T.R
YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
CHEMICAL ENGINEERING DEPARTMENT

# STUDY AND REMOVAL SOME SULFIDE COMPOUNDS FROM CRUDE OIL VIA ADSORPTION BY ZnO – NANOPARTICLE

M.Sc. THESIS

PREPARED BY: Amanj Wahab SAYDA
SUPERVISOR: Prof. Dr. Nahit AKTAS

VAN–2017

T.R
YUZUNCU YIL UNIVERSITY
INSTITUTE OF NATURAL AND APPLIED SCIENCES
CHEMICAL ENGINEERING DEPARTMENT

# STUDY AND REMOVAL SOME SULFIDE COMPOUNDS FROM CRUDE OIL VIA ADSORPTION BY ZnO – NANOPARTICLE

M.Sc. THESIS

PREPARED: Amanj Wahab SAYDA

VAN–2017

## ACCEPTANCE and APPROVAL PAGE

This thesis entitled "STUDY AND REMOVAL SOME SULFIDE COMPOUNDS FROM CRUDE OIL VIA ADSORPTION BY (ZnO-NANOPARTICLE)" presented by Amanj Wahab SAYDA under supervision of Prof. Dr. Nahit AKTAŞ in the department of Chemical Engineering has been accepted as a M. Sc. thesis according to Legislations of Graduate Higher Education on 18/05/2017 with unanimity of the members of jury.

| | |
|---|---|
| Chair: Prof. Dr. Nahit AKTAŞ | Signature: |
| Member: Doç. Dr. Şenol KUBİLAY | Signature: |
| Member: Yrd. Doç. Dr. Zeynep Şilan TURHAN IRAK | Signature: |

This thesis has been approved by the committee of The Institute of Natural and Applied Science on 02./06../2017. with decision number 2017..26-1

T.C.

Signature.........

Director of Institute

# THESIS STATEMENT

All information presented in the thesis obtained in the frame of ethical behavior and academic rules. In addition all kinds of information that does not belong to me have been cited appropriately in the thesis prepared by the thesis writing rules.

Signature

Amanj, Wahab SAYDA

# ABSTRACT

## STUDY AND REMOVAL SOME SULFIDE COMPOUNDS FROM CRUDE OIL VIA ADSORPTION BY ZnO – NANOPARTICLE

SAYDA, Amanj Wahab
M. Sc. Thesis, Chemical Engineering
Supervisor: Prof, Dr. Nahit AKTAS
2017, 84 pages

Because of the dangerous of the refractory sulfur in the oil and the problems it causes to the environment where human beings are living with other creatures as well as using fuel or other types of energy, sulfur causes decay of the operation systems and the spring of certain gases such as SO and $SO_2$.

For that reason such the one just mentioned above, this study has been devoted to remove sulfur out of oil at the stage of preparing oil for purification, particularly in case of the existence of sulfur in a high ratio in the pure oil. In this field, the ration of sulfur compounds becomes 1.9640 w.t%.

Used the adsorption methods by using zinc oxide non-particle ZnO 80 nm for high activity, we can measure the effect of time i. e. sticking time, where the ratio of sulfur adsorbent increases with time to an extent that it reaches a saturation state where the effect does not increase. The effect of temperature is one of the other factors that their effect on the adsorption process was studied 25-45 $^0$C, where the decrease in the removal of sulfur compounds showed an increase in temperature.

The results obtained at throughout this study show a decrease at the process of adsorption, for adsorption takes place with absorption, whereas the width of zinc oxide non-particle ZnO shows important results with the increase of the density from 0.1 to 0.5 g and the stability of the ratio 38 $^o$C heat temperature and according to the system.

**Keywords:** Adsorption process, Crude oil, Sulfur compounds, Zinc oxide nanoparticle.

# ÖZET

## ÇİNKO OKSİT NANOPARTİKÜLLERİ TARAFINDAN ADSORPSİYON YOLUYLA HAM PETROLDEN SÜLFÜR İÇERİKLERİNİN İNCELENMESİ VE TASFİYES

SAYDA, Amanj Wahab
Yüksek Lisans Tezi, Kimya Mühendisliği Bölümü
Tez Danışmanı: Prof. Dr. Nahit AKTAŞ
Mayıs 2017, 84, sayfa

Ham petrolde bulunan sülfür içeriği oldukça büyük bir tehlike arz etmekte, insanlarla diğer canlıların yaşadığı çevreye zarar vermekte, işletim sistemlerinin aksamasına ve bozulmasına ayrıca SO ve $SO_2$ gibi toksik gazların yayılımına sebep olmaktadır.

Bu çalışma bu sebeplerden dolayı sülfür içeriği yüksek olan ham petroller başta olmak üzere, ham petrolden sülfürün tasfiyesi amacıyla hazırlanmıştır.Calışmanın yürütüldüğü petrol alanında sülfür içeriklerinin oranı %1.9640 düzeyindedir. Yüksek etkililik için çinko oksit nanopartikülleri yoluyla kullanılan adsorpsiyon metotları sayesinde zamanın etkililiğini (yüzeye tutulma süresi) hesaplayabilirizçünkü.

Zamanla sülfür adsorbentinin oranı yükselmektedir ancak doyma noktasına ulaştıktan sonra etkisi daha fazla artmamaktadır. Adsorpsiyon süreci üzerinde onemli bir etkisi bulunan sıcaklık faktorü 25-45 °C incelenmiştir. Sıcaklık arttıkça tasfiye edilen sülfür içeriğinin oranında bir azalma olmuştur ancak 38 °C stabil sıcaklıkta çinko oksit nanopartiküllerinin genişliğinde ve 0.1-0.5 g arasında değişen yoğunlukların artışında onemli sonuçlar elde edilmiştir.

**Anahtar kelimeler**: Ham petrol, Çinko oksit nanopartikülleri, Adsorpsiyon süreci ve sülfür içerikleri.

# ACKNOWLEDGMENT

At the end of my thesis, I would like to thank all those people who made this thesis possible and an unforgettable experience for me.

Firstly, I would like to express my deepest sense of gratitude to my supervisor Prof. Dr. Nahit AKTAS for the continuous support and help me to get finish my MSc study, course work, laboratory and academic research. I would never forget all the chat and moment he had spent with me.

I would also like to thank, all the teachers, at Yuzuncu Yil University, Faculty of, Engineering department of Chemical Engineering

Finally, I would like to thank my family, my parents, my brothers, and sisters, and my children and my very sincere thanks go to my wife for supporting me spiritually throughout writing this thesis and my life in general, I would not have been able to complete this thesis without their continuous love and encouragement.

## TABLE OF CONTENTS

**Pages**

**Pages**

# LIST OF TABLES

**Tables** **Pages**

# LIST OF FIGURES

**Figures** **Pages**

# SYMBOL AND ABBREVIATION

Some symbols and abbreviations used in this study are presented below, along with descriptions.

| **Symbol** | **Description** |
|---|---|
| **R** | Alkyl radicals |
| **C** | Carbon |
| **O** | Oxygen |
| **S** | Sulfur |
| **N** | Nitrogen |
| **Ni** | Nickel |
| **V** | Vanadium |
| **Fe** | Iron |
| $SO_2$ | Sulfur dioxide |
| $CS_2$ | Carbon disulfides |
| $SO_3$ | Sulfur trioxide |
| $CH_3SCH_3$ | Dimethyl sulfide |
| $CH_3SSCH_3$ | Dimethyl disulfide |
| **G** | Gram |
| **L** | Litter |
| $^{O}C$ | Celsius |
| $F^{o}$ | Fahrenheit |

| **Abbreviations** | **Description** |
|---|---|
| **PAHs** | Polyaromatic hydrocarbons |
| **BC** | Before Christy |
| $H_2S$ | Hydrogen sulfide |
| **ZnO** | Zinc oxide |

| **Abbreviations(continue)** | **Description** |
|---|---|
| **CnH2n+2** | Generic molecular formula of alkane |
| **CnH2n** | Formula of Naphthenic hydrocarbons |
| **RCS** | Mercaptans |
| **NHDS** | Non-Hydrodesulphurization |
| **ODS** | Oxidative desulfurization |
| **BDS** | Biodesulfurization |
| **NPs** | Nanoparticles |
| **$\Delta H$** | Enthalpy |
| **BET** | BrunauerEmmett-Teller |
| **GC** | Gas chromatography |
| **Ce** | The equilibrium concentration |
| **Qo** | Maximum amount of adsorption |
| **KL** | Langmuir constant |
| **W.t %** | Ratio percentage |
| **PPM** | Part per million |
| **API** | American Petroleum Institute |
| **PTB** | Pounds per thousand barrel |
| **CST** | Centistokes |

# 1. INTRODUCTION

Crude oil is the world's largest and most extensive source of energy that is consumed as vehicle fuels such as gasoline, jet fuel, diesel and so on (Hosseini and Hamidi, 2014). Crude oil is an extremely complex mixture consisting of alkanes (A), naphthenes (N), olefins (O), monoaromatic, polyaromatic hydrocarbons (PAHs), steranes, hopanes , and some trace components containing sulfur and nitrogen etc. the content of sulfur in crude oil can vary from 0.05% to 10% (Hua et al., 2004 ).

Sulfur compounds are present in crude oil as mercaptans, mono- and disulfide dies with the general formula R-SH, R-S-$R_1$, R-S-S-$R_1$, where R and $R_1$ are the alkyl radicals. Mercaptans are very corrosive whereas mono- and disulfide are not. Examples of cyclic sulfur compounds are thiophenes and benzothiophene3- (Chaudhuri, 2011). Hydrogen sulfide $H_2S$ gas is a common gaseous pollutant which is colorless, odorous, highly toxic, corrosive for pipelines and poisonous for catalysts (Hazrati et al., 2014).

Health effects attributed to sulfur oxides are due to exposure to sulfur dioxide, sulfate aerosols, and sulfur dioxide adsorbed onto particulate matter. Alone, sulfur dioxide will dissolve in the watery fluids of the upper respiratory system and be absorbed into the bloodstream. Sulfur dioxide reacts with other substances in the atmosphere to form sulfate aerosols. Since most sulfate aerosols are part of PM 2.5 (Anonymous, 1998).

The hazardous sulfur compounds are emerged from the sour crude oil over an extended period of time, and the evolution of these compounds produces a serious environmental and safety problem. Not only the evolution of the sulfide compounds does, such as hydrogen sulfide and sulfur dioxide, from sour crude oil, create a serious environmental and safety problem, but also these compounds attack the metal components of the oil well, as well as pipelines and storage tanks, causing brittleness and/or corrosion of the metal components (Collins et al., 1998). The production of hydrocarbon fuels with low sulfur contents and organic aromatics gains rising importance among researchers. Hydrocarbon fuels containing high contents of sulfur compounds have gained tremendous interest not only from scientific societies but also from governmental organizations (Darwish, 2015).

Therefore, desulfurization of crude oil is extremely important in the petroleum processing industry. Several processes have been proposed in the past to deal with the problem of removing these compounds from crude oil. The most important and common industrial process is that of treating the fuel under high temperatures and high pressures with hydrogen. This process is called hydrodesulfurization HDS and has received extensive attention since its discovery in 1930’s (Campos-Martin et al., 2010). Desulfurization refers to processes to remove sulfur; in general, methods for deep desulfurization of liquid hydrocarbon fuels can be classified into catalytic hydrodesulfurization HDS with improved and new catalysts, chemical oxidation, adsorption, extractive desulfurization, and biodesulfurization by using special bacteria among them, selective adsorption appears to be one of the promising approaches for ultra-deep desulfurization (Zhou et al., 2006).

Oxidative desulfurization ODS has been considered as a further new technology for the reduction of sulfur In ODS. This desulfurization process includes two stages: (i), oxidation in a first step; and (ii), and eventually liquid extraction. It is evident that the greatest advantages of the ODS process are low reaction temperature (Campos-Martin et al., 2010). Author process Desulfurization by extraction is based on the fact that organosulfur compounds are more stable than hydrocarbons in a solvent. One of the most attractive features of the extraction method is its applicability at low temperature and pressure (Song, 2014).

The adsorption desulfurization process of sulfur compounds in crude oil is an economically viable method for the attainment of diesel oil with low sulfur content. Adsorptive desulfurization processes are considered among the most economically attractive techniques due to their simple operating conditions and the availability of inexpensive and regenerable adsorbents such as reduced metals, metal oxides, alumina, metal sulfides, zeolites, silica, and activated carbon (Al Zubaidi et al., 2015). The ability of nanotechnology to enhance catalytic activity opens the potential to replace expensive catalysts with lower amounts of inexpensive Nanocatalysts (Safaei-Ghomi et al., 2013). Although zinc oxide has high sulfur compounds removal efficiency (Song, 2014). Zinc oxide nanoparticles have a great advantage to apply to a catalytic reaction process due to their large surface area and high catalytic activity (Kumar et al., 2013).

## 1.1. The Aim of This Study

The present study focusing on the removing sulfur compounds and its different compounds in the crude oil which include (mercaptans, thiophenes, thiophene, dibenzothiophenes, dihydrogen sulfur) in the process of adsorption by using zinc oxide nanoparticle 80 nm workers by using a conical flask.

This study aims at:

1- Keeping and removing sulfur compounds.

2- Reducing the environmental pollution.

3- Collecting crude oil from sulfur compounds which make the process of purification and reoccurring easier.

4- Reducing the other compounds which occur with sulfur like the compounds of amines or carboxyl oxide.

5- Reducing the process of corrosion in the oil system (filtering systems and distillation**).**

# 2. GENERAL INFORMATION

## 2.1. Crude oil

The uses of crude oil as a fuel have been known already before the Christian era, with Persia as a supplier of the western world. Two hundred years BC the Chinese used kerosene for the lamps in the emperor’s palace. Crude oil is an organic liquid substance often found below the Earth’s surface. It is made up of thousands of molecules composed of different hydrogen and carbon atoms. Such compounds are called hydrocarbons (Qabazard and Fantini, 2011).

The crude oil formation occurs by various hydrocarbons combining with certain minerals such as sulfur under extreme pressure. Modern day scientists have proven that most if not all crude oil fields were created by the remains of small animal and plant life being compressed on the seabed by billions of tons of silt and sand several million years ago.

When small sea plants and animals die they will sink, they will then lie on the seabed where they will decompose and mix with sand and silt. During the decomposition process, tiny bacteria will clean the remains of certain chemicals such as phosphorus, nitrogen, and oxygen (Anonymous, 2016)a.

Crude oil is the largest and most widely used source of energy in the world. Major portions of the crude oils are used as transportation fuels such as gasoline, kerosene (jet fuel) and diesel (Abel Adekanmi and Folorunsho, 2012). Crude oil is a complex mixture consisting of 200 or more different organic compounds, mostly alkanes single bond hydrocarbons, and smaller fraction aromatics six-ring molecules such as benzene, $C_6H_6$ (Devold, 2013). The nature of the crude depends on the original biological source material and the geochemical forces to which it has been subjected (Grimwood, 2001).

Although exactly how crude oil originated is not established, it is generally agreed that crude oil is derived from marine animal and plant debris subjected to high temperatures and pressures. It is also suspected that the transformation may have been catalyzed by rock constituents. Regardless of their origins, crude oil is mainly constituted of hydrocarbons mixed with variable amounts of sulfur, nitrogen, and oxygen compounds. Metals in the forms of inorganic salts or organometallic compounds are present in the crude mixture in trace amounts, the ratio of the different constituents in crude oil, however, varies appreciably from one reservoir to another (Kasali et al., 2011).

## 2.2. Classification of crude oil

The varied and complex composition of crude oil has been recognized by petroleum chemists for many years. Engl and Hofer record several methods of classification dating back to 1900. Early American nomenclature in this regard is well stated by Bacon and Hamor (Smith, 1968). The classification falls into two categories

1- Those proposed by chemical engineers interested in refining crude oil.

