	Activated carbon
MMT	Montmorillonite
HCL	Hydrochloric acid
π	Pi-complexation bond
C_i	Initial concentration of model oil
Ce	Final concentration of model oil
qe	Equilibrium adsorption capacity
q_{max}	Adsorption constant-Langmuir
K_L	Adsorption constant-Langmuir
K_F	Adsorption constant-Freundlich
n	Adsorption constant-Freundlich
R_L	Separation factor
R^2	Correlation of coefficient

PENJERAPAN DISULFURISASI OLEH DIBENZOTHIOPHENE MENGGUNAKAN PENJERAP BERASASKAN BENTONIT

ABSTRAK

Desulfurisasi penjerapan telah menjadi salah satu tumpuan penyelidik sejak dekad yang lalu kerana penggunaan tenaga yang lebih rendah, mesra alam dan kos yang lebih murah. Dalam tesis ini, penjerap berasaskan bentonit digunakan untuk mengurangkan kepekatan dibenzothiophenes di dalam minyak model. Pada fasa awal eksperimen ini, lima jenis penjerap berasaskan bentonit yang berbeza (bentonit tulen, bentonit yang dicuci asid, Ni-bentonit, natrium-bentonit, dan magnesium-bentonit) telah disediakan. Kelima-lima bahan penjerap berasaskan bentonit ini telah diuji dalam keadaan biasa, dan hasilnya menunjukkan bahawa Ni-bentonit mempunyai penyahsulfuran yang tertinggi, iaitu 49.8%. Seterusnya, Ni-bentonit diuji dengan dua jenis kepekatan minyak model yang berbeza pada 100 ppm DBT dan 1000 ppm DBT. Keputusan menunjukkan bahawa Ni-bentonit berprestasi buruk dalam 100 ppm DBT dalam minyak model. Jadi, 1000 ppm DBT digunakan untuk minyak model Kemudian, Nikel-bentonit diuji dengan beberapa parameter lain. Parameter pertama yang dikaji ialah kesan dos penjerap ke atas desulfurisasi. Keputusan menunjukkan nilai optimum dos Ni-bentonit adalah antara 1.0 g. Seterusnya parameter yang diuji ialah kesan suhu terhadap peratusan disulfurisasi. Keputusan menunjukkan bahawa nilai suhu optimum untuk penyahsulfuran minyak model adalah 40°C. Ujian parameter ketiga ialah masa sentuhan antara penjerap dan penjerap. Keputusan menunjukkan bahawa nilai masa sentuhan yang optimum untuk penyahsulfuran minyak model adalah 2 jam. Parameter terakhir yang diuji ialah kesan peratusan pemuatan logam. Keputusan menunjukkan bahawa 30% pemuatan nikel memberikan penyahsulfuran yang tertinggi, iaitu 55%. Untuk model penjerapan, Keputusan menunjukkan bahawa proses penjerapan lebih sesuai dengan model isoterma Langmuir berbanding model isoterma Frreundlich.

ADSORPTIVE DESULPHURIZATION OF DIBENZOTHIOPHENE BY USING BENTONITE -BASED ADSORBENT

ABSTRACT

Adsorptive desulphurization has been one of the focus of the researchers over the past decade due to its lower energy consumption, environmentally friendly, and cheaper alternative. In this study, bentonite-based adsorbents are used to reduce the concentration of dibenzothiophenes in the model oil. Five different kinds of bentonite-based adsorbents; pure bentonite, acid-washed bentonite, Ni-bentonite, sodium-bentonite, and magnesium-bentonite, were prepared. These five bentonite-based adsorbents were tested under normal ambient conditions, and the result showed that Ni-bentonite has the highest desulphurization at 49.8%. Then, Ni-bentonite was tested in two different ranges DBT concentration; 100 ppm and 1000 ppm. The result shows that Ni-bentonite performed poorly in 100 ppm DBT model oil. Therefore, 1000 ppm of DBT model oil is chosen instead. Then, Nickel-bentonite is subjected to different parameters tests. In the effect of adsorbent dosage study, the result showed that the optimum desulfurization of Ni-bentonite dosage is 1.0 g. For the effect of temperature study, the result showed that the optimum temperature for desulphurization is 40°C. Regarding the effect of contact time between the adsorbent and adsorbate, the result showed that the optimum contact time for desulphurization 2 hours. The last parameter tested is the effect of the percentage of metal loading. The result showed that 30% of nickel loading provides the highest desulphurization percentage, at 55%. In the present study, the adsorption process was found to fit the Langmuir isotherm model better than Freundlich isotherm.

CHAPTER 1 INTRODUCTION

1.1 Dibenzothiophene and Bentonite

Energy consumption worldwide has been rising due to the blooming of many industries. Fossil fuel, known as petroleum, is one of the crucial sources of energy on the earth. Diesel, kerosene, and fuel oil are examples of petroleum fractional distillation products used to generate energy. Diesel is commonly used for heat engines such as trucks, buses, and diesel generators. Kerosene is famous for its usage in jet engines due to its low freezing point. While, fuel oil is mainly used to power the ships involved in international navigation (Audrey Errard, 2022). In the process of combustion of petroleum fractional distillation products, it releases energy and obnoxious Sulphur oxide (SO_X)

The nature of petroleum itself contains different kinds of sulphur compounds. Thus, when petroleum is combusted, the sulphur compound is converted into sulphur oxide. Among many kinds of sulphur compounds present in petroleum, dibenzothiophene is the one that to be focused on in the research. Dibenzothiophene (DBT) consists of two benzene rings fused to a central thiophene ring. It is a colorless solid that is chemically somewhat like anthracene (Ho, 2004).

