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Efficient Exploitation of Al-Mishraq

Sulfur Solid Wastes

**A Project Submitted as Partial Fulfillment for The Requirements
of the Degree of Bachelor of Science in Mining Engineering**

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Abstract

Al-Mishraq Sulfur Solid Wastes (foam) are exploited as a potential and priceless feedstock for Activated Carbon (AC) prepared through thermal activation method. Iodine number surface area employed in identifying the AC. The as-obtained AC was applied in the desulphurization of dibenzothiophene (DBT) from synthetic gasoline. A 56.95 % as a maximum removal efficiency of DBT from model gasoline was obtained at 20°C for a contact time of 60 minutes using 25 mL of 100 mg/L DBT solution and 0.25 g of the AC. The adsorption data have analyzed for their adsorption isotherms, and the consequences followed the following order: Freundlich model > Langmuir model> Temkin model, suggesting the heterogeneity and porosity of the as-prepared adsorbent. The present investigation offers a cheap and potential feedstock to create AC as an adsorbent for model gasoline fuel desulphurization.

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Nomenclature

Symbol	Description
MSM	Mishraq sulfur mine
AC	Activated carbon
DBT	Dibenzothiophen
IL	Ionic liquid
WHO	World health organization
HDS	Hydro desulfurization
ODS	Oxidative desulfurization
BDS	Bio desulfurization
EDS	Extractive desulfurization
PDS	Pervaporation desulfurization
ADS	Adsorptive desulfurization
MOF	Metal organic framework
PVDS	Pervaporation desulfurization
PVC	Polyvinyl chloride
IN	Iodine adsorption
BT	Benzothiophene
DMPT	Dimethylbnzothiophene
S-MInteraction	Sulfur-metal interaction
I.R	Infrared spectroscopy
U.V	Ultraviolet spectroscopy
P.M.R	Proton magnetic resonance spectroscopy
R ²	Coefficient of determination
BET	Brunauer-Emmett-teller
WMS	Wild mustard stems
FESEM	Field emission scanning electron microscopy
XRD	X-ray diffraction
FTIR	Fourier transform infra-red spectroscopy
TAG	Thermal gravimetric analysis
PPM	Part per million
MPA	Mica pascal
RPM	Round per minute

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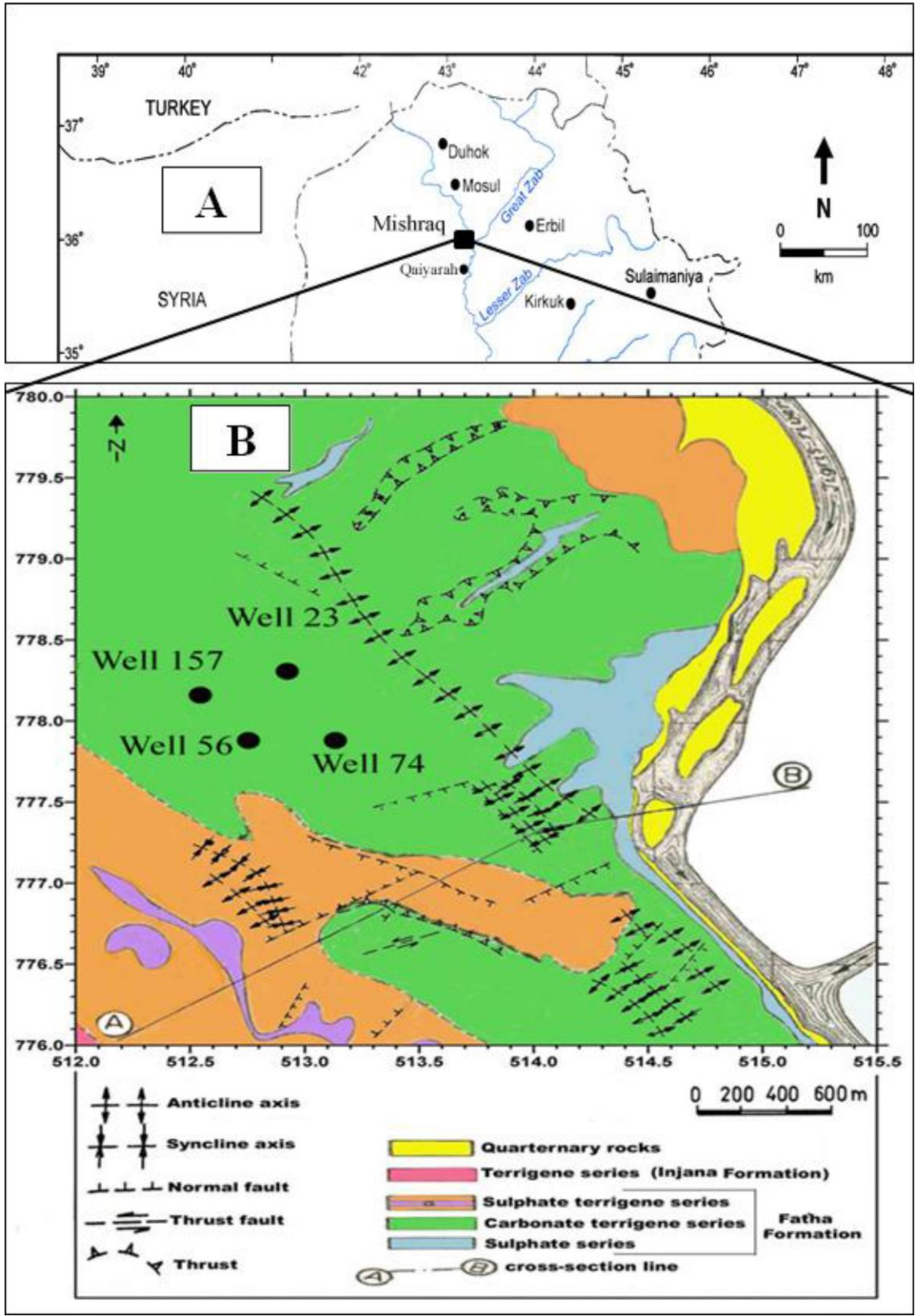
1-1 introduction

This chapter deals with a general overview of the Al-Mishraq mine, purification methods used to purify sulfur and considerations of different desulfurization processes.

AL Mishraq raw sulfur

Mishraq Sulfur Mine (MSM), one of the most important mines in the Middle East, is located in North Iraq, about 45 Km southeast of Mosul (Figure1-1A). It contains about 100-250 million tons of bioepigenetic sulfur) within the Middle Miocene Fat'ha Formation. It extends for about 10 km² within a doubly plunging anticline on the west bank of the Tigris[1].

Bitumen, widespread in MSM, is present in the Euphrates and Fat'ha Formations. This bitumen causes problems in drilling and well log acquisition and interpretation. Northern part of the mine contains higher concentrations of bitumen than the southern part; therefore, the first sulfur mining concentrated in the southern part Previous studies of the Mishraq Mine focused on the origin and formation of native sulfur and hydrological factors in native sulfur and the role of tectonic, sedimentological, and there have been no published studies concerning the origin of bitumens in this area [1].



(Figure 1-1) Map of North Iraq showing the location of Mishraq area , Geologic map of Mishraq area showing the well locations.

1-2 Sulfur purification from bitumen impurities

The sulfur industry is the second extractive industry in Iraq after oil, and the annual production rate of sulfur is estimated at one million tons. The Iraqi Mishraq sulfur purification methods differ from the standard sulfur purification methods because the Mishraq sulfur ore contains a low percentage of heavy bitumen hydrocarbons, which leads to pollution of the resulting sulfur with this bituminous material due to its tendency to dissolve with this substance. For this reason, it was necessary to follow purification methods that differ from the traditional. purification methods used in the production of sulfur.