2- Those presented by geologists and geochemists as an aid to understanding the source, maturation, and history. The first type of classification is concerned with the quantities of the various hydrocarbons present in crude oil and their physical properties, such as viscosity and boiling point. The second type schemes of interest to geologists are concerned with the molecular structures of oils because these are keys to their source and geological history. One of the schemes developed in U.S. bureau of mines (smith, 1927 lane, and Garton, 1935).

3- Crude oil is classified into paraffinic, naphthenic, and intermediate types according to their distillate fractions at different temperature and pressure (Selley, 1985). Later several classification schemes have been published including, paraffin’s, naphthenes, aromatics, asphaltenes, the composition of an example crude oil is presented 40 to 80% Saturates 15 to 40% Aromatics 0 to 20% Resins and Asphaltenes .The composition of 636 crude oils from around the world have been compared by Tissot and Welte, Tissot and Welte found that 95% of the crude oils produced around the world fell into this distribution (McMillen et al., 2001).

## 2.3. The composition of crude oil

Crude oil refers to a wide range of natural hydrocarbon substances and refined products, each having a different chemical composition. Crude oil is a mixture of the highly variable proportion of hydrocarbon but differs from lighter oils to heavier oils and bitumen (Younes, 2012). Crude oil products have a wide variety of forms that vary from gaseous and liquid fuels to near solid machinery lubricants. In addition, asphalt – the residue of many refinery processes and once considered a useless by-product – is now a premium value product for highway surfaces, roofing materials, and miscellaneous waterproofing uses. Crude petroleum is a mixture of compounds that boil at different temperatures, and so can be separated into a variety of different generic fractions by distillation.

The terminology of these fractions has been bound by the utility and often bears some relationship to their composition. The molecular composition of petroleum covers a wide range of boiling points and hydrocarbon compounds. These compounds have widely varying carbon numbers together with other compounds containing nitrogen, oxygen, and sulfur, as well as metallic (porphyrinic) constituents (Speight, 2011).The crude oil mixture is composed of the following groups:

1. Hydrocarbon compounds (compounds made of carbon and hydrogen).
2. Non-hydrocarbon compounds.
3. Organometallic compounds and inorganic salts (metallic compounds) (Matar and Hatch, 1994).

### 2.3.1. Type of hydrocarbon

Compounds solely made of carbon and hydrogen is called hydrocarbons. These hydrocarbons are classified as paraffin, naphthenes, aromatics, and olefins. Crude oil contains these hydrocarbons in different proportions, except olefins, which are produced during processing. Paraffin is saturated with hydrocarbons. The homologous series of these hydrocarbons are called alkanes (Chaudhuri, 2011). The hydrocarbons in crude oil can generally be divided into four categories:

1-Paraffins: Alkanes are saturated hydrocarbons having the general formula $CnH_2n+_2$. The simplest alkane, methane $CH_4$, is the principal constituent of natural gas. Methane, ethane, propane, and butane are gaseous hydrocarbons at ambient temperatures and atmospheric pressure. They are usually found associated with crude oils in a dissolved state. Normal alkanes (n-alkanes, n-paraffin) are straight-chain hydrocarbons having no branches. Crude oils contain many short, medium, and long-chain normal and branched paraffin's (Selley, 1985).

These can make up 15 to 60% of crude oil and have a carbon to hydrogen ratio of 1:2. These are generally straight or branched chains, but never cyclic compounds. Paraffin is the desired content in crude and what are used to make fuels. The shorter the paraffin is, the lighter the crude oil (Anonymous, 2016)b.

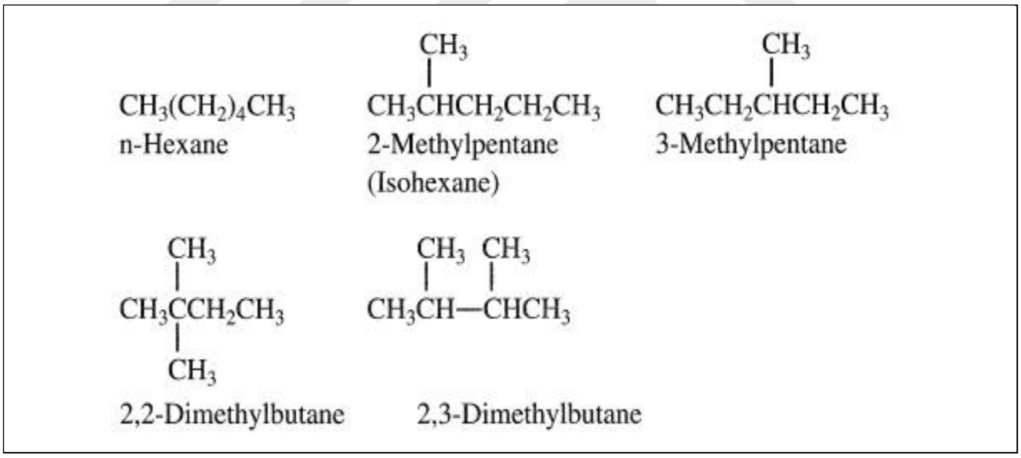


Figure 2.1. Type of paraffin of hydrocarbon in crude oil (Matar and Hatch, 1994).

2. Naphthenes. Naphthenic hydrocarbons have the formula $C_nH_{2n}$. All bonds of carbon with hydrogen are saturated. As such, naphthenic hydrocarbons in crude are also relatively stable compounds. Naphthenic hydrocarbons are the most abundant class of hydrocarbons in most crude oils. Their composition in oil can vary from 25 to 75%. Usually, a number of naphthenes in crude oil fraction increases as the boiling point of the fraction also increase. However, there is an exception. The number of naphthenic

hydrocarbons decreases with an increasing boiling temperature for heavy oils. This can be explained on the basis of the increasing of aromatic compounds in heavy oils (Simanzhenkov and Idem, 2003).

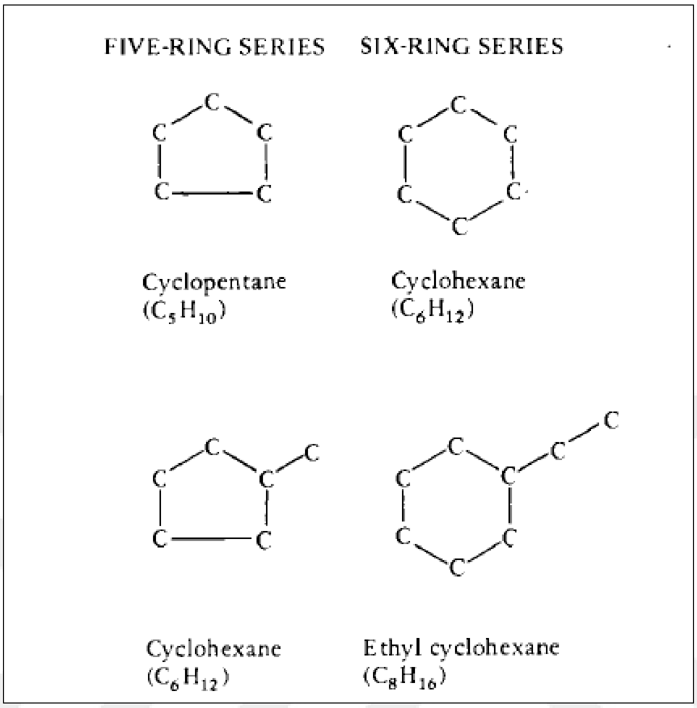


Figure 2.2. The naphthalene compounds in crude oil (Selley, 1985).

3-Aromatics: Aromatic compounds have special characteristics of aromaticity. Which include low hydrogen: carbon atomic ratio C-C bonds that are quite strong and of between such bonds in alkanes and those in alkenes tendency to undergo substitution reactions rather than the addition reactions characteristic of alkenes; and delocalization of electrons over several carbon atoms. Many toxic substances environmental pollutants, and hazardous waste compounds, such as benzene, naphthalene, and chlorinated phenols, are aroma like compounds (Manahan, 2009).

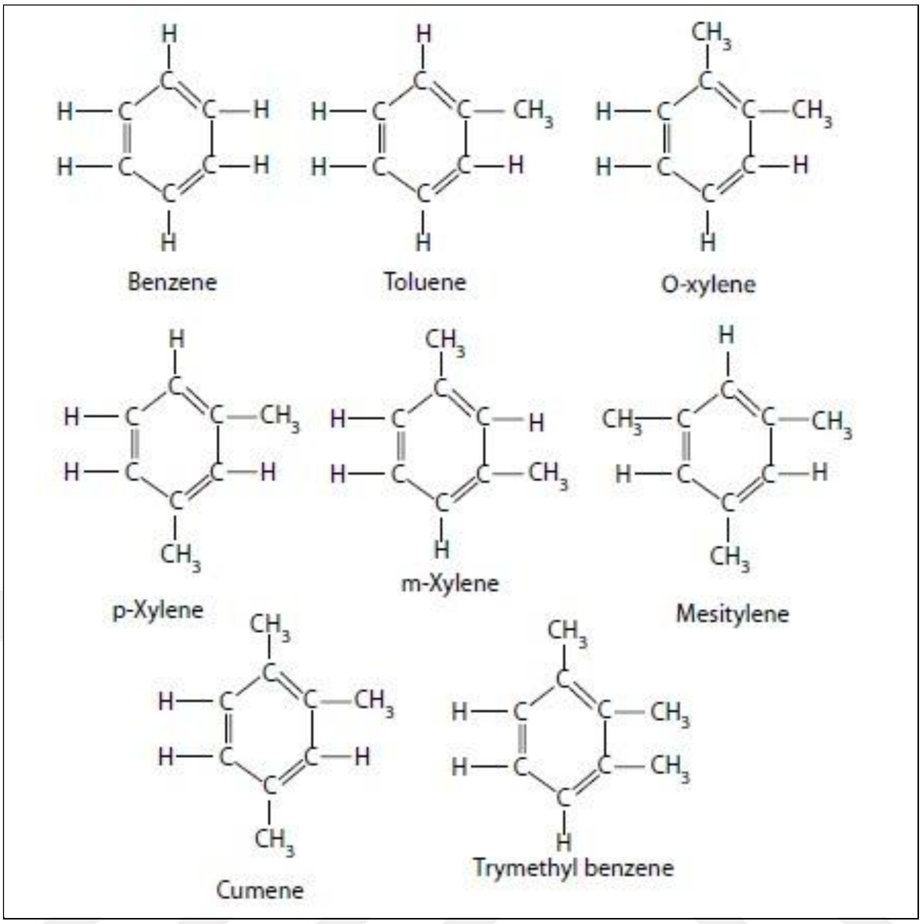


Figure 2.3. Aromatic compounds in crude oil (Chaudhuri, 2011).

4-Asphaltics: The asphaltene fraction, like the resins, is defined as a soluble class, namely the fraction of the crude oil precipitating in light alkanes like pentane, hexane or heptane. This precipitate is soluble in aromatic solvents like toluene and benzene. The asphaltene fraction contains the largest percentage of heteroatoms O, S, and N and organometallic constituents Ni, V, Fe in the crude oil (Aske et al., 2002).

### 2.3.2. Non-hydrocarbon compounds

Crude oils contain considerable amounts of organic non-hydrocarbon constituents. Those constituents when present in organic compounds, atoms other than carbon and hydrogen are called heteroatoms. Sulfur-, nitrogen-, oxygen- containing compound varies in crude oil (Duissenov, 2013).

### 2.3.2.1. Sulfur compounds

The sulfur content of crude oil varies from less than 0.05% to more than 14 wt % but generally, falls in the range 1 to 4 wt.% crude with less than 1 wt % sulfur is referred to as low-sulfur, and that with more than 1 wt % sulfur is referred to as high-sulfur (Spieght, 2000). The levels of sulfur compounds may be also measured by ppm range from 1000– 30000 ppm (Patil et al., 2011). The sulfur in crude oil is present as organic sulfur compounds, $H_2S$ and small amounts of elemental sulfur. The sulfur content of crude oil depends on its origin. The main sulfur compounds are organic sulfides or disulfides. Mercaptans and thiophenes have existed in the low boiling fractions. The sulfur is found mainly as thiophene derivatives such as benzo- and dibenzothiophenes in the higher boiling fractions (Stirling, 2000).

### 2.3.2.2. Nitrogen compounds

The nitrogen content of crude oil range from trace amounts to 0.9% by weight. Compounds of nitrogen in crude oils are unwelcomed because of catalyst poisoning and formation of gum in fuel oils. Nitrogen compounds, which can easily separate، include the basic nitrogen compounds, pyridines, quinolines,3-methylpyridine and nonbasic nitrogen compounds indoles, pyrroles and carbazoles, amides (Yasin et al., 2013).

### 2.3.2.2. Oxygen compounds

Crude oil generally contains less oxygen than sulfur. Even though it is not abundant, oxygen can play a consequential role; in particular, it is responsible for petroleum acidity (Wauquier, 1995). Oxygen compounds fall into two parts, original that existed with crude oil during its formation and unoriginal that formed by oxidation after extracting crude oil and they are accumulated in heavy distilled and distillation residues. Oxygen is found in the (Younes, 2012).carboxylic acids, cresyl ic acid, phenol, and naphthenic acid. Naphthenic acids are mainly cyclopentane and cyclohexane derivatives having a carboxyalkyl side chain.

In general, the total acid content of crude oil is low but may reach as much as 3%, as in some California crude. Non-acidic oxygen compounds such as esters, ketones, and amides are less abundant than acidic compounds (Jukić, 2013).

#### 2.3.2.3. Organometallic compounds

Many metals occur in crude oils. Some of the more abundant are sodium, calcium, magnesium, aluminum, iron, vanadium, and nickel. They are present either as inorganic salts, such as sodium and magnesium chlorides or in the form of organometallic compounds, such as those of nickel and vanadium as in porphyrins. Calcium and magnesium can form salts or soaps with carboxylic acids. These compounds act as emulsifiers, and their presence is undesirable (Matar and Lewis, 1994).

## 2.4. Sulfur compounds

Sulfur compounds are present in crude oil in a wide range of both aliphatic and aromatic forms and mainly concentrated in the heavy part of the crude oil (Ali, et al., 2009). However, crude oil contains sulfur (third most abundant element in crude oil after carbon and hydrogen usually in the form of organic sulfur compounds. Sulfur compounds exist in various forms and can be classified into four main groups: mercaptans, sulfides, disulfides, and thiophenes. It is an undesirable component because it forms sulfur dioxide $SO_2$ during fuel oil combustion (Adeyi et al., 2014).

The sulfur content of a crude oil is important for a number of reasons. Downstream processes such as catalytic cracking and refining will be adversely affected by high sulfur contents. During an oil spill, the sulfur content becomes a health and safety concern for cleanup personnel. In addition, if high sulfur oils are burning, they can produce dangerous levels of sulfur dioxide (Jokuty and Paula, 1996). Sulfur dioxide

$SO_2$ is a colorless, non-inflammable, toxic gas with a characteristic pungent smell and acidic taste (Ashar, 2016).

### 2.4.1. The Chemical and physics properties of sulfur compounds in crude oil

Sulfur contents in crude oil are in different shapes such as free elemental sulfur, hydrogen sulfide, carbon disulfides $CS_2$, mercaptans RCS and thiophenes (Vaezi et al., 2011).This category can be divided into two compounds: Sulfur oxides $SO_{X,}$ Sulfur is responsible for the emission of sulfur oxides SOx resulting from the combustion of fuels used in transportation. Several sulfur oxides are gaseous $SO_3$, $SO_2$, SO (Fadhel, 2010). Sulfur dioxide $SO_2$ is composed of one sulfur atom S and two oxygen atoms O, making it an oxide. Sulfur dioxide, at room temperature, is a toxic, non-flammable, colorless gas and heavier than air. It has a strong pungent, irritating odor familiar to the smell of a just-struck match. Sulfur trioxide $SO_3$ is composed of one sulfur atom S and three oxygen atoms O making it another oxide. Sulfur trioxide, at room temperature, is a very reactive colorless gas. It acts as an oxidizing agent (Donohue MJ, 2014).