Bentonite is the adsorbent used to conduct the adsorptive desulphurization for this research. It is a type of clay that can swell and mainly consist of montmorillonite. The montmorillonite consists of chemical components such as Aluminum Oxide, Magnesium Oxide, Silicon dioxide, potassium oxide, iron(ii) oxide, and Calcium Oxide. It is formed when ancient volcanic ash submerged in the seawater absorbed a lot of minerals and nutrients to become clay (Wan Ngah et al., 2011). Bentonite has a structure of one alumina sheet and two contracting tetrahedral silicate sheets. These two sheets of material are stacked so that there is enough gap for metal ions to be filled inside (Alexandre and Dubois, 2006). Being a part of the

clay material group, Bentonite is a widely available material. It also has a lower cost compared to other types of adsorbents. Besides, it is also proven that Bentonite has good intrinsic adsorption capacity (Toor et al., 2015).

1.2 Problem Statement

Air pollution is a severe problem in Malaysia. According to the Malaysia Department of Environment (MDOE), open burning, power stations, and motor vehicles are the main contributor to air pollution (Nizam et al., 2013). Carbon Monoxide, Nitrogen Dioxide, and Sulphur Dioxide are the primary sources of air pollution. From 2007 to 2008, sulphur dioxide emissions increased from 158,120 metric tons to 161,193 metric tons (Nizam et al., 2013). This is a massive issue as the presence of sulphur dioxide in the air can cause pollution such as acid rains and severely damage human health (Rall, 1974). The sulphur dioxide presence is attributed to the combustion of petroleum for energy generation, especially in the power station industry. In 2008, 12,865 metric tons of sulphur dioxide were released solely by motor vehicles (Nizam et al., 2013). The number is expected to increase exponentially due to the massive growth of vehicle possession in Malaysia. Motor vehicles in Malaysia mainly use fuel such as diesel and petrol as a source of energy. Before commercializing this fuel, it must be subjected to desulphurization to reduce the sulphur concentration.

There have been many ways to conduct the desulphurization process. The most common way is by hydrodesulphurization (HDS). However, this technique requires extreme operating conditions and expensive catalysts. Therefore, adsorption process is another appropriate way to conduct the desulphurization process. Adsorptive desulphurization involves the removal of sulphur through physicochemical adsorption (Dalai, 2021). It is a low-cost process and does not involve extreme operating conditions. Moreover, the adsorbents used are primarily widely available materials and low cost. Among them, bentonite clay has been gaining some attention from researchers. However, the sulphur removal efficiency of bentonite clay is a little less than

expected. Hence, the idea is to impregnate bentonite with a different metal. For example, by impregnating Zinc into bentonite clay, the desulphurization percentage increased from 45% to 60% (Ahmad et al., 2017). Thus, for this research, other metal ions such as Magnesium, Nickel, and Sodium are impregnated into the bentonite clay. The purpose is to determine their desulphurization based on the dosage, temperature, adsorption time, sulphur concentration, and metal percentage.

1.3 Objectives

The objectives of this research are

I.   To evaluate the adsorptive desulfurization of bentonite impregnated with a different metal group.

II.   To study the effects of operating parameters: adsorbent dosage, temperature and contact time.

III. To investigate the impact of metal loading on bentonite's adsorptive desulfurization.

IV.   To study the adsorption isotherm model of adsorptive desulphurization by a bentonite-based adsorbent

1.4 Scope of thesis

Adsorptive desulfurization has been widely studied due to its ability to conduct desulfurization at high efficiency with low cost and non-intensive energy process. Thus, understanding the adsorbent properties and the parameters affecting the desulfurization. This project aims to determine the optimum parameters of bentonite-based adsorbent in the desulfurization of model oil. First, five different kinds of bentonite-based are tested under standard c to decide which one is in the model oil's desulfurization. Once it is determined, the bentonite-based adsorbent is subjected to other different parameters such as concentration of model oil, adsorbent dosage, temperature, contact time, and percentage of metal loading. Throughout the testing, UV-spectrophotometer is used to obtain the reading of absorbance value. Finally,

adsorption isotherm models are also being fitted to determine the relationship between the adsorbent and adsorbate.

CHAPTER 2: LITERATURE REVIEW

This chapter focuses on different kinds of desulphurization techniques with further emphasis on different materials used as adsorbents for adsorptive desulphurization.

2.1 Different Sulphur Removal Techniques

There are many ways to conduct desulphurization. They are hydrodesulphurization , oxidative desulphurization, extractive desulphurization, biodesulphurization and adsorptive desulphurization.

2.1.1 Hydrodesulphurization (HDS)

It is considered one of the old methods in conducting the desulphurization process. HDS is used worldwide to remove sulphur from the petroleum refinery industry. HDS consisted of two routes of the mechanism. The first one is the direct removal of sulphur atoms to form biphenyl. The second route has two steps. Firstly, the sulphur molecule is partially hydrogenated(AL-Hammadi et al., 2018). The second step is eliminating the sulphur molecule through the hydrogenolysis of the C-S bond. It is a fact that HDS is an established process. Thus, it has been the main reason industries still prefer HDS over other methods. However, there are some disadvantages to this method. In order to conduct an optimum HDS process, the operating condition must be high, for instance, 300- to 400 ∘C and 5 to 13 MPa (Méndez et al., 2017). HDS also requires expensive catalysts such as Co or Ni. Furthermore, HDS also releases hydrogen sulfide, which is considered a pollutant.

