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Desulfurization of Light Naphtha from Al-Diwaniya Refinery by Using Modified Calcite Adsorbent

A Thesis
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By

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بِسْمِ اللَّـهِ الرَّحْمَـٰنِ الرَّحِيمِ

يَرْفَعِ اللَّهُ الَّذِينَ آمَنُوا مِنكُمْ
وَالَّذِينَ أُوتُوا الْعِلْمَ دَرَجَاتٍ ۚ
وَاللَّهُ بِمَا تَعْمَلُونَ خَبِيرٌ

صدق اللَّهُ العظيم

سورة المجادلة (١١)

Dedication

This thesis is dedicated to:

My **Father** and my brother **Saad** who had passed away before seeing this

moment, are

with me in every step.

To which heaven is under her feet, my dear mother.

To my wife and companion, and to my soul my son and my daughter.

My beloved brothers and sisters.

All my teachers: my second family.

My friends who encourage and support me.

All the people in my life who touch my heart, I dedicate this research to

them.

Ahmed Qasim

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A special thanks to my close friends

Sajjad Sarhan,Thamer,Mustafa, Mohand, Shahad,Alaa ,Gofran and Huda.

AHMED

Abstract

This study used the adsorption method to remove sulfur compounds from light naphtha fuel by using calcite and modified calcite as adsorbents. The calcite was prepared from chicken eggshells by heating and activation methods, and it was modified by mixing it with commercial activated carbon as equal weight ratios. XRD and FTIR characterized the adsorbents, and Brunauer, Emmett, and Teller (BET) evaluated their surface areas.

Light naphtha from the Al-Diwaniyah refinery, with a sulfur concentration of 776 ppm, was used in batch adsorption studies. Various operation conditions that affect the adsorption process were studied, as temperature (20–40 °C), weight of the adsorbent (1-3 g) per 100 ml of light naphtha, and contact time (15–45 min) at constant mixing speed (300 rpm). In this study, the Minitab programme-Box-Behnken design was used to design experiments, which is considered more straightforward and accurate because it shows the effect of each dependent factor on the adsorption efficiency and removal ratio. Results and analysis show that the increase in temperature, the amount of adsorbent, and contact time increasing the removal efficiency. The analysis of adsorption equilibrium isotherms shows that the experimental data follows the Freundlich isotherm model for adsorbents. According to the results of the study, the optimum removal percentages of sulfur content of light naphtha by using calcite and modified calcite as adsorbents equal 61% (303 ppm) and 79% (163 ppm), respectively.

Finally, the results proved that using modified calcite(mixing of equal weight ratio of calcite and commercial activated carbon) as an adsorbent for adsorptive desulfurization is better than calcite in terms of removal percentage.

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LIST OF ABBREVIATIONS

Abbreviations	Definition
AC	Activated carbon
ADS	adsorptive desulfurization
ANOVA	Analysis of variance
API	American petroleum institute
BBD	Box-Behnken design
BDS	Biodesulfurization
BET	Brunauer-Emmett-Teller
BT	Benzothiophenes
CAC	Commercial activated carbon
DBTs	Dibenzothiophenes
DS	Desulfurization
EDS	Extractive desulfurization
EPA	Environmental Protection Agency
FTIR	Fourier –Transform Infrared Spectroscopy
GAC	Granular activated carbon
HDS	Hydrodesulfurization
JCPDS	Joint Committee on Powder Diffraction Standards
LHSV	Liquid hour space velocity
L.N	Light naphtha
LPG	Liquefied petroleum gas
MAC	Modified activated carbon

M-calcite	Modified calcite
min	Minute
MMT	Metals impregnated montmorillonite clay
MOFs	Metal-organic frameworks
ODS	Oxidative desulfurization
pH	Acidity measurement
ppm	Part per million
R^2	Correlation coefficient
RSM	Response surface methodology
rpm	Rotate per Minute
SEDS	Solvent Extractive desulfurization
SOCs	Sulfur organic compounds
Temp.	Temperature
WES	White eggshell
XRD	X-ray diffraction

NOMENCLATURES

Symbols	Definition	Unit
β_0	Intercept coefficient	dimensionless
βi	Linear effect (slope)	dimensionless
βii	Squared effect	dimensionless
βij	The interaction effect of linear	dimensionless
C_e	Equilibrium concentration of adsorbate	mg/L
k	Number of factors	dimensionless
K_F	Freundlich isotherm constant	[(mg/g) (L/mg)$^{1/n}$]
K_L	Langmuir isotherm constant	(L/mg)
N	Number of tests	dimensionless
n	Freundlich favorability constant	dimensionless
q	Adsorbate adsorbed/amount of adsorbent	mg/g
q_e	Equilibrium adsorption capacity of the adsorbent	mg/g
q_m	Saturation capacity at maximum	(mgS/g.adso.)
R	Predicated response	dimensionless
r	Replicate the number central point	dimensionless
S_o	Initial sulfur concentration	ppm
S_f	Final sulfur concentration	ppm

Chapter One

Introduction

Chapter One

Introduction

1.1 Introduction

Demand for crude oil as a source of energy is increasing as the global economy grows. Crude oil is either considered sweet (with a sulfur concentration of less than 0.5%) or sour (with a sulfur content of greater than 0.5%). The location of a crude oil reservoir is a key factor in determining its sulfur concentration**(Alardhi et al., 2022)**. Market prices for crude oil are based mostly on its sulfur content and API, with a preference for crude oil with a low sulfur content **(Demirbas et al., 2015)**.

When it comes to sulfur compounds in feedstock derivatives (fuels), the Environmental Protection Agency (EPA) and other environmental protection organizations are constantly revising their requirements.

Oil derivatives such as gasoline, kerosene, and diesel fuel contain sulfur compounds, which are among the most toxic elements impacting the environment due to their offensive odor, corrosive nature, and ability to poison chemical catalysts. In order to comply with strict environmental requirements, it is normal practice to keep the sulfur concentration as low as feasible **(Humadi et al., 2023;Yu et al., 2023).**

As a result, in order to comply with the extremely low levels of sulfur, which are less than 10 ppm, worldwide rules have been mandated. A primary objective must continue to be the creation of a desulfurization technology that is both effective and economically feasible. Although hydrodesulfurization, also known as HDS, is commonly used in industry, it is not very effective at removing refractory sulfur compounds (such as dibenzothiophene (DBT) and alkyl-substituted DBTs), and it must be able to withstand difficult circumstances (such as high temperature, high pressure, high hydrogen consumption, and so on). There have been, fortunately, developments in several other technologies, such as adsorption desulfurization, extractive desulfurization, oxidative desulfurization, biodesulfurization, and so on**(Jiao et al., 2023)**.

Adsorptive desulfurization (ADS) stands out among these approaches because of its many benefits, such as its efficiency, energy savings, low cost, environmental friendliness, and operational safety. Also it is very effective at removing refractory sulfur compounds such as DBT and alkyl-substituted DBTs and it is not consuming hydrogen **(Zhang et al., 2023)**.

Calcite's adsorptive performance for desulfurization light naphtha from Al-Diwaniya refinery has been studied as a novelty in light of this, and the synthesis of calcite adsorbent with unique and useful modifications has been studied. The commercial activated carbon used in the synthesis of these modifications was mixed with calcite.

1.2 Objectives of the Work

The purpose of this job is to study the adsorptive desulfurization (ADS) of light naphtha (776 ppm) provided from the refinery of AL-Diwaniya, which can be done as follows:

1- Preparation of calcite ($CaCO_3$) as an adsorbent from chicken eggshells by using heating and activation methods, then Characterization of the calcite preparation by XRD, FTIR, and surface area. Also, enhancement of calcite activity for ADS by modification (mixing it with commercial activated carbon), then characterization of modified calcite by XRD, FTIR, and surface area.

2- Investigation of calcite and modified calcite activity for ADS of light naphtha in batch process by studying variables (temperature 20–40 °C, weight of the adsorbent 1–3 g per 100 ml of light naphtha, and time 15–45 min) by using Minitab 2017 Response Surface Methodology (RSM), Box-Behnken design (BBD), and examination adsorption isotherm Langmuir and Freundlich.

Chapter Two

Literature Review

Chapter Two

Literature Review

2.1 Crude Oil Refinery

Large industrial facilities called petroleum refineries process crude oil into a variety of useful byproducts like LPG, gasoline, kerosene, aviation fuel, diesel, fuel oil, wax, asphalt and feedstocks for the petrochemical industry**(Speight, 2020).**

To begin the process of refining crude oil, it must first be separated into the basic stocks that will serve as the foundation for the final products. In order to accomplish this crude oil fractionation, the oil is first separated into a series of boiling point fractions that satisfy the distillation criteria and share some of the attributes of the finished products. This is done in the crude distillation units**(Jones and Pujadó, 2006)**.

A typical refinery process flow diagram is shown in **Figure (2.1) (Al-Moubaraki and Obot, 2021).**

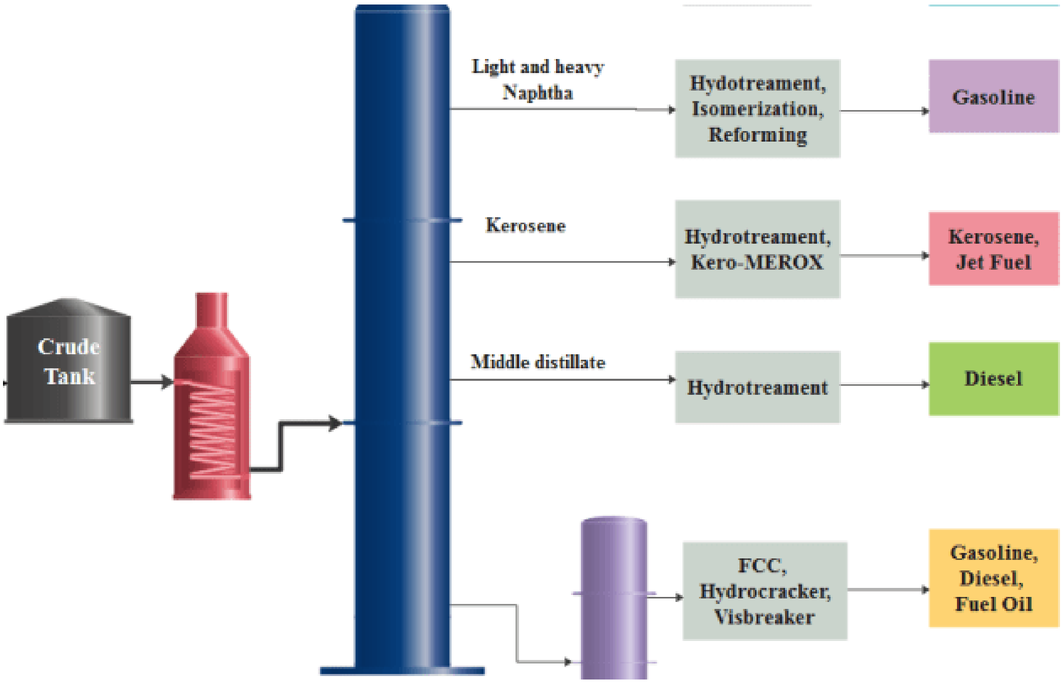

Figure (2.1): Units of crude oil refinery(Al-Moubaraki and Obot, 2021)

2.2 Naphtha

Naphtha is a byproduct of crude oil processing that is an intermediate hydrocarbon liquid. The lightest of the crude distillation liquid distillates, it consists of C5 through C10 hydrocarbons and boils between 38°C and 150°C. Naphtha is produced from the refinery's various secondary processing units as well as from the atmospheric distillation of crude oil.. Naphtha is not a direct petroleum fuel like kerosene, diesel and fuel oil; however, it is a feedstock in the plastics industry**(Shaw and Sahni, 2014)**.

Naphtha's physical characteristics are determined by the specific types of hydrocarbons it contains, with aromatic hydrocarbons having the greatest solvent power and straight-chain aliphatic compounds having the least **(Hassan et al., 2012)**.

One of the main feedstocks used in refineries for the manufacturing of gasoline is naphtha. Where natural gas is not available, naphtha is turned into hydrogen for use in the hydro processing units of refineries. Sometimes, naphtha is used in gas turbines or boilers **(Parkash, 2010)**.

Naphtha is produced in the refinery by secondary processing such as distillate hydrocrackers, delayed Coker units, and residual hydrocrackers as well as gas processing equipment that separates LPG from field gases. Based on their boiling range, heavy and light naphtha can be separated from one another.**(Parkash, 2010)**.

2.2.1 Light Naphtha

Naphtha with a lower number of carbon atoms in its molecules (between 5 and 6) boils at a lower temperature (between 30°C and 90°C) **(Khalid, 2015)**. It is one of the top fuels in the world and a significant source of automobile fuel (gasoline). Whereas in the traditional method, the light naphtha is obtained using an atmospheric distillation column, the hydrotreating process is then used to remove sulfur compounds, followed by a reforming unit, and the end result is gasoline**(Jarullah et al., 2020)**.

light naphtha, which could be as high as 10–15 volume percent of a crude oil, as light naphtha compounds are also produced in downstream process units**(Aboul-Fotouh et al., 2019)**.

2.2.2 Heavy Naphtha

The boiling point of heavy naphtha is between 90°C and 200 °C, and its molecules have 6-12 carbon atoms. It is used as a feed for refinery catalytic reformers that transform the lower-octane naphtha into reformate and has been used in the petrochemical industry due to its higher concentration of aromatics and naphthenes**(Joo and Suh, 2022).**

2.3 Sulfur Compounds:

Sulfur can be found in crude oil in a number of forms and concentrations. Depending on the nature and origin of the crude oil, the sulfur level can be anywhere from negligible to well over 80,000 ppm. For example, the sulfur content of Iraqi crude oils is between 22600 ppm and 33000 ppm. **(El-Gendy and Speight, 2015**; **El-Gendy and Nassar, 2018)**.

Sulfur compounds present in chemicals can harm the catalysts that are used in oil refining and lead to the formation of corrosion on equipment. Also have effects on the environment because when sulfur dioxide combines with water and air, it forms sulfuric acid, which is the main component of acid rain that causes deforestation.

The origin and boiling point range of the fraction indicated the presence of sulfur compounds in petroleum. The levels of sulfur compounds in crude oil increase with the increase in boiling point during distillation. However, the medium distillate fractions may have a higher sulfur content than the higher boiling point fractions. The breakdown of high molecular weight molecules during distillation is responsible for this **(Speight, 2014**; **Singh et al., 2016**).

Sulfur exists in both its elemental and organosulfur complex forms. There are two main types of organosulfur compounds: aliphatic (mercaptans, sulfides, and disulfides) and aromatic (thiophenes, benzothiophenes, dibenzothiophenes, and their alkylic derivatives**(Kurniawan et al., 2021)**.

Figure (2.2) shows sulfur compounds in crude oil**(Hossain et al., 2019)**.

Due to their low reactivity, aromatic sulfur compounds are more challenging to remove from liquid fuels via the conventional method known as the hydrodesulfurization process (HDS), even under optimal operating conditions. Because of this, they are classified as refractory sulfur compounds**(Gooneh-Farahani and Anbia, 2023)**.

Naphtha contains a variety of sulfur compounds, including mercaptans, disulfides, sulfides, and thiophenes; of these, thiophenes are the most refractory. The naphtha's sulfur compound contents change depending on the naphtha's origin**(Antos and Aitani, 2004)**.

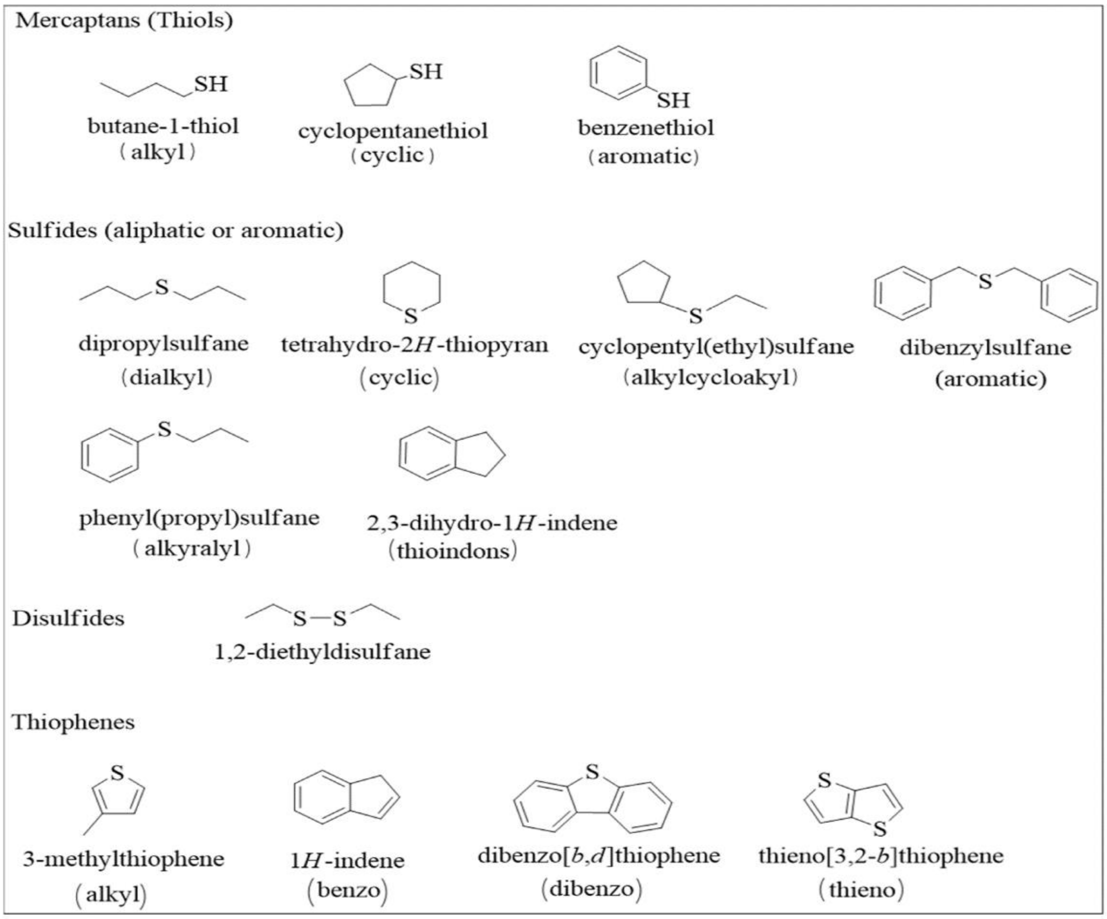

Figure (2.2): Types of the sulfur compounds for crude oil(Hossain et al., 2019).