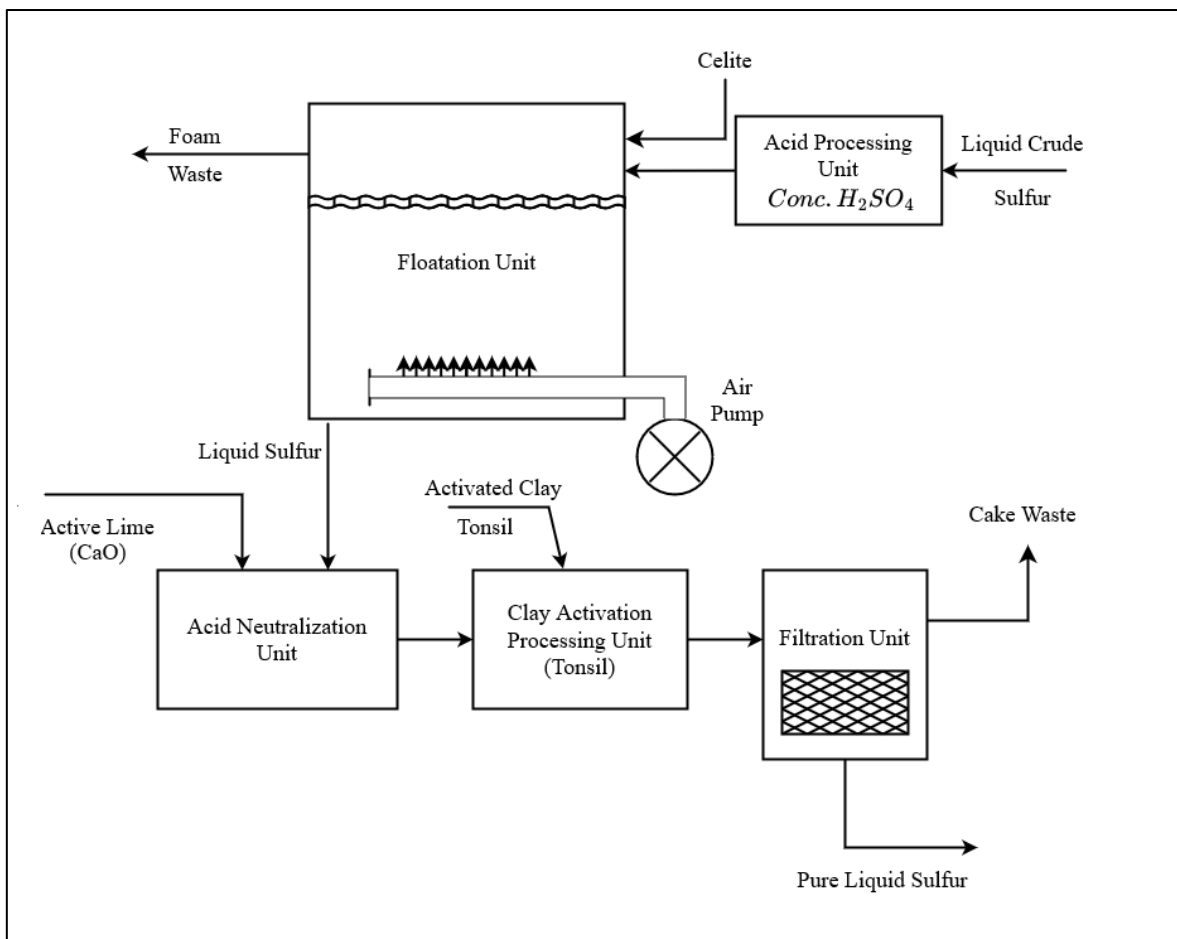
1-3 The old Bolognese filtration unit:

The project started production at the beginning of the seventies, and during this period it relied on purifying sulfur by what was termed the Bolognese method, in reference to the company that built the unit. This method relied on charring the bitumen impurity by treating it with concentrated sulfuric acid. Where these organic materials are oxidized as a result of the action of the acid. The liquid raw sulfur produced from the field is mixed with concentrated sulfuric acid and a small amount of silica dust under the trade name (Celite). So that a large part of the tar impurities present in the raw sulfur is transformed into a carbonic substance that is adsorbed on the surface of the silica dust, and the mixture is taken to the insulation container, where compressed air is pumped from the bottom of the container to float the adsorbed carbon impurities to be in the form of a foam called a foam layer, where this layer is skimmed and sent to the solid waste accumulation depot. As for the lower layer, which contains sulfur, it is sent to the neutralizer container, where quicklime powder (calcium oxide CaO) is added to the

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mixture, the remaining unreacted sulfuric acid, and then the liquid sulfur is filtered in the filter unit, where quantities of activated clays (Tonsil) are added to sulfur. As an adsorbent on which carbon granules and the remaining bitumen materials and inorganic impurities are adsorbed on those clays as a filter medium to be filtered.

Pure sulfur through it, and after a period of time, that layer is lifted and replaced, and it is thrown in the form of pieces known as cake, which contain a percentage of sulfur and the materials adsorbed on it, and are sent to the solid waste accumulation warehouse as well. (Figure 1-2) gives an illustration of the nature of the treatments included in the Polish method.



(Figure 1-2) The Polish Method [1]

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Previously, it is found that this method produces two types of solid sulfur waste, which contains a percentage of sulfur estimated at about (65 - 90%) in addition to an amount of carbon and other materials, known as Foam and Cake, by stacking them on top of each other, so they will be dealt with on one material, which is the solid waste of the old method.

This method, despite its ability to produce sulfur with internationally acceptable specifications, was suffering from many important problems such as high corrosion rates in the equipment as a result of the use of concentrated sulfuric acid in large quantities, as well as the high percentages of gas, liquid and solid pollutants (foam and cake) that are expelled.

As a result of the production process, in addition to the limitation of the method's work within certain proportions of the bitumen impurity in sulfur, not exceeding one percent by weight, and these problems were reflected in their entirety on the economic feasibility of the entire project. This unit continued production until 1990, when it was replaced by a new unit that oxidizes and carbonizes the bitumen impurity by thermal treatment. that catalyzes a reaction between sulfur and hydrocarbon, whereby hydrogen sulfide gas is formed and the hydrocarbon converted to solid carbon, which is filtered.

1-4 Economic consideration of desulfurization processes of fuel

Currently, hydrodesulfurization process is the only method that has seen industrial applicability but hydrogen demand and high- temperature requirement leading to high overall cost are the greatest challenges. Most of the processes described above are still operating at a laboratory stage and are not appeal to industrialists yet. This could be because the technology to

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harness them on a large scale is still under development or equipment and material needed for large-scale application are difficult to operate [2].

Vehicle releases significant amounts of sulfur oxides (SO_x) to the atmosphere. The air pollution due to SO_x causes ozone layer depletion, acid rain, and also reduces soil fertility [3]. According to the survey of the World Health Organization (WHO) [4], every year, around 3 million people die prematurely due to air pollution. Besides, the presence of sulfur compounds in petroleum products causes corrosion problems in petroleum refinery equipment and also poisons downstream catalysts [5]. The sulfur removal from petroleum fuels and intermediate products is essential to protect the environment and human life from air pollution and thus, as shown in Table (1-1), different countries have imposed different rules and regulations on the allowable sulfur limit (ppm) in transportation fuel desulfurization of refinery main products such as petroleum gas, gasoline, jet and diesel fuels lubricants, bitumen, wax and petrochemicals is of environmental, health and economic values towards meet changing societal needs [2]. Achieving low sulfur (<10 ppm) or zero content in transportation fuel requires different combinatoric factors ranging from cost, fuel type, methods of desulfurization, fuel source etc.