2.1.2 Oxidative desulphurization

It is a desulphurization technique whereby an oxidant is used to oxidize the sulphur compound into sulfone, which is more polar. The compounds are removed by using a polar solvent. In order to oxidize the sulphur compound, a catalyst and oxidant are required. The commonly used oxidants are hydrogen peroxide, ozone, and tertbutyl hydroperoxide (Rajendran et al., 2020). Among them, hydrogen peroxide is regarded as the better oxidant. On the other hand,

the catalyst used can be metal oxides, zeolites, metal-organic frameworks, polyoxometalate, and carbon(Rajendran et al., 2020). The operating condition to conduct is low compared to HDS. This is a huge plus because the structure of the petroleum compound will not be damaged. Although oxidative desulphurization seems a possible commercial method, it has some significant disadvantages. For instance, the oxidants used have low selectivity towards the petroleum from the real-life feedstock, which causes the yield of the petroleum will also be severely reduced. This is due to the removal of the hydrocarbon part of the sulphur compound.

2.1.3 Extractive desulphurization

This desulphurization uses extractants such as acetonitrile, dimethyl sulfoxide, dimethylformamide, ethylene glycol, furfural, and polyethylene glycol. These solvents are chosen due to their high partition coefficient for aromatic compounds, non-toxic and high chemical, and thermal stability. The prominent advantage of this is that it does not affect the structure of the compounds in the fuel and can be operated in mild conditions (Sharma et al., 2013). However, research has shown that using these traditional extractants has low desulphurization while causing a considerable loss in fuel volume ((Sharma et al., 2013). Therefore, new extractants have been chosen with advancements in research, which are called ionic liquids. Ionic liquids have the advantage of not causing a massive loss in fuel volume and having better desulphurization. Some ionic liquids are 1-butyl-3-methylimidazoliumdicyano, methanide, and imidazolium (Ibrahim et al., 2015; Raj et al., 2019). The disadvantages of using these ionic liquids are their complexity in regeneration while being expensive.

2.1.4 Biodesulphurization

This desulphurization is done by using microorganisms or enzymes such as Rhodococcusrhodochrous. Agrobacterium, Alcaligenes, Bacillus, Brevibacillus, and Corynebacterium (Mohebali and Ball, 2016). The prominent advantage of this technique is that it can selectively remove the sulphur compound without altering the hydrocarbon fragment of

the removed sulphur compound. The way biodesulphurization works can be described with the example of the removal of DBT by using Rhodococcusrhodochrous. Four enzymes of Rhodococcusrhodochrous keep its nutrient from DBT and produce a final product of 2-hydroxybiphen (Mohebali and Ball, 2016). The disadvantages of this technique are the high cost of the media culture for these microorganisms and bacteria. Besides that, separating the oil and microbial biomass is a considerable as a tough process.

2.1.5 Adsorptive desulphurization

Adsorptive desulphurization is a process that extracts organic sulphur compounds from petroleum fractions. It is being done via either physisorption or chemisorption. It saves money on hydrogen because it works at such a low temperature and pressure. The adsorbent's textural properties significantly affect its adsorptive desulphurization. A vast surface area, pore volume, and many surface-active sites, as well as a high degree of structural strength and stability, make this material desirable (Dutta, 2007).

2.2 Adsorbents studied in adsorptive desulphurization

Many materials have been studied and potentially used as adsorbents recently: metal oxides, zeolite, mesoporous material adsorbents, and activated carbon and clay.

2.2.1 Metal oxides

Metal oxides are a good candidate for adsorbents due to their various desirable features, including ease of synthesis, high structural stability, and insolubility in common solvents. Al_2O_3, SiO_2, ZnO, TiO_2, and mixed metal oxides are the most often utilized metal oxide adsorbent. Al_2O_3 is particularly intriguing to researchers since it is inexpensive, readily available, and simple to prepare. Doping metal oxides with transition metals such as Ag, Zn, and Ni significantly increased their adsorption capability. The adsorption ability of alumina (Al_2O_3) for the removal of thiophene by adding Ag, Ni, and Zn. The result shows that silver has the highest adsorption effectiveness of the four metals (Liao et al., 2015).

Other research also has examined the adsorptive desulphurization of TiO_2-CeO_2 mixed metal oxide in jet fuel ((Watanabe et al., 2021). The surface-active oxygen species on TiO_2-CeO_2 acted as active sites and adsorbed sulphur molecules via electron donor-acceptor interaction. As a result, this mixed metal adsorbent was discovered to reduce the sulphur level of jet fuel to less than one part per million (Watanabe et al., 2021).

2.2.2 Zeolite

Zeolites are three-dimensional crystalline aluminosilicates with enormous exterior surface areas. Because of their stable skeletal structure and capacity to execute cation exchange, zeolites are more widely researched. The adsorption capacity and selectivity of metal cation-exchanged zeolites towards sulphur compounds are reported to be exceptionally high due to metal-based active sites on the surface. This is due to their tunable porosity for size-selective adsorption, high ion-exchange capacity, and good thermal stability. Na/Y, Ni/Y, La/Y, and Ce/Y are some examples of zeolites that have been used as adsorbents. Na/Y zeolite performed much better than other metal-exchanged Y zeolites due to its greater surface area and absence of nitrogen or aromatic chemicals in the feed (Yoosuk et al., 2020). However, the adsorptive ability of Na/Y zeolite reduces dramatically when aromatics and nitrogen compounds are included in the feed.

2.2.3 Mesoporous material-based adsorbent

MCM-41, SBA-15, and KIT-6 are some of the mesoporous adsorbents. MCM-41 is a mesoporous member of the silicate and aluminosilicate family. MCM-41 has a large surface area, well-ordered pores, and a large pore volume (Alvarado-Perea et al., 2020). Findings show that sulphur compounds have been removed from model oil and natural fuel feedstocks using MCM-41.

Mesoporous materials, such as MCM-41, are significantly unstable when it comes to heat; thus, their application is hampered. Adding organic molecules to MCM-41's structure can

help it become stabilized. Adding CuO to MCM-41 facilitated the absorption of sulphur compounds via the acid-base interaction, which is how sulphur is absorbed (Shan et al., 2011).