2.4 Methods of Desulfurization

Desulfurization may be roughly categorized depending on the presence or absence of hydrogen, the fate of sulfur compounds, and the nature of the desulfurization process itself (physical, chemical, or both). The sulfur compounds might be decomposed and removed, eliminated from the process stream without decomposition, or decomposed solely, depending on the nature of the alteration that occurred. **Figure (2.3)** several of their possible permutations have been deemed promising. **(Saleh et al., 2016)**

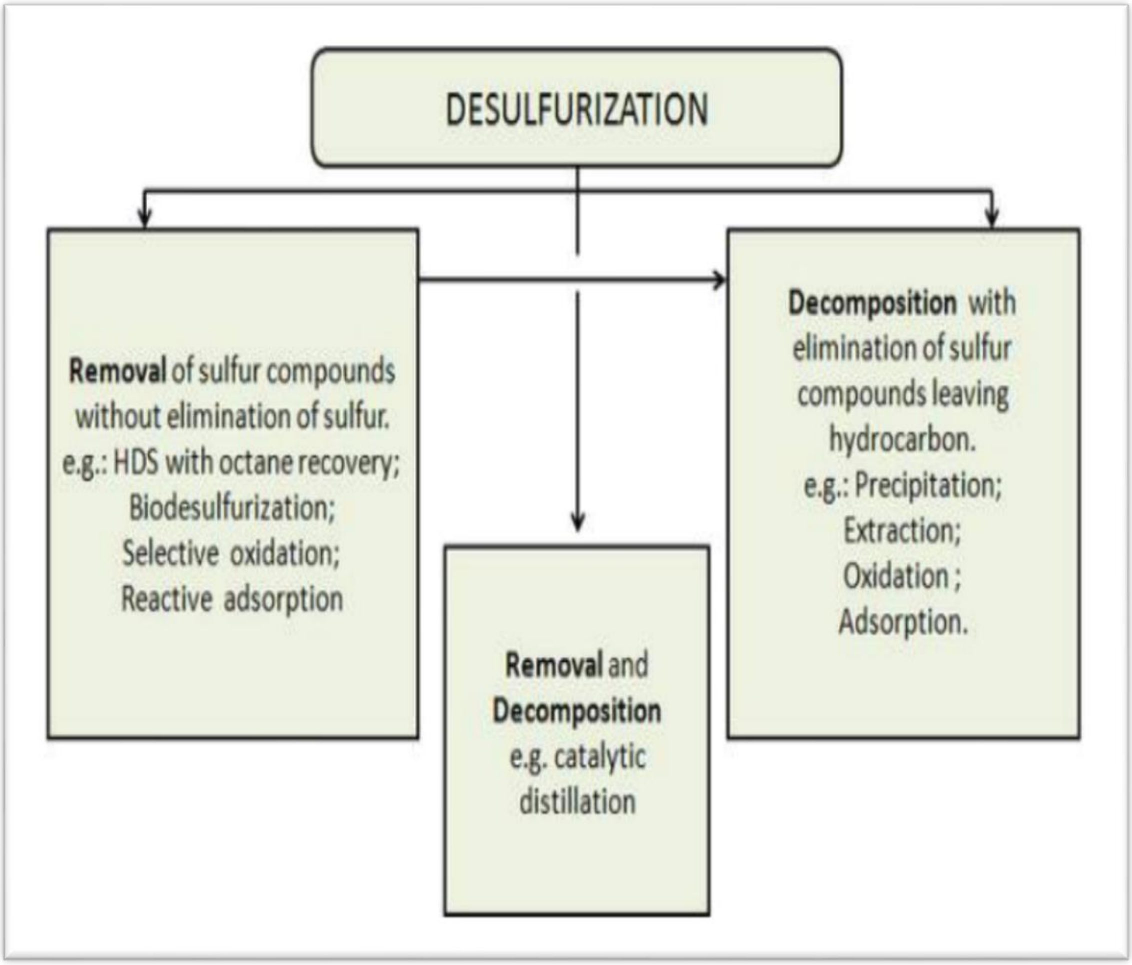

Figure (2.3): Desulfurization processes are divided up into several categories based on the nature of the sulfur compound modifications made throughout the purification procedure. (Saleh et al., 2016)

2.4.1 Hydrodesulfurization (HDS)

The hydrodesulfurization process is a chemical reaction that requires a catalyst. That used to remove or eliminate sulfur from petroleum products and natural gas. The HDS process converts a variety of organo-sulfur compounds into both hydrogen sulfide and sulfur-free organic molecules. Using metal catalysts like CoMo/Al_2O_3 or NiMo/Al_2O_3, this process is being carried out by catalytic treatment with hydrogen at pressures between 10 bar and 180 bar and temperatures between 290 °C and 455 °C. By adjusting hydrotreatment conditions and applying the right catalysts, refineries may generate especially limited sulfur**(Mamuad and Choi, 2023)**.

Naphtha is typically desulfurized by the hydrodesulfurization process. This method is widely used because it is effective at removing sulfur from aliphatic sulfur compounds and some thiophene spices. This is done in the presence of certain catalysts at high temperatures and pressures. Despite its benefits, current hydrodesulfurization technology falls short of the ultra-low sulfur requirement due to difficulties in treating benzothiophenes (BTs) and dibenzothiophenes (DBTs)**(Beshkoofeh, 2023)**.

2.4.2 Oxidative Desulfurization (ODS)

Since the ODS technology does not require exceptionally high temperatures and just air pressure is needed to achieve reaction, it is possible to define it as a promising technique**(Alwan, 2021)** . First, the sulfur is oxidized to sulfoxide or sulfones in the presence of an oxidation agent like potassium ferrate, tetra butyl hydroperoxide, hydrogen peroxide, ozone, molecular oxygen, etc., and because this is a selective oxidation, the OSCs retain their carbon-carbon bonds. Hydrogen peroxide (H_2O_2) is preferred over the other oxidant agents because it has a high oxidation reactivity, is cheap, safe, and selective. It may even be considered a green oxidant. Sulfur-containing compounds become more polar as they are oxidized. The second step is to use a polar solvent or adsorbents to extract the sulfoxides and sulfones from the oil phase**(Abdulhadi and Alwan, 2023)**

2.4.3 Solvent Extractive Desulfurizations (SEDS)

As an alternative to more complex methods, extractive desulfurization has been employed to eliminate sulfur compounds from liquid hydrocarbon fuels. Because sulfur compounds are more soluble in the solvent than in the feedstock, the solvent may be used to extract the sulfur compounds from the feedstock. This is a one-phase extraction procedure. Hydrocarbons and the solvent undergo the separation process in a device called a separator **(Siddiqui and Ahmed, 2016).**

Efficient removal of S-compounds from an EDS process requires the use of an extractant that meets the following specifications: high extractive capability, easy regeneration, immiscibility in fuel, high chemical and thermal stability, and environmental benignity**(Moheb-Aleaba and Khosravi-Nikou, 2023)**.

2.4.4 Biodesulfurizations (BDS)

It is a cost-effective substitute for the difficult and lengthy hydrodesulfurization of refractory heterocyclic-sulfur compounds like dibenzothiophene (DBT) and its derivatives. Desulfurization biocatalysts that maintain fuel's calorific value despite reducing sulfur content are in high demand due to increasing requirements**(Martzoukou et al., 2023)**

Biocatalysts for BDS synthesis have been in use since 1995, and a number of different types of bacteria, such as Arthrobacter, Rhodococcus erythropolis H-2, Rhodococcus sp. ECRD-1, and Sphingomonas subarctica T7b, have been utilized**(Zeelani and Pal, 2016)**.

The difficulties in BDS emerge from its slow biodegradation and the need for a suitable biocatalyst. The sensitive nature of living microbes makes it difficult to find out how to safely store, handle, ship, keep, and use them in the refinery environment**(Campos- Martin et al., 2010)**.

2.4.5 Adsorptive Desulfurization (ADS)

The removal of refractory sulfur compounds from liquid petroleum products using the standard hydrodesulfurization (HDS) approach is difficult. We're looking into several other methods as well. Adsorptive desulfurization (ADS) is a process that can be used as an alternative. In adsorption separation, a sulfur-removing adsorbent is used. In addition, it is possible under atmospheric conditions**(Yeole, 2023)**.

In either a fixed bed or a batch reactor, ADS can be used to clean petroleum-based fuels of sulfur compounds (**Liang et al., 2018**; **Yin et al., 2018**). There are a number of advantages to using adsorption for desulfurization rather than alternative methods**(Sharma et al., 2013**; **Saleh, 2015**; **Botana-de la Cruz et al., 2020**) based on:

- Its capacity to directly adsorb refractory thiophenic compounds employing a variety of solid adsorbent materials under mild operating conditions (room temperature and atmospheric pressure).

- This method of desulfurization is more cost-effective than others since it uses less energy without requiring complex equipment such as oxidizing agents or high-pressure hydrogen reactors in an adsorber structure.

- Ultradeep desulfurization is more practical for achieving sulfur-free fuel (less than 10 ppm).

- It is simple and inexpensive to regenerate adsorbents such as ionic liquids, silica, polymers, alumina, activated carbon, metal oxides, zeolites, clays, and so on.

- Adsorption methods require no skilled technicians or expensive equipment.

2.5 Adsorption

2.5.1 Definitions and Classifications

Adsorption is a surface process because it involves the movement of a molecule from a liquid or gaseous bulk to a solid surface, forming an interface layer between the two phases. In this layer, the interactions can be either physical or chemical**(Alaqarbeh, 2021)**.

Physical adsorption involves the interaction of an adsorbent and an adsorbate by the force of weak interparticle interactions, such as the forces of Van der Waals. The sulfur compounds do not undergo chemical changes since the adsorbent binds the organic sulfur compounds to the solid surface as a whole **(W. Ahmad et al., 2017)**. In contrast to the weaker van der Waals interaction caused by the exchange of electrons in physical adsorption, π-complexation between organosulfur compounds (SOCs) and the adsorbent is much more powerful in chemical adsorption. Some adsorption processes may involve both physical and chemical steps (**Ganiyu and Lateef, 2021**; **Yang et al., 2018**)

2.5.2 Mechanisms of Adsorption

The process of solute molecule adsorption onto an adsorbent can be divided into four main stages:

1-Bulk solution transport refers to the process by which an adsorbate is transferred from bulk solution to the adsorbent's surface.

2-Film diffusion transport involves adsorbate molecules moving across the liquid film that surrounds the adsorbent particles.

3- Diffusion on the internal surface of the pores, both in the liquid that is enclosed within the pores as well as the adsorbate that fills the pores.

4-There is adsorption and desorption occurring both inside the particle and on its external surface.

Any of those four stages listed above, or a combination of any of them, could serve as the rate-controlling step. For instance, if a chemical reaction comes after adsorption, it can go slower than diffusion, controlling the rate of removal.

Transport in the solution can be the rate-limiting stage in several large-scale adsorption processes**(SANYANGAR, 2016)**.

2.6 Variable Conditions Influencing on Batch Adsorption Process

2.6.1 Surface Area of Adsorbent

Granularity of the adsorbent plays an important parameter in treatment the adsorption technique due to surface area related inversely with particle size of adsorbent grain. Usually, the main adsorption is done as an external adsorption at adsorbent surface and slightly move inside the particle because only a few of the internal sites allow the adsorbate ion to propagation. Increasing surface area leads to the availability of suitable sites for adsorption **(Amal, 2018).**

2.6.2 Weight of Adsorbent

In general, amount of adsorbent is playing a main role in process of increasing removal of adsorbate form liquid phase to transport to solid phase at adsorbing sites. Increasing amount of adsorbent mass will provide more active exchangeable adsorption sites the extent of adsorption of a solute increase with the increase in the concentration of an adsorbent because the increase in adsorbent concentration translates into increased. However, the overall solute adsorption per unit weight of an adsorbent can decrease following the increase in adsorbent concentration due to interference caused by the interaction of active sites of an adsorbent **(Sidra, et al., 2018).**

2.6.3 Effect of Temperature

The temperature has two major effects on the adsorption process which is often accompanied by energy emission. Increasing the temperature is known to increase the rate of diffusion of the adsorbed molecules across the external boundary layer and the internal pores of the adsorbent particles, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate **(Barka, et al., 2011).** The nature of adsorption can be endothermic or exothermic where at endothermic state the heat and thus the kinetic energy of the molecules absorbed increases the ability to enter the pores of the steel phase and increase the speed of spread in it, so increase the adsorption process by increasing the temperature while at exothermic state the adsorbed amount decreases when the temperature increased, and raising the temperature will liberate the adsorbate(desorption) **(Amal, 2018).**

2.6.4 Effect of Contact Time

The contact time significantly affects the adsorption process. Also, contact time can influence the economic efficiency of the process as well as the adsorption kinetics. Therefore, contact time is another performance governing factor in adsorption process **(Sidra, et al., 2018).**

2.6.5 Effect of Agitation Speed

The absorbate up take based on assumption that film diffusion is rate limiting in adsorption process. Increased agitation speed causes low resistance of mass transfer due to reduction of the surface film diffusion, so the decreasing resistance to mass transfer and increasing the mass transfer until reaching equilibrium state **(Foo and Ahmed, 2010; Barka, et al., 2011).**

2.7 Adsorbents

Adsorbents have been used for purifying and separation purposes ever since ancient times. Some of the most popular options include activated carbon, zeolites, polymeric adsorbents, black carbon, clay and biosorbents.

Although many adsorbents are commercially available, choosing the right one for a given application can be challenging due to differences in matrix, porous structure, and adsorbent capacity. Only by developing a material with surface functional groups favorably impacting interactions with particular or polar adsorbates is it possible to achieve the capacity coupled with high sorption rates. The use of the polarity factor appears to be particularly crucial in the successful desulfurization of transportation fuels, as sulfur compounds are known to be somewhat more polar than hydrocarbons of similar nature.

New and improved adsorbents have been the focus of intensive research and development in this area. Adsorbents' adsorption capacities and selectivities can be improved through the addition of metals, composite adsorbents, mixed oxide supports, and other modifications to the physicochemical properties of the adsorbents' surfaces, pore channels, microstructures. (**Sun and Tatarchuk, 2016; Radhi and Mohammed, 2021)**.

2.7.1. Eggshells

Eggshells are a waste product of domestic and fast-food restaurants and can be gathered for free if a market exists. There were clearance sales on eggshells due to environmental contamination. The disposal of eggshells presents a number of difficulties, including cost, lack of convenient disposal options, unpleasant odor, diseases, and hardness. In addition, many tones of treated waste chicken eggshells are now being generated every day. The remainder of the eggshell is discarded since further processing would be too time- and money-consuming**(Mahmood et al., 2022; Al-Qaim, 2011).**

Eggshells are a biomaterial that can be used as an adsorbent since they are inexpensive, biocompatible, environmentally acceptable, easily renewable, and particularly stable in organic solvents**(Arunlertaree et al., 2007).**

2.7.1.1. Structure of the Eggshell

There are typically three layers to an egg shell: the cuticle, the stratum, and the membrane. There's different chemistry in each stratum. The cuticle layer, which is 10 µm thick and contains a pore channel, shields the egg from air moisture and bacteria while also facilitating gas exchange. The weight of an egg's calcite shell accounts for 9–12% of the whole egg. About 95% of an eggshell contains calcium carbonate, 1% is magnesium carbonate, 1% is calcium phosphate, and the remaining 4% is organic things, mostly protein. It’s well known that Calcium Carbonate ($CaCO_3$) can be found in eggshells.**(Ningrum et al., 2022;Yee Jian and Tunku Abdul Rahman, 2015).**

2.7.1.2 Calcium Carbonate (Calcite) in Eggshell as Adsorbent

Eggshells, seashells, and rocks all contain calcium carbonate (calcite), a naturally occurring compound that gives these objects their hardness and strength. On average, the calcium carbonate in a normal eggshell will amount to 2.2 grammes. A dry eggshell typically weighs

(5.5) grammes and is composed of calcium carbonate; however, these values might vary based on sources **(Lechtanski, 2000)**.

$CaCO_3$, or calcium carbonate, is a naturally occurring compound that makes up more than 4% of the earth's crust. It occurs naturally as marble, limestone, and chalk because of the long-term precipitation of coral and shells**(Mathur et al., 2016)**.

The decreasing availability of natural calcium carbonate began to cause worry. In addition, the aesthetic value of nature will be diminished as a result of the harvesting of natural limestone. Climate and environmental burdens, such as soil, water, and air pollution, are often linked to the quarrying of limestone**(Kittipongvises, 2017)**. That's why it's so important to find an acceptable substitute that can take its place without breaking the institution. This study suggests that used eggshells can be processed into a useful form of calcium carbonate.

2.7.2 Activated Carbon (AC)

The term "activated carbon" is used to describe a broad category of carbonized materials characterized by high porosity and surface area. Removal, retrieval, separation, and modification of different compounds in gases and liquids are only some of the many environmental and industrial uses for activated carbon**(Heidarinejad et al., 2020).**

Because of its limited sulfur capacity, ordinary AC requires frequent regeneration when employed as an adsorbent for ADS. Therefore, it's crucial to modify it in order to increase its sulfur capacity **(Zhang et al., 2016)**.

It is common knowledge that adsorbents derived from low-cost and easily accessible materials should be favored. Rice husk, oil palm, coconut shell, cork powder, tyres, and fly ash are all examples of carbonaceous materials widely used to produce AC **(Hanif et al., 2020)**.

2.8 Adsorption Isotherms

Until equilibrium is reached, the concentration of the adsorbed solute rises in adsorption systems. In a dynamic system, equilibrium is achieved when the adsorption and desorption rates are equal. At a given temperature and pressure, the equilibrium state is defined by the final concentration of solute in the liquid phase (mg S/l solution) and the amount of adsorbate present on the adsorbent (mg adsorbate/g adsorbent). One or more model equations, known as equilibrium isotherm equations, can be used to represent and fit these parameters.**(Lowell et al., 1991)**.

At a fixed temperature, the adsorption equilibrium of the adsorbate on the surface of an adsorbent is often described using adsorption isotherms**(Al-Ghouti and Da'ana, 2020)** .