Table (1-1)

Year-wise limit on sulfur (ppm) of gasoline and diesel imposed by developing countries

Country	Gasoline			
	2016	2017	2018	2019
USA	30	30	30	15
China	50	50	10	10
European Countries	10	10	10	10
India	150	50	50	50
Japan	10	10	10	10

Country	Diesel			
	2016	2017	2018	2019
USA	15	15	15	15
China	50	50	10	10
European Countries	10	10	10	10
India	350	350	50	50
Japan	10	10	10	10

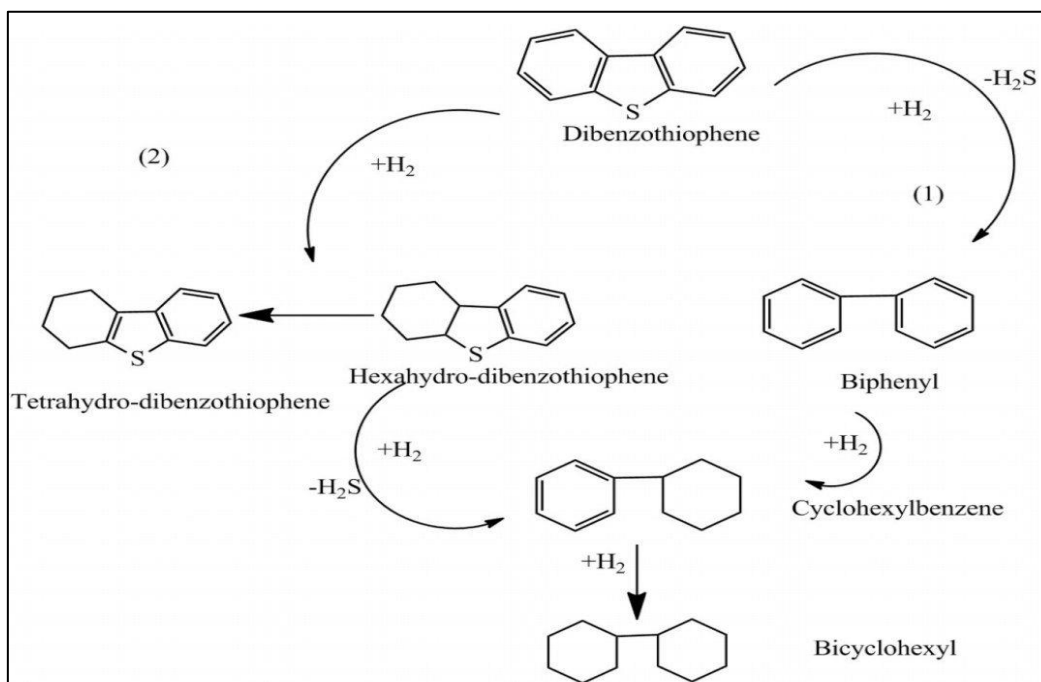
Desulfurization of fuel or from other sources is done by different technologies to remove the sulfur content to an acceptable threshold to meet regulatory standards [6]. These sulfur removal approaches include hydrodesulfurization (HDS), Oxidative desulfurization (ODS), bio-desulfurization (BDS), extractive desulfurization, precipitative desulfurization and adsorptive desulfurization [7].

The recent studies on desulfurization by the HDS, BDS, ODS (ILs), Extractive desulfurization (EDS) have been thoroughly elucidated[8].

1-5 Hydrodesulfurization

Hydrodesulfurization (HDS) is a catalytic process, which has been used in refineries since 1993 to remove sulfur compounds such as sulfides, disulfides from petroleum fractions [9]. The temperature and hydrogen pressure of HDS are usually kept in the range of 300 to 400 °C and 5 to 13 MPa, respectively [9]. Studies with model compounds have shown that the HDS reaction follows two different pathways[10]. The mechanism of HDS with DBT is shown in (Figure 1-3). The first route (1) involves direct desulfurization, where the sulfur atom is directly eliminated from DBT molecules and forms biphenyl. The second pathway (2) involves hydrogenation, where the DBT molecule is partially hydrogenated first before the elimination of sulfur by

hydrogenolysis of the C–S bond. Both pathways provide cyclohexylbenzene as a primary product.



(Figure 1-3) Possible pathways of HDS of DBT compound⁹.

The hydrodesulfurization catalysts are usually Co or Ni promoted Mo or W sulfide. $\gamma\text{-Al}_2\text{O}_3$ is the traditional support material for HDS catalysts as it provides a high surface area and high thermal and mechanical stabilities. Although the HDS process is commercially applied by refineries around the world, it has several unavoidable limitations. It is expensive as a high temperature and pressure process. The high consumption of costly hydrogen increases the operating cost [11].

1-6 Adsorptive desulfurization (ADS)

Adsorptive desulfurization is a relatively new technology for sulfur removal from fuel. It is highly popular among researchers due to its cheap nature and its relative ease of operation and adaptability to different fuel processors. It involves contacting fuel with an activated/ functionalized adsorbent to remove

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the sulfur from the fuel. Non requirement of hydrogen, operation under mild conditions of temperature (room temperature to around 100 °C) and adsorbent renewability make this method an economical method of desulfurization. Up till date, several different adsorbents have been focused and process technology has been modified to accommodate for ultra-low sulfur removal. Many of the reported materials and processes, with various mechanisms and process conditions, would be extensively explored [12].

1-6-1 Mechanisms of adsorption.

Adsorptive desulfurization is usually conducted with the use of solid sorbents of different porosity and functionalities to achieve maximum adsorptive capacity. The class of sorbents include Zeolites, Carbon, Metal organic framework (MOF), metal-oxides, metal-supported inorganics etc. [13]. Zeolites represent the class of aluminosilicates materials with $[\text{SiO}_4]^-$ $[\text{Al}_2\text{O}_3]^-$ for different applications in catalysis, related to hydrocarbon etc.[14]. In addition, it is widely used as membranes for gas separation (e.g. CO_2 capturing), and water purification via ion exchange processes [15]. Also, zeolites have been reported to have good adsorption capacities and potentials for organosulfur compounds (aromatic and aliphatic)[16]. Furthermore, modification of zeolites with various metals such as Cu^{2+} , Fe^{2+} , Ag^+ , Ni^{2+} , Zn^{2+} , Ce^{4+} , Pd^{2+} by ion exchange has been reported to significantly enhance the adsorption efficiency, selectivity and regeneration of aluminosilicates [17]. The mechanism of adsorption desulfurization of zeolites by reactive, selective and π complexation have been observed by virtue of different treatment approaches. Their efficiency is reported to be directly linked to improved characteristic properties such as pore size[18].

1-6-2 Effect of Porosity

The porosity of the adsorbents plays a crucial role in adsorption because it influences their adsorption capability. Moreover, during adsorptive desulfurization, there is the opportunity of selective separation of molecules that have different molecular size. This is true when the molecular size of the thiophenic derivative is smaller than the MOF pores. During adsorption, molecules can diffuse into the porous channels and become anchored at the active adsorption sites [19]. On the contrary, if the molecular size is similar or smaller than the pore sizes of the MOF, steric hindrances forbid the penetration inside the framework and adsorption cannot take place [20].

1-7 Oxidative desulfurization

Oxidative desulfurization (ODS) is an indirect two-steps process, where organic sulfur compounds from petroleum fractions are oxidized into corresponding more polar sulfones and sulfoxides in the presence of a suitable oxidant and a catalyst and then extracted using a suitable polar solvent [21-22-23]. Unlike HDS, it is operated at mild temperature and pressure conditions and does not cause damages to the structure of hydrocarbon. It was found that the electron density on sulfur atoms has a direct influence on the oxidation rate of sulfur compounds [24].

1-8 Extractive desulfurization

In EDS, extractants are used to extract the aromatic sulfur compounds from petroleum fractions at mild operating conditions without affecting the chemical structure of compounds present in fuels. A suitable solvent for extractive desulfurization should have a high partition coefficient for aromatic

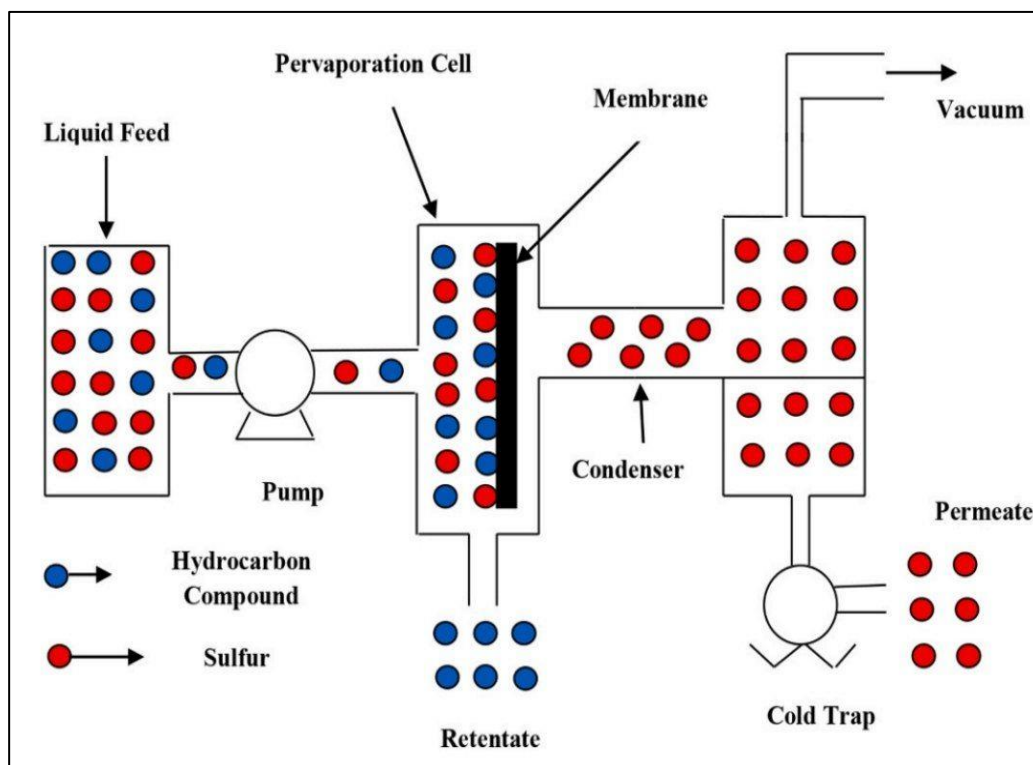
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sulfur compounds, negligible solubility in fuels, high thermal and chemical stabilities, nontoxicity, and low cost [25].