The gas includes petroleum/natural gas, and be part of this material gaseous compounds such as hydrogen sulfide $H_2S$, it occurs naturally in crude petroleum, natural gas, and hot springs. Hydrogen sulfide is a colorless, flammable, extremely hazardous gas with a “rotten egg” smell (Anonymous, 2017a).

### 2.4.2. Type of sulfur compounds

Each crude oil has its own types and proportions of sulfur compounds. As a general rule, however, the proportion, stability, and complexity of the compounds are greater in the heavier crude oil fractions. Hydrogen sulfide is a primary contributor to corrosion in refinery processing units (Simanzhenkov and Idem, 2003). Sulfur compounds are present in crude oil in a wide range of both aliphatic and aromatic forms and mainly concentrated in the heavy part of the crude oil (Ali et al., 2009). Sulfur-containing compounds are subdivided into two categories: non-polar sulfide, thiophenes and polar forms thiols commonly known as mercaptans. Dioctyl sulfide, dibenzothiophene, and tetra decanethiol were tested to represent sulfide, thiophenes, and mercaptans, respectively (Foss et al., 2010).

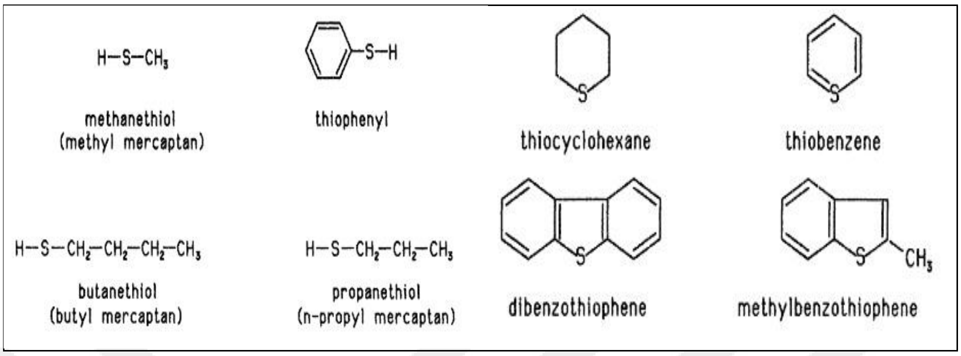


Figure 2.4. The sulfur compounds in crude oil (William and McCain 1990).

### 2.4.3. The effect of sulfur compounds

Environmental regulations all over the world are becoming more restrictive concerning the release of atmospheric pollutants associated with the flue gasses of combustion systems, particularly the emission of sulfur dioxide $SO_2$ (Adeyi et al., 2014). These gasses react with water in the atmosphere to form sulfates and acid rain which damaged buildings, destroys automotive paint finishes, acidifies the soil, and ultimately leads to loss of forests and various other ecosystems. Sulfur compounds are undesirable in refining process as they tend to deactivate some catalysts used in crude oil processing and cause corrosion problems in the pipeline, pumping, and refining equipment (Srivastava, 2012).

Hydrogen sulfide $H_2S$ is one of the most common sulfur components and is considered as an undesirable component in most industrial applications since sulfur impurities rapidly deactivate or poison catalysts, which are widely used in the chemical or petrochemical industries (Song, 2014). Today, the strongest motivation for the reduction of sulfur in fuels is due to environmental protection agency’s regulation which is imposing stringent limits for sulfur levels in transportation fuels (Daware et al., 2015) corrosion but also contributing considerably to acid rains and air pollution, deforestation, smog, and global warming, as well as several human health concerns such as cardiovascular disease, cancer, the creation of asthmatic symptoms and other respiratory diseases (Abel Adekanmi and Folorunsho, 2012).

## 2.5. Methods treatment of sulfur compounds in crude oil (Desulphurization processes)

Crude oil, a complex mixture of organic liquids, is the largest source of energy. Major portions of the crude oil are used as transportation fuels such as gasoline; diesel and jet fuel. Sulfur compounds represent one of the most common impurities present in the crude oil (Srivastava, 2012). Although its minor constituents of crude oil, their influence on processing costs can be major, some of the sulfur compounds that present problems to oil refiners. When burned in vehicles or power plants, high-sulfur fuels cause acid rain. For many refining processes, sulfur is a catalyst poison. Therefore, refiners devote a considerable amount of time and money to remove heteroatoms from intermediate streams and finished products (Duissenov, 2013).

The problem of deep removal of sulfur has become more serious due to the lower and lower limit of sulfur content in the final gasoline and diesel fuel products by regulatory specifications, and the higher and higher sulfur contents in the crude oils (Song, 2002). At present, oil desulphurization technology can be broadly divided into two categories which are hydrodesulfurization HDS and non-HDS NHDS (Song, 2014).

### 2.5.1. Hydrodesulfurization HDS

Hydrodesulfurization, a mild form of hydrocracking, is a refining process used to remove organic sulfur compounds from petroleum fractions. Organic sulfur compounds like thiols, sulfides, and thiophenes can be readily removed from petroleum fractions using conventional HDS catalysts, sulfided CoMo/Al2O3 I NiMo/Al2O3 compounds, and conventional reactors (Karagiannakis et al., 2013).

Currently, fuels desulfurization is performed with the aid of hydrodesulfurization processes HDS, typically operated in fixed-bed reactors under hydrogen-rich environment, elevated temperatures 300-400°C and a pressure ranging from 30 to 130 bar. Such a method is, on the one hand, is unsuitable for small-scale decentralized applications and, on the other hand, quite energy intensive when very low total sulfur content is desirable e.g. ≤ 2 ppmw.

The conventional reaction model of hydrodesulfurization of diesel fuel and fuel oil does not work effectively in the ultra-deep desulfurization range down to sulfur content 100 ppm or less. The catalyst volume must be three times more in the case of 50 ppm, and four times more if the aim is to reach the final sulfur content of 30 ppm (Rang et al., 2006).

### 2.5.2. Non-Hydrodesulphurization NHDS

The non-hydrodesulfurization processes include extraction, oxidation, adsorption, the combination of these processes, and the combination of these processes with hydrodesulfurization to reduce the consumption of hydrogen. The development of the mentioned processes is given, along with a discussion of recent studies in this field (Rang et al., 2006). A non-HDS technique, such as adsorptive desulfurization, relying on π-complexation bonding, is promising since the adsorption process could be accomplished at ambient temperature and pressure (Song, 2014).

#### 2.5.2.1. Oxidative desulfurization ODS

Oxidative desulfurization has been considered as a further new technology for the reduction of sulfur In ODS. This process includes two stages: (i), oxidation in a first step; and (ii), liquid extraction at the end. It is evident that the greatest advantages of the ODS process are low reaction temperature and atmospheric pressure, and that expensive hydrogen is not used in the process (Campos-Martin, 2010).

Oxidized by adding one or two oxygen atoms to the sulfur using appropriate oxidants without breaking any carbon–sulfur bonds, yielding the sulfoxide and sulfone, respectively. These oxidized compounds are then extracted from the light oil due to their increased relative polarity. The capital expenditure for ODS is less than for HDS as different fractions can be oxidized under low temperature and pressure conditions and expensive hydrogen is not required (Duissenov, 2012).

### 2.5.2.2. Extraction

Desulfurization by extraction is based on the fact that organosulfur compounds are more stable than hydrocarbons in a solvent. One of the most attractive features of the extraction method is its applicability at low temperature and pressure (Song, 2014). Extraction can be used for desulfurization because of higher solubility of organic sulfur compounds in the appropriate solvent than other hydrocarbons present in a petroleum fraction. The organic sulfur compounds are removed from the feed into the solvent, after which the mixture of sulfur-rich solvent and feed is separated (Music and Sertiæ-Bionda, 2013).

Many extraction processes that used for removing sulfur-containing compounds have been patented. Extraction with polyethylene methyl ether decreases sulfur content by 30% in petrol, diesel fuel, gas oil, and other raw oil fractions. The extraction process of gas oil with aqueous acetone, ethanol, mesityl oxide, and formic acid is also patented. The reduction of sulfur content was estimated to be in the range from 86 to 96% (Rang et al., 2006).

### 2.5.2.3. Biodesulfurization BDS

BDS is a new biocatalytic desulfurization method, which has been applied since the 1980s. According to the principle of enzyme catalysis for implementing the specific reaction for C-S bonds cleavage performed by microbiological flora, sulfides in crude oil can be turned into elemental sulfur that can be removed. In the process of desulfurization, the sulfur-containing pollutants are transformed into sulfides and $H_2S$ by biological reduction, and the elemental sulfur can be removed via the process of biological oxidation (Lin et al., 2010). For removal of sulfur from crude oil using sodium metabisulphite whose concentration is increased by culturing immobilized spores of Aspergillus flavors. Investigators investigated that 10 g, 50 g and 100g of immobilized spores of flavors remove 49.6%, 94.7% and 53.9% sulfur respectively when added to 100 ml the crude oil for seven days (Gawande and Kaware, 2014).

#### 2.5.2.4. Adsorptive desulfurization

Adsorptive desulfurization processes are considered among the most economically attractive techniques due to their simple operating conditions, availability of inexpensive and there-generable adsorbents such as reduced metals, metal oxides, alumina, metal sulfides, zeolites, silica and activated carbon (Darwish, 2015). Adsorption is the process whereby molecules from the gas (or liquid) phase are taken up by a solid surface; it is distinguished from absorption which refers to molecules entering into the lattice (bulk) of the solid material. Adsorption is governed by either physical or chemical force. In the former case, the adsorption is named physical adsorption physisorption, whereas in the latter case chemical adsorption chemisorption (Auroux, 2013).

## 2.6. Zinc oxide

Zinc is ubiquitous in the environment and occurs in the earth’s crust at an average concentration of about 70 mg kg. Zinc metal is not found freely in nature; rather it occurs in the +2 oxidation state primarily as various minerals such as sphalerite zinc sulfide, smithsonite zinc carbonate, and zincite, zinc oxide. Fifty-five zinc-containing minerals are known to exist. The most important commercial minerals, their molecular composition and zinc percentages (Choudhury et al., 2005). Zinc oxide is an inorganic compound with the formula ZnO. Zinc oxide is a white powder that is insoluble in water, and it is widely used as an additive in numerous materials and products including rubbers, plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants, and first-aid tapes. (Battez et al., 2008). Zinc Oxide has recently achieved special attention regarding potential electronic application due to its unique optical, electrical and chemical properties (Nawaz et al., 2011).

Zinc oxide, with its unique physical and chemical properties, such as high chemical stability, high electrochemical coupling coefficient, a broad range of radiation absorption and high photostability, is a multifunctional material. In materials science, zinc oxide is classified as a semiconductor in group II-VI, whose covalence is on the boundary between ionic and covalent semiconductors (Kołodziejczak-Radzimska and Jesionowski, 2014).

This semiconductor has several favorable properties, including good transparency, high electron mobility, and strong room-temperature luminescence. Those properties are used in emerging applications for transparent electrodes in liquid crystal displays, in energy-saving or heat-protecting windows, and in electronics as thin-film transistors and light-emitting diodes (Özgür et al., 2005).

Heterogeneous catalysis is being used in the fine chemicals industry because of the need for more environmentally friendly production technology. This tendency is assisted by the availability of novel catalytic materials and modern techniques of creating and investigating specific active sites on catalyst surfaces. Recently, bulk Zinc oxide has been employed as a heterogeneous catalyst for various organic transformations (Kumar et al., 2011). Many methods have been described in the literature for the production of Zinc oxide nanostructures such as laser ablation, hydrothermal methods, electrochemical depositions, sol–gel method, chemical vapor deposition, thermal decomposition, and combustion method. Recently, ZnO nanoparticles were prepared by ultrasound, a microwave-assisted combustion method, two-step mechanochemical-thermal synthesis, anodization, co-precipitation, and electrophoretic deposition (Kumar et al., 2013).

Zinc compounds such as zinc oxide and zinc carbonate are common scavengers to remove Sulfur compounds from crude oil. Zinc oxide is a commodity sorbent and good candidate for the removal of sulfur compounds in crude oil because it has high zinc content 80% and has well predictable reaction kinetics and absorption capacity. It is also readily available compared with other sorbents, such as molecular sieves or zinc-titanium oxide (Sayyadnejad et al., 2008).

## 2.7. Nanoparticle

Nanotechnology is a novel technology that has captured the whole world. It deals with the study of particles in atomic scale in order to control them. The main objective of most research works in the field of nanotechnology is to create new compounds or to bring about changes in existing materials (Aghebati-Maleki et al., 2014).

Nanoscience primarily deals with synthesis, characterization, exploration, and exploitation of nanostructured materials. These materials are characterized by at least one dimension in the nanometer range. A nanometer nm is one-billionth of a meter, or 10–9 m. One nanometer is approximately the length equivalent to 10 hydrogen or 5 silicon atoms aligned in a line (Pokropivny et al., 2007). Very small particles, so-called nanoparticles, have the ability to enter, translocate within, and damage living organisms. This ability results primarily from their small size, which allows them to penetrate physiological barriers and travel within the circulatory systems of a host (Buzea et al., 2007).

A nanoparticle is the most fundamental component in the fabrication of a nanostructure and is far smaller than the world of everyday objects that are described by Newton’s laws of motion, but bigger than an atom or a simple molecule that are governed by quantum mechanics (Horikoshi and Serpone, 2013).

The major goals in designing nanoparticles as a delivery system are to control particle size, surface properties and release of pharmacologically active agents in order to achieve the site-specific action of the drug at the therapeutically optimal rate and dose regimen (Mohanraj and Chen, 2006).

Nanoparticles have already been applied as drug delivery systems with great success. Nanoparticles provide massive advantages regarding drug targeting, delivery and with their potential for combine diagnosis and therapy and one of the major tools in Nanomedicine. There are many technical, challenges in developing the following techniques Virus-like systems for intracellular systems, Architecting of biomimetic polymers, control of sensitive drugs, functions of active drug targeting, bioresponsive triggered systems, systems interacting with me body smart delivery, nanochips for nanoparticle release, carriers for advanced polymers for the delivery of therapeutic peptide / proteins (Pal et al., 2011).

The objective of the Nanotechnology Particle Project is to establish a platform for developing the synthesis and functionalization technologies of nanoparticles, which is important for producing nanostructures and expressing nano-functions imparted as quantum size effect, through the expression of giving the great potential for use in applications in the electronic, chemical and mechanical industries, as well as in the related technologies using catalysts (Okuyama and Lenggoro, 2004).

The field of nanocatalysis (the use of nanoparticles to catalyze reactions) has undergone an explosive growth during the past decade both in homogeneous and heterogeneous catalysis. Since nanoparticles have a large surface-to-volume ratio compared to bulk materials, they are attractive candidates for use as catalysts.

Nanoparticles of metals, semiconductors, oxides and other compounds have been widely used for important chemical reaction (Baskar et al., 2014). The difference between homogeneous and heterogeneous catalysis is mainly due to the materials used as catalysts (molecular complexes in solution versus solid particles, often grafted onto a support), as well as to the catalytic reaction conditions applied (Philippot and Serp, 2013).

Most metals have been or can be produced in nanometric dimensions. NP is studied in particular and shows an optical resonance spectrum in the visible range, which is sensitive to the environmental conditions, size, and shape of NP. Their unique properties make it possible to envision a series of applications. Several metal oxides of nanometric dimensions have been created, but the most common ones، because they are produced on a large scale, are probably silica, titanium dioxide and zinc oxide (Ostiguy et al., 2010).