Adsorption isotherms are essential for optimizing the adsorbent used by describing the interaction between the adsorbate and the adsorbent. Adsorption analysis and prediction, therefore, require the connection of experimental equilibrium data via a theoretical or empirical equation. Adsorption isotherm data can be described experimentally using one of several mathematical models. The most commonly used equations for adsorption isotherms are those of Langmuir and Freundlich.**(Zaini et al., 2023;Horváth et al., 2023).**The adsorbent capacity was calculated as follows **(Azimi et al., 2017)**.

$$q = \frac{(C_0 - C_e)V}{w} \qquad \mathbf{(2.1)}$$

where q (mg/g) : is the amount of adsorbate that is adsorbed (mg) / amount of adsorbent (g), Ce and C_0 : are the initial and equilibrium concentrations of SOCs (ppm); V :is the volume of solution (Liter) and w is the adsorbent weight (grams)

2.8.1 Langmuir Isotherm

The Langmuir isotherm model predicts that maximal adsorption will take place when the adsorbate molecules form a saturated monolayer on the adsorbent surface, maintaining a constant adsorption energy. Neither the adsorbate nor the molecules on the surface move or interact with one another**(Pereira et al., 2022)**.

Good corrections to very favorable isotherms can be found using Langmuir equation, which describes the physical and chemical adsorption of solid adsorbents with equal active sites. Adsorption of organosulfur compounds, and more petroleum fuel desulfurization processes have been reported by many researchers to be well suited to the Langmuir model**.** The Langmuir equation can be expressed as follows**(Sanyangar, 2016).**

$$q_e = \frac{q_m K_L C_e}{1+K_l C_e} \qquad \textbf{(2.2)}$$

The linear form of the Langmuir equation appears below **(Ayawei et al., 2017)**

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad \textbf{(2.3)}$$

where

C_e: the solute concentration in bulk solution at equilibrium (mg S/l solution).

q_e: at equilibrium, the weight adsorbate per unit weight adsorbent (mg S/g adsorbent).

q_m: the saturation capacity (mg S/g adsorbent).

K_L: the Langmuir constant (l/mg).

2.8.2 Freundlich Isotherm

The first example of an empirical correlation is the Freundlich isotherm model. Non ideal, reversible and heterogeneous adsorption processes can be described by using the Freundlich isotherm because it implies multi-layer adsorption of heterogenous surfaces with interactions between adsorbate molecules and many different adsorption sites **(Al Zubaidi et al., 2015; Yadav and Singh, 2017)**. The Freundlich isotherm has fewer restrictions than the Langmuir isotherm when describing the adsorption behavior of organic materials and reactive compounds because it applies to physical or chemical adsorption and to homogeneous and heterogeneous surfaces. Some metals, dyes, oxygenated pollutants, organic pollutants, and SOCs in fuels were all adsorbed by the various adsorbents, and the results were found to be in perfect agreement with experimental data. The Freundlich equation is described as an experimental equation with the following form **(Kopsidas, 2016)**:

$$q_e = K_F C_e^{1/n} \qquad (\mathbf{2.4})$$

The linear form of the Freundlich isotherm is as follows equation **(Ayawei et al., 2017)**

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad \mathbf{(2.5)}$$

where

K_F [(mg/g) (l/mg) ¹⁄ n] and n (dimensionless of constant) are empirical constants of the Freundlich isotherm, which give an indicator of adsorption capacity and favorability, respectively.

2.9 Response Surface Methodology (RSM)

Minitab 17's fractional factorial design includes the RSM technique, which provides a systematic and efficient experimental strategy for analyzing the effect of the parameters through the use of statistical methods. It's ideal for analyzing how several variables work together to affect final results(**(Bashir et al., 2015)**. An experimenter who is worried about the response function's curvature may choose the three-level factorial design. RSM has seen increasing application in recent years. The methodology of the response surface (RSM) is an application of statistical strategies used for the purpose of:

1) Setting up a range of experiments (design) for appropriate response prediction.

2) Fitting a hypothesized (empirical) model to the knowledge obtained through the design chosen.

3) Determining optimal conditions for the input (control) variables included in the model that contribute to the maximum or minimum response within a selected area.

4) With the publication of the article mostly on Experimental Achievement of Optimum Conditions by Box and Wilson, systematic work on RSM began**(Verdooren, 2020)**.

Response surface designs can be divided into two categories **(Ranade and Thiagarajan, 2017)**:

- Central Composite Designs:

It is possible to link a complete quadratic model to a central composite design. Since designs can incorporate data from a well-planned factorial experiment, they are frequently utilized when a design plan requires sequential experimentation.

- Box-Behnken Designs:

With the same number of factors, box-Behnken designs are cheaper to operate because they require fewer design points than central composite designs. First- and second-order coefficients can be estimated efficiently, but factorial experiment runs cannot be accounted for. When compared to central composite designs, which can have up to five levels per component, Box-Behnken designs always use three levels per factor. Box-Behnken designs, in contrast to centralized composites, never test all elements at their maximum or minimum values.

2.10 Previous Studies

Al Zubaidy et al. (2013) studied the adsorptive desulfurization of diesel fuel from a petrol station in Sharjah/ UAE with an initial concentration of sulfur content 410 ppm using commercial activated carbon (CAC) at 5% by mass as an adsorbent in batch work. The authors found that sulfur content reduced from 410 ppm to 251 ppm at room temperature with a time contact of two hours and a rotation speed of 500 rpm for a batch shaker.

Al Zubaidi et al. (2015) studied the effects of 10% granular charcoal activated (GAC) mass loading on the adsorption of sulfur compounds from industrial diesel oil. The diesel oil used had an initial sulfur level of 398 ppm, and it was purchased from a petrol station in Sharjah, United Arab Emirates. Using the Langmuir and Freundlich isotherm equations, they analyzed the equilibrium isotherms for sulfur adsorption on GAC. At room temperature, with a contact duration of one hour and a rotation speed of 300 rpm, the ADS of diesel fuel employing GAC displayed high efficacy in removing sulfur, with a value of 20.94% relative to the original sample. The Langmuir isotherm was shown to be the most efficient equilibrium model for this process.

Saleh and Danmaliki. (2016) looked at the possibility of using discarded rubber tyres as an inexpensive adsorbent for adsorptive desulfurization of dibenzothiophene from fuel by converting them into activated carbon. In order to dissolve 150 mg of dibenzothiophene, the authors used one liter of model fuel (hexane85% and tolune15%) in batch mode. At room temperature, the adsorbent and the refractory sulfur compound were mixed together in a solution and agitated until equilibrium was reached. Isotherm experiments were done, and the adsorption data was a good fit for the Freundlich isotherm model after 90 minutes of adsorption at an adsorbent weight of 0.5 g in where the adsorption capacity was 8.6 mg/g.

Ahmad et al. (2017) studied the selectivity of acid-modified montmorillonite (MMT) clay for adsorption of sulfur compounds found in commercial kerosene and diesel (0.0542 and 1.041 sulfur wt%, respectively). Cr ,Fe, Mn , Ni, Co, , Pb, Zn, and Ag were among the metals used in the wet impregnation process to add new properties to MMT.The initial adsorption trial lasted 1 hour, used a 1.5 g adsorbent concentration, and was conducted at 25 degrees Celsius with 20 milliliters of fuel. Zn-MMT was found to be responsible for the significant desulfurization observed. Adsorption through Zn-MMT was able to achieve maximum desulfurization of 76% in the case of kerosene and 77% in the case of diesel.

Saleh et al. (2017) treated activated carbon with manganese oxide to further improve its surface properties for adsorptive desulfurization of model fuels of thiophene, BT, and DBT in a mixture of hexane (85 vol%) and toluene (15 vol%). An optimum metal loading of about 10% showed significant adsorptive desulfurization efficiency. Experimental tests were conducted in batch mode with isotherms and kinetics study. The adsorption experimental data were best fitted to Temkin isotherm models and pseudo-second order kinetic. Adsorption capacities of 4.5, 5.7, and 11.4 mg S/ g adsorbent were obtained for the adsorption of thiophene, BT, and DBT, respectively. The same trend of DBT>BT>T was observed for the adsorption capacities in the fixed bed mode experiments.

Zhu et al. (2018) prepared the composite material (MOF-5@AC) and put it through some ADS tests using n-heptane containing either 400 ppm of thiophene, dimethyl sulfide, or n-propyl mercaptan as the simulated fuel and 100 parts per million (ppm) of thiophene, BT, or DBT dissolved in n-heptane. For the thiophenic sulfur compounds in particular, the results displayed that the composite material's performance was higher than that of the two raw components. While the removal rate increases and the sulfur capacity falls with decreasing concentration, the authors discovered that the agent-to-oil ratio remained constant throughout. At 400 ppm sulfur concentration, the adsorbent reached its maximum removal efficiency of 48.6% and its maximum sulfur capacity of 11.34 mg S/g adsorbent. When compared to the original materials, the reuse performance also saw an important enhancement. The microstructure, morphology, and desulfurization capabilities of composite materials are highly influenced by the ratio of their raw components. The best desulfurization removal performance was seen in MOF-5@AC with a ratio of 1:5.

Yahya and Hussein. (2019) used molecular sieve 13X in a fixed bed column and ran the experiment at (15-30 gm of molecular sieve 13X ,1.5-6.0 h-1, LHSV,600-1650 ppm sulfur content in feedstock, and adsorption temperatures of 25°C and 40°C to see how selective adsorption is affected by the removal of sulfur compounds of heavy naphtha from the refinery of Dura. At 3.0 h-1 LHSV, 20 gr (13X) weight, and 25°C temperature, sulfur content in H.N was decreased from over 600 ppm to less than 1 ppm, making it an ideal operating setting for removing sulfur compounds.

Abbas and Ibrahim. (2020) investigated the desulfurization of L.N. (light naphtha) employing adsorption catalysts white eggshell and granular activated carbon at ambient pressure in a batch unit under differing operating conditions of hydrogen peroxide to LN percentages, pH, moderate temperature, contact time, and catalyst amount. When WES or GAC was used as a catalyst in catalytic desulfurization, the process achieved a maximum efficiency of 56.78% and 81.73% , respectively, at (H_2O_2/LN) ratios of 4, pH equal 1, agitation speeds of 400 rpm, temperatures of 80°C and 85°C, and contact times of 150 minutes.

Naife. (2021) looked into the efficacy of adsorption desulfurization employing Ni and Cu as single-binary metals put into modified activated carbon (MAC) for removing the sulfur compounds of Iraqi light naphtha, which is produced in the AlDora refinery. Experiments were conducted in a batch unit at room temperature with a constant initial sulfur concentration of 155 ppm for 50 ml of light naphtha, varying the MAC dosage, agitating speed, and contact time by 300 minutes.

Increases in MAC dose, agitation speed, and contact duration all resulted in greater DS percentage results, with the author showing a higher DS percentage by AC/Ni-Cu (66.45) % at a speed of 500 rpm and 1 gm dose than DS (29.03%) by activated carbon AC. The adsorption capacities of AC/Ni, AC/Cu, and AC/Ni-Cu MAC were observed at 16, 15, and 20 mg sulfur/g MAC, respectively.

Flihh and Ammar.(2022) used a hydrothermal methodology to synthesize a zeolitic imidazolate framework (ZIF-67) as an active adsorber for removing dibenzothiophene (DBT) from a liquid simulated fuel using the adsorptive desulfurization technique. The Surface area of the synthesized ZIF-67 was quite large, coming in at 1159.9 m^2/g. ZIF-67 had a high adsorption uptake of DBT (100 ppm) (86.12 mg/g) for model fuel under the best conditions of adsorber dose = 1 g/L, adsorption period = 3 h, and constant room temperature. The equilibrium analysis demonstrated that using the Freundlich isotherm streamlined the procedure.

Ali et al., 2023 studied the adsorptive desulfurization of diesel fuel from Al-Diwaniya refinery with an initial concentration of sulfur content of 12000 ppm using commercial activated carbon(CAC) as an adsorbent(31.45 gm per 500 ml of diesel) in batch work at a time of 40 min, a temperature of 60 °C, and a rotational speed of 500 rpm. The removal ratio was 95%..

Table (2.1): Summary of Previous Works

Authors	Conditions	Results
Al Zubaidy et al., 2013	ADS sulfur compounds produced from commercial diesel fuel on CAC. The initial sulfur concentration of the diesel oil was 410 parts per million.	Using CAC at 5% by mass and room temperature was shown to be 39% effective in removing sulfur.
Al Zubaidi et al., 2015	ADS of sulfur compounds produced from commercial diesel fuel on GAC. The initial sulfur content of the diesel oil was 398 parts per million.	When comparing the original sample at room temperature to the ADS of diesel oil using GAC, sulfur removal effectiveness was found to be 20.94%, which is quite good. Langmuir isotherm was found to be more efficient in the equilibrium analysis.
Saleh and Danmaliki., 2016	AC was synthesized by discarded rubber tyres as an adsorbent for ADS in model fuel (150 ppm DBT in hexane at 85% and tolune at 15%).	Adsorption data was fit to the Freundlich isotherm model at 0.5 g adsorbent weight and 8.6 mg/g capacity.
Ahmad et al., 2017	MMT clay was used as an adsorbent for ADS diesel and kerosene (0.0542 and 1.041 sulfur wt%, respectively). Zn, Cr, Ni, Co, Mn, Pb, Fe, and Ag were used for the wet impregnation process for MMT.	Zn-MMT was able to achieve maximum desulfurization of 76% in the case of kerosene and 77% in the case of diesel.
Saleh et al., 2017	AC was treated with manganese oxide to further improve its surface properties for ADS of model fuels of thiophene, BT, and DBT in a mixture of hexane (85 vol%) and toluene (15 vol%) in batch mode.	An optimum metal loading of about 10% showed significant ADS efficiency. The experimental data were best fitted to Temkin isotherm models and pseudo-second order kinetic. Adsorption capacities of 4.5, 5.7, and 11.4 mg S/ g adsorbent were obtained for the adsorption of thiophene, BT, and DBT, respectively.

Zhu et al., 2018	The adsorption of simulated fuels (400 ppm thiophene, dimethyl sulfide, or n-propyl mercaptan dissolving in n-heptane, and 100 ppm thiophene, BT, or DBT dissolved in n-heptane) onto a composite material (MOF5@AC) was studied.	The composite material exceeded the raw components, especially for thiophenic sulfur compounds. At 400 ppm sulfur concentration, the highest sulfur capacity was 11.34 mg S/g adsorbent, and the best removal rate was 48.6%.
Yahya and Hussein., 2019	A molecular sieve (13X) was used as an adsorbent for ADS of heavy naphtha (600-1650 sulfur content in ppm) in a fixed bed reactor.	At 600 ppm sulfur content, the highest desulfurization was 99% at (3.0 h-1 LHSV, 20 gramms molecular sieve of bed weight, and 25 °C.
Abbas and Ibrahim., 2020	Eggshell was used as a catalyst to remove SOCS from light naphtha (14 sulfur concentration in ppm).	At (H_2O_2/LN) ratios of 4, pH values of 1, agitation speeds of 400 rpm, temperatures of 80 °C, and times of 150 min in a batch process. The best efficiency for WES catalytic desulfurization was 56.78.
Naife., 2021	Ni and Cu as single binary metals put into MAC were used as an adsorbent for ADS of 50 ml of light naphtha (155 ppm sulfur concentration)	The best efficiency for AC/Ni-Cu MAC catalytic desulfurization was 66.45 at room temperature in a batch process at a speed of 500 rpm, a 1 g dose, and a contact time of 300 min.
Flihh and Ammar., 2022	ZIF-67 was used as an adsorbent for ADS of model fuel (100 ppm DBT)	Adsorption data fit the Freundlich isotherm model with an 86.12 mg/g capacity
Ali et al., 2023	CAC was used as adsorbent for ADS of diesel at initial concentration 12000 ppm	The removal ratio was 95% at 31.45 gm of CAC per 500 ml diesel in batch work at time 40 min, temperature 60°C and rotational speed of magnetic stirrer= 500 rpm

Chapter Three

Experimental Work

Chapter Three

Experimental Work

3.1 Introduction

Current research experiments are presented in this chapter and comprise of the following procedures:

1.Preparation of calcite from eggshells as an adsorbent.

2.Modification of calcite as an adsorbent.

3. To investigate and evaluate the desulfurization efficiency of producing adsorbents and adsorption isotherms, we carried out batch adsorption experiments for light naphtha using the MINITAB 2017 - BBD method.

3.2 Materials

3.2.1 Eggshells

chickens Eggshells were collected from homes, restaurants and hatcheries in large quantities in order to extract an adsorbent from them.

3.2.2 Activated Carbon

Commercial activated carbon was chosen as an adsorbent since it is widely regarded as the best adsorbent due to its surface area. The active carbon used was from the commercial market.

3.2.3 Chemicals

Table (3.1) details the various chemicals employed in the experiments. No additional purification of the compounds was performed before their use.

Table (3.1): Chemicals used in adsorbents preparation

Material	Purity	Chemical formula	Vender
Deionized water	99 %	H_2O	Diwaniya refinery
Hydrochloric acid	99%	HCl	German

3.2.4 Fluid Feedstock

Light naphtha in this study was obtained from AL-Diwaniya Refinery with a sulfur content of 776 ppm as one of the atmospheric distillation products.

Tables (3.2) show the properties of light naphtha tested in Al-Diwaniya refinery

Table (3.2): Properties of the light naphtha

property	value
API	71
Initial boiling point, (°C)	42
Ending boiling point(°C)	130
Reid vapor pressure at 37.8°C	8.5
Sulfur content, (ppm)	776

3.3 Apparatus

The experimental equipment is summarized in **Table (3.3)**

Table (3.3): Apparatus used in Experiments

No.	Apparatus	Specification	Company
1	Magnetic stirrer heater with an attached hot plate	Variable speeds (100- 1800 rpm) and temperatures (30-300 °C)	Alfa
2	Oven	Maximum (220 degrees Celsius)	Heraeus
3	Electronic balance	Optimal weight (220 g) Lowest weight (0.001 g)	Sartorius
4	pH meter	Digital	Hanna Instruments
5	Industrial grinder	Electrical	China
6	200 Mesh sieve	Stainless steel sieve	Gilson
7	Filter paper	Qualitative filter paper possesses a pore size of between 15-20µm	Imco

3.4 Adsorbents Preparation

3.4.1 Preparation of Calcite

The preparation process of calcite from eggshells as an adsorbent following a similar procedure by previous researcher **(Sembiring et al., 2021)** was as follows: Eggshells were washed in distilled water until they were free of dirt and debris. They were then sun-dried for 24 hours and mashed in an industrial grinder. Sieving was used to achieve a grain size that is small enough to pass through a sieve with a mesh size of 200 (0.075mm). After being sieved, they were heated for 15 minutes at

110°C, followed by activation with a solution of 0.1 M HCl for 48 hours. Finally, after being filtered and cleaned with deionized water until the pH level reached 7, after that, in an oven preheated to 150 °C for 30 min, the adsorbents were activated.