BA-15 is one of the most used ADS adsorbents; a claim stated that CeO_2 is in SBA-15 and can hold 0.165mmole/g of thiophene due to a strong bond between the S and Ce parts of it. In addition, because Ce was distributed throughout the small spaces of SBA-15, there were more surface metal active sites, resulting in a higher adsorption capacity of SBA-15 with CeO_2 added to it than the parent SBA-1.

KIT-6 has a bi-continuous cubic structure with interconnected cylindrical pores ranging from 8 to 10 nm (Wang et al., 2014) . It is impregnated with copper by using an ultrasound-assisted method. The experiment was designed to investigate thiophene adsorptive desulphurization. The result has shown that ultrasound assisted in forming a more significant number of Cu+2 active sites on the surface of the KIT-6 adsorbent, thereby increasing its ADS capacity. (Subhan et al., 2014).

2.2.4 Activated Carbon

Due to its low cost, high surface area, high porosity, and tunable pores, activated carbon (AC) is a widely used adsorbent. It can be made from various materials such as rice husk, bamboo, old tires, wood, fruit stone waste, waste plastic, and coconut shell. However, it also has been found that the adsorption of sulphur compounds is dependent on the type and quantity of oxygen functional groups (such as carboxylic acid, pyrone, lactone, and phenolic group) present on the activated carbon surface. Thus, researchers have attempted surface modification methods such as acid oxidation and impregnation of mono- or bimetals to form active metal sites and surface oxygen functional groups.

In terms of oxidation modification, Li et al. have used aqua regia to treat the ordered mesoporous carbon (CMK-3) material, resulting in the formation of carboxyl groups on the surface (Li et al., 2018). . The capacity of the surface-modified CMK-3 to adsorb sulphur

saturation was nearly double that of the parent CMK-3. Saleh et al. also investigated the ADS of DBT using manganese oxide incorporated activated carbon (MnO/AC) which showed a promising result.

For the impregnation of a different kind of mono- or bimetals into the activated carbon, Danmaliki et al. reported that the adsorption capacity of AC with Ce– Fe has increased (Danmaliki and Saleh, 2017). Ce and Fe active sites in this material enhance the material's adsorption capacity via complexation and the S–M-bond.

Besides activated carbon, nanotubes and graphite were also investigated for adsorptive desulphurization. This is due to their similar surface functionalities to activated carbons. Jha et al. have investigated the adsorption of carbon nanotubes (CNTs) and carbon nanofibers (CNFs) by using 250 ppm of DBT in a model diesel fuel. The result reported maximum adsorption of 43% and 35%, respectively.

2.2.5 Clay

Clays are naturally occurring short-range organized aluminosilicates. They, like zeolites, have a high adsorption capacity. Additionally, they are cheap and environmentally friendly. Ishaq et al. have examined the adsorption of DBT on acid-treated bentonite. The results show that the modified bentonite has adsorption capacities of 84.4 mg/g and 99.5 mg/. In addition, modified bentonite has increased surface roughness, active sites, and porosity. This makes it more effective at adsorption than parent bentonite.

2.3 Effect of different parameters for adsorptive desulphurization

Some parameters can affect the adsorptive desulphurization. They are adsorbent dosage, temperature, contact time and adsorbent regeneration.

2.3.1 Adsorbent dosage

The adsorption capacity of sulphur removal increases as the adsorbent dosage is increased. This is because of an increased number of accessible active sites. Ishaq et al. observed that

increasing the adsorbent dosage from 0.01 to 0.05 g/L enhanced the percentage of DBT adsorption to up to 98 percent. A similar pattern with acid-treated activated charcoal also has been observed. Ishaq et al. and Song et al. concluded that when the adsorbent dosage exceeded the optimal value, no further significant change in DBT adsorption occurred. This is mainly due to a lack of sulphur compounds that are not readily available for subsequent adsorption.

2.3.2 Temperature

Temperature is a critical process parameter in adsorption. It affects both the rate of adsorption and absorption capacity. The rate of adsorption is expected to rise as the temperature increases. When sulphur gains more heating energy, it penetrates the pores of adsorbents more quickly and eventually overcomes the activation energy barrier. Temperature's effect on adsorption capacity also depends on the adsorption process's type. Exothermic or endothermic processes are possible. Ishaq et al. also investigated the effect of temperature on DBT adsorption on bentonite. The results indicated that adsorption capacity increased as the temperature increased (Ishaq et al., 2017). This is because the diffusion rate via the pores of bentonite increases.

2.3.3 Contact time

The adsorption time of any adsorbent has a significant effect on its adsorption efficiency. In general, as the adsorption time rises, its capacity increases until it achieves equilibrium. For example, Ishaq et al. investigated bentonite's adsorption capability using DBT. An increase in adsorption time from 1 to 160 minutes had increased the adsorption capacity of bentonite from 45 mg S/g to 99.5 mg S/g. However, the further increase resulted in no significant change because of equilibrium. In this regard Zhang et al. explained that as adsorption time increased, adsorbates increasingly occupied the active sites of the adsorbent until they reached a saturation point, at which maximum adsorption occurred (Zhang et al., 2018). Therefore, adsorption can no longer happen on a large scale.

2.3.4 Adsorbent Regeneration

Adsorbent regeneration is the most crucial factor in evaluating the industrial viability of adsorptive desulphurization. The adsorptive desulphurization process regenerates the adsorbents using either a thermal or chemical approach. The thermal method involves using heat to increase the boiling points of organic sulphur compounds in the presence of air or inert gas. However, this approach damages adsorbents' structural stability and generates toxic H_2S and SO_x during sulphur combustion (Lee and Valla, 2019).