In recent decades, extractive desulfurization using ionic liquids (ILs) has drawn much attention as it avoids problems such as solvent loss and contamination[26]. Ionic liquids are classified as green solvents. Their high thermal and chemical stability, non-flammability, and negligible vapor pressure make them efficient solvents for desulfurization [27].

1-9 Pervaporation desulfurization

The separation of organic sulfur compounds by pervaporation is comparatively a newly developed technology. Researchers give attention to PVDS due to low energy consumption, and easy to scale up. In pervaporation desulfurization, dense and nonporous polymeric membranes separate the sulfur compounds from other hydrocarbons based on their solubility, affinity, and diffusivity [28]. (Figure 1-4) shows a schematic diagram of the pervaporation desulfurization process [28].



(Figure 1-4) Pervaporate desulfurization process[28].

1-10 Bio desulfurization

Bio desulfurization involves the use of microorganisms or enzymes as catalysts to remove organic sulfur compounds from petroleum distillates. Microorganisms selectively remove organic sulfur atoms, without affecting the hydrocarbon moiety of the organo-sulfur compound [29].

1-11 Activated carbon

Activated carbon (AC) is a well-known adsorbent that can be used efficiently for removal of a broad spectrum of pollutants from air, soil and liquids. Adsorbents are usually porous solids, and adsorption occurs mainly on the pore walls inside particles. Examples are AC (adsorbs mainly organics), silica

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gel and activated alumina (adsorb moisture), zeolites and molecular sieves and synthetic resins. Among them, AC is more efficient adsorbent for elimination of many pollutants [30].

Applications of (AC) are enormous. It is important to use is for gasoline vapor emission control canisters in automobile. AC can act as a filter material in air cleaning filters for removal of gases and vapors in the industrial environment. Especially impregnated grades are used in cigarette filters to adsorb some of the harmful components of tobacco, and as the catalyst or carrier of catalytically active substances. Heavy metal ions such as mercury, lead and cadmium in drinking waters are very dangerous even in trace amount, and adsorption method for removing these ions can be essential for water and waste water contaminated by heavy poisonous metal ions [31]. Activated carbon can be used for removal of poisonous heavy metal ions from aqueous solutions. Adsorption in this case is due to the surface complex formation between the metal ions and the acidic surface function group of AC. Adsorption is due to the surface complex formation between the metal ions and the acidic surface function group of AC. The removal efficiency is influenced by various factors, such as solution concentration, solution pH, ionic strength, nature of adsorbate, adsorbent modification procedure, Physical properties (surface area, porosity), and the chemical nature of AC [31].

Highly colored waste streams such as result from dyeing operations can be cleaned-up by activated carbon. Its first use came into prominence through its use as an adsorbent for certain poisonous gases in gas masks in World War I. It has been reported that coal carbons are 99% effective for dye removal and could accept dye loadings as 0.40 kg dye per kg of AC. In order to make it economical, fixed bed systems containing granular carbon could be used in

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tertiary treatment of wastewater. Although there are many chemical, physical, and biological methods of treating water contaminated with industrial and municipal wastes to produce safe and palatable drinking water, none of them have the potential of AC treatment[32].

1-11-1 Preparation of Active Carbon

Any carbonaceous materials (animal, plant, or mineral origin) with high concentration of carbon can be simply changed into activated carbon (using both chemical or gas activation methods). The most common raw materials are wood, charcoal, nut shells, fruit pits, brown and bituminous coals, lignite, peat, bone and paper mill waste (lignin), synthetic polymers like Polyvinyl chloride PVC, are used for manufacturing of activated carbon. Activated carbon obtained from hard wood is preferable for adsorption because charcoal obtained from soft wood, such as pinewood, is very unstable and readily crumbles. It has been reported that the best grades of AC are obtained from the coconut shell and apricot pits. Activated carbons are commonly prepared by two basic processes:

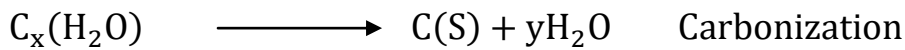
1- Physical or gas activation method, and 2- Chemical activation. The choice of activation method is also depending upon the starting material and whether a low or high density, powdered or granular carbon is desired.

In gas activation method the raw material with less than 25% moisture, is carbonized first at 400 - 500 °C to eliminate the bulk of the volatile matter and then the carbon is subjected to oxidizing gases usually carbon dioxide or steam at 800-1000 °C or and with air at low temperature, for selective oxidation [33]. The oxidation is preceded usually by a primary carbonization of raw material. The pyrolysis of wood starts at temperature about 225 °C.

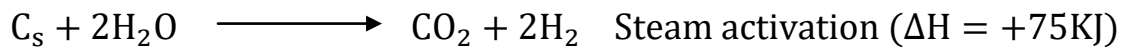
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Carbon is oxidized by atmospheric oxygen is oxidized to CO₂, so the air should be excluded or very controlled during carbonizing and activation. Steam and carbon dioxide act as mild oxidizing agents at 800-1000 °C as follow:

Eq. 1-1



Eq. 1-2



Eq. 1-3



achieved by washing with organic solvents, mineral acids, caustic soda, steam, or dry heat under vacuum but powdered form is very difficult. High-density starting materials such as coconut shells are used for preparation of AC for gas phase applications.

The relative capacity of different carbons is best assessed by trial upon the water to be treated. The pore structure limits the size of molecules that can be adsorbed, and the surface area limit the amount of material that can be adsorbed, assuming suitable molecular size. For screening purposes many manufacturers test their products upon standard solutions to yield iodine, molasses, phenol and methylene blue numbers. The most commonly applied gas adsorption tests are carbon tetrachloride and benzene activity tests. Concentration of organic contaminants can affect the adsorption process [34].

1-11-2 Comparing and Combining Physical and Chemical Processes

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Activated carbons can be produced by physical, chemical, or combined activation processes, resulting in sorbents with well-distributed porosity and high surface areas. However, the mechanisms of activation are very different for both processes, and the resultant carbons possess different chemical and physical properties.

The first significant difference between physical and chemical processes is the number of stages required for activation and the temperature at which activation takes place. Chemical activation is conducted in one step, whereas physical activation is usually a two-step process of carbonization and activation. The temperatures employed in chemical activation (200-800°C) are lower than those required for physical activation (typically 800-1100°C), resulting in different burn off rates of the carbon skeleton. Often, it is reported that the carbon yields in chemical activation are greater than those for physical activation. As a result of this temperature difference, chemically activated carbons lack the semiconductor-redox properties seen in physically activated carbons. This is due to the restriction of the formation of graphite zones resulting from the low temperatures used in chemical processes.

Another significant difference relates to the pore-size distribution. Rodriguez and Molina [35] reported that chemical activation of lignocellulosic precursors with ZnCl_2 resulted in the same micropore volume as CO activation but with a higher yield. They found that as a consequence of chemical activation, the porosity is more developed, leading to carbons having similar micropore volumes but with larger mesopore volumes. Physical activation with CO was reported to open and widen the micro porosity, but at high temperatures, there was an ablation of the exterior of the particle, resulting in low carbon yields. Lopez [36] investigated the variable effects of CO and ZnCl_2 activation on carbons from wood monolith. In

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contrast to chemical activation, physical activation resulted in smaller surface areas, smaller yields, and significant pore differences. Pore investigations implied that the micropore and mesopore size distributions were closer in physical activation carbons than in chemically activated carbons[37].