3.4.2 Preparation of Modified Calcite

The preparation process of modified calcite includes mixing the calcite that was previously prepared with commercial activated carbon in equal weight ratios by using the planetary ball mill equipment at the Petroleum Research and Development Centre- Ministry of Oil, as shown in **Figure (3.1)**

Figure (3.1): planetary ball mill machine

A planetary ball mill (specifications shown in **Appendix A1**) was created for uses requiring very fine powder. Colloidal grinding is only one of the many uses for it, which also performs in grinding and mixing applications with soft, tough, brittle, fibrous, dry, and wet materials .

Figure (3.2) shows adsorbents for calcite, commercial activated carbon and modified calcite.

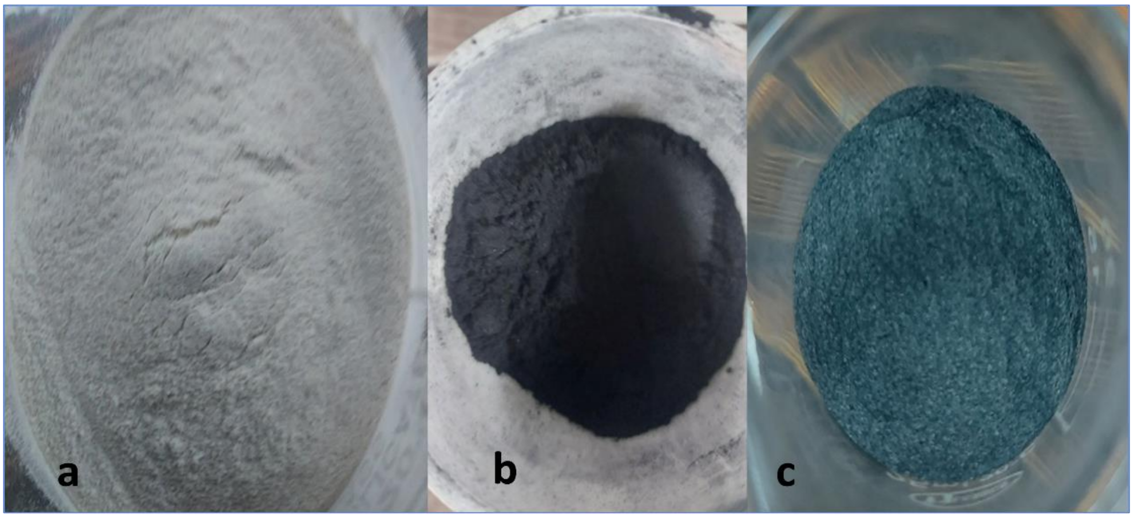

Figure (3.2): (a) Calcite, (b) Commercial Activated Carbon, and (c) Modified Calcite

3.5 Operating Conditions for Batch Adsorption Experiments

Table (3.4) shows the parameters that used in experiments.

Table (3.4): Factors and its ranges.

Factor	Range		
Wight of adsorbent, gm/100 ml L.N	1	2	3
Time, min	15	30	45
Temperature, °C	20	30	40

3.6 Experiment Design

Adsorption experiments were designed using MINITAB 2017, which contains the Box-Behnken design, which is a type of response surface methodology. According to BBD, the necessary number of experiments to cover the system of investigated variables is **(Qasim and Alwan, 2023)**

$$N = 2K(K - 1) + r. \qquad (\mathbf{3.1})$$

Where :

K: number of factors.

N: number of experiments.

r: replicate the number central point (3-6).

According to BBD, only three values (-1,0,1) were allowed for the variables in the analysis., with the distance between each level having values that are equal to one another. This means that the number of experiments for three variables with three levels was between fifteen and eighteen, dependent on the parameter r (replicates) in the formula. The chosen studied variables are temperature, adsorbent dosage, and contact time with ranges of 20-40 C°, 1- 3 g, and 15-45 minutes, respectively, to investigate the activity of the adsorbent in light naphtha ADS process as listed in **Table (3.5)**, the experimental design by Minitab version 2017 as shown in **Table (3.6)**

Table (3.5): Variables and their levels that are independent

Variables	Symbols		Level		
	Coded	Actual	-1	0	1
Temperature (°C)	x1	X1	20	30	40
Adsorbent dosage (g)	x2	X2	1	2	3
Contact time (min)	x3	X3	15	30	45

Table (3.6): BBD matrixes

	Design of parameters				Design of parameters				Design of parameters		
Runs	x_1	x_2	x_3	Runs	x_1	x_2	x_3	Runs	x_1	x_2	x_3
1	1	0	-1	6	0	1	1	11	0	0	0
2	-1	0	1	7	0	-1	-1	12	-1	0	-1
3	1	-1	0	8	0	0	0	13	0	1	0
4	1	1	0	9	0	0	0	14	-1	1	0
5	0	-1	1	10	1	0	1	15	-1	-1	0

An equation for estimating predicted values and optimizing the system may be obtained by fitting the results of experiments for the impacts on temperature (x_1), the amount of adsorbent (x_2), and the time of contact (x_3) on ADS as a second-order polynomial **(Qasim and Alwan, 2023)**

$$R\% = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \varepsilon \qquad \mathbf{(3.2)}$$

β_0: intercept coefficient, R: predicated response, β_i : linear effect (slope) of input variable x_i , β_{ii} : squared effect ,β_{ij} :the interaction effect of linear by linear between two input variables x_i , ε ; random error.

3.7 Batch Adsorption Experiments and Desulfurization Efficiency

The tests were carried out at atmospheric pressure with a constant mixing speed in batch mode. Powdered adsorbents have been used because they provided more surface area for mass transfer and require less agitation to remain suspended. Desulfurization efficiency was determined by dividing the amount of sulfur removed from the fuel by the amount of sulfur that was initially present in the fuel using the following equation **(Qin et al., 2018):**

$$R\% = \frac{S_o - S_f}{S_0} \quad \textbf{(3.3)}$$

Where

S_o: the initial sulfur concentration for liquid fuel (ppm)
S_f : the measured sulfur concentration for liquid fuel (ppm)

The AL-Dura Refinery evaluated the sulfur level of its liquid fuels using an American-made ANTEK 9000N/S analyzer calibrated to ASTM D-5453 and an X-ray fluorescence instrument calibrated to ASTM D-4294.

3.7.1 Batch Adsorption Procedure for Calcite and Modified Calcite

1- Put a certain amount (100 ml) of light naphtha in a conical flask.

2- Put the conical flask on the magnetic stirrer heater at a constant mixing speed (300 rpm) and adjust the temperature according to the conditions of the experiment.

3-. Put the calcite as an adsorbent into the conical flask after knowing its weight according to the experiments.

4- After the end of the specified time according to the conditions of the experiments for adsorption, the adsorbent particles were removed from the fuel using filter sheets, and the fuel samples were collected separately for sulfur analysis.

5- These steps repeated in 15 experiments in different conditions.

6- The same procedure for calcite was carried out with modified calcite adsorbent and the same light naphtha to adsorbent ratio.

6- Figure (3.3) shows these steps.

Figure (3.3): Batch adsorption

3.8 Characterization Tests of Adsorbents

3.8.1 X-Ray Diffraction (XRD)

The method (XRD) is used as a "fingerprint" for identifying phases in prepared materials. The principle upon which this method rests is the observation that the diffraction patterns of various compounds in solid samples vary. Preparation adsorbents were measured using (XRD) with a (Shimadzu, Japan, XRD-6000) instrument set to 35 kV and 30 mA of radiation (λ= 1.54060) A. Diffractograms were captured at a rate of 5 degrees per minute, covering a range of 2 θ from 2° to 80°. Tested in the College of Materials Engineering – Department of Ceramics and Building at the University of Babylon.

3.8.2 Surface Area

The Ministry of Oil's Petroleum Research and Development Centre measured the surface area of the absorbents after they had been prepared. Using Thermo Analyzer/USA and the Brunauer, Emmett, and Teller (BET) technique.

3.8.3 Fourier Transforms Infrared Spectroscopy (FTIR)

The FTIR spectrum for produced adsorbents were analyzed to learn more about the chemical groups and acid sites present. Using an IR-Affinity-1 from Shimadzu, Japan, and operating in the range of (4000-550) cm^{-1}, an attempt was made to carry out the test at the Petroleum Research and Development Center/Ministry of Oil.

Chapter four

Results and Discussion

Chapter four

Results and Discussion

4.1 Introduction

In the first section including XRD, surface area, and Fourier transform infrared spectrophotometry (FTIR), are used to learn more about the manufactured adsorbents and determine their properties.

The second section covers batch experiments carried out by BBD for ADS light naphtha using calcite and modified calcite as adsorbents, and statistical analysis ANOVA was studied and the effect of each of the operating conditions on the adsorption efficiency. Isotherm models of each produced adsorbent are also shown in this section.

4.2 Prepared Adsorbents Characterization

4.2.1 Investigation by XRD

4.2.1.1 Calcite

The XRD pattern for prepared adsorbent is shown in **Figure (4.1).** The XRD diffractogram at 2θ shows many peaks that are consistent with the presence of calcium carbonate $CaCO_3$ in the activated adsorbent, which is supported by the diffraction pattern of the JCPDS data.

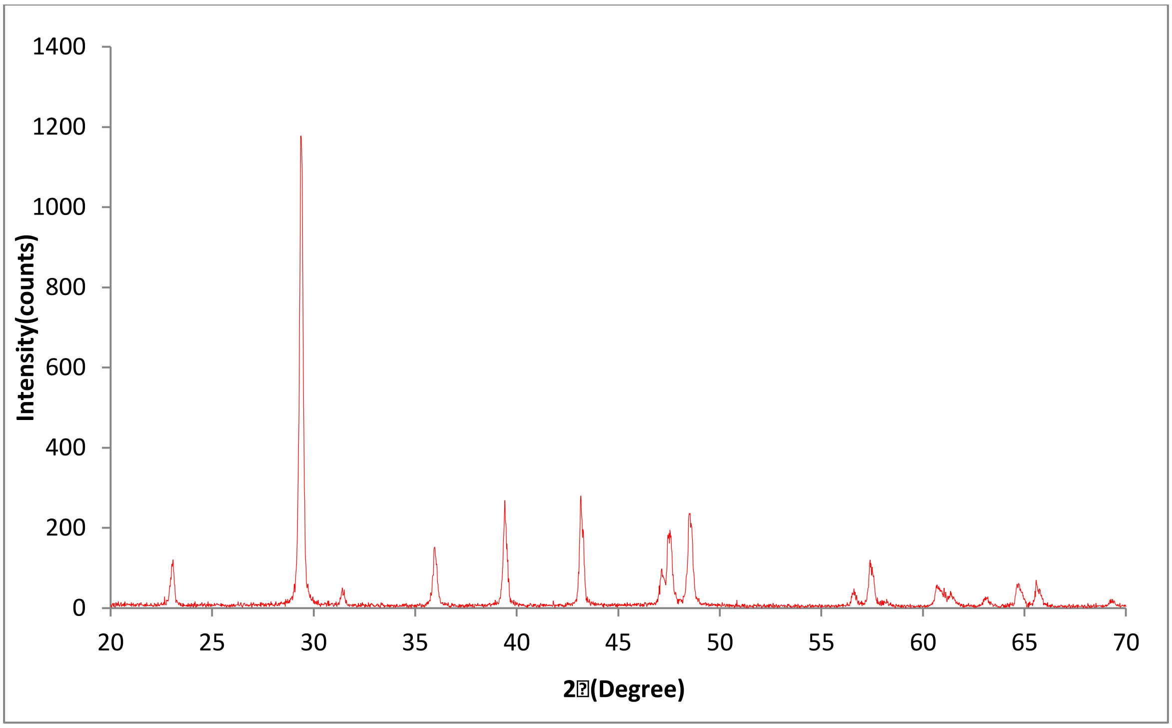

Figure (4.1): XRD pattern for prepared calcite as an adsorbent

4.2.1.2 Modified Calcite

As shown in **Figure (4.2),** the XRD spectrum for both calcite and modified calcite, the XRD for calcite shows many peaks at 2θ 29.3°, 31.4°,39.4,47.1°,48.5°, 56.6°, 57.4°, 60.6° and 64.7° which correspond to the presence of $CaCO_3$ **(Sembiring et al., 2021)**. While the XRD pattern for modified calcite exhibited three sharp peaks at about 2θ equal to 26°, 29°, and 50° that revealed crystalline carbonaceous structure **(Kennedy et al., 2007)** , the other peaks 23° and 44° indicated the presence of calcite **(Sembiring et al., 2021)**

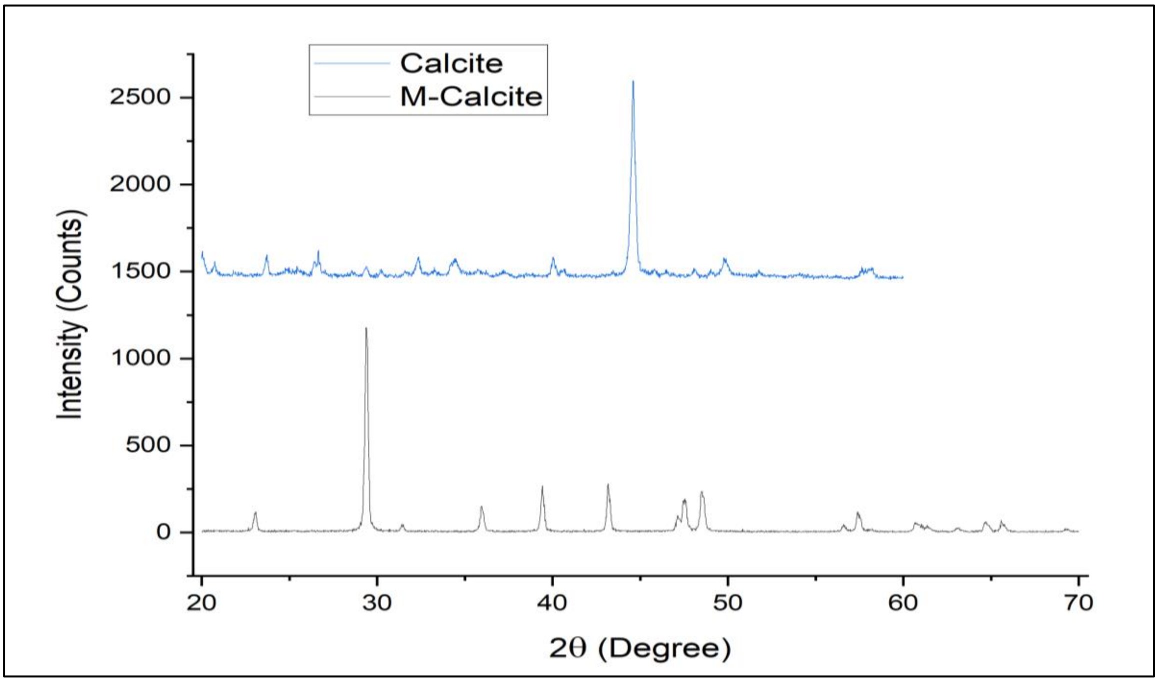

Figure (4.2): XRD pattern for calcite and modified calcite (M-calcite)

4.2.2 Investigation by FTIR

4.2.2.1 Calcite

Figure (4.3) illustrates the FTIR spectra of prepared $CaCO_3$ from eggshell, in which the spectra analysis shows an apparent peak at 711,872, 2516 cm $^{-1}$. At 1487 cm^{-1}, there is a very strong absorption peak from eggshell particles, which is likely due to the presence of carbonate minerals in the eggshell matrix. The existence of a hydroxyl (-OH) group or an acidic hydrogen (H+) group that indicated by the presence of peaks 3400 and 2516 cm^{-1}. The two peaks, noted clearly at about 712, and 872 cm^{-1}, respectively**(M. Ahmad et al., 2012; Tizo et al., 2018).** A better understanding of how contaminants interact with the organic membrane based on calcium carbonate under controlled conditions can help in the future to come up with compact treatment methods that work best. **(Ningrum, Humaidi, Sihotang, and Bonardo, 2022)**.

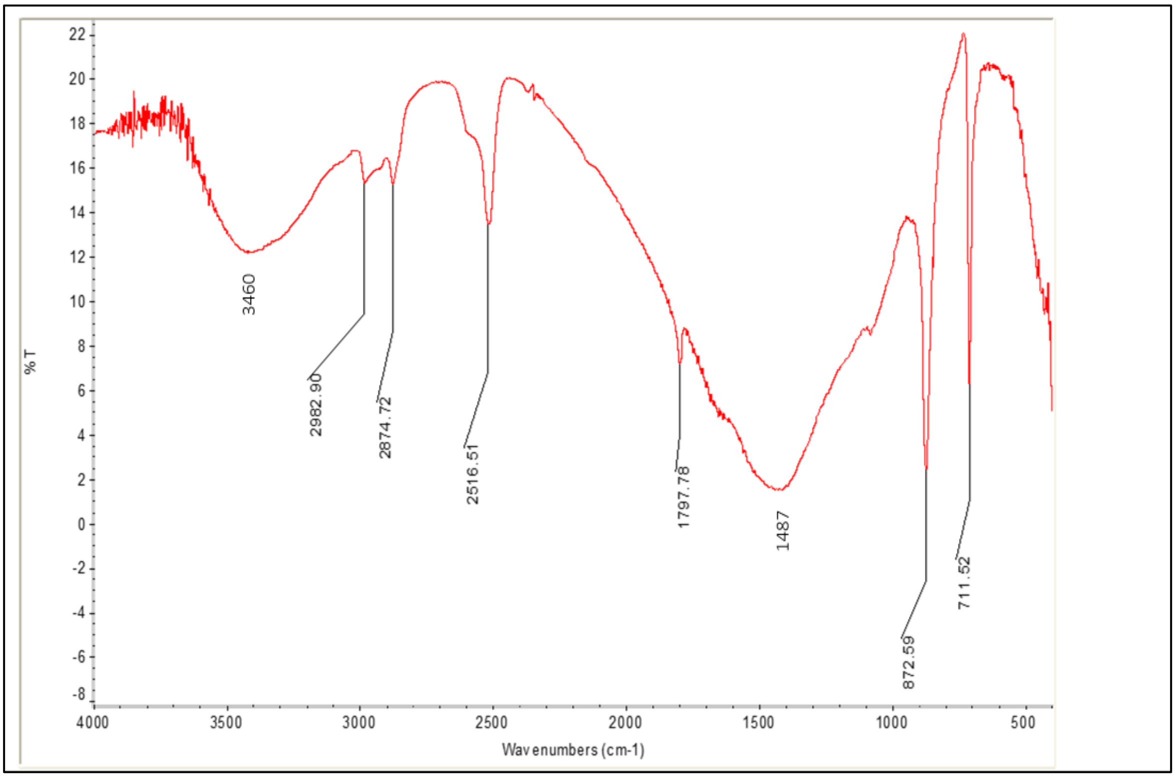

Figure (4.3): FTIR spectra for prepared calcite

4.2.2.2 Modified Calcite

Figure (4.4) illustrates the FTIR spectra for prepared calcite ($CaCO_3$) from eggshell only (red curve), activated carbon only (aqua curve), and mixed of them (green), in which the spectra analysis for calcite prepared from eggshell (red curve) shows an apparent peak at 711,872, 2516 cm $^{-1}$. At 1487 cm^{-1}, there is a strong peak of eggshell particles, which is highly linked to the presence of carbonate minerals in the eggshell matrix. The hydroxyl (-OH) group and the acidic hydrogen (H+) group can be seen in peaks at 3400 and 2516 cm^{-1}. The two peaks, which are noted clearly at about 712, and 875 cm^{-1}, respectively, indicated the presence of calcium carbonate **(M. Ahmad et al., 2012; Tizo et al., 2018)**, whereas the FTIR spectra for M-calcite (the green curve) have the parks closed to the origin calcite, and this represents an improvement the understanding of complex interferences and interactions between $CaCO_3$ and activated carbon.