On the other hand, the adsorbents are washed directly with various organic solvents such as ethanol, methanol, toluene, and dichloromethane for the chemical technique. This method produces no emissions, hence making it preferable. Some parameters need to be addressed to obtain high adsorbent regeneration. They are based on Lee and Valla, 2019:

I.   The way of sulphur is adsorbed on the adsorbent, whether physically or chemically

II.   The polarity of the solvent

III.   The leaching tendency of active metals of the adsorbent to washing

2.4 Mechanism of adsorptive desulphurization

There are three different types of chemisorption interaction that occur during the adsorptive desulphurization process. They are pi complexation, acid-based interaction, and direct sulphur metal interaction.

2.4.1 Pi,π complexation

This type of interaction has two ways. First, it involves the transfer of electrons from the π orbitals of organic sulphur compounds to the vacant s-orbitals of adsorbent metal (Alvarado-Perea et al., 2020; Danmaliki and Saleh, 2017). Second, it involves the transfer of electron atoms from the d-orbitals of adsorbent metal atoms to anti-bonding π orbitals of organic sulphur compounds (Alvarado-Perea et al., 2020; Danmaliki and Saleh, 2017). For this kind of interaction, adsorbents such as zeolite, metal oxide, activated carbon, and mesoporous-based adsorbent have it.

2.4.2 Acid -base interaction

Through Lewis acid-base interaction, metal sites such as Fe, Cr, Al, Cu, Zn, Co, and Ag on the adsorbents operate as Lewis acidic sites and bond with the basic sulphur atoms in organic sulphur compounds (Danmaliki and Saleh, 2017; Yoosuk et al., 2020).

2.4.3 Direct sulphur-metal interaction

It is accomplished by donating lone pair electrons from sulphur atoms in organic sulphur compounds to metal atoms in adsorbents. Zeolite, metal oxide mesoporous-based adsorbent, and activated carbon also have this kind of interaction. (Danmaliki and Saleh, 2017; Yoosuk et al., 2020).

Table 1 summarize some of the research that has been done to determine the type of mechanism in adsorptive desulphurization.

Table 1: Comparison of sulphur removal mechanism done in past research

Adsorbent	Adsorbate	Type of mechanism	Reference
Copper-Montmorillonite	Model oil with Thiophene	π-complexation and acid base interaction	(Habimana et al., 2018)
Argentum- zeolite Y	Model oil with Thiophene	π-complexation and direct sulphur interaction	(Song et al., 2013)
Aluminum/Activated Carbon	Model oil with DBT	π-complexation and acid base interaction	(Ganiyu et al., 2016)

Argentum-Al$_2$O$_3$	Real fuel with benzothiophene and DBT	π-complexation and acid base interaction	(Neubauer et al., 2017)
Acid treated charcoal	Model oil with DBT	Acid base interaction	(Shah et al., 2018)

CHAPTER 3: MATERIAL AND METHOD

3.1 Materials

Bentonite was used as an adsorbent to remove the sulphur compound from the model oil. The sulphur compound is Dibenzothiophene (DBT), while the model oil is pure 95% n-hexane. A hydrochloric acid solution is used to wash the bentonite prior to the impregnation of the metal ion. The bentonite is impregnated with different kinds of metal from Nickel (II) Nitrate, Magnesium Chloride, and sodium hydroxide. All organic materials were obtained in reagent grade purities and used as received without modification.

Table 2: Materials used, supplier and its purpose

Chemical	Supplier	Purpose
Bentonite	Fisher Scientific	The adsorbent itself.
Hydrochloric Acid (HCl)	QRëC	To wash away all the remaining organic component inside the bentonite.
n-Hexane	Fisher Chemical	The solvent in model oil.
Magnesium Chloride	Acros Organics	The Mg precursor for bentonite impregnation.
Sodium Hydroxide	R&M chemicals	The Na precursor for bentonite impregnation.
Nickel (II) Nitrate	Acros Organics	The Ni precursor for bentonite impregnation.
Dibenzothiophene	Acros Organics	The sulphur compound.