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1-12 The aim of the study

The present study objects to separate the carbon materials from the residues of purifying the sulfur Al-Mishraq, which is a mixture of sulfur and carbon resulting from the process of carbonizing the hydrocarbon impurities, and then studying the adsorption ability of the pollutants (di benzo thiophenes) from the gasoline model.

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2-1 Literature review

This chapter deals with previous studies from several researchers about the adsorption of DPT. In this section, some references are mentioned to show how they are related to this study.

Latif H. Ali and Khalid A. Al-Ghannam (1979) Separated the bituminous impurity incorporated with the elemental sulphur in the Mishraq deposit by solvent extraction. The extract was further fractionated by column chromatography and the fractions were studied spectroscopically (IR, UV, and p.m.r.) The observation that the bituminous material is basically asphaltic (ca. 80% of the total weight, precipitated by straight-chain pentane) with no detection of light components, coupled with the p.m.r. results on carbon type distribution, may add support to the existing theories about the origin of elemental sulphur in the Mishraq region. Elemental analysis of bitumen samples isolated from Frasch sulphur when compared with those isolated from borehole samples using identical isolation techniques may indicate that a reaction between elemental sulphur and the bituminous impurity is taking place under the thermal conditions of the Frasch Process [38].

Muhammad Imran Din, et.al. (2017) derived an extensive variety of AC from agricultural and commercial waste materials. Compared different activating agents for AC and concluded that, although basic treatment gives a better yield, it incurs greater expense, and it may also cause bursting of the tube furnace. Neutral activation treatment is safe to carry out but gives a relatively lower yield which is also economically unfavorable. So, acidic activation is the best treatment that, if carried out under highly controlled conditions, may provide a better surface area and microporosity [39].

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Melanie Iwanow , et.al. (2020) discussed the preparation of activated carbon materials along selected examples of precursor materials of available production and modification methods and possible characterization techniques. evaluated the preparation methods for activated carbon materials with respect to its use as catalyst support and identified important parameters for metal loading. Accordingly, the catalyst must be developed individually for the different applications according to the desired requirements based on empirical and theoretical knowledge [40].

Hala Saad Jasim Mohamed (2020) studied three types of bituminous materials found in different conditions in Mishraq sulfur Mine: Bituminous materials of Frasch sulfur mine, Natural bituminous materials, Bituminous materials extracted from a depth of about 200 m without exposing to Frasch process conditions. The optimum conditions were determined to obtain a nearperfect reaction between the concentrated sulfuric acid and the bituminous materials (0.3ml conc. H₂SO₄, 160-170°C, 2.5h). Pure sulfur was filtered using the Soxhlet and toluene as a solvent. The specifications of pure sulfur were in conformity with the Iraqi standard 2119 for 2002 [41].

Ali A. Hussein and Abdelrahman B. Fadhil (2021) employed an equivalent blend of date pits and olive stones (w/w) as a low cost precursor for AC synthesis by the ZnCl₂ activation method. The adsorptive action of the synthesized AC was inspected toward the desulfurization of dibenzothiophene (DBT). The maximum % removal of DBT reached 92.86% under optimum conditions of 0.30 g of the AC, a contact period of 60 minutes, at 40°C, and 25 mL of 200 mg/L DBT solution. The adsorption data followed the pseudo-second-order kinetic model, while Freundlich isotherm model described best the adsorption data. This investigation presents a cheap and effective adsorbent for both model and commercial gasoline fuel desulfurization [42].

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Biswajit Saha, et.al. (2021) studied different adsorbents under varying conditions, and a comparative study can identify high performing materials for ADS. While most studies were on lab-scales and batch systems, a continuous adsorptive desulfurization system using real feedstocks can enhance its commercial potential. Metal oxide, zeolite, mesoporous material, MOF, and carbon-based adsorbents have potential for ultra-low fuel production, but further research on adsorbent durability, regeneration, and reuse is needed for successful scale-up [43].

Baraa M. Mohammed-Taib and A. B. Fadhil (2021) successfully synthesized a high quality and surface area AC (1286.0 m²/g) from a nonedible feedstock viz. wild mustard stems (WMS) through the ZnCl₂ activation method. The as-created AC was influential in the ADS of DBT with an efficiency of 96.02% at relatively mild conditions of 0.40 g AC dose, a contact period of 30 minutes at 30°C. The ADS data fitted well to the Langmuir adsorption isotherm due to its higher R² value (R² = 0.9924) than other models, suggesting multi-layers' adsorption of DBT onto the AC. The so-obtained AC was also effective towards the ADS of the commercial gasoline with a removal efficiency of 91.33% employing 1.0 g of the AC [44].

Saheed A. Ganiyu and Saheed A. Lateef (2021) reported several materials (mesoporous materials, zeolites, supported metals/metal oxides and clay), process conditions and results of adsorptive desulfurization of fuel with a particular interest in the ultra-deep removal of recalcitrant sulfur compounds such as thiophene, Benzothiophene BT, Dibenzothiophene DBT and Dimethylbnzothiophene DMPT. also reported that the physicochemical properties of the adsorbent such as surface area, pore volume and chemical nature of the adsorption surface area are important criteria for effective adsorption process. In the case of zeolites, diffusion limitation is one the

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drawbacks of the effective adsorption process and hierarchical zeolites have been studied with good results reported. Also, incorporation of metal oxides with supports such as zeolites and/or mesoporous materials are yielding encouraging results by improving the physicochemical properties of the sorbents which consequently increase the activity of the adsorbent, investigation into the in-situ changes in the chemical nature of the adsorbed compounds which could affect the stability of the adsorbent is highly necessary [45].

Mohamed W. Alkhafaji, et.al. (2021) revealed that bitumens from the Mishraq Mine were subjected to alteration processes by biodegradation and water washing. Deuterium isotope values of asphaltenes indicate that these bitumens are not affected by abiotic oxidation. These bitumens are slightly biodegraded (level 2–3 of Peters and Moldowan, 1993) [46]. Their normal alkanes are partially removed, although the terpanes and steranes are intact. Dibenzothiophene/phenanthrene (DBT/P) values of all samples are low, due to water washing. Normal alkanes and isoprenoid ratios, biomarker characteristics of terpanes and steranes, and carbon isotopic composition of saturated and aromatic fractions indicate that these bitumens were generated from early mature carbonate source rocks containing sulfur-rich marine organic matter deposited under marine reducing conditions. The Upper Jurassic to Lower Cretaceous Chia Gara Formations are the most likely source rocks for these bitumens [47].

Chapter Three

In this chapter, the practical features of the project were explained.

3-1 Methodology

In practical features of the project were explained from the beginning of the extraction of the raw material (foam), its diagnosis and application for the adsorption of sulfur compounds (DPT) from the gasoline model. The practical part and measurements were made in collaboration with University of Mosul College of Science, Department of Chemistry, Industrial Research Laboratory.

3-2 Chemicals and materials

Foam extracted from sulfur Al-Mishraq, petroleum ether, n-hexane, sodium hydroxide, hydrochloric acid, di-benzothiophene, iodine, sodium thiosulfate, starch, ethylene glycol mono ethyl ester.

3-3 Preparation of adsorbent

In a beaker, 50 g of foam is weighed and 50 ml of 20% sodium hydroxide solution is added to foam, then the mixture is heated on a water bath at a temperature of 80-90 °C for two hours with continuous stirring, then filtered through a filter paper and washed. The precipitate is washed several times with hot water and dried at a temperature of 80 ° C for 1 hour. The precipitate is treated with 100 ml of petroleum ether using Soxhlet extraction apparatus

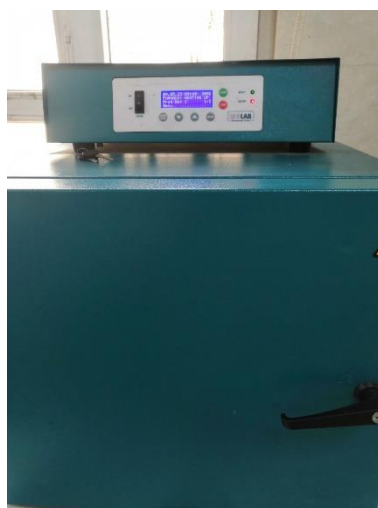
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(Figure 3-1) until the solvent becomes colorless, it is distilled and the bituminous material is dried at a temperature of 105 °C for 24 hours.