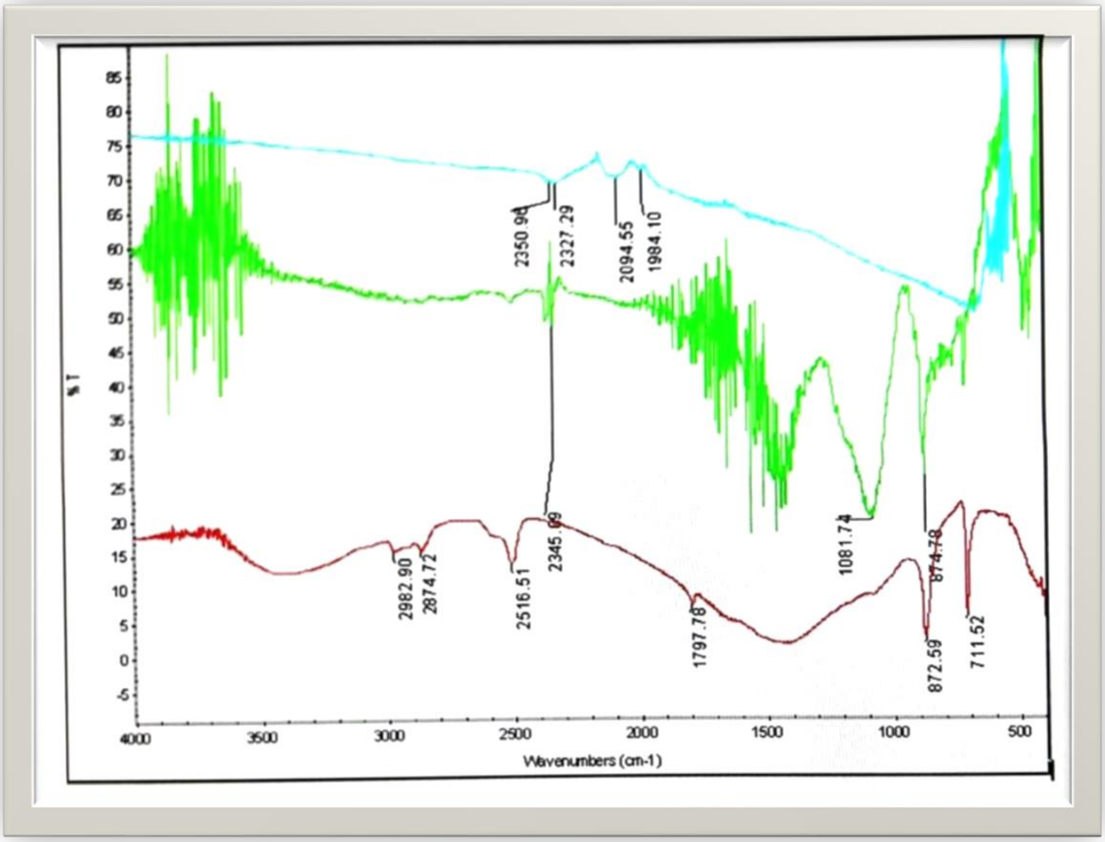

Figure (4.4): FTIR for calcite,M-calcite and AC

4.2.3 Investigation by Surface Area

4.2.3.1 Calcite

The surface area of the adsorbent powder was calculated at about 1 m^2/g using the BET method.

4.2.3.2 Modified Calcite

The surface area of the adsorbent powder was calculated at about 356 m^2/g using the BET method.

4.3 Adsorptive Desulfurization Studies for Calcite

4.3.1 Adsorptive Desulfurization Results

Table (4.1) shows the adsorptive desulfurization (ADS) by prepared $CaCO_3$ adsorbent for all experiments designed according to BBD. Minitab 17 was used to fit the experimental batch results to a second order polynomial (quadratic model) with BBD, and the sulfur removal effectiveness was found to be in the 45-60% range. The fitting product shows that a regression equation in uncoded variables for using $CaCO_3$ adsorbent is:

$$R\% = 32.6 + 0.688\ X1 - 1.08\ X2 - 0.014\ X3 - 0.00167\ X1^2 + 0.583\ X2^2 - 0.00074\ X3^2 - 0.0250\ X1\ X2 + 0.0500\ X2\ X3 \quad \textbf{(4.1)}$$

Table (4.1): Experimental (actual) value for sulfur removing efficiency for all runs for calcite.

Run	Temp.°C	Adsorbent,gm	Time,min	R%	Run	Temp.°C	Adsorbent,gm	Time,min	R%
1	40	2	15	57	9	30	2	30	50
2	20	2	45	47	10	40	2	45	58
3	40	1	30	56	11	30	2	30	55
4	40	3	30	60	12	20	2	15	46
5	30	1	45	51	13	30	3	15	53
6	30	3	45	56	14	20	3	30	50
7	30	1	15	51	15	20	1	30	45
8	30	2	30	52					

As noted from the ANOVA in **Table (4.2)**, the F-value is 11.19 for regression, and it was greater than the tabulated value for Fisher`s (F=4.77). The high R^2 (0.9527) and high values for adjusted R^2 (0.8676) indicate that the model's assumptions are reasonably consistent with the data.

Moreover, based on actual results and ANOVA, temperature has the highest effect on sulfur adsorption, whereas other parameters effects are ordered as follows; adsorbent dosage and adsorption time via their F-value of 86.13, 11.93 and 1.16 for temperature, weight and contact time, respectively. The sulfur removal efficiency of ADS increased as temperature, adsorbent weight and contact time increased. The results analysis shows the optimum sulfur removal efficiency is 61% at the following operation conditions; 40 °C, 3 grams and 45 minutes for temperature, adsorbent dosage and adsorption time, respectively, as shown in **Figure (4.5)**.

Table (4.2): ANOVA results for the calcite quadratic

Source	DF	Adj SS	Adj MS	F Value	P Value
Model	9	270.317	30.035	11.19	0.008
Linear	3	266.250	88.750	33.07	0.001
Temp (X_1)	1	231.125	231.125	86.13	0.000
Adsorbent dosage (X_2)	1	32.000	32.000	11.93	0.018
Time (X_3)	1	3.125	3.125	1.16	0.330
Square	3	1.567	0.522	0.19	0.896
Temp*Temp (X_1)^2	1	0.103	0.103	0.04	0.853
Adsorbent dosage*Adsorbent dosage (X_2)^2	1	1.256	1.256	0.47	0.524
Time*Time (X_3)^2	1	0.103	0.103	0.04	0.853
2-Way Interaction	3	2.500	0.833	0.31	0.818
Temp*Adsorbent dosage (X_1) (X_2)	1	0.250	0.250	0.09	0.772
Temp*Time (X_1) (X_3)	1	0.000	0.000	0.00	1.000
Adsorbent dosage*Time (X_2) (X_3)	1	2.250	2.250	0.84	0.402

4.3.2 Effect of Studied Variables on ADS for Calcite

4.3.2.1 Effect of Temperature on Desulfurization Removal

It is noted in **Figure (4.5)**, that the sulfur removal efficiency from naphtha increases steadily with temperature, compared with the increase in the sulfur removal efficiency resulting from increasing the adsorbent dosage. Higher temperatures accelerate light naphtha spread across the external borders and internal pores within the adsorbent material. So, at increasing temperature, increasing mobility and reducing viscosity of large OSCs molecules thereby produce a swelling effect with the internal structure of the adsorbent**(Abdus-Salam et al., 2016)** , or the pores enlarging came by breaking chemical bonds or oxidizing molecules on the surface during the heating step in preparation, consequently, they run into adjustments in physical properties, leading to a rise in surface area and a resulting enhancement in adsorption **(Sembiring et al., 2021)**.

4.3.2.2 Effect of Adsorption Dose on Desulfurization Removal

According to **Figure (4.5),** the optimal desulfurization efficiency was achieved when the adsorbent weight levels were raised while keeping all other variables constant. Calcite's greater weight means more available adsorption surface area. So, the adsorption capacity of the adsorbent is improved because of the increased in number of active sites on its surface **(Abbas and Ibrahim, 2020)**.

4.3.2.3 Effect of Contact Time on Desulfurization Removal

The results in **Figure (4.5)** show that desulfurization efficiency improved as a function of increased processing time. This is likely the result of longer reaction times between the liquid reactants. which leads to a great chance of adhesion of sulfur compounds to surface adsorbents

(Saad et al., 2012). The desulfurization efficiency did not change after 90 minutes. For this reason, we accept a quasi-equilibrium saturation and assume a steady state approximation. This is because, throughout the first 90 minutes, there are the most free surface sites available for adsorption.

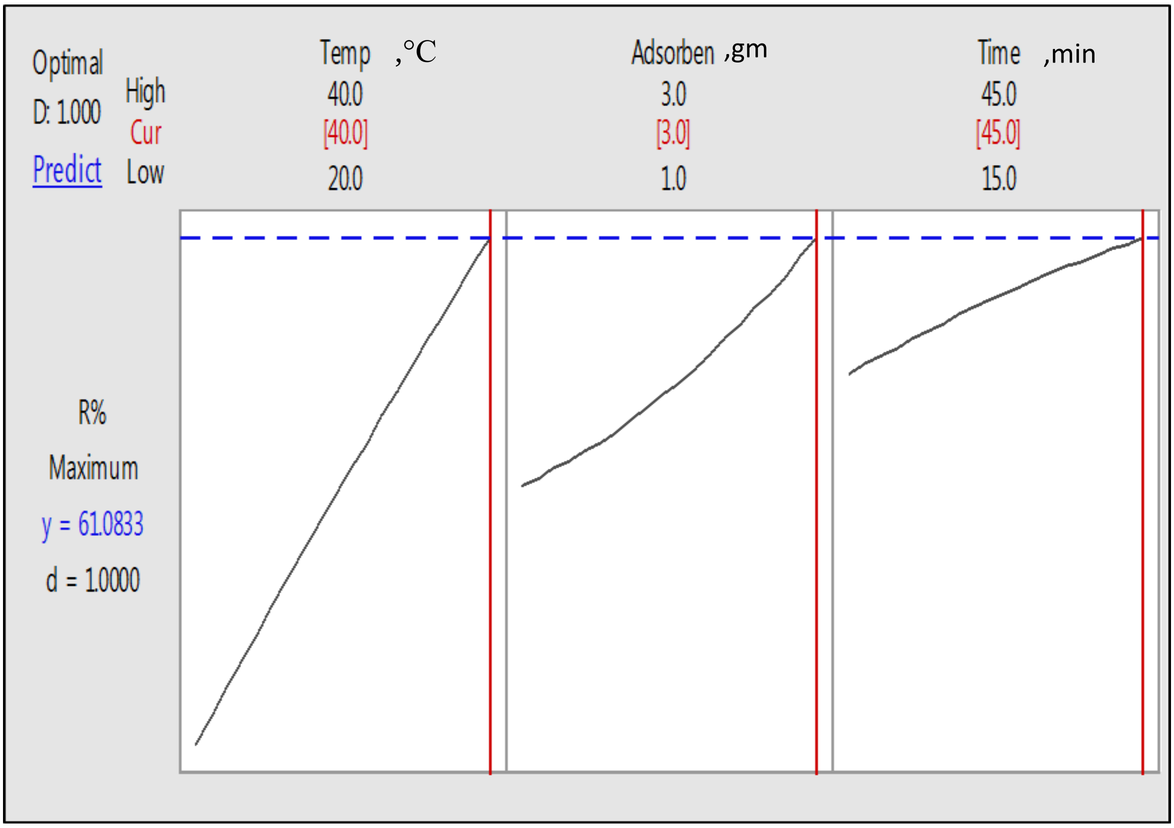

Figure (4.5): Optimum conditions for light naphtha ADS process with calcite adsorbent; 40 °C, 3 grams and 45 minutes for temperature, adsorbent dosage, and adsorption time respectively, also the figure show the general effect of studied variables on sulfur removing efficiency as temperature, adsorbent dosage, and adsorption time increasing.

Figure (4.6) to **Figure (4.8)** show the contour chart, which illustrated the interaction effect of each two variables on sulfur removal efficiency. As it was shown when studying the individual effect of each variable, the removal ratio increases with the increase of the variables.

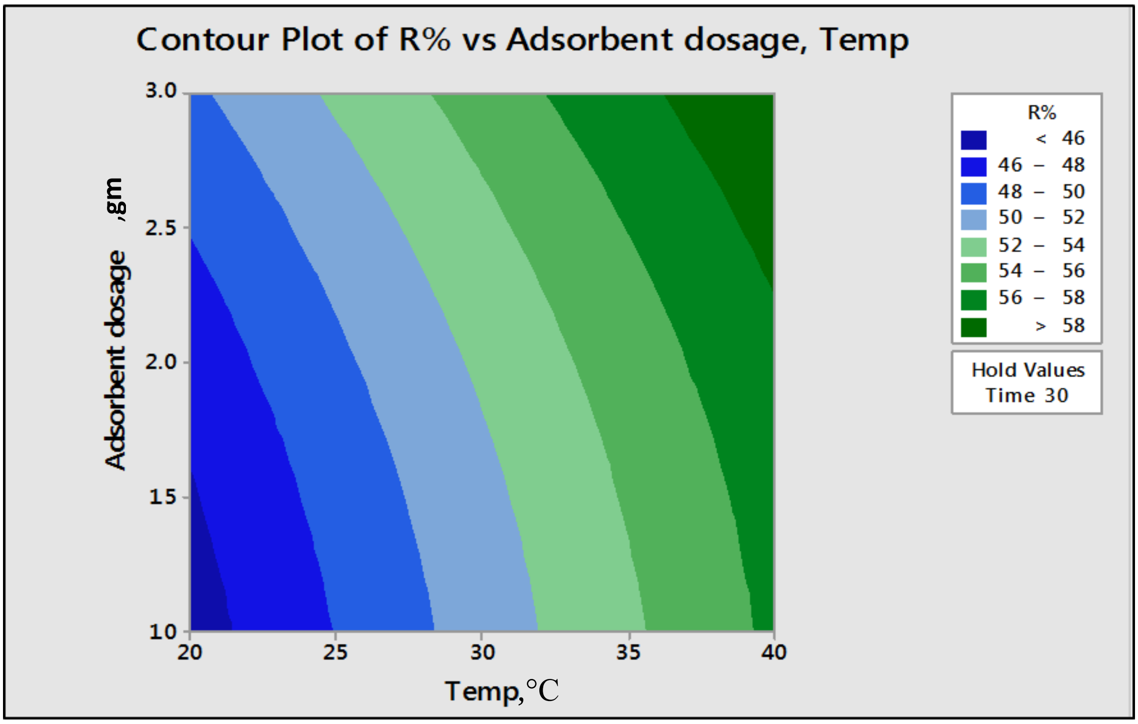

Figure (4.6): Interaction- effect of temperature and adsorbent weight on sulfur removal efficiency while kept adsorption time at 30 minutes for calcite.

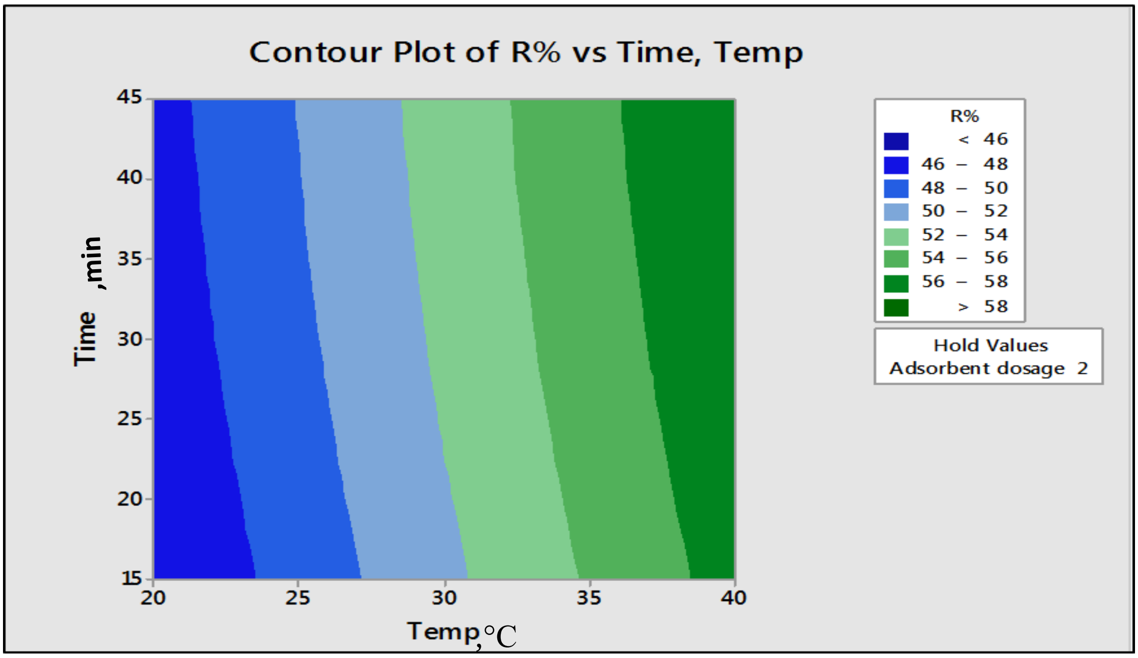

Figure (4.7): The interaction effect of temperature and adsorption time on sulfur removal efficiency while kept adsorption dosage 2 grams for calcite.