Nanoparticles are generally formed by two different processes based on coarser particles, the top-down process leads to smaller particles mainly by mechanical comminution in bottom-up processes, and nano-sized particles are formed by gas phase or liquid phase reactions (Anonymous, 2013). Two main approaches are used in nanotechnology. In the ‘‘bottom-up’’ approach, materials and devices are built from molecular components which assemble themselves chemically according to the principle of molecular recognition. In the ‘‘top-down’’ approach, nano-objects are constructed from larger entities without atomic-level control. Larger to smaller: a materials perspective: A number of physical phenomena become pronounced as the size of the system decreases. These include statistical, mechanical effects, as well as quantum mechanical effects, for example, the ‘‘quantum size effect’’ where the electronic properties of solids are altered with great reductions in particle size . This effect does not come into play by going from macro to micro dimensions. However، it becomes dominant when the nanometer size range is reached (Chaturvedi et al,. 2012).

## 2.8. Adsorption

Until the early twentieth century when adsorption processes were more fully understood. However, as early as 1550 BC, carbon was recognized for its adsorptive qualities and used in the purification of medicine. Adsorption is the accumulation of atoms, ions, or molecules from a gas or liquid at the surface, known as the adsorbent (Eigenbrodt and Rooney, 2014).

Adsorption is the association of an adsorbate compound into a surface of their compounds (adsorbent), usually in a liquid-solid or vapor-solid system, while absorption involves the redistribution of a compound from the aqueous phase into a volume of material. In geochemical systems, however, the two are often indistinguishable and the term adsorption is almost used (Kadhim, 2006).

Adsorption is related to the removal of a substance called an adsorbate from the gaseous or liquid phase by a solid material called an adsorbent. The adsorption process is recognized as an important process in the field of separation technology. The adsorption process is primarily studied by fitting the data to Freundlich, Langmuir, and BrunauerEmmett-Teller BET equations (Khan, 2012).

The behavior of an adsorbing substance onto surfaces has been interpreted by thermodynamic, statistical, mechanical, and more complicated mathematical treatments. More than forty theories have been devel claimed that the theory can be used for adsorption from gas or liquid phases. Regarding the precision and range of validity, the proposed theory is an improvement on other methods, especially the BET method. According to this theory, the adsorption system where particles are adsorbed on a solid surface or on another phase should be considered as an open system in mechanical and thermal equilibrium (Bajpai and Rajpoot, 1999).

Adsorption at various interfaces has concerned scientists since the beginning of this century. This phenomenon underlies a number of extremely important processes of utilitarian significance. The technological, environmental and biological importance of adsorption can never be in doubt. Its practical applications in industry and environmental protection are of paramount importance. The adsorption of substrates is the first stage in many catalytic processes. The change in concentration of a given substance at the interface as compared with the neighboring phases is referred to as adsorption. Depending on the type of phases in contact, we can consider this process in the following systems: liquid-gas, liquid-liquid, solid-liquid and solid-gas (Dąbrowski, 2001).

The solid-fluid interfaces are governed by specific and specific interactions between the atoms at the solid surface and the molecules approaching the surface of the liquid phase. In particular, heterogeneous catalysis is based on a sequence of steps which involve adsorption of reactants at the surface of the solid material, surface reactions and desorption of final products (Auroux, 2013). The solid-liquid interface plays a crucial role in many important industrial processes such as detergency, flotation, and deinking. In many of these applications, the use of surfactant mixtures improves significantly the performance over those of single component systems. In processes such as enhanced oil recovery (Somasundara and Huang, 1997).

The adsorption isotherm is one of the most important criteria for an adsorption process. In practice, the uptake of adsorptive of a given catalyst material is a decisive quantity, since a high uptake usually means a (desired) high catalyst efficiency. The adsorption isotherm data of a novel adsorption system is linearized and non-linearized methods. To establish the most appropriate adsorption equilibrium correlation, the accuracy in parameters prediction of both linear and nonlinear isotherm models was compared and discussed (Christmann, 2011).They can be subdivided according to the interaction mechanism between the sulfur compound and the adsorbent. Adsorptive desulfurization is based on the physical adsorption of sulfur compounds on the surface of a solid adsorbent. Desulfurization by reactive adsorption involves the chemical interaction between the adsorbent and the sulfur compounds. Once the phenomenon stops, the adsorbent can be regenerated by eliminating $H_2S$, S, or SOx, depending on the applied process. The efficiency of the method is defined by the adsorbent properties, including adsorption capacity, selectivity for sulfur compounds, durability, and regeneration of spent adsorbent (Alavi and Hashemi, 2014).

Adsorption one of the powerful treatment processes for the removal of dyes from water is adsorption. Adsorption techniques have been proven successful in removing colored organics (Erdem et al., 2004).

### 2.8.1. Type of adsorption

The adsorption can be divided into two types, physical, physisorption or Fadhel chemical, chemisorption based on the nature of the adsorbent-sorbate interaction (Fadhel, 2010).

#### 2.8.1.1. Physical Adsorption or Physisorption

Physical adsorption takes place due to Van der Waals forces and electrostatic forces in molecules with a permanent dipole moment. In physical adsorption, the forces that attract a molecule to the surface do not change the adsorbate molecule and are usually weak (Darwish, 2015).

The forces and adsorption energy usually not exceeding 80 kJ mol-, with typical energies being considerably less. Physically adsorbed molecules may diffuse along the surface of the adsorbent and typically are not bound to a specific location on the surface. Physisorption plays a major role during separation and enrichment processes at and near phase boundaries (Webb, 2003). Physisorption plays a major role during separation and enrichment processes at and near phase boundaries (Christmann, 2011).

Physical Adsorption or Physisorption is characterized by:

a) Low temperature, always under the critical temperature of the adsorbate

b) Type of interaction: Intermolecular forces (van der Waals forces)

c) Low enthalpy: $\Delta H < 20$ KJ mol-

d) Adsorption takes place in multilayer

e) Low activation energy (Wang et al., 2007).

#### 2.8.1.2. Chemical adsorption or chemisorption

Chemisorption involves the formation of chemical bonds between the adsorbate and adsorbent is a monolayer, often with a release of heat much larger than the heat of condensation. Chemisorption, consisting of a chemical reaction confined to the solid surface, does involve rearrangement of electrons of both adsorptive molecules and surface atoms, yielding new surface terminations(Auroux, 2013). Chemisorption occurs usually at temperatures much higher than the critical temperature, is a specific process which can only take place on some solid surfaces for a given gas. (Dąbrowski, 2001) The adsorption capacity is, however, reduced because chemisorption is limited to unimolecular coverage of the adsorbate on the active sites (Brauer,1981). In chemisorption the force of attraction is very strong, therefore adsorption cannot be easily reversed (Anonymous, 2017b).

### 2.8.2. Mechanism of adsorption

The catalytic cycle is the principle of catalytic action. The mechanism of a catalyzed reaction can be described by the sequence of elementary reaction steps of the cycle, including adsorption, surface diffusion, chemical transformations of adsorbed species, and desorption, and it is the basis for deriving the kinetics of the reaction (Deutschmann et al., 2009). Many different types of isotherms have been observed in the literature, these isotherms could have very different shapes depending on the type of adsorbent, the type of adsorbate and intermolecular interactions between the liquid and the surface (Dowdy and Lindsay, 1981).

The mechanism of ions adsorption on porous adsorbents may involve three steps; (i) diffusion of the ions to the external surface of adsorbent; (ii) diffusion of ions into the pores of adsorbent; (iii) adsorption of the ions on the internal surface of the adsorbent. The first step of adsorption may be affected by MB ions concentration and agitation period. The last step of the adsorption is considered as a rate-determining step and as a relatively rapid process (AL-Asadi, 2013).

### 2.8.2.1. Langmuir model

The Langmuir equation is the most widely used model for adsorption processes (Putra et al., 2009). Often the amount adsorbed is measured as a function of the partial pressure or concentration at a given temperature and the result expressed as an adsorption isotherm (Abdueva, 2006). The Langmuir equation relates the coverage or adsorption of molecules on a solid surface to gas pressure or concentration of a medium at the solid / liquid interface at a fixed temperature. Langmuir isotherm has been successfully used in many adsorption systems, for example, wine clarification (Sun et al., 2007; Sarmento et al., 1999) and waste water treatment (Hameed et al., 2008). It was suggested that this isotherm can also be used for protein adsorption onto a solid surface with an assumption of no intermolecular interactions between adsorbed molecules (Li and Li, 2007). However, this could be erroneous because proteins are large amphoteric polymers that would result in multilayer adsorption on solid-phase.

The model was originally developed for physical adsorption of gasses onto porous solids. However, it was found to model chemisorption’s very well (Seader and Henley, 2006). For Langmuir adsorption, suggested that adsorption was due to chemisorption’s, while suggested it was due to physical adsorption. The latter is characterized by adsorbate adhering weakly to a solid surface and is relatively weaker compared to chemisorption. Strong adsorption systems are characterized by combinations of both which can be seen in adsorption of amoxicillin on activated carbon (Putra et al., 2009).

There are many approaches in deriving isotherms. The most common method is through a kinetic approach (Tien, 1994). The effect of ionic strength cannot be accounted by the Langmuir equation that assumes a constant ion-surface affinity. The isotherm will always predict that adsorption will increase until saturation. For salt competition adsorption, additional variables are required. But adding more terms complicates analysis and therefore, a more direct approach is always preferred such as analyzing just one solute component in solution (Theng, 1980). The Langmuir linear isotherm is expressed in equation Ce/Q = 1/K + (a/K) Ce (1)

Where Ce is the equilibrium concentration (mg l-), Qo is the maximum amount of adsorption (mg/g) corresponding to complete monolayer coverage and KL which is constants related to the binding strength, respectively or sometimes called Langmuir constants. The fitting of adsorption data to Langmuir isotherm equation is investigated by plotting Ce/Qe versus Ce (Ramakrishna and Viraraghavan, 1997). It is an empirical isotherm derived from a proposed kinetic mechanism. Is based on four hypotheses:

1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.

2. Adsorbed molecules do not interact.

3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent. For liquids adsorbate adsorbed on solids adsorbent (Sun et al., 2012**)**.

#### 2.8.2.2. Freundlich adsorption isotherm

The isotherm was developed by Herbert Freundlich in 1909, originally used to represent the isothermal variation in gas adsorption empirically. It relates the quantity of adsorbed gas relative to the unit mass of solid-phase with pressure (Seader and Henley 2006). The Freundlich equation is an adsorption isotherm, which a curve is relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact (Rahimi and Vadi, 2014).

The adsorption isotherm of Freundlich is one of the most important isotherms that deal with adsorption at the solid-liquid interface, which has been introduced by (Herbert Max finallyFreundlich) a German scientist in (Laider and Meisen, 1982). Most of the surfaces are heterogeneous, so the change in potential energy is regular, and the adsorption sites are not equivalent in energy R (Bitton and Marshall, 1980), hence the multi-layer formation is highly expected**.** Freundlich equation could be written as follows: (Atia et al., 2006)

$$Q = Kf\ Ce1/n \tag{2}$$

$$LogQ = \log Kf + (1/n) \log Ce \tag{3}$$

The term **n** represents heterogeneity and cooperatively in adsorption which is a temperature dependent constant, with **n > 1** indicating favorable adsorption and **n > 10** indicating the adsorption process is irreversible (Zheng et al., 2009 & Theng, 1980).For **n** equals to 1, the isotherm equation is reduced to Henry‟s**Cr = k Ce** According to (Parfitt et al., 1983), this simple expression does not usually apply over the whole concentration range thus its validity is uncertain. He added that the isotherm is derived from consideration of heterogeneity of the surface when applied to gas adsorption on solids. Therefore, if data for liquid adsorption fit the equation, it is possible that the solid surface is heterogeneous; however, this is not proven.

The limitation of the Freundlich isotherm has no saturation term. It fails at high pressure for gas adsorption. The reason for that is in gas adsorption, the adsorbed component; Cr varies directly with pressure until the saturation pressure is reached. Beyond this point, there should be no adsorption but the model would suggest Cr will keep on increasing. Similarly, for adsorption from solution, because the isotherm describes the Cr as a function of solute concentration Ce, Cr always increases indefinitely with the solution concentration (Sharma and Agarwal, 2001).

## 2.9. Gas chromatography (GC)

The development of GC as an analytical technique was pioneered by Martin and Synge (1941); they suggested the use of gas-liquid partition chromatograms for analytical purposes. When dealing with liquid-liquid partition chromatography, they predicted that the mobile phase need not be a liquid but may be a vapor.

The concept of gas chromatography was envisioned in the early forties but unfortunately, little notice was taken of the suggestion (Anonymous, 2016)c. Gas chromatography GC systems can separate different components of gaseous mixtures, and are important analytical tools for a variety of disciplines, including environmental analysis, methane gas probes, and homeland security and pollution monitoring. However, most modern GC devices suffered the problems of low detection speed, sensitivity, and poor stability (Sun et al., 2012). Gas chromatography has the advantage to measure the components of interest in a compositional background. It will first separate the components of interest from the bulk composition in a separation column and then leads the components over a detector. The separation column for the measurement of sulfur components can be chosen in packed and capillary type (Lenior, 2009).

The gas chromatography is used to analyze compositions of the gas and liquid phases in crude oil, in the crude reservoir the proportions of gas, liquid, and solid depend on subsurface conditions and on the phase diagram envelope of the petroleum mixture. The recombined compositions based on the gas and liquid according to the measured gas/oil ratio are those of the reservoir fluid. To obtain compositions of a reservoir fluid, a reservoir sample is flashed into gas and liquid phases at ambient conditions (Zeng et al., 2012).

# 3. MATERIALS AND METHODS

## 3.1. Introduction

This chapter includes the details of experimental work of the present study. The target is to experimentally investigate the effect of zinc oxide nanoparticle to remove the sulfur compounds from crude oil, and see the Influence of temperature and the mass of catalyst contact time on the process of desulfurization.

## 3.2. Materials

### 3.2.1. Apparatus

Table 3.1. List of tools and equipment’s.

| Tools | Uses |
|---|---|
| Electronic balance type Ntrols mod. Mark 2200 with ± 0.05g accuracy | Weighing |
| Heater IKA-RET basic C in IKA China | Heating |
| Stopwatch | Time |
| Batch reactor with the magnetic and stirrer | Shaker |
| MULTI-Thermometer | Measuring temperature |
| EDXRF sulfur analyzer Fxe-400s (TANAKA, Japanese) | Measuring sulfur |
| Cylinder, Beaker, Funnel, Conical flask, Volumetric flask, stirrer, Stand | Glass wear |
| RAYPA DO-50 Drying oven Digit, R. Espinar, S.L. | Drying |

### 3.2.2. Crude oil

The crude oil used in this research was obtained from jambour field from Kirkuk-Iraq; and the total sulfur content present initially is 19640 ppm. Crude oil for experimental work was carried out on sample of the temperature carried out nature 38 $^{O}$C. The physical and chemical properties which are shown in table are below.

Figure 3.1. Crude oil.

Table 3.2. Shows chemical properties of crude oil.

| **Chemical properties** | **Crude oil** | **Method** |
|---|---|---|
| Sp.Gr. at 60/60 $F^{o}$ | 0.8289 | ASTM D-1298 |
| API | 39.2 | ASTM D-1298 |
| Water & sediment (vol. %) (BS&W) | Water = 0.30 %<br>Sediment = 0.36 % | ASTM D-4007 |
| Salt content (PTB) | Nil | ASTM D-3230 |
| Asphaltene (wt. %) | 0.3% | ASTM D-6560 |
| Total Sulfur content by x-Ray Fluoresce. (%wt.) | 1.9640 wt.% | ASTM D-4294 |
| Viscosity (cst) 40 $^{o}C$ | 3.6 cst | ASTM D-7042 |

### 3.2.3. Zinc oxide nanoparticle powders

Zinc oxide nano used for this experiential it is 80 Nanoparticle.