(Figure 3-1) Soxhlet extraction apparatus.

The produced carbonaceous material produced was then crushed and sieved to obtain certain particles size (140 μm). The obtained particles were thermal activated at (500°C) for 1h using Muffle furnace (Figure 3-2).



(Figure 3-2) Muffle furnace.

The resulting activated carbon (AC) was washed by 5% HCl and DW, then kept in a sealed container for further use. The AC yield was calculated as follows [48]:

$$\text{Ac yield \%} = \frac{\text{Weight of AC}}{\text{Weight of feed stock}} \times 100 \dots\dots\dots(3 - 1)$$

3-4 Characterization of the adsorbent (AC)

The specific surface area of the suggested adsorbent was determined using ethylene glycol mono ethyl ester retention method [49] The adsorptive capacity of the said adsorbent, such as iodine adsorption number (IAN) which measures the micro porosity level in the AC, was determined following the method given elsewhere [50]:

$$\text{IN(mg\g)} = \frac{(V_b - V_s) \times N \times (126.9) \times 1.5}{M} \dots\dots\dots(3 - 2)$$

where, V_b and V_s are volumes of sodium thiosulphate solution necessary for the blank thiosulphate solution (mol/l), 126.9 is iodine atomic weigh, and M is the implemented quantity of the AC (g).

3-5 Model gasoline preparation

A 0.20 g of DBT was dissolved in 1 L n-hexane to prepare a DBT stock solution of 200 mg/L. Diverse solutions of DBT (10–100 mg/mL) were

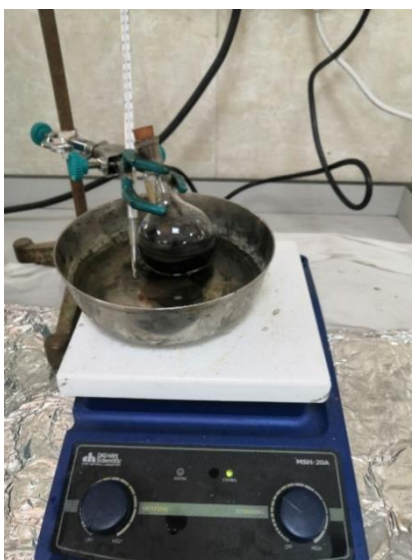
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prepared, and then implemented in determining the calibration curve, which was exploited for the determination of the concentration of DBT after the ADS process. Then, the absorbance of the designed solutions was measured and plotted against their absorbance at the maximum wavelength (λ_{\max}) of 325 nm. The obtained calibration curve exhibited linearity with a correlation coefficient of (R^2) of 0.9992.

3-6 The Adsorptive desulfurization (ADS) of model gasoline

The ADS of model gasoline using the as-created AC was investigated via batch adsorption experiments. The ADS experiments were carried out by mixing 25 mL of 100 mg/L DBT stock solution with the proper amount of the AC in a round bottom flask. The mixture was stirred at the specified

temperature on a magnetic stirrer at 100 rpm until attaining the equilibrium (figure 3-3). After equilibrium, the AC was stripped from the solution by filtration, and the final concentration of DBT in the filtrate was analyzed by UV – Vis spectrophotometer at 325 nm (figure 3-4).



(figure 3-3) Hotplate magnetic stirrer.

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The optimization of the ADS conditions was achieved by adopting numerous experiments, which studied the effect of DBT initial concentration (20–100 mg/L), the AC dose (0.1 g – 0.50 g), temperature (10°C – 50°C), and contact time (5–120 minutes) on the percentage removal of DBT.



(Figure 3-4): UV.-Vis spectrophotometer.

The adsorption capacity (mg/g) and the DBT adsorption percentage (DBT %) of the as-synthesized were calculated using Equations (3) and (4), respectively:

$$q_e = \frac{(C_0 - C_e)V}{W} \dots\dots\dots(3 - 3)$$

$$\text{DBT}\% = \frac{(C_0 - C_e)}{C_0} \times 100 \dots\dots\dots(3 - 4)$$

where, C_0 and C_e indicates the initial and equilibrium concentration of DBT (mg/L), V represents the volume of the model oil, and W refers to the AC (g).

3-7 Adsorption isotherms

Information relating to the adsorbent capability can be obtained from the equilibrium inspection of adsorption. The surface properties and the adsorbent affinity can be expressed by definite constant values, which can be derived from the adsorption isotherm. The latter can also be employed to compare the adsorbents' capacities for various contaminants. Analyzing the equilibrium data can be achieved by commonly identified adsorption isotherms. The experimental data of the adsorption isotherms [51].

Chapter Four

4-1 Results and Discussion

In this part, the results obtained from this study of (DPT) adsorption process from gasoline are discussed.

4-2 Characterization of AC:

The specific surface area of the suggested adsorbent was determined using ethylene glycol mono ethyl ester retention method (EGME) surface area, adsorptive capacity and moisture content are given in Table (4-1). The following table shows surface area (SA) of activated carbon prepared from Al-Mishraq sulfur residue through two processes. Its value is 531.25 after physical activation process.

Table (4-1) Properties of The AC

Property	AC
Iodine adsorption number (mg/g)	531.25
SA_{EGME} (m²/g)	522.4
Moisture (wt. %)	3.23

The activation temperature dramatically influences the physical and chemical features, textural structures, and the functional groups on the AC surface Table (4-2).

Table (4-2) Effect of the activation temperature on the AC yield and surface area.

Temperature(°C)	Yield% (AC)	Surface area (IN(mg/g))
400	86.54	329.3
500	88.37	531.25
600	87.15	527.3
700	81.32	521.56

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A progressive decline in the AC yield occurred with raising the activation temperature, as shown in Table 3, due to the precursor further devolatilisation and dehydration. According to Rodriguez-Reinoso [52], during the activation, pores development proceeds through three stages. In the first stage, the opening of earlier unreachable pores occurs, while new pores are created through the selective activation in the second stage. Lastly, widening of the formed pores occur. It is evident from Table 3 that raising the activation temperature above the optimum ones declined the AC yield due to the further loss of the volatile's ingredients. Table 3 demonstrated that the SA of the AC samples enhanced with raising the activation temperature. This consequence attributes to the further removal of volatiles with the increment of temperature, resulting in new micro-pores. The best SA was obtained at 500°C activation temperature. Temperatures above 500°C lessened the SA because of the degradation of the micro-pores walls, resulting in the transformation of micro-pores into mezo-pores and macro-pores.

4-3 Adsorptive desulphurization efficiency:

The ADS of model gasoline fuel was inspected through batch adsorption experiments. Therefore, the influences of the DBT initial concentration, AC dosage, ADS temperature, and ADS contact period on the adsorptive efficiency of DBT were individually examined.

Due to the occurrence of diverse concentrations of S-aromatic compounds in petroleum fractions, it is significant to assess S-compounds initial concentration at a given mass of the AC. Accordingly, the elimination of DBT form model gasoline was inspected by changing the DBT initial concentration from 20 to 100 mg/L using 25 mL of DBT solution at 20°C for 120 min

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contact time with 0.25 g of the AC. As demonstrated in Table (4-3), the increment in the DBT initial concentration was accompanied by an increase in the amount of DBT adsorbed. This result ascribes to the rise in mass transfer driving force because the concentration gradient progressed between the AC's bulk solution and surface [12]. With rising concentration, extra molecules of DBT will enclose the AC active sites leading to further adsorption. Ishaq and Sadare [53] announced similar consequences upon the ADS of DBT using bentonite, acid-activated, magnetite nanoparticle loaded bentonite and pomegranate leaf, as adsorbents, respectively.