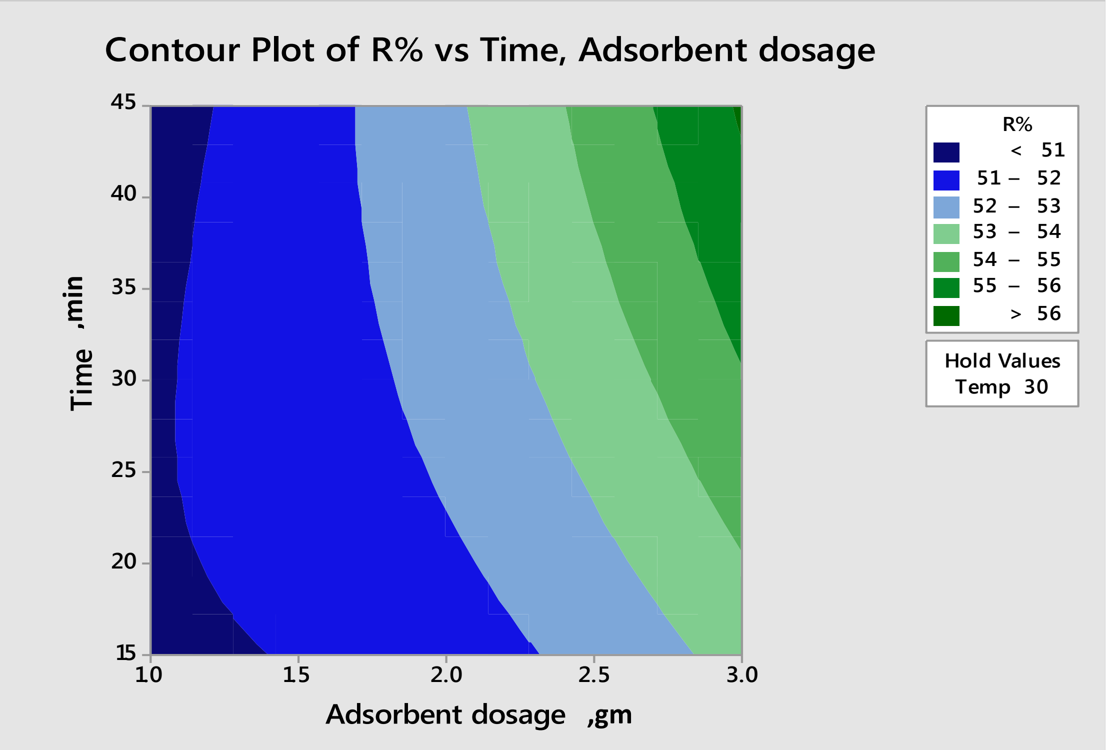

Figure (4.8): The interaction effect of adsorption time and adsorbent dosage on sulfur removal efficiency while kept temperature at 30 °C for calcite.

Figure (4.6) illustrates the interaction effect between temperature and adsorbent weight at hold value for time (30 min) and to what extent it affects sulfur removal efficiency, where it was shown that the best removal between (3grams) and (2.3grams) adsorbent weight and the temperature is approximate (37 to 40°C), while **Figure (4.7)** illustrates the interactions between temperature and time at hold value for adsorption dosage (2grams) and to what extent it affects sulfur removal efficiency, where it was shown that the best removal between (37 °C) and (40 °C) temperature and the optimum time is approximate to 45 min).**Figure (4.8)** illustrates the interactions between time and weight at the hold value for temperature (30 °C) and to what extent it affects sulfur removal efficiency, where it was shown that the best removal between 32 min and 45 min time and the weight is approximately (2.7 to 3 grams).

4.3.3 Adsorption Isotherm for Calcite

Adsorption isotherm for SOCs on calcite at different temperatures (20,30 and 40 °C), As well known the Langmuir and Freundlich isotherms are two models that can be used to describe the adsorption process. **Figure (4.9)** and **Figure (4.10)** show the Langmuir and Freundlich isotherms at different temperatures, respectively.

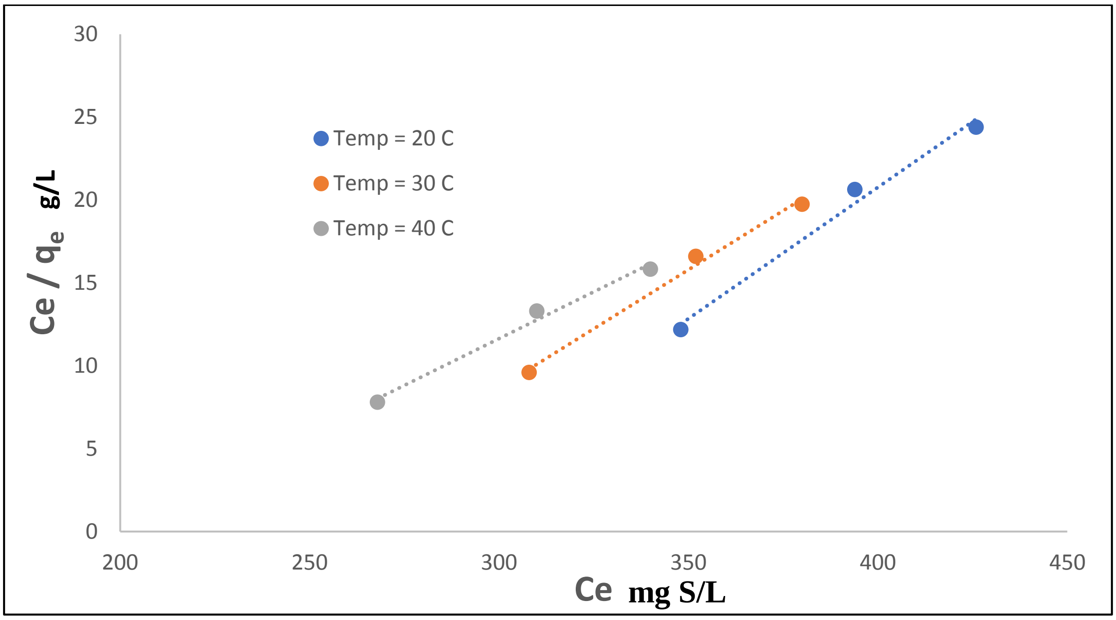

Figure (4.9): Langmuir isotherm for OSCs adsorption onto calcite adsorbent at different tempertures.

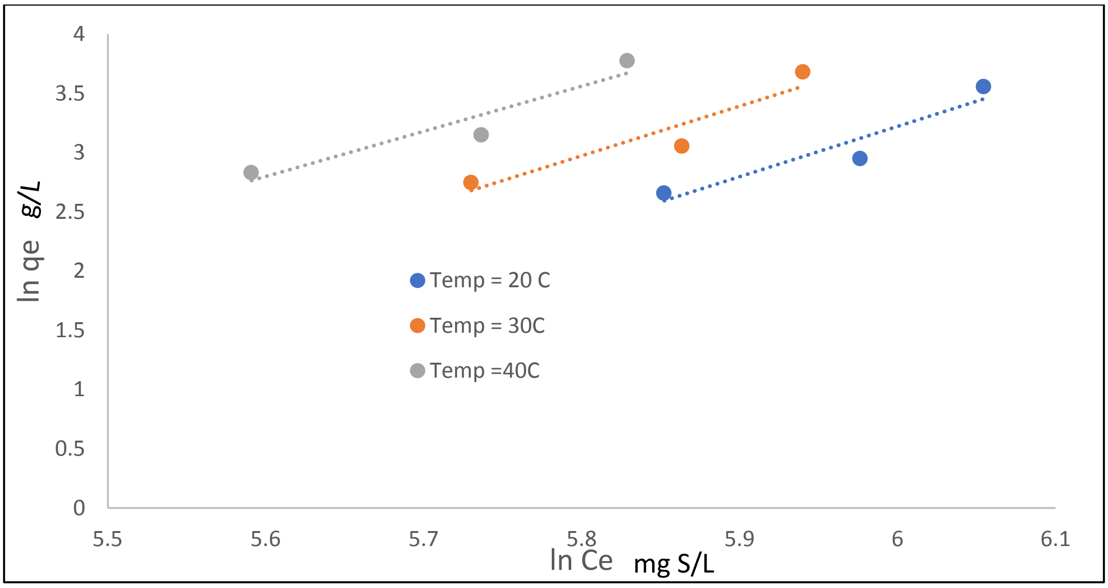

Figure (4.10): Freundlich isotherm for OSCs adsorption onto calcite adsorbent at different tempertures.

The isotherm model parameters values for Langmuir and Freundlich can be found at **Table (4.3).**

Table (4.3): Langmuir and Freundlich model parameters for calcite

	Langmuir constants				Freundlich constants		
Temp.(°C)	q_m (mg S/g)	K_L(L/mgS)	R^2		K_F[(mgS/g) (L/mg S) $^{1/n}$]	n	R^2
20	-6.60	-1.94×10^{-3}	0.9002		2.15×10^{-10}	0.235	0.895
30	-7.42	-2.17×10^{-3}	0.886		5.31×10^{-10}	0.238	0.8824
40	-9.24	-2.38×10^{-3}	0.9085		8.66×10^{-9}	0.262	0.9047

Table (4.3) displays that the Langmuir model's fit to experimental data on the adsorption of sulfur compounds onto calcite as an adsorbent yields a negative slope. This can happen if the constants are determined in an experimental part that is too steep. Although the correlation coefficient for the Langmuir model is the closest to 1, the adsorption behavior of the studied systems is inconsistent with this assumption., and the Freundlich isotherm is more appropriate for describing that adsorption of Socs within the given concentration range.**(Shikuku, Zanella, et al., 2018)**. These figures showed that experimental data fit the Freundlich isotherm. This result indicates that the adsorption of SOCs on the adsorbent occurred on a heterogeneous surface area and was multilayer.

4.4 Adsorptive Desulfurization Studies for M-calcite

4.4.1 Adsorptive Desulfurization Results

Table (4.4) shows the adsorptive desulfurization (ADS) by a modified calcite adsorbent for all experiments designed according to BBD. Minitab 2017 was used to fit the experimental batch results to a second-order polynomial (quadratic model) with BBD, and the sulfur removal effectiveness was found to be in the 46-79% range. The fitting product shows that a regression equation in uncoded variables for using $CaCO_3$ adsorbent is:

Regression Equation in Uncoded Units

$$R\% = 40.1 - 0.666\ X1 + 4.34\ X2 + 0.585\ X3 + 0.01065\ X1^2 + 0.839\ X2^2 - 0.00529\ X3^2 + 0.1224\ X1\ X2 - 0.00150\ X1\ X3 \qquad \textbf{(4.2)}$$

Table (4.4): Experimental (actual) value for sulfur removing efficiency for all runs for M-calcite.

Run	Temp.°C	Adsorbent,gm	Time,min	R%	Run	Temp.°C	Adsorbent,gm	Time,min	R%
1	40	2	15	59	9	30	2	30	60
2	20	2	45	63	10	40	2	45	64
3	40	1	30	52	11	30	2	30	61
4	40	3	30	79	12	20	2	15	57
5	30	1	45	54	13	30	3	15	67
6	30	3	45	75	14	20	3	30	71
7	30	1	15	46	15	20	1	30	49
8	30	2	30	61					

As noted from the analysis of variance (ANOVA) in **Table (4.5)**, the F-value is 37.02 for regression, which is greater than the tabulated value for Fisher`s (F=4.77). The high R^2 (0.9852) and high values for adjusted R^2 (0.9586) indicate that the model's assumptions are reasonably consistent with the data.

Moreover, based on actual results and ANOVA, weight has the highest effect on sulfur adsorption, whereas other parameters effects are ordered as follows; time and temperature via their F-values of 295.55, 25.41 and 6.79 for adsorbent weight, adsorption time, and temperature, respectively. The sulfur removal efficiency of ADS increased as adsorbent weight, time, and temperature increased. The results analysis shows the optimum sulfur removal efficiency is (79%) at the following operation conditions; 40 °C, 3 grams and 45 minutes for weight, time and temperature, respectively, as shown in **Figure (4.11)**.

Table (4.5): ANOVA results for the M- calcite quadratic

Source	DF	Adj SS	Adj MS	F Value	P Value
Model	9	1166.45	129.61	37.02	0.000
Linear	3	1147.37	382.46	109.25	0.000
Temp (X_1)	1	23.77	23.77	6.79	0.048
Adsorbent dosage (X_2)	1	1034.66	1034.66	295.55	0.000
Time (X_3)	1	88.95	88.95	25.41	0.004
Square	3	12.88	4.29	1.23	0.392
Temp*Temp (X_1)^2	1	4.18	4.18	1.20	0.324
Adsorbent dosage*Adsorbent dosage (X_2)^2	1	2.60	2.60	0.74	0.428
Time*Time (X_3)^2	1	5.23	5.23	1.50	0.276
2-Way Interaction	3	6.20	2.07	0.59	0.648
Temp*Adsorbent dosage (X_1) (X_2)	1	5.99	5.99	1.71	0.248
Temp*Time (X_1) (X_3)	1	0.20	0.20	0.06	0.819
Adsorbent dosage*Time (X_2) (X_3)	1	0.00	0.00	0.00	1.000

4.4.2 Effect of Studied Variables on ADS for M-calcite

4.4.2.1 Effect of Adsorption Dose on Desulfurization Removal

As shown in **Figure (4.11)**, when the adsorbent weight quantities were increased, the percentage desulfurization efficiency also increased, assuming all other variables remained constant. The increased weight of modified calcite indicates an increase in the adsorbent's surface area. Increased the number of active sites on the surface of the adsorbent, thereby enhancing its adsorption capacity**(Üçer et al., 2006).**

4.4.2.2 Effect of Temperatures on Desulfurization Removal

The results demonstrated that when the system temperature was increased, the percentage desulfurization efficiency also increased, assuming all other variables remained at their optimal levels, as shown in **Figure (4.11)**. Higher temperatures accelerate light naphtha spread across the external borders and internal pores within the adsorbent material. So, at increasing temperature, increasing mobility and reducing viscosity of large OSCs molecules thereby produce a swelling effect within the internal structure of the adsorbent**(Abdus-Salam et al., 2016)** .

4.4.2.3 Effect of Time on Desulfurization Removal

As can be seen in **Figure (4.11**), the percentage desulfurization efficiency improved as the desulfurization time for sulfur in light naphtha increased, holding all other factors constant. This could be because it is common knowledge that the sulfur content of a solution will be better treated thermally or in contact with surface area adsorbents for a longer period of time if the time of desulfurization is increased relative to the time spent desulfurizing the solution. Therefore, the adsorbent has a greater capacity for sulfur conversion or adsorption. Therefore, the efficiency of light naphtha desulfurization will be increased.**(Abbas and Ibrahim, 2020)**. The desulfurization efficiency did not change after 120 minutes. For this reason, we accept a quasi-equilibrium saturation and assume a steady state approximation. This is because, throughout the first 120 minutes, there are the most free surface sites available for adsorption.

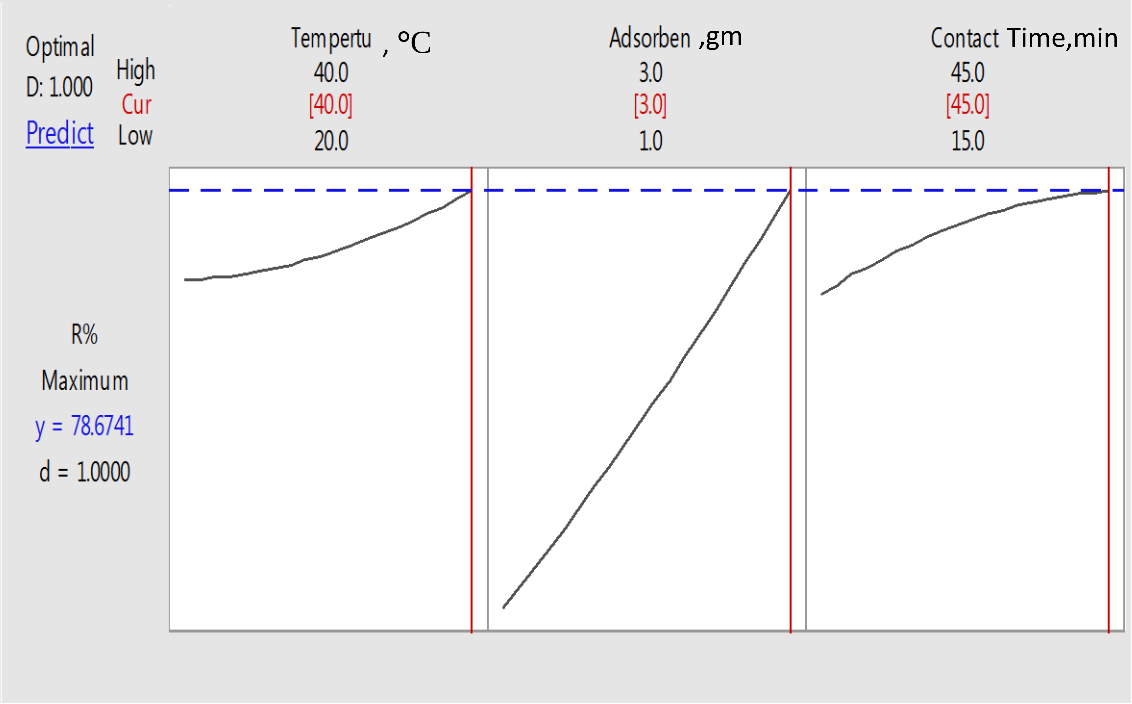

Figure (4.11): Optimum conditions for light naphtha ADS process with modified calcite adsorbent; 40 °C, 3 grams and 45 minutes for temperature, adsorbent dosage, and adsorption time respectively, also the figure show the general effect of studied variables on sulfur removing efficiency as temperature, adsorbent dosage, and adsorption time increasing.

Figure (4.12) to **Figure (4.14)** show the contour chart, which illustrated the interaction effect of each two variables on sulfur removal efficiency. As it was shown when studying the individual effect of each variable, the removal efficiency increases with the increase of variables.