3.2 Research Flow

Figure 1 shows the flow diagram of the research project. The research is about the adsorptive desulphurization of DBT using a bentonite-based adsorbent. Preparation of the bentonite impregnation, adsorptive desulphurization, and sulphur concentration analysis have been be carried out using methodologies that will be described later.
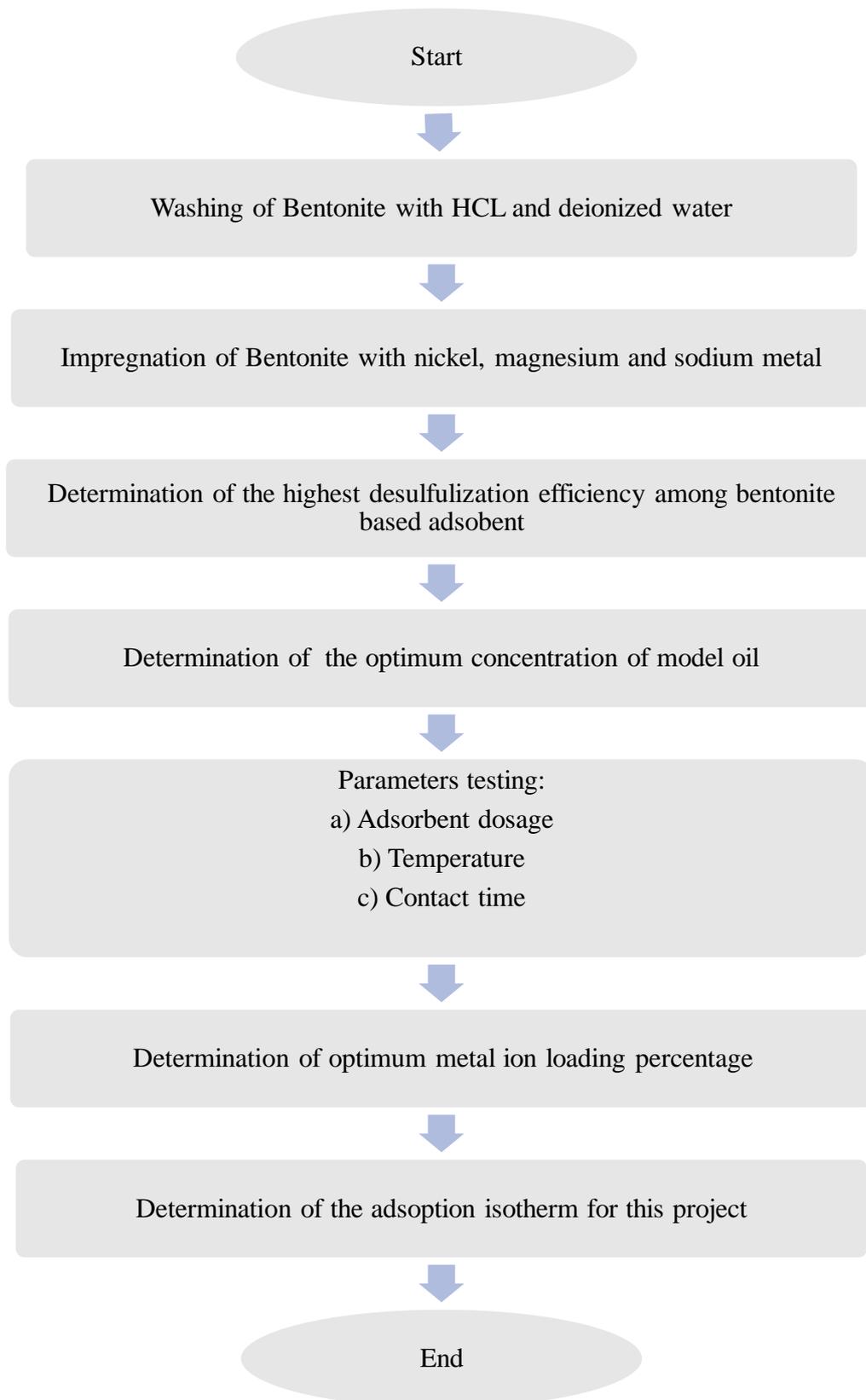
Figure 1:Research Plan flowchart

3.3 Method

3.3.1 Impregnation of bentonite with different kind of Metal

One hundred grams of bentonite is prepared and washed with 100 ml of 0.1M of HCl solution. The mixture is stirred on the heat plate for 3 hours. The mixture is filtered using filter paper, and the bentonite is rewashed with deionized water to remove the remnants of HCL. After the washing process, the mixture is again filtered to obtain the residue. The residue is left to dry in the oven overnight. The next day, the bentonite is ground until it becomes a fine powder.

The metal chosen for the impregnation of adsorbents are nickel, magnesium, and sodium; their respective precursor are magnesium chloride, nickel nitrate, and zinc nitrate sodium. For the impregnation step, 10 g of the bentonite is mixed with the precursor solution. First, the mixing process is conducted so that only 10% of the metal is loaded inside the bentonite. (The detailed calculation to obtain the 10% metal loading inside the bentonite is shown in the Appendix 1). Next, each solution is stirred on the hot plate for 2 hours at 60°C. The solution is then filtered by using filter paper to obtain the residue. Once the residue is obtained, it is left inside the oven overnight to be dried. The impregnated bentonites are ground the next day until they become a fine powder. Afterward, the impregnated bentonites are calcinated in the furnace at 750 °C for 4 hours. Finally, it was left for a few hours to cool down and kept in an airtight bottle for further use.

3.3.2 Desulphurization of model oil

Model oil is prepared by adding 1.0 g of DBT into 1.0 liter of hexane. Then, 20 ml of the model oil was taken, and 1.0 g of impregnated bentonites were added to the Erlenmeyer flask. Next, the model oil is stirred on a hot plate with a magnetic stirrer for one hour at 30°C. During the stirring process, the Erlenmeyer flask is covered with a lid being done

under the fume hood. The model oil is then filtered through a filter paper. The filtrate is then stored inside a round flask for analysis purposes.

Two critical experiments needed to be conducted before testing other parameters. The first experiment is determining desulphurization among bentonite-based adsorbents, which are Ni-bentonite, magnesium-bentonite, and sodium-bentonite. The second experiment is determining the optimum concentration of model oil by using the bentonite-based adsorbent with the highest desulphurization from the previous experiment. For the second experiment, 100 ppm and 1000 ppm of DBT in model oil are tested. Once the highest desulphurization among bentonite-based adsorbent and optimum model concentration is determined, the other parameters can be tested. The parameters tested during the desulphurization of model oil are the adsorbent dosage, temperature, contact time, and percentage of metal loading. The procedure is the same for each of the parameters tested.