The influence of the as-created AC dosage on the ADS of DBT was examined using various amount of the so-obtained AC in the range of (0.1 g – 0.50 g). The ADS experiments were studied at 20°C using 25 mL of 100 mg/L DBT solution for 120 minutes contact period. Positive progress in the ADS efficiency was observed as the AC dosage increased from 0.1 g to 0.25 g, as demonstrated in Table(4-3). This consequence is due to the increment of the AC particles with increasing the AC amount implemented, leading to more surface area and extra adsorption sites available for DBT molecules attachment [54]. This increment in the amount of DBT adsorbed relates to the ability of DBT to form π - π dispersive interactions between the aromatic ring in DBT and the grapheme layers on AC[55]. AC dosage beyond 0.25 g had insignificant effect on the DBT removal % as a result of the unavailability of the adsorbate in the medium. Thus, AC amount of 0.25 g was selected as the best dosage for ADS of DBT.

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Table (4-3): Influence of the DBT initial concentration, AC quantity, temperature, and contact period on the removal of DBT.

Initial concentration (mg/L)	Adsorbed amount of DBT (mg/g)	Dose of AC (g)	DBT removal (%)
20	1.18	0.1	28.431
40	2.32	0.15	31.339
50	2.88	0.25	55.048
70	3.93	0.35	38.113
80	4.52	0.4	28.651
100	5.50	0.5	28.573
150	8.06		
200	10.05		
0.25 g of AC; 25 mL DBT; 20°C;120 minutes		100 mg/L DBT; 25 mL; 20°C;120 minutes	
Temperature (°C)	DBT removal (%)	Time (minutes)	DBT removal (%)
10	44.349	10	32.199
20	55.048	20	36.984
30	49.565	30	38.113
40	46.070	40	40.747
50	45.250	50	48.328
		60	56.951
		90	55.468
		120	55.048
100 mg/L DBT; 0.25 g of AC; 25 mL DBT;120 minutes		100 mg/L DBT; 0.25 g of AC; 25 mL DBT;20°C	

The ADS performance and mechanism of S-containing compounds elimination from petroleum cuts are greatly influenced by the process temperature. Accordingly, different temperatures ranged from (10°C- 50°C) were tested upon inspecting the effect of temperature on the ADS% of DBT by the as-prepared AC. These experiments were achieved using 0.25 g of the AC with 25 mL of 100 mg/L DBT concentration for 120 minutes contact

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time. Outcomes demonstrated in Table (4-3) revealed that the DBT removal % enhanced with rising temperature. The best removal efficiency attained at 20°C. This observation may attribute to the endothermic nature of the DBT adsorption by the AC. Besides, with rising temperatures, the mobility of DBT molecules in the solution phase enhances due to declining the solution's viscosity [56]. Also, when the temperature rises, there is a chance for the pore to widen to some extent, hence overcoming the activation energy barrier [53]. Furthermore, the DBT molecules diffusion rate in the AC pores increases with temperature [12]. These findings were in line with those announced by Yaseen [57], Sadare and Fadhil [58] upon the ADS of DBT from model fuels employing corn cobs derived AC, pomegranate leaf, and PET derived AC as adsorbents, respectively. Nonetheless, when the temperature exceeded 30°C, a decline in the DBT removal% was noticed. This finding ascribes that raising the temperature over the ambient resulted in an increment in the molecular kinetic energy, which weakens the attractive forces between DBT molecules on the AC surface, leading to a diminish in the ADS efficiency [57].

The impact of the working period on the DBT elimination AC was examined in the range of 10–60 minutes, as depicted in Table (4-3). Batch experiments were accomplished using 25 mL of 100 mg/L DBT at 20°C with 0.25 g of the AC. It was noticed that the DBT removal % enhanced with prolonging the contact time. However, removal efficiency of 32.199% was accomplished at the first ten minutes of the adsorption. The highest removal % was obtained at a contact time of 60 minutes. The prolonged period had no impact on the removal efficiency of DBT because vacant pores ready for the adsorption are no longer exist. The AC originated from corn cobs exhibited the maximum removal of DBT at a longer contact time [57].

4-4 Adsorption isotherms

The AC adsorption nature was examined through testing the adsorption data to diverse models of isotherms, including the Langmuir, Freundlich, and Temkin, which are demonstrated in Eq (4-1),(4-2) and (4-3) respectively:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \dots\dots\dots (4 - 1)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \dots\dots\dots (4 - 2)$$

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \dots\dots\dots (4 - 3)$$

where C_e , q_e , q_m , and K_L represents the equilibrium concentration (mg/L), the capacity of adsorption (mg/g), Langmuir maximum adsorption capacity constant (mg/g), and the Langmuir constant (pronounces the adsorbate relative affinity). K_F and n belong to the Freundlich adsorption capacity and intensity, respectively. For Temkin isotherm, K_T , and b represent the equilibrium binding constant (L/g) and constant related to the adsorption heat (J/mol).

The Langmuir isotherm elucidates that the adsorption process happens on the homogeneous adsorbent surface, which owns specific active positions and energies, with the absence of adjacent interaction and steric hindrance among the adsorbate molecules [59].

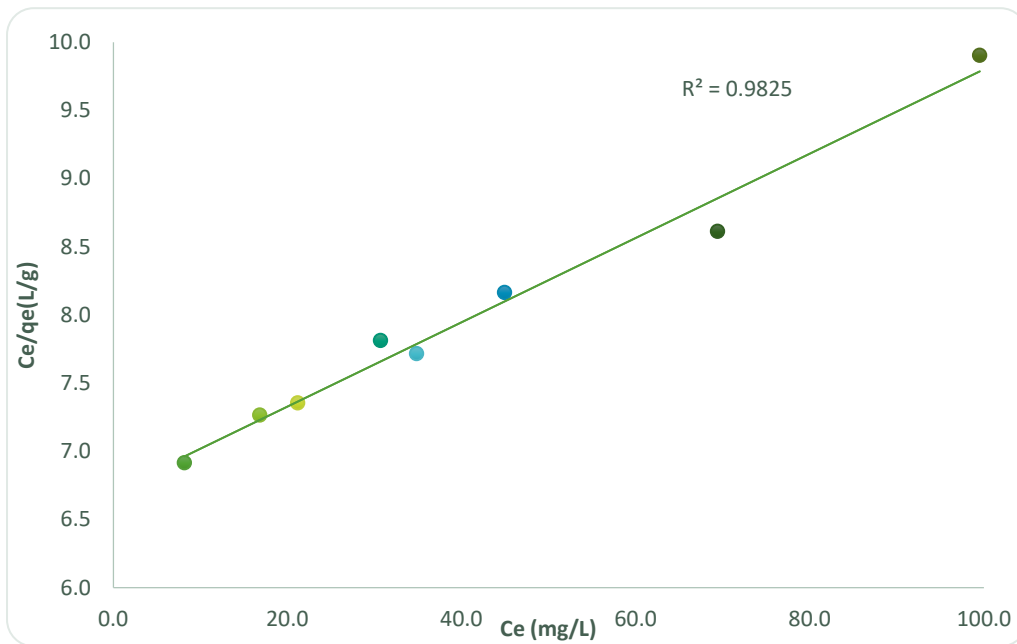
The Langmuir constants q_m and K_L could respectively be obtained from the slope and intercept of the linear plot of C_e (mg/L) versus C_e/q_e (g/L) (Figure

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4-1). The separation factor (R_L), which offers the Langmuir isotherm characteristic, can be calculated using the following formula [60]:

$$R_L = \frac{1}{1 + C_0 K_L} \dots\dots\dots (4 - 4)$$

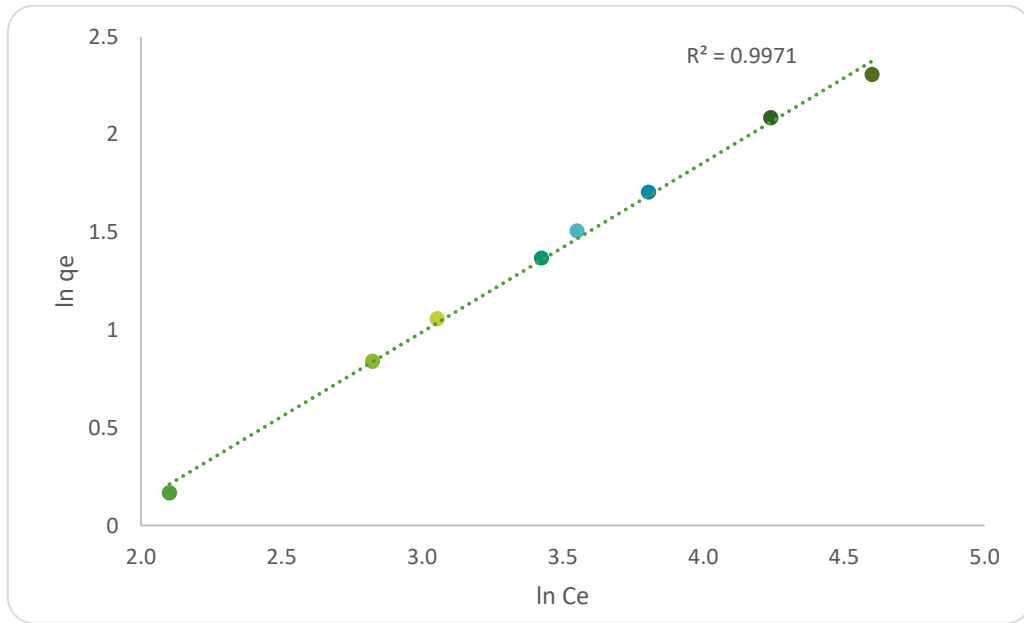
The DBT adsorption by the as-synthesised AC is favourable due to the separation factor obtained for DBT adsorption is $0 < R_L < 1$.