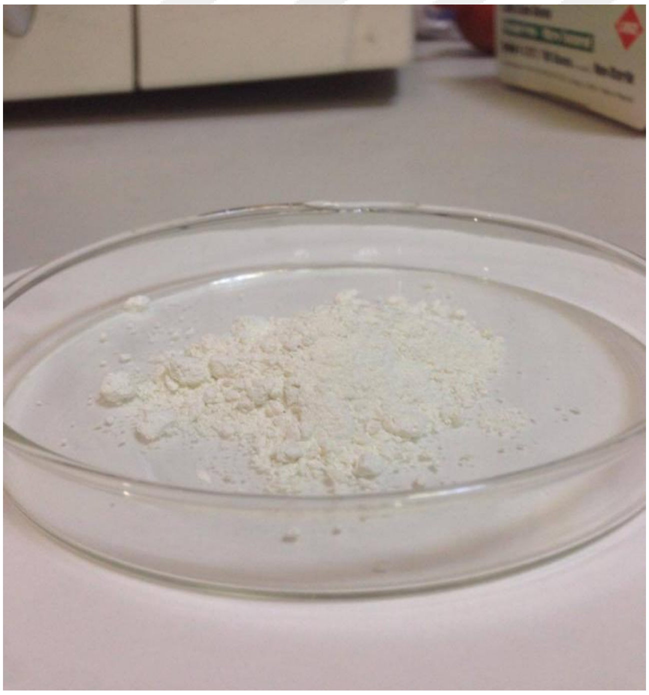


Figure 3.2. Zinc oxide nanoparticle 80 nm.

### 3.2.4. Other chemicals used

The chemical Materials that were used in experimental work are listed in Table

Table 3.3. Shows other chemical marital use in experimental.

| Substance | Formula | Molecular Weight | Specific Gravity* | Melting Point($^{o}$C) | Supplier | Purity% |
|---|---|---|---|---|---|---|
| Methanol | $CH3OH$ | 32.04 | 0.792 | — | B.D.H | 99.9 |
| Toluene | $C6H5CH3$ | 44 | 0.866 | — | G.C.C | |

### 3.3. Experimental procedure

The desulfurization process using the zinc oxide nanoparticle adsorbent was investigated at different levels of the amount of sorbent material used 0.1 wt. % - 0.5 wt. %, operating temperatures 25, 30, 35, 40, and 45 $^{o}$C and contact times 20, 40, 80,160, and 320 min according to the following procedure:

Batch adsorptive desulphurization experiments were performed by contacting 0.1g of the adsorbent-Activated zinc oxide powder with 50 ml of crude oil. The experiment was performed on a magnetic stirrer (model A-034) for a period of 1 hour at 400 rpm using 250 ml flask containing 50 ml of crude oil sample and 0.1 g of adsorbent at Carried out of nature temperature 38$^{o}$C by Heater IKA-RET basic C in IKA China. Continuous mixing was provided during the experiment by agitating at constant speed 400 rpm, for better mass transfer with high interfacial area contact.

The remaining sulfur in each sample after adsorption was determined by EDXRF Sulfur Analyzer Fxe-400s TANAKA, Japanese, Then it is used the MULTI-Thermometer to know the exact temperature and stay the degree of temperature on 38$^{o}$C without the effect of

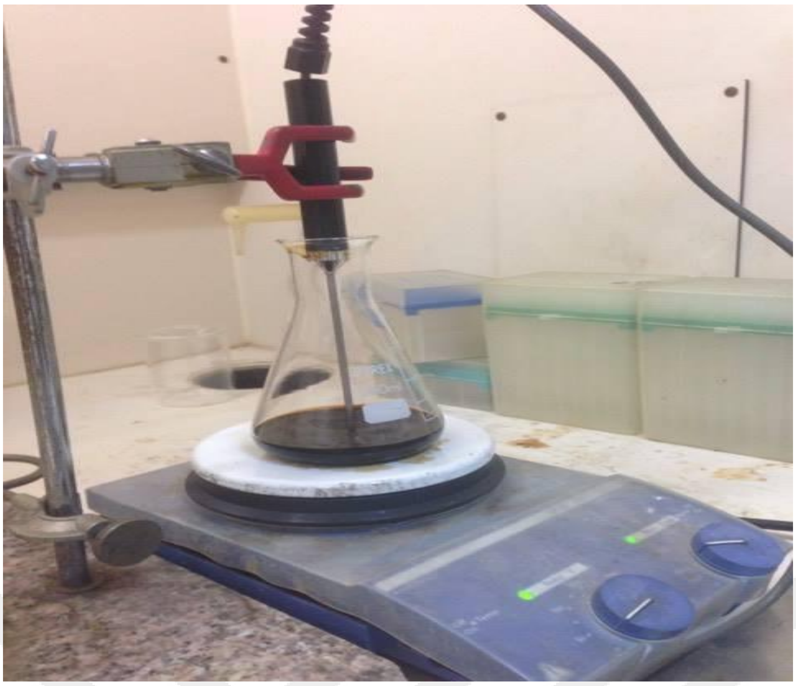


Figure 3.3. Adsorption process.

Different temperatures are used for experimental. Finally weight the zinc oxide nanoparticle for all experimental by electronic balance type Ntrols mod. Mark 2200. All this procedure is done it inside the hood and use batch process to desulfuration from crude oil and the methodically by three step.

Figure 3.4. Edxrf Sulfur Analyzer Fxe-400s.

### 3.3.1. Effect of change the dosage of zinc oxide

ZnO utilization experiments Study of Change the amount of zinc oxide nanoparticle with a time of reaction contacted time, should be carried out the crude oil of nature of temperature and constant time. Then it is taken 50 ml of crude oil in conical flask volume 250 ml. the temperature of the crude Carried out of nature temperature 38$^oC$ by Heater IKA-RET basic C (in IKA China).then Weighted different amount 0.1, 0.2, 0.3, 0.4 and 0.5 g from zinc oxide nanoparticle and added to the 50 ml from crude oil in the conical flask and shaker with a magnetic stirrer at a rate of 400 oscillations /min for 1 hour. Then Use centrifuge Hettich, ZENTRIFUGEN, D-78532 Tuttlingen, ROTINA 420R, Germany, to separation the catalyst ZnO from the crude oil after each experimental, the mixture was centrifuged at 4500 rpm for 15 min at room temperature. Finally Preparation of all samples for tests by a glass tube.

Figure 3.5. Centrifuge.

### 3.3.2. Effect of temperature

By temperature utilization an experiment, the study of Change is used to show the effects of temperature with time of reaction constant time. they added 50 ml of crude oil in conical flask 250 ml. then Weight 0.1g from zinc oxide nanoparticle for all experiential and added to the 50 m from crude oil and use different temperature at 25, 30, 35, 40, and 45 $^{0}$C by Heater IKA-RET basic C in IKA China, and shaker with magnetic stirrer at a rate of 400 oscillations /min for 1 hour. Then Use centrifuge Hettich, ZENTRIFUGEN, D-78532 Tuttlingen, ROTINA 420R, Germany. to separation the catalyst ZnO from the crude oil after each experimental, the mixture was centrifuged at 4500 rpm for 15 min at room temperature. Finally Preparation of all samples for tests by a glass tube.

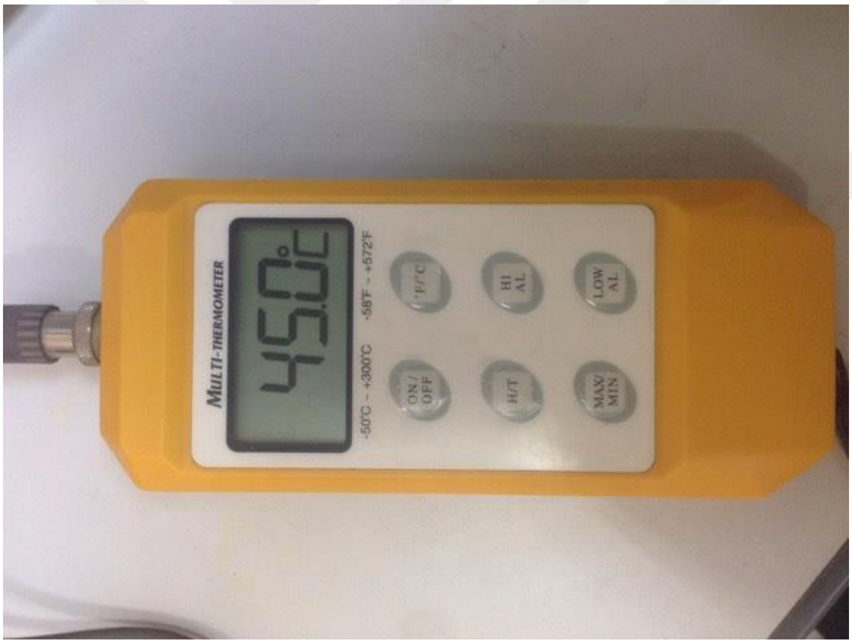


Figure 3.6. Multi-thermometer.

### 3.3.3. Effect of contact time

These experiments will be carried out at fixed ZnO 0.1 g with crude oil concentration. We use different time for these experiments. Then added 50 ml of crude oil in conical flask 250 ml. then Weight 0.1 g from zinc oxide nanoparticle and added to the 50 ml from crude oil and the temperature carried out nature at 38 $^{o}$C by Heater IKA-RET basic C in IKA China, and shaker with magnetic stirrer at a rate of 400 scillations /min for different time 20, 40, 80,160, and 320 min.

Then Use centrifuge Hettich, ZENTRIFUGEN, D-78532 Tuttlingen, ROTINA 420R, Germany, to separation the catalyst ZnO from the crude oil after each experimental, the mixture was centrifuged at 4500 rpm for 15 min at room temperature Finally Preparation of all samples for tests by a glass tube.

# 4. RESULTS AND DISCUSSION

Many experiments have been done to measure the qualification of the adsorption process using zinc oxide nanoparticle to remove the sulfur compounds from crude oil in Kirkuk from jambour field as well the ratio of sulfur compounds large So reducing the ratio is important, zinc oxide where it has been studied the effect of the time, effect the temperature, and the effect dosage of adsorbent factor. The result showed that there was an effect to the numbered factors from as the following in the figure diagram 3.1, 3.2, 3.3.

## 4.1. The result of effect dosage zinc oxide NPs

In this change we notice the great decrease at the density of the content of sulfur and pure oil at the stable increase of the adsorbent material in every time at the stability of the Retention time and the heat temperature and that supports.

The theory of the increasing of the adsorptive process with the increase of the running path in which at 0.1 g and the time with temperature constant note that 220 ppm from the sulfur compounds was adsorbent, while in the second step when added 0.2 g note that 285 ppm from the sulfur compounds adsorbent than appears increase from the adsorb by increase the amount of the catalyst zinc oxide nanoparticle, so stable increase from the catalyst 0.3, 0.4, 0.5 g of zinc oxide note that increase running path from the removal of sulfur compounds 333, 360, 490 ppm and is shown below in the table (4.1), and figure (4.1).

This means the amount of dosage of catalyst plays a role in adsorption but if used in large areas it must reach an appropriate quantity with the appropriate size of the solute.

Table 4.1. Result the effect of amount of ZnO.

| No of samples | Dosage of catalyst | Results w.t% | Sulfur removal (ppm) |
|---|---|---|---|
| 1 | 0.1 | 1.9420 | 220 |
| 2 | 0.2 | 1.9355 | 285 |
| 3 | 0.3 | 1.9307 | 333 |
| 4 | 0.4 | 1.9280 | 360 |
| 5 | 0.5 | 1.9150 | 490 |

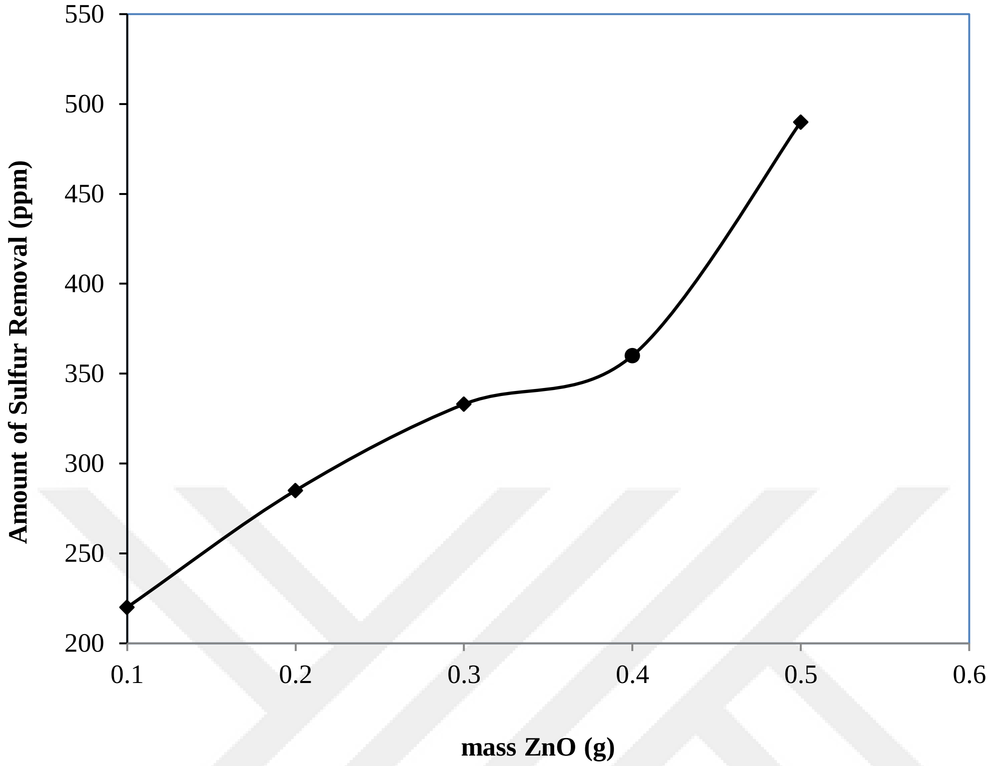


Figure 4.1. Diagram the effect amount of catalyst.

In a study related with adsorption by zinc oxide nanoparticle. The result of dosage of zinc oxide is compared with kinds of literature. The comparison results showed that the amount of catalyst has a great effect on the increase of adsorption with different absorbent, whenever added more amount regularly the curve between the adsorption and amount of catalyst increase showed in the diagram (4.1).Similar results were found by several authors, (Kaynar et al., 2014), (Sayyadnejad et al., 2008).

In our study related with adsorption use another material such as active carbon, Manganese dioxide, where found with an increase from the amount of catalyst increasing removal by adsorption, similar results (Al Zubaidy et al., 2013), ( Al Zubaidi et al., 2015), (Adeyi et al., 2014).

## 4.2. The result of effect of temperature

According to table 4.2. The influence of temperature on adsorption between crude oil and zinc oxide nanoparticle showed increase of temperature the adsorption it decreases, it is shown in 25 $^0$C higher rate of adsorption equal to 740 ppm the removal of sulfur compounds in crude oil, followed by 30, 35, 40 and 45 $^o$C as 530, 490, 220 and 130 ppm respectively. The decrease of the density of the content of sulfur and pure oil in the second change the increase of the heat temperature of the pure oil.

Shows a stable increasing of the heat temperature of the pure oil in every time the density of the pure oil sulfur content decrease at the same time proves that the heat temperature increases but backward at which at increase the temperature the adsorption decrease following this in below figure 4.2.