3.3.3 Sulphur Analysis

The sulphur analysis is conducted by using UV-spectrophotometer. A calibration curve is constructed first before doing any testing. The calibration is constructed by varying the concentration of DBT in model oil to 200 ppm, 400 ppm, 600 ppm, 800ppm, and 1000 ppm. The calibration curve is shown in Figure 2.
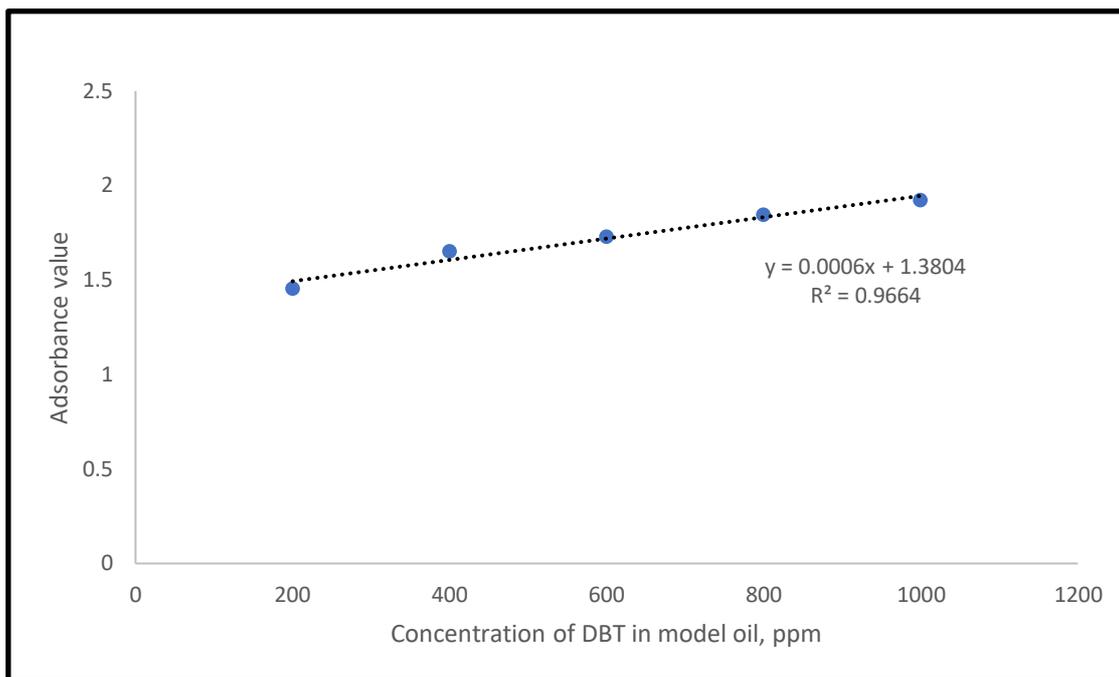
Figure 2:Calibration curve of DBT in model oil

Since the R^2 of the calibration curve is more significant than 0.95, it can be used for further calculation. Once the calibration curve is obtained, sulphur analysis is conducted. For the testing, the wavelength of the UV-spectrophotometer is set to be 325 nm. Next, a blank which contains only the solvent is tested to obtain a 0.00 absorbance value. Once the zero-absorbance value is obtained, the actual testing can be done. One thing to be noted is that since the solvent used for the model oil is quickly evaporated and toxic, quartz cuvettes are used alongside the cuvette cover.

The reading of the UV- spectrophotometer for each sample, which is the absorbance value, is taken three times. For each of the absorbance values, the final concentration, C_e of the model oil can be determined by using the linear equation from the calibration curve, which is:

$$y = 0.0006x + 1.3804 \quad (Equation\ 1)$$

Since the y-value is the absorbance value, it can be substituted into the equation to obtain the final concentration of model oil. Once the C_e is obtained, the

desulphurization can be calculated using the formula below since the initial concentration of model oil, C_i is already known, 1000 ppm.

$$Desulfurization = \frac{C_i - C_e}{C_i} * 100\% \quad (Equation\ 2)$$

The desulphurization calculated from each absorbance value is averaged. Finally, a graph is formed with x-axis as the parameter and y-axis as the desulphurization.

3.3.4 Adsorption model

The adsorption model or isotherm can be defined as a graphical representation showing a relationship between adsorbate that has been adsorbed and adsorbate that remained inside the test medium at equilibrium (Desta, 2013). In this research, adsorption is graphically represented to describe the relationship between the amount of DBT adsorbed and the amount of DBT remaining in the model oil at equilibrium. In order to test what kind of model fits the adsorptive desulphurization of DBT, two well-known isotherms were tried: Freundlich and Langmuir.

Three different C_i of model oil is prepared, with concentrations of 500 ppm,700 ppm, and 1000 ppm. Each of them is subjected to adsorptive desulphurization by using 0.5 g of Ni-bentonite for 1 hour at 30°C. After one hour, their absorbance value is recorded, and their C_e is calculated. Once their C_e is determined, equilibrium adsorption capacity, qe is calculated by using the formula:

$$q_e\left(\frac{mg}{g}\right) = \frac{C_i - C_e}{W} * V \quad (Equation\ 3)$$

Whereby W is the amount of adsorbent used, which is 0.5g, and V is the volume of the model oil which is 20 ml. Once q_e is determined, the linearized Freundlich and Langmuir equation can create the adsorption model. Those linearize equations are shown below:

Langmuir linearized equation

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (Equation\ 4)$$

Freundlich linearized equation

$$lnq_e = \frac{1}{n} lnq_e + lnK_f \quad (Equation\ 5)$$

When these equations are plotted, the result will be a straight line. Finally, the constant adsorption parameter ; (K_L, q_{max}, n and K_F) can be determined by the y-intercept of the plotted graph.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Effect of Different Metal Impregnation on Bentonite

Nickel, magnesium, and sodium are chosen metals to be impregnated into bentonite. These metals are chosen because they are from different of group of periodic tables. Sodium from the group 1 alkali metal, magnesium from group 2 alkaline earth metal, and nickel are part of the transition metal group. Since they are from different groups, they have different chemical properties. Thus, impregnation of each of them will bring different effects towards desulphurization . The impregnation of metal is done through the wet impregnation method. This method is chosen due to its simplicity, fast process, and inexpensive. One way to know whether the impregnation is successful is by looking at the bentonite color changes. This can be seen in figure 3 below, whereby the impregnation of nickel to bentonite causes the bentonite color to change from light brown to green. The green color is attributed to precursor metal which is Ni (II) ion.
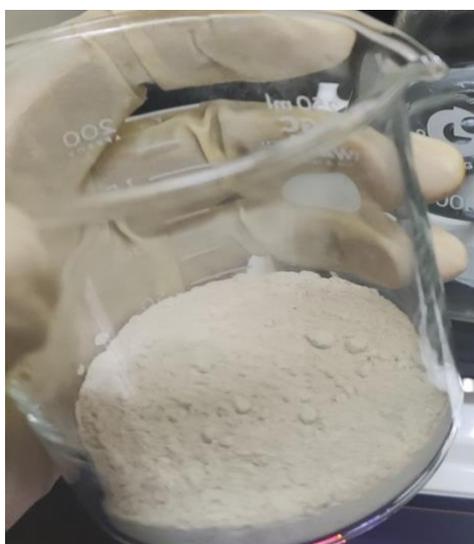
Figure 3:Pure bentonite