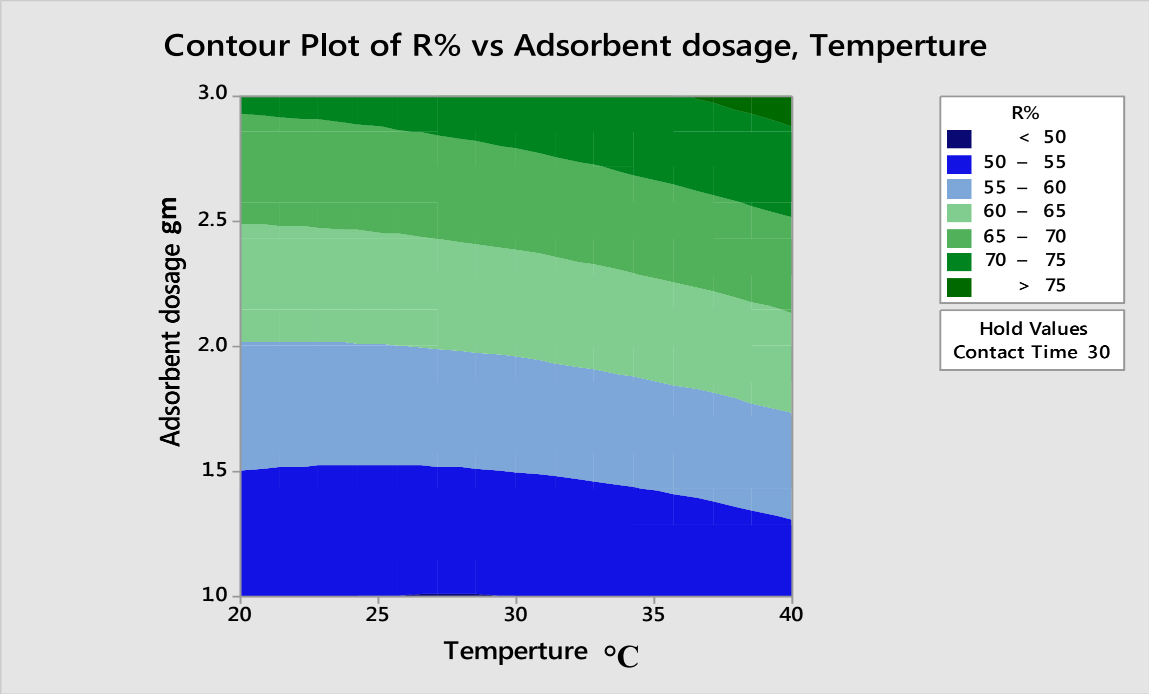

Figure (4.12): The interaction effect of temperature and adsorbent dosage on sulfur removal efficiency while kept adsorption time at 30 minutes for modified calcite.

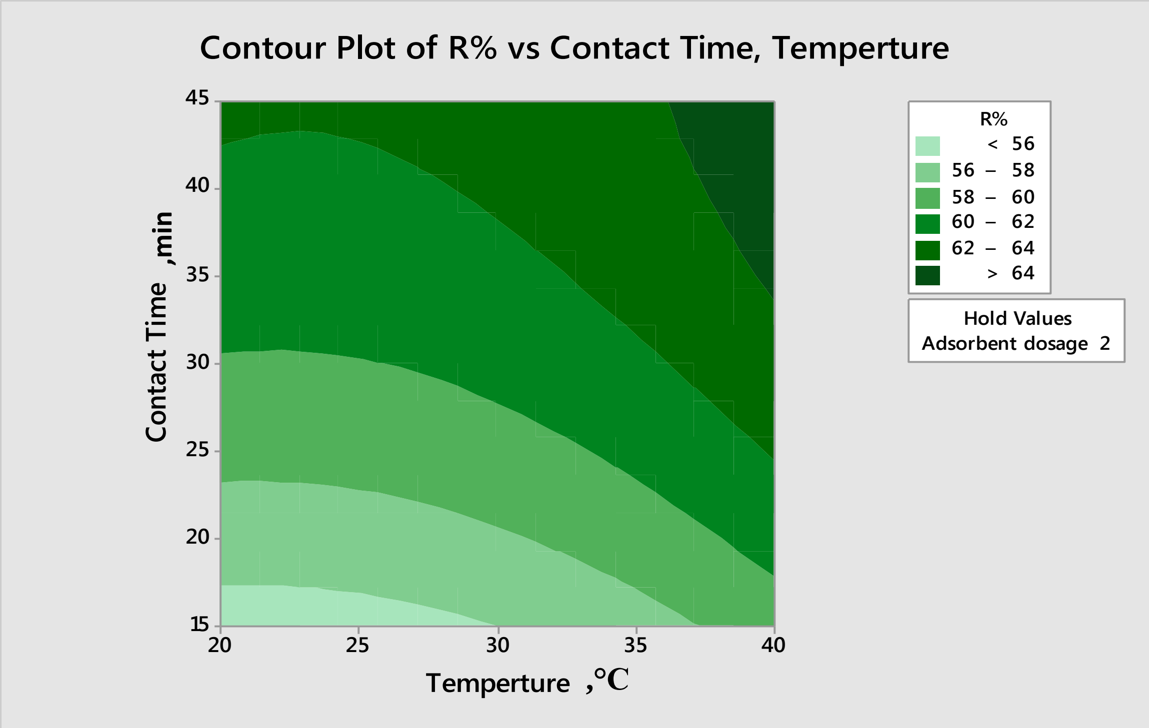

Figure (4.13): The interaction effect of temperature and adsorption time on sulfur removal efficiency while kept adsorption dosage 2 grams for modified calcite.

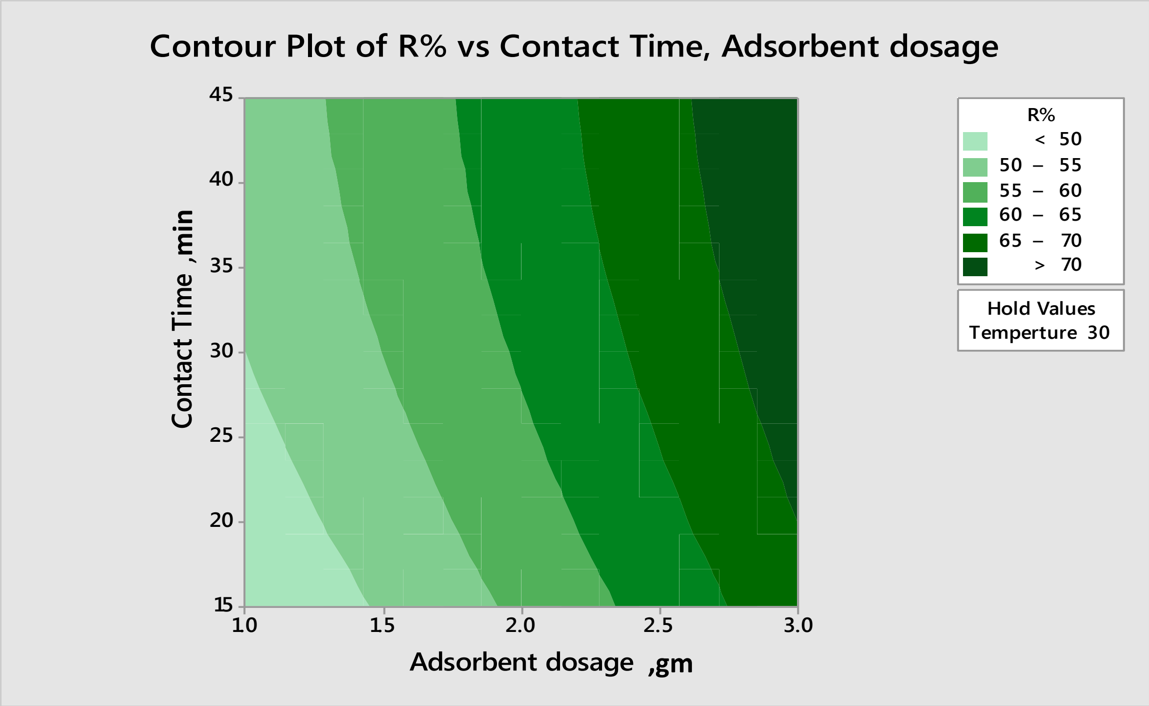

Figure (4.14): The interaction effect of adsorption time and adsorbent dosage on sulfur removal efficiency while kept temperature at 30 °C for modified calcite.

Figure (4.12) illustrates the interaction effect between temperature and adsorbent weight at hold value for time (30 min) and to what extent it affects sulfur removal efficiency, where it was shown that the best removal between (2.8grams) and (3grams) adsorbent weight and the temperature is approximate 36 to 40 °C, while **Figure (4.13)** illustrates the interactions between temperature and time at hold value for adsorption dosage (2grams) and to what extent it affects sulfur removal efficiency, where it was shown that the best removal between (34 min) and (45 min) time and the temperature is approximate 37 to 40°C).**Figure (4.14)** illustrates the interactions between time and weight at the hold value for temperature (30 °C) and to what extent it affects sulfur removal efficiency, where it was shown that the best removal between 20 min and 45 min time and the weight is approximately (2.7 to 3 grams).

4.4.3 Adsorption Isotherm for M-calcite

Adsorption isotherm for SOCs on modified calcite at different temperatures (20,30 and 40 °C), As is well known, both Langmuir and Freundlich may be used to characterize the adsorption process. **Figure (4.15)** shows the Langmuir isotherm for different temperatures and **Figure (4.16)** shows the Freundlich isotherm for different temperatures.

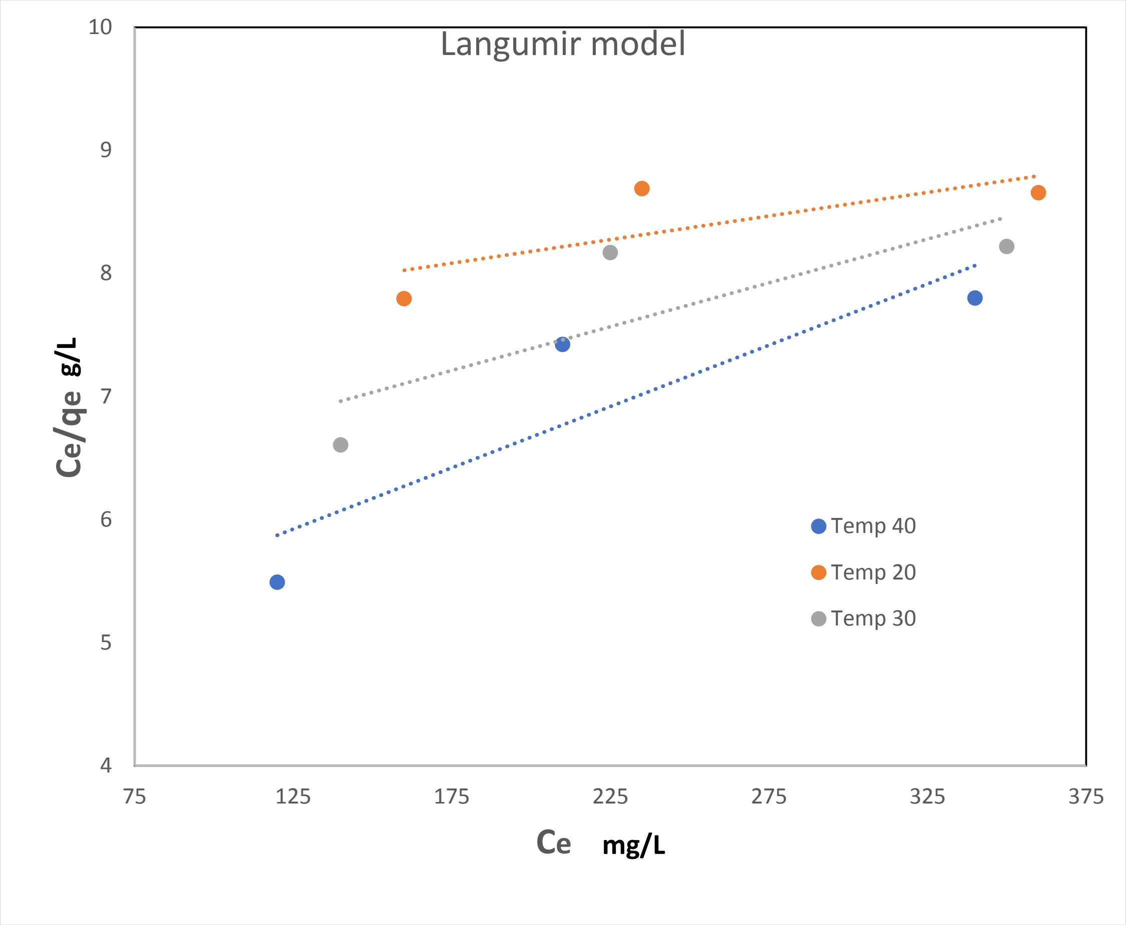

Figure (4.15): Langmuir isotherm for OSCs adsorption onto modifed calcite adsorbent at different tempertures.

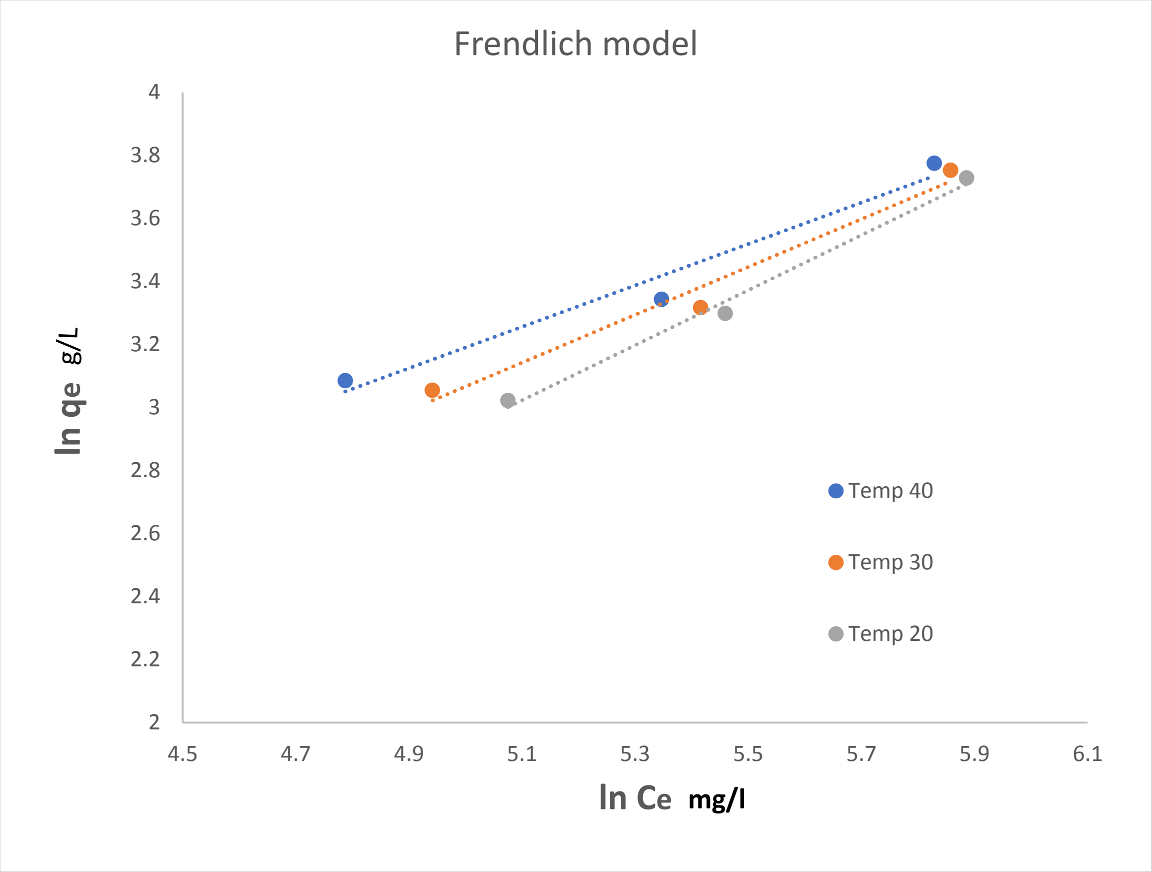

Figure (4.16): Freundlich isotherm for OSCs adsorption onto modified calcite adsorbent at different tempertures.

The isotherm model parameters values for Langmuir and Freundlich can be found in **Table (4.6)**

Table (4.6): Langmuir and Freundlich model parameters for M-calcite

	Langmuir constants				Freundlich constants		
Temp.(°C)	q_m (mgS/g)	K_L (L/mg S)	R^2		K_F [(mgS/g) (L/mg S) ⅟ n]	n	R^2
20	263	5.12×10^{-4}	0.60		0.24	1.14	0.97
30	140	1.2×10^{-3}	0.70		0.48	1.31	0.97
40	100	2.14×10^{-3}	0.80		0.90	1.5	0.99

The experimental data provided here closely follows the Freundlich isotherm, as shown in the **Table (4.6)**. This concludes that SOCs adsorption on the adsorbent occurred on a surface that was both heterogeneous and multilayered. If n is greater than 1, it suggests physical adsorption; if it's less than 2, it suggests adsorption is just moderately challenging**(Das et al., 2016; Li et al., 2016; Shikuku, Kowenje, et al., 2018)**

Chapter five

Conclusions and Recommendations

Chapter Five

Conclusions and Recommendations

5.1 Conclusions

This study yielded the following conclusions:

1.Characterization tests of prepared calcite and M-calcite revealed:

•Adsorbents were successfully synthesized by several processes, and the XRD spectrum conformed to that.

• All adsorbents were found to have oxygen-rich functional groups on their surfaces, as shown by the FTIR study spectra.

• Calcite's surface area was found to have been enhanced (from 1 m^2/g to 356 m^2/g) when activated carbon (568 m^2/g)was added, as measured by the BET method.

2. The efficiency of M-calcite as an adsorbent was higher than that of calcite in batch mode; the removal ratio for M-calcite was 79%, while it was 61% for calcite in the same conditions of the experiment.

3. After studying the adsorption desulfurization results that were conducted in calcite and M-calcite, the following was concluded:

•Temperature, weight of the adsorbent and time of contact were directly affected by the removal ratio, and the increase in the values of the factors led to a greater removal ratio efficiency.

• We note that the experiment (4) yields the best results with calcite as an adsorbent, where the sulfur content of light naphtha decreased from 776 ppm to 465 ppm and the conditions used were (temperature=40°C, weight=3 gm and contact time=30 min) and the removal ratio was 60%.

- Also, experiment (4) shows the best results with M-calcite as an adsorbent. Operating conditions were contact time =30 min, adsorbent weight =3 gm, temperature = 40 °C and the removal ratio was 79%.

4. The Freundlich isotherm provided the best fit to the experimental data for adsorptive desulfurization using the produced adsorbents, with correlation coefficients very near unity.