Through the results we can choose the best temperature for adsorption process.

Table 4.2. Result the effect of temperature.

| No of samples | Temperature $^O$C | Results w.t% | Sulfur removal ppm |
|---|---|---|---|
| 1 | 25 | 1.8900 | 740 |
| 2 | 30 | 1.9110 | 530 |
| 3 | 35 | 1.9150 | 490 |
| 4 | 40 | 1.9420 | 220 |
| 5 | 45 | 1.9510 | 130 |

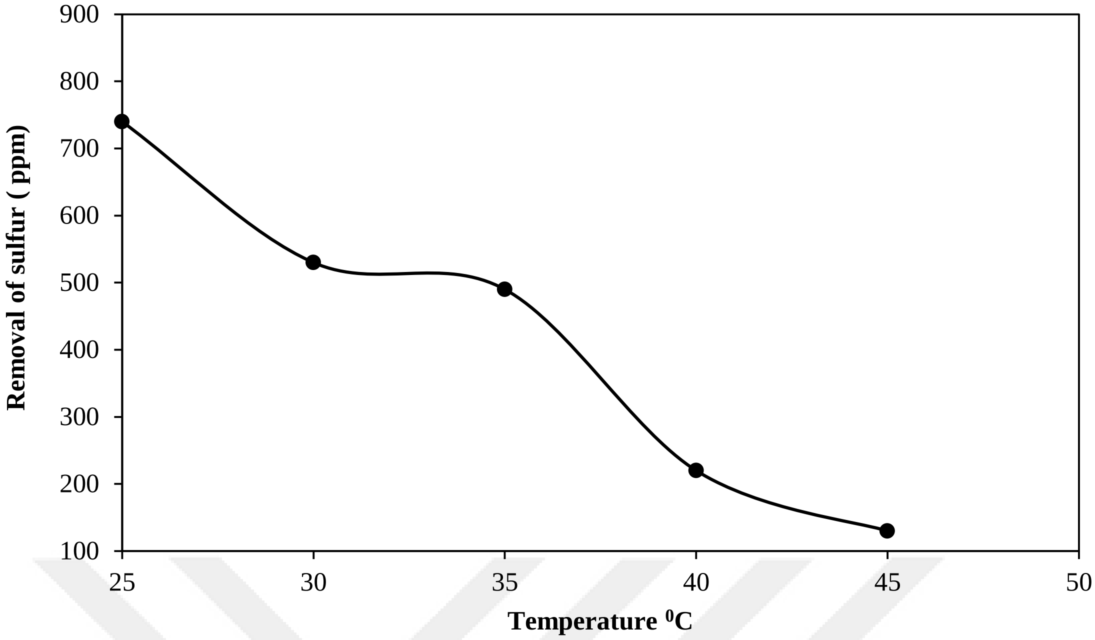


Figure 4.2. Diagram the effect of temperature.

In this study we evaluate the effect of temperature within the experimental thermal range 25-45 °C on adsorption process using zinc oxide nanoparticle and the results are showed that the temperature increase regularly the adsorption decrease and compared with (Suteu, 2005), (Al-Obady and Al-Shimmery, 2012).

## 4.3. The result of effect contact time

Of ratios that we got we noticed a significant decrease in the density of sulfur material. Therefore the adsorption process of proving adsorption mechanism of activity, it is a perfect way to get rid of dangerous sulfur materials. That is in pure nanoparticle oil connectivity tiny zinc oxide.

These studies have showed that the increase in the survival of pure oil with the adsorbent material that has a positive effect on the activity of adsorption, make a big difference between the first study, and the second study, which confirms that this reaction occurs rapidly and a large activity in the temperature nature of crude oil, but when we increase the time we see adsorption happens a little bit and took constant a path in the 80 mint and top.

In the time 20, 40 min the curve of the removal of sulfur compounds 437,582 ppm, toward top but in the 80 min increase the curve after stopped to increase and took the curve right line because the adsorbent material Saturation then time increase 160 , 320 min does not make a big influence on the removal of sulfur compounds. This is shown below table 4.3 and figure 4.3.

Table 4.3. Result the effect the contact time.

| No of samples | time | Results w.t% | Sulfur removal ppm |
|---|---|---|---|
| 1 | 20 | 1.9203 | 437 |
| 2 | 40 | 1.9058 | 582 |
| 3 | 80 | 1.8980 | 660 |
| 4 | 160 | 1.8970 | 670 |
| 5 | 320 | 1.8965 | 675 |

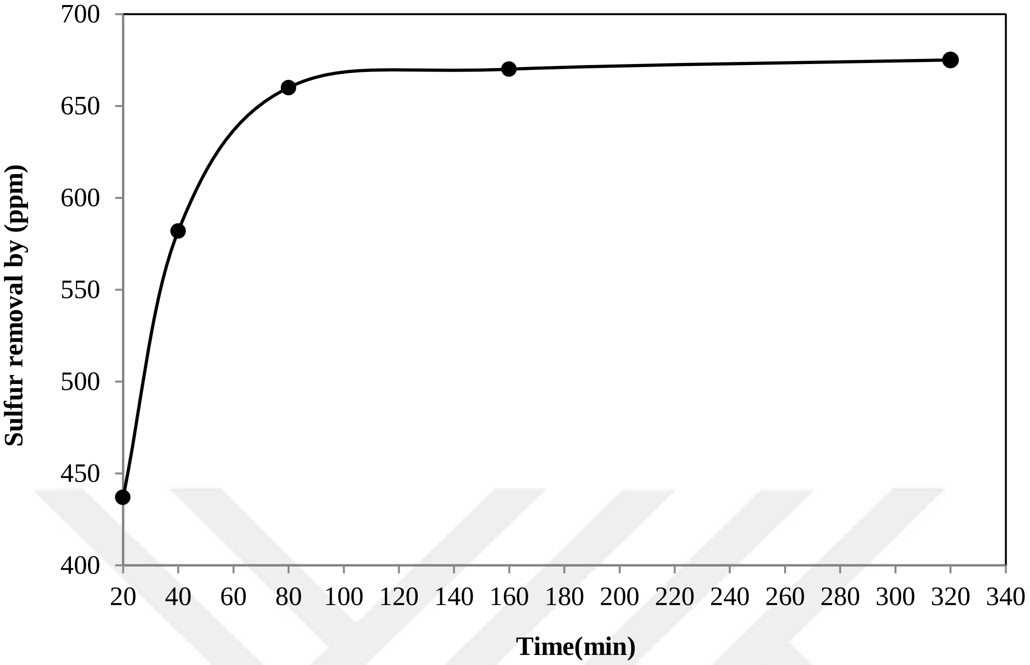


Figure 4.3. Diagram the effect of contact time.

These results of time dependence of sulfur compounds adsorption experiments are shown in figure. 4.3 are compared with (Kaynar et al., 2015), (Hosseini and Hamidi and 2014) literatures, the comparison results showed that the adsorption of sulfur compounds has been investigated onto nanoporous zinc oxide nanoparticle powders as a function of time in the range of 20–360 min shows the variation of curve and percentage sorption with shaking time for crude oil. It is clear that the sorption efficiency increases rapidly during the first 80 min and becomes constant.

## 5. CONCLUSION

This study showed that the process of adsorption is to reduce the accompanying sulfur compounds.

1- Easy technique needs no using complex processes.
2- Cheap.
3-Rapid process and fast results, so we can remove the sulfur compounds in a great way.
4- High qualification of removing.
5- Can be used practically in refineries.

# REFERENCE

Abdueva D, 2006. Probe-target hybridization modeling and its application to the analysis of microarrays, **2**(1): 17-57.

Abel Adekanmi A and Folorunsho A, 2012. Comparative analysis of adsorptive desulphurization of crude oil by manganese dioxide and zinc oxide, ***Research Journal of Chemical Sciences***, ***2***(8): 14-20.

Adeyi AA, Popoola LT, Yusuff AS, Olateju II, Grema AS, 2014. Kinetics analysis and dosage effects of manganese dioxide adsorbent on desulphurization of crude oil***. J. of Bioprocessing and Chemical Engineering.*** **1**(2): 1-6.

Aghebati-maleki L, Salehi B, Behfar R, Saeidmanesh H, Ahmadian F, Sarebanhassanabadi M, Negahdary M, 2014. Designing a hydrogen peroxide biosensor using catalase and modified electrode with magnesium oxide nanoparticles, ***Int. J. Electrochem. Sci,*** **9**(2014): 257-271.

Al Zubaidi I, Darwish NN, El Sayed Y, Shareefdeen Z, Sara Z, 2015. Adsorptive desulfurization of commercial diesel oil using granular activated charcoal, ***Int'l Journal of Advances in Chemical Engg***., & Biological Sciences, **2**(1): 15-18.

AL-Asadi ZAK, 2013. Effect of zinc oxid on the bentonite ability for removing Methylene blue from solution, ***J. Baghdad for Sci,*** **10**(2): 446-447.

Alavi SA, Hashemi SR, 2014. A review on diesel fuel desulfurization by adsorption process, ***international conference on chemical, agricultural, and biological sciences***, (ICCABS'2014), 33-36.

Ali MF, Abdullah M, Shakil A, 2009. Chemical desulfurization of petroleum fractions for ultra-low sulfur fuels." ***fuel processing technology***, **90**(4): 536-544.

Anonymous, 1998. ***Pollution Prevention and Abatement Handbook, Toward Cleaner Production***. Washington, DC: World Bank Group, chapter **3**, 179-441.

Anonymous, 2013. ***Nanomaterials***: report. Weinheim: Wiley-VCH. (pp. 10-25, Rep.).

Anonymous, 2016 a. Petroleum Formation, (n.d.). Retrieved December 06, 2016, from ***http://www.petroleum.co.uk/formation***

Anonymous, 2017a.United States Department of Labor. (n.d.). Retrieved January 10, 2017, from ***https://www.osha.gov/OshDoc/data_Hurricane_Facts/hydrogen_sulfide_fact.html***

Anonymous, 2016b. The Classification of Petroleum. (n.d.). Retrieved September 27, 2016, from ***http://www.petroleum.co.uk/classification***

Anonymous, 2011b. An introduction to petroleum refining and the production of ultra-low sulfur gasoline and diesel fuel. ***The international council on clean transportation***. Bethesda, Maryland, US.

Anonymous, 2017b. Adsorption Isotherm. (n.d.). Retrieved January, from ***http://vlab.amrita.edu/?sub=2&brch=190&sim=606&cnt=1***

Anonymous, 2016c. CHROMacademy | HPLC training | GC training | Mass Spec & SPE training | HPLC troubleshooting,from ***http://www.chromacademy.com/***

Ashar NG, 2016. Advances in sulphonation techniques, ***springerBriefs in applied sciences and technology***, chapter **2**: 9-19.

Aske N, Orr R, Sjöblom J, 2002. Characterisation of crude oil components، **2**: 2-8.

Atia AA, Farag FM, Youssef AE, 2006. Studies on the adsorption of dodecylbenzenesulfonate and cetylpyridinium bromide at liquid/air and bentonite/liquid interfaces. Colloids and Surfaces A: ***Physicochemical and Engineering Aspects***, **278**(1-3): 74-80.

Auroux A, 2013. Calorimetry and thermal methods in catalysis. ***Springer Berlin Heidelberg***, chapter **1**: 1-50.

Bajpai AK, Rajpoot M, 1999. Adsorption technique – A review, ***journal of scientific & industrial research***, **58**: 844-860.

Baskar C, Baskar S, Dhillon RS, 2014. ***Biomass Conversion the Interface of Biotechnology, Chemistry and Materials Science. Berlin: Springer Berlin***, Chapter **5**: 187-196.

Battez AH, González R, Viesca J, Fernández J, Fernández JD, Machado A, Riba J, 2008. CuO, $ZrO_2$ and ZnO nanoparticles as antiwear additive in oil lubricants. Wear, **265**(3-4): 422-428.

Bitton G, Marshall KC, 1980. Adsorption of microorganisms to surfaces. New York: Wiley, **25**(5): 969-970.

Brauer H, Varma YB, 1981. Design and operation of adsorption equipment. Air Pollution Control Equipment, ***springer-Verlag***, 307-333.

Buzea C, Pacheco II, Robbie K 2007. Nanomaterials and nanoparticles: Sources and toxicity. Biointerphases, **2**(4): 1-103.

Campos-Martin J, Capel-Sanchez M, Perez-Presas P, Fierro J, 2010. Oxidative processes of desulfurization of liquid fuels,***Journal of Chemical Technology & Biotechnology***, **85**(7): 1-33.

Chaturvedi S, Dave PN, Shah N, 2012. Applications of nano-catalyst in new era. ***Journal of Saudi Chemical Society***, **16**(3): 307-325.

Chaudhuri UR, 2011. Fundamentals of petroleum and petrochemical engineering, Boca Raton: ***CRC Press***. Chapter **1**: 1-23.

Chinese academy of sciences, Beijing, China. ***Intech open access publisher***, **3**: 51-66.

Choudhury H, Stedeford T, Donohue J, Ingerman L, Osier M, Fransen M, MacDonald AR, 2005. Toxicological review of zinc and compounds, ***EPA***. **2**(1): 3-5.

Christmann K, 2011. ***Modern Methods in Heterogeneous Catalysis Research***. Lecture presented at Freie Universität in German, Berlin. 1-39.

Collins BC, Mestetsky PA, Savaiano NJ, 1998. Method of removing sulfur compounds from sour crude oil and sour natural gas, ***Ulllted States Patent***, **11**: 1-6.

Dąbrowski A, 2001. Adsorption — from theory to practice. ***Advances in Colloid and Interface Science***, **93**(1-3): 135-224.

Darwish NN, 2015. ***Adsorption Study of Desulfurization of Diesel Oil Using Activated Charcoal*** (Unpublished master's thesis). American University of Sharjah, chapter **1**: 14-21.

Daware GB, Kulkarni AB, Rajput AA, 2015. Desulphurization of diesel by using low cost adsorbent, ***International Journal of Innovative and Emerging Research in Engineering***, **2**(6): 69-73.

Deutschmann O, Kneozinger H, Kochloefl K, Turek T, 2009. ***Heterogeneous Catalysis and Solid Catalysts***, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, chapter **2**: 7-23.

Devold H, 2013. Oil and gas production handbook an introduction to oil and gas production, transport, refining and petrochemical industry, All rights reserved, chapter **3**: 21-38.

Donohue MJ, 2014. ***Sulfur Part I: Sulfur and Sulfur Compounds in the Environment***(pp.1-21,Rep.No.7)report. Washington: ***Http://www.toxipedia.org/display/toxipedia*.**

Dowdy RH, Lindsay WL, 1981. ***Solid Phase-Solution Equilibria in Soils,ASA Special Publication Chemistry in the Soil Environment***, chapter **10**: 183-201.

Duissenov D, 2012. Production and processing of high sulfur crude and associated gas, NTNU Det skapende unversitet, Trondheim, **7**: 19-22.

Duissenov D, 2013. Production and processing of sour crude and natural gas - challenges due toincreasing stringent regulations, Norwegian University of Science and Technology, chapter **7**: 32-33.

Eigenbrodt C, Rooney E, 2014. Adsorption of 1, 4 –Dioxane on activated carbon with regeneration by titanium dioxide/***Ultraviolet Light***, **2**: 9-40.

Erdem E, Karapinar N, Donat R, 2004. The removal of heavy metal cations by natural zeolites. ***Journal of Colloid and Interface Science***, **280**(2): 309-314.

Fadhel ZS, 2010. ***Desulfurization of Light Diesel Fuel Using Chloramine T and Polymer Supported Imidation Agent***, MSc thesis, Chemical Engineering Department, University of Technology, Baghdad, **2**(2010): 22-29.