Figure 4: Nickel-bentonite

The effect of impregnating metal into bentonite is tested for it desulphurization. Apart from testing the impregnated bentonite adsorbents, two other kinds of bentonite-based adsorbent were also tested. They are pure bentonite and "washed" bentonite. "Washed" bentonite is bentonite that had been washed with HCl and deionized water. On the other hand, pure bentonite is bentonite without any prior changes. The result for desulphurization among five of these bentonite-based adsorbents is shown in the Figure 5.
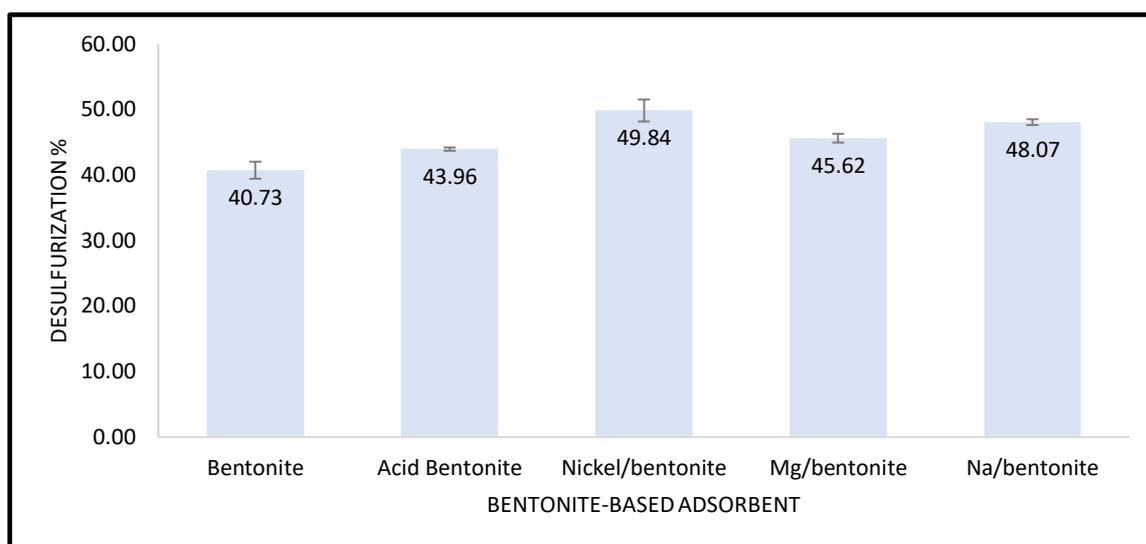
Figure 5: Desulphurization of different bentonite-based adsorbents

[Condition: 10% metal loading, 1.0 g adsorbent dosage, 30°C operating temperature, 20 ml of 1000 ppm of DBT in model oil & 1.0 of hour contact time]

Ni-bentonite has the highest desulphurization, which is at 49.8%. Following the second place is Na-bentonite with a slightly lower desulfurization at 48.1%. The third is Mg-bentonite, with 45.6 % of desulphurization. For the last two places, both bentonite and "washed bentonite" have 40% and 43% desulphurization. Based on the result above, it is shown that bentonite does have the capability to adsorb sulphur compounds from model oil. Washing bentonite with HCl followed by deionized water does increase its adsorption capacity. This is because the HCl removed all the organic material inside the bentonite (Nizam et al., 2013). The result also shows that the impregnation of metal onto the "washed bentonite" does increase the adsorption capacity. Ni-bentonite has the highest desulphurization may be attributed to nickel being part

of the transition metal group in the periodic table because it is similar to the research done by Yi et al., 2013. The research involved copper (II) modified bentonite used to desulphurize the model oil. The metal used was copper, which is also a of transition metal. The research stated that the sulphur atom quickly loses electron pairs since its low electronegativity. Thus, it quickly forms S-M σ bonds with the Cu(II) (Yi et al., 2013). Since nickel is also a part of transition metal, similar interaction may happen. Waqas Ahmad's research (2017) also shows that Nickel-MMT has high desulphurization in kerosene (41%) and diesel (55.9%). Since Ni-bentonite has better desulphurization than the rest, it is chosen to be tested for other parameters.

4.2 Effect of DBT concentration

It is crucial to determine the optimum DBT concentration of model oil that can yield high desulphurization based on the adsorbent used. The adsorbent potential can be fully utilized by knowing the optimum range. In order to study this effect, two sulfur concentrations in model oil are prepared: 1000 ppm (high concentration) and 100 ppm (low concentration). The procedure section has already mentioned the preparation of 1000 ppm of the model. On the other hand, 100 ppm of DBT in model oil is prepared through the dilution method by using the formula:

$$M_1 V_1 = M_2 V_2 \quad (Equation\ 6)$$

M_1 is the initial concentration of DBT in model oil, M_2 is the desired concentration of DBT in model oil , V_2 is the volume of model oil with desired DBT concentration and V_1 is the initial volume of model oil. The adsorptive desulphurization of model oil is done by using Ni-bentonite. The model oil used has two different concentrations, which are 100 ppm of DBT in model oil and 1000 ppm of DBT in model oil. The result for their desulphurization in figure 6 below.