5.2 Recommendations for Future Studying

1-Enhancement of M-calcite effectiveness and selectivity can be investigated by mixing activated carbon with calcite at different ratios to determine the optimal conditions for this composite adsorbent.

2-Using adsorptive desulfurization for calcite and M-calcite as adsorbents in continuous mode.

3-Using solvents for regeneration of the adsorbents and studying kinetics for adsorption.

4-Using other real fuels such as (kerosene, diesel) and simulated fuel compounds such as BT(Benzothiophene) and DBT(Dibenzothiophene).

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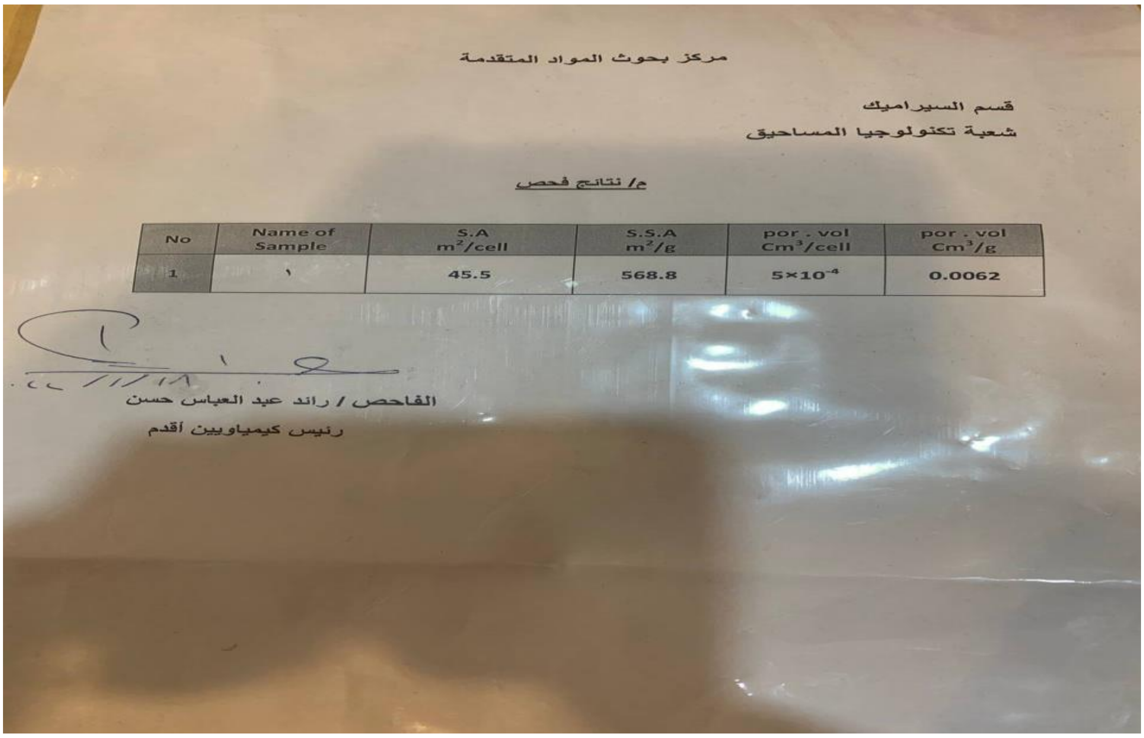
Appendices

Surface Area of Adsorbents



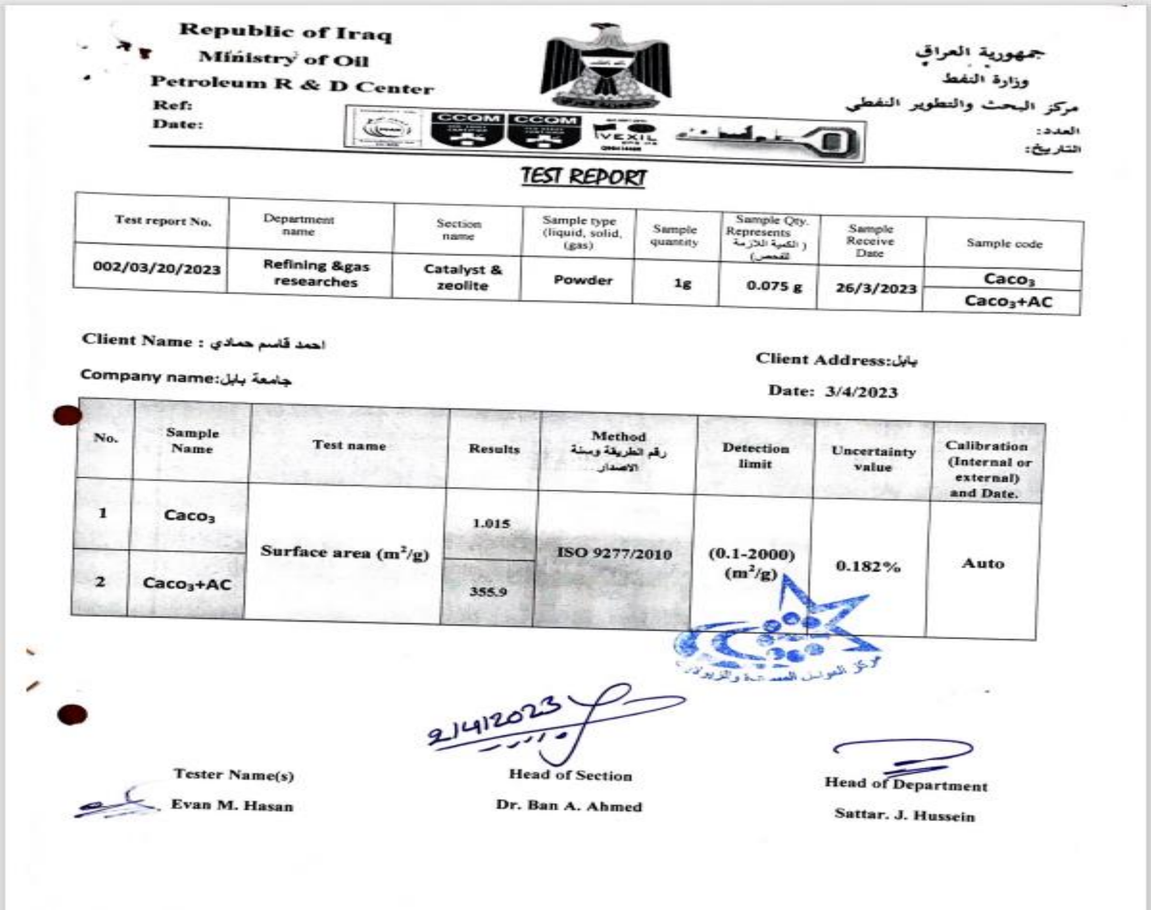
مركز بحوث المواد المتقدمة

قسم السيراميك
شعبة تكنولوجيا المساحيق

م/ نتائج فحص

No	Name of Sample	S.A m^2/cell	S.S.A m^2/g	por . vol Cm^3/cell	por . vol Cm^3/g
1	١	45.5	568.8	5×10^{-4}	0.0062

الفاحص / رائد عبد العباس حسن
رئيس كيمياويين أقدم



Republic of Iraq
Ministry of Oil
Petroleum R & D Center
Ref:
Date:

جمهورية العراق
وزارة النفط
مركز البحث والتطوير النفطي
العدد:
التاريخ:

TEST REPORT

Test report No.	Department name	Section name	Sample type (liquid, solid, (gas)	Sample quantity	Sample Qty. Represents (الكمية اللازمة للفحص)	Sample Receive Date	Sample code
002/03/20/2023	Refining &gas researches	Catalyst & zeolite	Powder	1g	0.075 g	26/3/2023	$CaCO_3$
							$CaCO_3$+AC

Client Name : احمد قاسم حمادي

Company name:جامعة بابل

Client Address:بابل

Date: 3/4/2023

No.	Sample Name	Test name	Results	Method رقم الطريقة وسنة الاصدار	Detection limit	Uncertainty value	Calibration (Internal or external) and Date.
1	$CaCO_3$	Surface area (m^2/g)	1.015	ISO 9277/2010	(0.1-2000) (m^2/g)	0.182%	Auto
2	$CaCO_3$+AC		355.9				

2/4/2023

Tester Name(s)
Evan M. Hasan

Head of Section
Dr. Ban A. Ahmed

Head of Department
Sattar. J. Hussein

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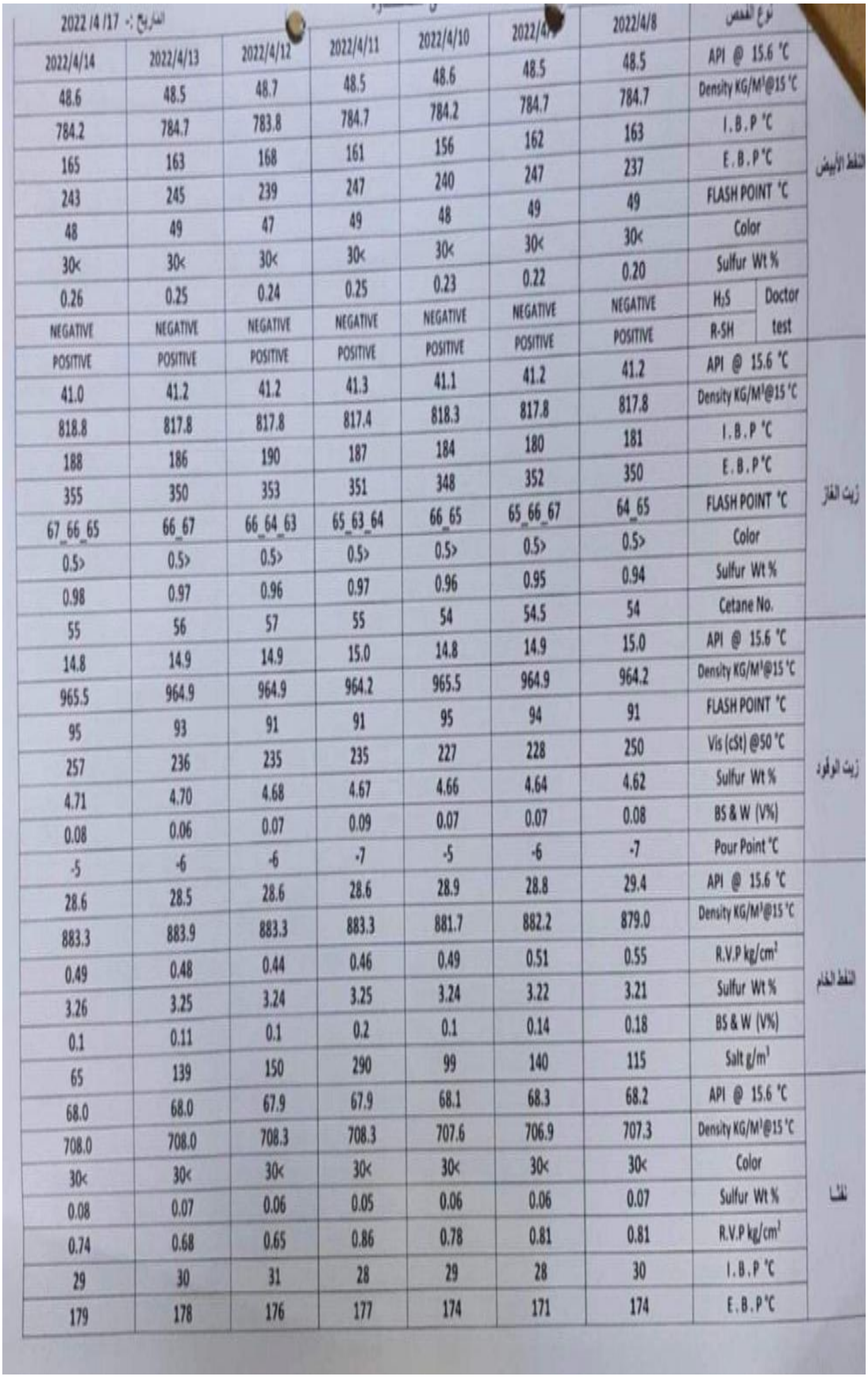
- Batch-wise processing with max. 1 x 220 ml sample
- 2 x 20 ml sample per batch with stacked jars

Specifications of Products in Al-Diwaniya Refinery



التاريخ :- 2022 /4 /17

	نوع الفحص	2022/4/8	2022/4/	2022/4/10	2022/4/11	2022/4/12	2022/4/13	2022/4/14
النفط الأبيض	API @ 15.6 °C	48.5	48.5	48.6	48.5	48.7	48.5	48.6
	Density KG/M^3@15 °C	784.7	784.7	784.2	784.7	783.8	784.7	784.2
	I.B.P °C	163	162	156	161	168	163	165
	E.B.P °C	237	247	240	247	239	245	243
	FLASH POINT °C	49	49	48	49	47	49	48
	Color	30<	30<	30<	30<	30<	30<	30<
	Sulfur Wt %	0.20	0.22	0.23	0.25	0.24	0.25	0.26
	Doctor test H_2S	NEGATIVE	NEGATIVE	NEGATIVE	NEGATIVE	NEGATIVE	NEGATIVE	NEGATIVE
	R-SH	POSITIVE	POSITIVE	POSITIVE	POSITIVE	POSITIVE	POSITIVE	POSITIVE
زيت الغاز	API @ 15.6 °C	41.2	41.2	41.1	41.3	41.2	41.2	41.0
	Density KG/M^3@15 °C	817.8	817.8	818.3	817.4	817.8	817.8	818.8
	I.B.P °C	181	180	184	187	190	186	188
	E.B.P °C	350	352	348	351	353	350	355
	FLASH POINT °C	64_65	65_66_67	66_65	65_63_64	66_64_63	66_67	67_66_65
	Color	0.5>	0.5>	0.5>	0.5>	0.5>	0.5>	0.5>
	Sulfur Wt %	0.94	0.95	0.96	0.97	0.96	0.97	0.98
	Cetane No.	54	54.5	54	55	57	56	55
زيت الوقود	API @ 15.6 °C	15.0	14.9	14.8	15.0	14.9	14.9	14.8
	Density KG/M^3@15 °C	964.2	964.9	965.5	964.2	964.9	964.9	965.5
	FLASH POINT °C	91	94	95	91	91	93	95
	Vis (cSt) @50 °C	250	228	227	235	235	236	257
	Sulfur Wt %	4.62	4.64	4.66	4.67	4.68	4.70	4.71
	BS & W (V%)	0.08	0.07	0.07	0.09	0.07	0.06	0.08
	Pour Point °C	-7	-6	-5	-7	-6	-6	-5
النفط الخام	API @ 15.6 °C	29.4	28.8	28.9	28.6	28.6	28.5	28.6
	Density KG/M^3@15 °C	879.0	882.2	881.7	883.3	883.3	883.9	883.3
	R.V.P kg/cm^2	0.55	0.51	0.49	0.46	0.44	0.48	0.49
	Sulfur Wt %	3.21	3.22	3.24	3.25	3.24	3.25	3.26
	BS & W (V%)	0.18	0.14	0.1	0.2	0.1	0.11	0.1
	Salt g/m^3	115	140	99	290	150	139	65
نفثا	API @ 15.6 °C	68.2	68.3	68.1	67.9	67.9	68.0	68.0
	Density KG/M^3@15 °C	707.3	706.9	707.6	708.3	708.3	708.0	708.0
	Color	30<	30<	30<	30<	30<	30<	30<
	Sulfur Wt %	0.07	0.06	0.06	0.05	0.06	0.07	0.08
	R.V.P kg/cm^2	0.81	0.81	0.78	0.86	0.65	0.68	0.74
	I.B.P °C	30	28	29	28	31	30	29
	E.B.P °C	174	171	174	177	176	178	179

الخلاصة

في هذه الدراسة استخدمت تقنية الامتزاز لإزالة مركبات الكبريت من وقود النفثا الخفيفة باستخدام الكالسيت والكالسيت المعدل كمواد مازة، حيث تم تحضير الكالسيت من قشور البيض بطريقة التسخين والتفعيل بعد ذلك تم تعديله من خلال خلطه مع الكاربون المنشط التجاري بنسب وزنية متساوية حيث تم الحصول على خصائص المواد المازة المحضرة من خلال فحص حيود الأشعة السينية(XRD)ومطياف الاشعة تحت الحمراء(FTIR) وقياسات المساحات السطحية(BET) .

حيث استخدم وقود النفثا الخفيفة بتركيز كبريتي ٧٧٦ جزء في المليون من مصفى الديوانية في دراسات دفعية (batch-studies) حيث تمت دراسة ظروف التشغيل المختلفة التي تؤثر على عملية الامتزاز، مثل درجة الحرارة (٢٠-٤٠ درجة مئوية) ، ووزن المادة المازة (١-٣ غم) لكل ١٠٠ مل من النفثا الخفيفة ، وزمن التلامس (١٥-٤٥ دقيقة) بسرعة خلط ثابتة (٣٠٠ دورة في الدقيقة)، في هذه الدراسة، تم استخدام تصميم برنامج Minitab-Box-Behnken لتصميم التجارب، والذي يعتبر أكثر وضوحًا ودقة لأنه يوضح تأثير كل عامل معتمد على كفاءة الازالة ونسبة الإزالة حيث تظهر النتائج والتحليل أن الزيادة في درجة الحرارة وكمية المادة المازة ووقت التلامس تؤدي الى زيادة في كفاءة الإزالة. كذلك يوضح تحليل مساواة توازن الامتزاز (adsorption-isotherm) للدراسات الدفعية للمواد المازة بانها تتبع موديل (Freundlich).

وفقًا لنتائج الدراسة، فإن النسب المثلى لإزالة محتوى الكبريت من النفثا الخفيفة باستخدام الكالسيت والكالسيت المعدل كمواد مازة تساوي ٦١٪ (٣٠٣ جزء في المليون) و ٧٩٪ (١٦٣ جزء في المليون) على التوالي.

أخيرًا، أثبتت النتائج أن استخدام الكالسيت المعدل (الناتج من خلط نسبة وزنية متساوية من الكالسيت مع كاربون المنشط التجاري) كمادة مازة لإزالة الكبريت أفضل من الكالسيت من حيث نسبة الإزالة.

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قسم الهندسة الكيمياوية

إزالة الكبريت من النفثا الخفيفة لمصفى الديوانية باستخدام الكالسيت المعدل كمادة مازة

رسالة مقدمة الى
كلية الهندسة –جامعة بابل
كجزء من متطلبات نيل درجة الماجستير في علوم الهندسة الكيمياوية

من قبل

أحمد قاسم حمادي

بأشراف

أ.د حميد حسين علوان

١٤٤٥ه **٢٠٢٣م**