Foss M, Gulbrandsen E, Sjöblom J, 2010. Corrosion science "oil wetting and carbon dioxide corrosion inhibition of carbon steel with ferric corrosion products deposits." ***Corrosion, the journal of science and engineering***, **66**: 2 -11.

Gawande PR, Kaware JP, 2014. Desulphurization techniques for liquid fuel a review, ***International Journal of Engineering Technology***, management and applied Sciences, **2**(7): 2349-4476.

Grimwood MJ, 2001. ***Crude Oil Derived Petroleum Products In The Aquatic Environment: Priorities For Control***. R&D Technical ***Report*** P75/i688. United Kingdom.

Hameed B, Mahmoud D, Ahmad A, 2008. Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste. ***Journal of Hazardous Materials***, **158**(1): 65-72.

Hazrati N, Abdouss M, Vahid A, Miran Beigi AA, Mohammadalizadeh A, 2014. Removal of H2S from crude oil via stripping followed by adsorption using ZnO/MCM-41 and optimization of parameters, ***International Journal of Environmental Science and Technology Int***. J. Environ, **11**: 997-1006.

Horikoshi S, Serpone N, 2013. Introduction to nanoparticles, ***Wiley-VCH Verlag GmbH & Co. KGaA***, **1**(1): 1-23.

Hosseini H, Hamidi A, 2014. ***Sulfur Removal of Crude Oil by Ultrasound-Assisted Oxidative Method***, International Conference on Biological, Civil and Environmental Engineering, March 17-18, 2014 Dubai (UAE).

Hua R, Wang J, Kong H, Liu J, Lu X, Xu G, 2004. Analysis of sulfur-containing compounds in crude oils by comprehensive two-dimensional gas chromatography with sulfur chemiluminescence detection. J. Sep. ***Science Journal of Separation Science***, **27**(9): 691-698.

Jokuty, Paula, 1996. ***Properties of Crude Oils and Oil Products. Ottawa: Environment Canada***, Environmental Technology Advancement Directorate, Emergencies Science Division, Environmental Technology Centre, chapter **1**: 1-10.

Jukić A, 2013. ***Petroleum Refining and Petrochemical Processes, Faculty of Chemical Engineering and Technology University of Zagreb***, Fkitmcmxix, 1-18.

Kadhim LH, 2006. ***Adsorption of Some Dyes on Surface of White Iraqi Kaolin Clay, M.Sc***. Thesis, University of Kufa, Iraq.

Karagiannakis G, Baltzopoulou P, Dolios I, Konstandopoulos AG, 2013. "Liquid-phase adsorptive desulfurization of diesel fuel", 9th Panhellenic Scientific Chemical Engineering Congress, **2**(7): 1-9.

Kasali AA, Abiola O, Peters F, Aliyu H, Ikpe A, 2011. Petroleum chemistry, National open university of nigeria, **3**(1): 1-9.

Khan AA, 2012. Theory of adsorption equilibria analysis based on general equilibrium constant expression, T¨Ub˙itak, **36**: 219-231.

Kołodziejczak-Radzimska A, Jesionowski T (2014). Zinc oxide—from synthesis to application: A review. ***Materials,*** **7**(4): 2833-2881.

Kumar BV, Naik, HS, Girija D, Kumar BV, 2011. ChemInform abstract: ZnO nanoparticle as catalyst for efficient green one-pot synthesis of coumarins through knoevenagel condensation, chemInform, **43**(4): 615-621.

Kumar SS, Venkateswarlu P, Rao VR, Rao GN, 2013. Synthesis, characterization and optical properties of zinc oxide nanoparticles. ***Int Nano Lett International Nano Letters***, **3**(1): 1-6.

Laider KJ, Meisen JM, 1982. Physical chemistry, benjamin cummings publishing company, California, pp 775.

Lenior T, 2009. ***Analytical Techniques for the Determination of Sulphur Components in Flue Gas***, Fuel gas and natural gas (Master's thesis, VU University Faculty of Exact Sciences / Amsterdam) Amsterdam: Vrije Universiteit, (pp. 1-35).

Li W, Li S, 2007. A study on the adsorption of bovine serum albumin onto electrostatic microspheres: Role of surface groups. Colloids and Surfaces A: Physicochemical and Engineering Aspects, **295**(1-3): 159-164.

Lin L, Hong L, Jianhua Q, Jinjuan X, 2010. Progress in the technology for desulfurization of crude oil, China petroleum processing and petrochemical technology, **12**(4): 1-6.

Manahan SE, 2009. ***Fundamental of sustainable chemical science***, CRC press, chapter **9**: 307-336.

Matar S, Hatch LF, 1994**.** ***Chemistry of Petrochemical Processes***. Houston: Gulf Pub, chapter **3**: 49-107.

Matar S, Lewis FH, 1994.***Chemistry of Petrochemical Processes***. Houston: Gulf Pub, chapter **1**: 1-26.

McMillen SJ, Magaw RI, Carovillano RL, 2001. ***Risk-based Decision-making for Assessing Petroleum Impacts at Exploration and Production Sites***. Washington, D.C.: U.S. Dept. of Energy. Chapter **3**: 46-57.

Mohanraj VJ, Chen Y, 2006. Research Article Nanoparticles – A Review, ***Tropical Journal of Pharmaceutical Research***, **5**(1): 561-573.

Muzic M, Sertiæ-Bionda K, 2013. Alternative processes for removing organic sulfur compounds, ***Chem. Biochem. En***, **27**(1): 101–108.

Nawaz HR, Solangi BA, Zehra B, Nadeem U, 2011. Preparation of nano zinc oxide and its application in leather as a retanning and antibacterial agent, ***Canadian Journal on Scientific and Industrial Research***, **2**(4): 164-170.

Okuyama K, Lenggoro W, Iwaki T, 2004. Nanoparticle preparation and its application - a nanotechnology particle project in japan. proceedings, ***International Conference on MEMS, NANO and Smart Systems, ICMENS***, **4**(4): 1-4.

Ostiguy C, Roberge B, Woods C, Soucy B, 2010. ***Engineered Nanoparticles: Current knowledge about OHS Risks and Prevention Measures***, Montréal: Institut de recherche Robert-Sauvé en santé et en sécurité du travail. **4**(2): 5-10.

Özgür U, Alivov YI, Liu C, Teke A, Reshchikov M A, Doğan S, Morkoç H, 2005. A comprehensive review of ZnO materials and devices. J. Appl. Phys. ***Journal of Applied Physics***, **98**(4): 1-103.

Pal SL, Jana U, Manna PK, Mohanta GP, Manavalan R, 2011. Nanoparticle: An overview of preparation and characterization, ***Journal of Applied Pharmaceutical Science***, **1**(6): 228-234.

Patil MS, Bhattacharyulu YC, Kulkarni SR, 2011. Desulfurization of hydrocarbon liquid fuels by adsorption, ***Journal of Engineering Research and Studies***, **2**(1): 81-98.

Philippot K, Serp P, 2013. ChemInform Abstract: ***Concepts in Nanocatalysis, ChemInform, Wiley-VCH Verlag GmbH & Co***. KGaA, **44**(38): 1-54.

Pokropivny V, Lohmus R, Hussainova I, Pokropivny A, Vlassov S, 2007. ***Introduction to Nanomaterials and Nanotechnology***. Tartu: Tartu University Press, **1**: 7-13.

Putra EK, Pranowo R, Sunarso J, Indraswati N, Ismadji S, 2009. Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: Mechanisms, isotherms and kinetics. Water Research, **43**(9): 2419-2430.

Qabazard HM, Fantini M, 2011. ***I Need to Know: An Introduction to the Oil Industry & OPEC***. Vienna, Austria: OPEC Secretariat, Public Relations & Information Dept, chapter **1:** 12-25.

Rahimi M, Vadi M, 2014. Langmuir, Freundlich and Temkin Adsorption Isotherms of Propranolol on Multi-Wall Carbon Nanotube, ***Science journal of modern drug discovery and drug delivery research***, 1-3.

Ramakrishna K, Viraraghavan T, 1997. Dye removal using low cost adsorbents. ***Water Science and Technology***, **36**(2-3): 189-196.

Rang H, Kann J, Oja V, 2006. Advances in desulfurization research of liquid fuel, ***oil shale A Scientific-Technical Journal, Estonian Academy Publishers***, **23**(2): 164-176.

Safaei-Ghomi J, Ghasemzadeh MA, Zahedi S, 2013. ZnO Nanoparticles: A highly effective and readily recyclable catalyst for the one-pot synthesis of 1,8-dioxo-decahydroacridine and 1,8-dioxooctahydro-xanthene Derivatives, ***Sociedad Química de México***, **57**(1): 1-7 .

Sarmento M, Oliveira J, Slatner M, Boulton R, 1999. Kinetics of the adsorption of bovine serum albumin contained in a model wine solution by non-swelling ion-exchange resins. ***Journal of Food Engineering***, **39**(1): 65-71.

Sayyadnejad MA, Ghaffarian HR, Saeidi M, 2008. Removal of hydrogen sulfide by zinc oxide nanoparticles in drilling fluid, ***International Journal of Environmental Science & Technology***, **5**(4): 565-569.

Seader JD, Henley EJ, 2006. Separation process principles. ***Hoboken, NJ: John Wiley & Sons***. **1**(2): 2-34.

Selley RC, 1985. ***Elements of Petroleum Geology***, New York: W.H. Freeman and co. Second edition, Academic press. Chapter **2**: 14-33.

Sharma S, Agarwal GP, 2001. Interactions of proteins with immobilized metal ions: A comparative analysis using various isotherm models. ***Analytical Biochemistry***, **288**(2): 126-140.

Simanzhenkov V, Idem R, 2003. ***Crude Oil Chemistry***, New York: Marcel Dekker, chapter **1**: 1-70.

Smith HM, 1968. ***Qualitative and Quantitative Aspects of Crude Oil Composition***, Washington: U.S. Bureau of Mines;. **1**: 3-6.

Somasundara P, Huang L, 1997. Adsorption Behavior of surfactant mixtures at solid-liquid interface, ***Polish J. Chern***, **71**: 568-582.

Song C, 2002. New approaches to deep desulfurization for ultra-clean gasoline and diesel fuels, ***anl.gov***, **47**(2): 438-444.

Song HS, 2014. ***Desulfurization by Metal Oxide/Graphene Composites*** (Unpublished master's thesis). University of Waterloo, Ontario, Canada, 1-7.

Speight JG, 2000. The desulfurization of heavy oils and residua, marcel dekker, Inc. ***All right reserved***, **1**(2): 1-38

Speight JG, 2011.The refinery of the future. ***London: Elsevier***. Chapter **1**: 1-37.

Srivastava VC, 2012. An evaluation of desulfurization technologies for sulfur removal from liquid fuels. ***RSC Adv***., **2**(3): 759-783.

Stirling D, 2000. ***The Sulfur Problem: Cleaning up Industrial Feedstocks***. Cambridge, UK: Royal Society of Chemistry. Chapter **1**: 1-9.

Sun JHF, Cui D, Li H, Cai HY, Zhang LL, Chen X, 2012. ***Design, Modeling, Microfabrication and Characterization of the Micro Gas Chromatography Columns***. State Key Laboratory of Transducer Technology, Institute of Electronics, **3**: 51-65.

Sun X, Li C, Wu Z, Xu X, Ren L, Zhao H, 2007. Adsorption of protein from model wine solution by different bentonites. ***Chinese Journal of Chemical Engineering***, **15**(5): 632-638.

Theng BK, 1980. ***Soils with Variable Charge***, Lower Hutt, New Zealand Society of Soil Science.

Tien C, 1994. Fixed-bed adsorption calculations. adsorption calculations and modelling, ***Elsevier***,121-166.

Vaezi R, Atashi H, Tabrizi FF, 2011. A novel optimization approach for $H_2S$ expulsion from crude oil, ***International Journal of Chemical Engineering and Applications***, **2**(5): 342-345.

Wang W, Chen H, Wang A, 2007. Adsorption characteristics of Cd (II) from aqueous solution onto activated palygorskite. ***Separation and Purification Technology***, **55**(2): 157-164.

Wauquier JP, 1995. ***Petroleum Refining.*** Paris: Éditions Technip, chapter **1**: 1-15.

Webb PA, 2003. Introduction to chemical adsorption analytical techniques and their applications to catalysis, ***MIC Technical Publications***, **1**: 1-12.

William D, McCain Jr, 1990. The properties of petroleum fluids, ***pennwell published company***, **1**(2): 1-45.

Yasin G, Bhanger MI, Ansari TM, Naqvi SMSR, Ashraf M, Ahmad K, Talpur FN 2013. Quality and chemistry of crude oils, ***Journal of Petroleum Technology and Alternative Fuels***, **4**(3): 53-63.

Younes MA, 2012. ***Crude Oil Exploration in the World***. Rijeka, Croatia: InTech. Chapter **3**: 48-70.

Zeng H, Zou F, Lehne EYJ, Zhang D, 2012. Gas chromatograph applications in petroleum hydrocarbon fluids. ***Advanced gas chromatography - progress in agricultural, biomedical and industrial applications***, **17**(2012): 363-388.

Zheng H, Liu D, Zheng Y, Liang S, Liu Z, 2009. Sorption isotherm and kinetic modeling of aniline on Cr-bentonite. ***Journal of Hazardous Materials***, **167**(1-3): 141-147.

Zhou A, Ma X, Song C, 2006. Liquid-Phase adsorption of multi-ring thiophenic sulfur compounds on carbon materials with different surface properties, ***The Journal of Physical Chemistry B J. Phys. Chem. B***, **110**(10): 4699-4707.

# APPENDIX INDEX

## GENİŞLETİLMİŞ TÜRKÇE ÖZET
## (EXTENDED TURKISH SUMMARY)

## ÇİNKO OKSİT NANOPARTİKÜLLERİ TARAFINDAN ADSORPSİYON YOLUYLA HAM PETROLDEN SÜLFÜR İÇERİKLERİNİN İNCELENMESİ VE TASFİYES

SAYDA, Amanj Wahab
Yüksek Lisans Tezi, Kimya Mühendisliği Bölümü
Tez Danışmanı : Prof. Dr. Nahit AKTAŞ
Mayıs 2017, 84 sayfa

Ham petrolde bulunan sülfür içeriği oldukça büyük bir tehlike arz etmekte, insanlarla diğer canlıların yaşadığı çevreye zarar vermekte, işletim sistemlerinin aksamasına ve bozulmasına ayrıca SO ve $SO_2$ gibi toksik gazların yayılımına sebep olmaktadır.

Bu çalışma bu sebeplerden dolayı sülfür içeriği yüksek olan ham petroller başta olmak üzere, ham petrolden sülfürün tasfiyesi amacıyla hazırlanmıştır. Çalışmanın yürütüldüğü petrol alanında sülfür içeriklerinin oranı %1.9640 düzeyindedir. Yüksek etkililik için çinko oksit nanopartikülleri yoluyla kullanılan adsorpsiyon metotları sayesinde zamanın etkililiğini (yüzeye tutulma süresi) hesaplayabiliriz çünkü

Zamanla sülfür adsorbentinin oranı yükselmektedir ancak doyma noktasına ulaştıktan sonra etkisi daha fazla artmamaktadır. Adsorpsiyon süreci üzerinde önemli bir etkisibulunan sıcaklık faktorü 25-45°C incelenmiştir. Sıcaklık arttıkça tasfiye edilen sülfür içeriğinin oranında bir azalma olmuştur ancak 38° stabil sıcaklıkta çinko oksit nanopartiküllerinin genişliğinde ve 0.1-0.5 g arasında değişen yoğunlukların artışında önemli sonuçlar elde edilmiştir.

**Anahtar kelimeler**: Ham petrol, Çinko oksit nanopartikülleri, Adsorpsiyon süreci ve sülfür içerikleri

## 1.GİRİŞ

Ham petrol, dünyanın benzin, benzin ve benzin gibi yakıtlar olarak tüketilen dünyanın en büyük ve en geniş enerji kaynağıdır, Jet yakıtı, dizel ve benzeri (Hosseini and Hamidi, 2014). Ham petrol, alkanlar (A), naftenler (N), olefinler (O), monoaromatik, poliaromatik hidrokarbonlar (PAH), steranlar, hopanlar ve kükürt ve azot içeren bazı eser bileşenlerini içeren son derece kompleks bir karışımdır. Ham petroldeki kükürt içeriği% 0.05 ila% 10 arasında değişebilir (Hua ve ark., 2004). Ham yağda merkaptanlar olarak kükürt bileşikleri bulunur, mono- ve disülfür genel formül R-SH, R-S-R1, R-S-S-R1 ile ölür ve burada R ve Rı alkil radikalleridir. Merkaptanlar çok aşındırıcı iken, mono- ve disülfür yoktur. Siklik kükürt bileşiklerinin örnekleri, tiyofenler ve benzotiofen3- dir (Chaudhuri, 2011).

## 2. GENEL BİLGİLER

### 2.1. Ham petrol

Ham petrol, çoğunlukla alkanlar tekli bağ hidrokarbonları olan 200 veya daha fazla farklı organik bileşikten ve benzen, C6H6 gibi daha küçük fraksiyon aromatik altı-halkalı moleküllerden oluşan kompleks bir karışımdır (Devold, 2013). Hamurun doğası orijinal biyolojik kaynak materyaline ve maruz kaldığı jeokimyasal kuvvetlere bağlıdır (Grimwood, 2001).

### 2.2. Ham petrolün sınıflandırılması

1- Ham petrolü rafine etmek isteyen kimya mühendisleri tarafından önerilenler.

2- Jeologlar ve jeokimyacılar tarafından kaynak, olgunlaşma ve tarihin anlaşılmasına yardımcı olan kişiler.

### 2.3. Ham petrolün kompozisyonu

1. Hidrokarbon bileşikleri (karbon ve hidrojen bileşikleri).
2. Hidrokarbon olmayan bileşikler.
3. Organometalik bileşikler ve inorganik tuzlar (metalik bileşikler) (Matar and Hatch, 1994).

### 2.4. Kükürt bileşikleri

Kükürt bileşikleri çeşitli formlarda bulunur ve dört ana gruba ayrılabilir: merkaptanlar, sülfürler, disülfitler ve tiyofenler. Yakıtın yakılması sırasında kükürt dioksit SO2 oluşturması nedeniyle istenmeyen bir bileşen (Adeyi et al., 2014).

### 2.5. Ham petrolde kükürt bileşiklerinin arıtımı (Desülfürizasyon işlemleri)

1- Hidrodesülfürizasyon HDS
2- Hidrodesülfürizasyon NHDS (Oksidatif kükürt giderme ODS, Ekstraksiyon, Biyodosulfürizasyon BDS, Adsorpsiyon kükürt giderme)

### 2.6. Çinko Oksit

Çinko oksit ve çinko karbonat gibi çinko bileşikleri, kükürt bileşiklerini ham petrolden uzaklaştırmak için kullanılan yaygın temizleyicilerdir. Çinko oksit, hammadde emülsiyonu ve ham petroldeki kükürt bileşiklerinin uzaklaştırılması için iyi bir adadır. Yağ oranı% 80 olduğu için iyi tahmin edilebilir reaksiyon kinetiği ve emme kapasitesine sahiptir. Ayrıca, moleküler elekler veya çinko-titanyum oksit gibi diğer sorbentlere kıyasla kolayca bulunur (Sayyadnejad ve ark., 2008).

# 3. MATERYAL VE YÖNTEM

## 3.1. Giriş

Bu bölüm, bu çalışmanın deneysel çalışmasının ayrıntılarını içermektedir. Hedef, kükürt bileşiklerini ham petrolden çıkarmak için çinko oksit nanopartikülünün deneysel olarak araştırmak ve kükürt giderme işlemi üzerindeki sıcaklığın ve katalizör temas süresinin kütlesini görmektir.

## 3.2. Malzemeler

### 3.2.1. Cihaz

### 3.2.2. Ham petrol

Bu araştırmada kullanılan ham petrol, Kerkük-Irak'tan gelen jambour tarladan alınmıştır ve başlangıçta bulunan toplam kükürt içeriği 19640 ppm'dir. Deneysel çalışma için ham petrol, 38 ° C sıcaklıkta yapılan bir sıcaklık örneği üzerinde gerçekleştirildi.

### 3.2.3. Çinko oksit ZnO tozları

Çinko oksit nano bu deneyimsel için 80 Nanopartikül kullanılmıştır.

## 3.3. Deneysel Prosedür

Çinko oksit nanopartikül adsorbentini kullanan kükürt giderme işlemi, ağırlıkça% 0,1 oranında kullanılan sorbent materyalinin farklı seviyelerinde araştırıldı.

Ağırlıkça% - 0.5 %, Çalışma sıcaklığı 25, 30, 35, 40 ve 45 oC ve temas süreleri 20, 40, 80, 160 ve Aşağıdaki prosedüre göre 320 dakika.

# 4. SONUÇLAR ve DEĞERLENDİRME

## 4.1. Dozaj çinko oksitin sonuçları.

Adsorptif işlemin, 0.1 g'da ve sıcaklık sabitiyle birlikte sülfür bileşiklerinden 220 ppm çıktığında adsorbe ettiği çalışma yolunun artışı teorisi, ikinci aşamada 0.2 g eklendiğinde Adsorbe edilen kükürt bileşiklerinden gelen 285 ppm, adsorpsiyondan görülen artış, katalizör ZnO miktarını arttırarak, 333, 360, 490 ppm sülfür bileşiklerinin uzaklaştırılmasından itibaren çalışma yolunu artıran ve aşağıda tablo (4.1) ve şekil (4.1) 'de gösterilen katalizörün 0.3, 0.4, 0.5 g ZnO notundan istikrarlı bir şekilde artması,

Çinko oksit nanopartikül ile adsorpsiyon ile ilgili bir çalışmada. Çinko oksit dozunun sonucu literatür çeşitleri ile karşılaştırılmıştır. Karşılaştırma sonuçları, katalizör miktarının, farklı emici madde ile adsorpsiyon artışı üzerinde büyük bir etkiye sahip olduğunu, düzenli olarak eklendiğinde, adsorpsiyon ve katalizör miktarı arasındaki eğri şemada (4.1) gösterdiğini gösterdi. Benzer sonuçlar, Birkaç yazar (Kaynar ve diğerleri, 2014), (Sayyadnejad ve ark., 2008)

## 4.2. Etki sıcaklığının sonuçları

Çizelge 4.2'ye göre. Ham yağ ve çinko oksit nanopartikül arasındaki adsorpsiyon üzerindeki sıcaklığın etkisi, adsorpsiyonu düşürdüğü sıcaklık artışını gösterdi, ham petroldeki kükürt bileşiklerinin giderilmesi için 25 $^{0}$C daha yüksek adsorpsiyon oranının 740 ppm'e eşit olduğunu ve bunu takiben 30, 35 40 ve 45 $^{o}$C'de sırasıyla 530, 490, 220 ve 130 ppm olarak bulunmuştur. İkinci safhadaki kükürt ve saf yağın yoğunluğunun azaltılması, saf yağın ısı sıcaklığının yükselmesini değiştirir.

Saf yağın kükürt içeriğinin yoğunluğunun her düşüşü her seferinde saf yağın ısıtma sıcaklığının istikrarlı bir şekilde arttığını gösterir, bununla birlikte ısı sıcaklığının arttığını, ancak bunu izleyen sıcaklıkta adsorpsiyonun azaldığı sıcaklığın arttığını gösterir 4.2.

Bu çalışmada, çinko oksit nanopartikül kullanılarak adsorpsiyon işlemi üzerine 25-45 ° C deney sıcaklığı aralığındaki sıcaklığın etkisini değerlendirdik ve sonuçlar düzenli olarak adsorpsiyonun arttığını ve (Suteu, 2005), (Al- Obady ve Şimmery, 2012).

### 4.3. Etki sonuçları Temas Saati

Bu çalışmalar adsorpsiyon maddesiyle saf yağın hayatta kalma oranının artmasının, adsorpsiyon aktivitesini olumlu yönde etkilediğini ve ilk çalışmada ve bu reaksiyonun hızla gerçekleştiğini doğrulayan ikinci çalışmada büyük fark yarattığını göstermiştir Ham petrolün sıcaklık doğasında büyük bir etkinlik,

Ancak zaman kazandığımızda adsorpsiyonun biraz arttığını ve 80 nane ve üstte bir yol izlediğini görüyoruz. 20, 40 dakika süreyle, sülfür bileşiklerinin 437,582 ppm'den yukarı doğru, ancak 80 dakikaya doğru çıkması eğrisi arttıkça eğri arttı ve eğri sağa çıktı çünkü adsorbent madde doygunluğu, daha sonra 160, 320 dakika arttı. Kükürt bileşiklerinin uzaklaştırılması üzerinde büyük bir etkisi yoktur. These results of time dependence of sulfur compounds adsorption experiments are shown in figure. 4.3 are compared with (Kaynar et al., 2015), (Hosseini and Hamidi and 2014) literatures

## 5. SONUÇ

Bu çalışma adsorpsiyon sürecinin eşlik eden kükürt bileşiklerini azaltmak olduğunu gösterdi.

1- Kolay teknik, karmaşık süreçler kullanarak hayır ihtiyaç duyar.

2- Ucuz.

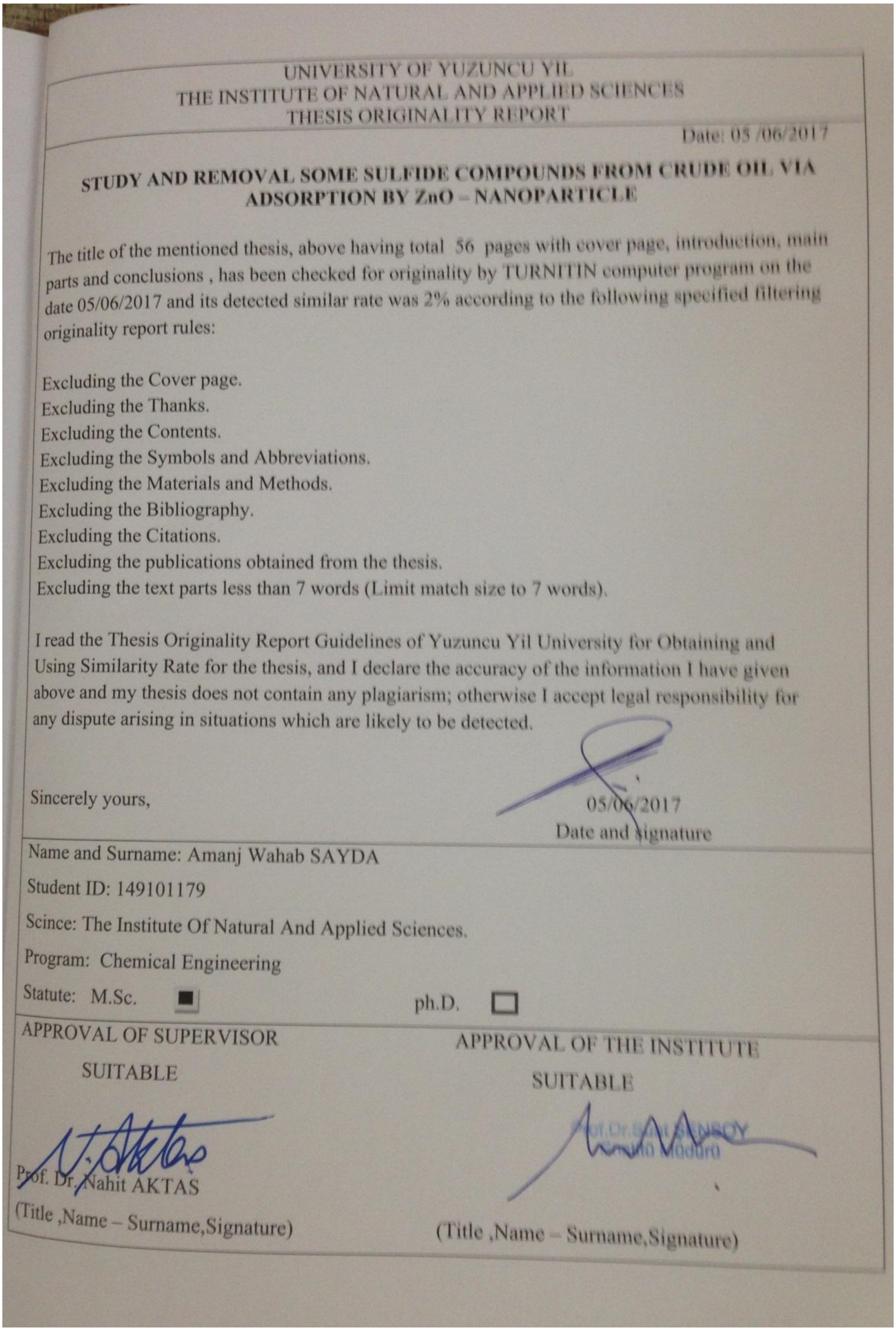
3- Hızlı işlem ve hızlı sonuçlar, bu nedenle kükürt bileşiklerini harika bir şekilde çıkarabiliriz.

4- Yüksek kaldırma kalifikasyonu.

5- Rafinerilerde pratik olarak kullanılabilir.

# CURRICULUM VITAE

He was born in khormatoo of Kirkuk from Iraq; He completed the primary and secondary education in Khormatoo town. During the years of 1992-1999 he had studied in Tikrit University, the College of Science, and Department of Chemistry. In 2004 he had graduated from here. At the September of 2014 he started my master study in Yuzuncu Yil University



UNIVERSITY OF YUZUNCU YIL
THE INSTITUTE OF NATURAL AND APPLIED SCIENCES
THESIS ORIGINALITY REPORT

Date: 05 /06/2017

## STUDY AND REMOVAL SOME SULFIDE COMPOUNDS FROM CRUDE OIL VIA ADSORPTION BY ZnO – NANOPARTICLE

The title of the mentioned thesis, above having total 56 pages with cover page, introduction, main parts and conclusions , has been checked for originality by TURNITIN computer program on the date 05/06/2017 and its detected similar rate was 2% according to the following specified filtering originality report rules:

Excluding the Cover page.
Excluding the Thanks.
Excluding the Contents.
Excluding the Symbols and Abbreviations.
Excluding the Materials and Methods.
Excluding the Bibliography.
Excluding the Citations.
Excluding the publications obtained from the thesis.
Excluding the text parts less than 7 words (Limit match size to 7 words).

I read the Thesis Originality Report Guidelines of Yuzuncu Yil University for Obtaining and Using Similarity Rate for the thesis, and I declare the accuracy of the information I have given above and my thesis does not contain any plagiarism; otherwise I accept legal responsibility for any dispute arising in situations which are likely to be detected.

Sincerely yours,

05/06/2017
Date and signature

Name and Surname: Amanj Wahab SAYDA
Student ID: 149101179
Scince: The Institute Of Natural And Applied Sciences.
Program: Chemical Engineering
Statute: M.Sc. ■ ph.D. ☐

APPROVAL OF SUPERVISOR
SUITABLE

N. Aktas
Prof. Dr. Nahit AKTAS
(Title ,Name – Surname,Signature)

APPROVAL OF THE INSTITUTE
SUITABLE

Prof.Dr.[illegible] [illegible]NSOY
[illegible] Müdürü
(Title ,Name – Surname,Signature)