(Figure 4-1) Langmuir linear isotherm

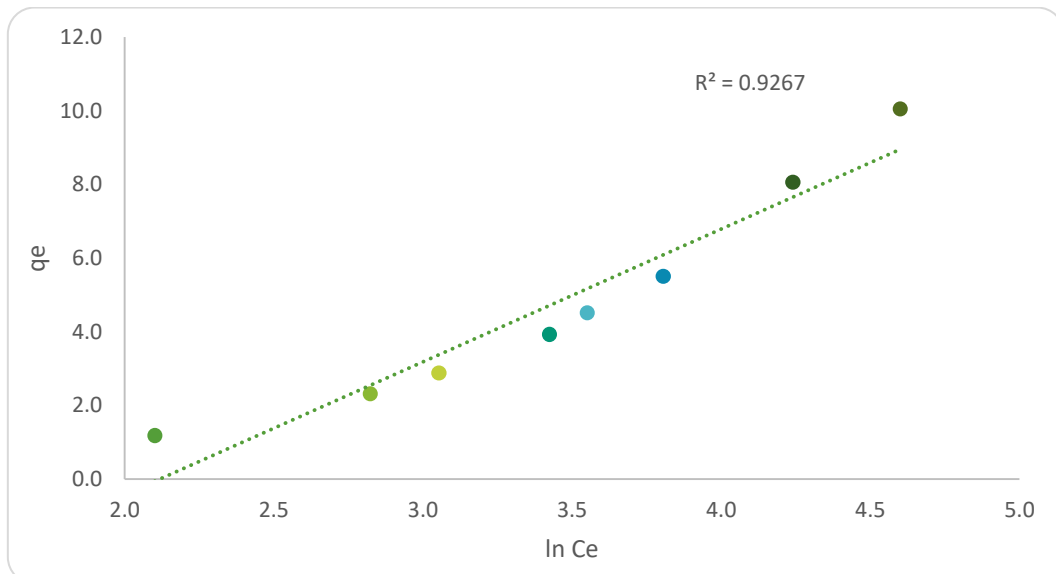
The Freundlich model of adsorption describes heterogeneity with a uniform distribution of heat of adsorption on the adsorption surface [59]. This isotherm's liner plot gives the Freundlich constants, n , and K_F , which can respectively be obtained from the slope and intercept of plotting $\ln q_e$ versus $\ln C_e$ (Figure 4-2). The adsorption is favorable if the value of n is above 1.0. In this work, the n value was 1.60, suggesting that DBT adsorption by the so-obtained AC is favorable.

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(Figure.4-2) Freundlich linear isotherm

The Temkin model (Figure.4-3) relies on the interaction between the adsorbent and adsorbate regardless of the extremely high and low concentrations. This model suggests that the heat of adsorption declines with covering the adsorbent surface of the adsorbate molecules[57].



(Figure.4-3) Temkin isotherm

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The Langmuir, Freundlich, and Temkin constants are displayed in Table (4-4), The DBT adsorption over the AC followed the following order:

$$\text{Freundlich model} > \text{Langmuir model} > \text{Temkin model}$$

This conclusion was drawn from the relatively higher R^2 value ($R^2 = 0.9971$) for Freundlich isotherm than that of Langmuir isotherm ($R^2 = 0.9825$). This model suggests the porous and heterogeneous nature of the AC. The higher R^2 values for the Freundlich model compared to other models suggest multilayer adsorption of DBT onto the as-synthesized AC. The q_m of the ADS of DBT from model gasoline using the AC was 32.34 mg/g. This value is higher than those established for the activated alumina (22.60 mg/g) [61], mesoporous carbon (5.13 mg/g) [62], and AC clothes (25.77 mg/g) [52].

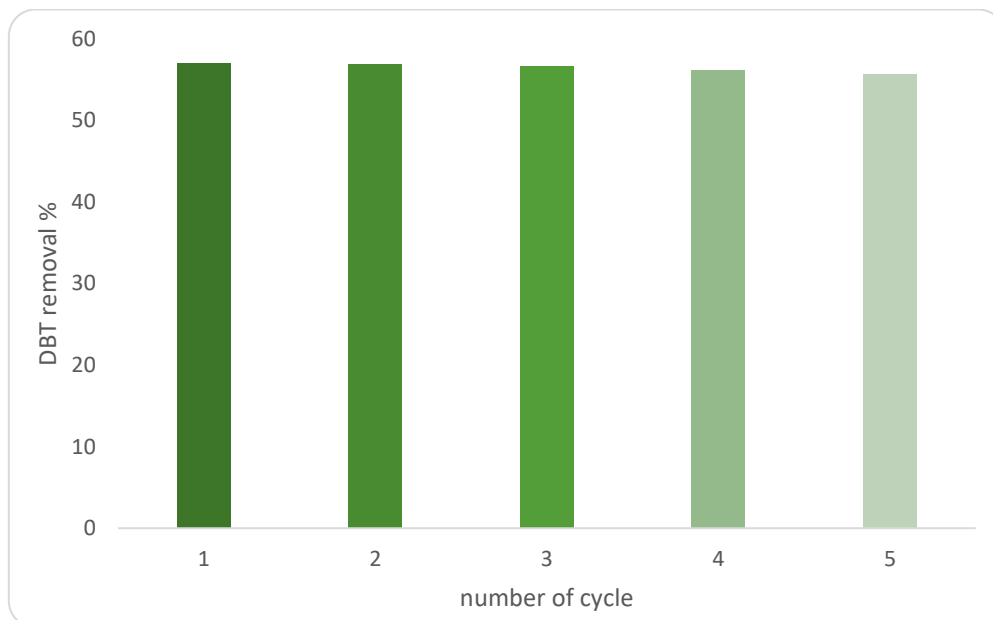
Table (4-4) Langmuir, Freundlich, and Temkin constants for DBT adsorption onto the AC.

Langmuir isotherm				Freundlich isotherm			Temkin isotherm		
q_m	K_L	R_L	R^2	n	K_F	R^2	B(mg/g)	A(L/g)	R^2
32.34	0.0046	0.684	0.982	1.606	0.865	0.997	7.629	3.604	0.926

Recycling performance

The AC employed in the ADS of DBT from model gasoline was collected, regenerated, and then implemented again for the same purpose. The consumed AC was treated with n-hexane in a Soxhlet apparatus and then dried at 100°C to be utilized later in the ADS of DBT from the synthetic model under the optimal conditions obtained previously. The consequences in (Figure.4-4) revealed that the DBT elimination by the regenerated AC decreased slightly with the increasing number of the reusability cycles.

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(Figure.4-4): Effect of the AC reusability on DBT removal %.

The first cycle of the removal amounted to 56.95% compared to 55.68 % for the 5th cycle, which means that the surface of the AC still possesses active sites ready for the elimination of DBT. Thus, the attained outcomes suggested that the AC created from foam is an efficient adsorbent to eliminate S-containing compounds from fuels.

Chapter Five

5 - Conclusions

Al- Mishraq sulfur ore contains a low percentage of heavy bitumen hydrocarbons, which leads to pollution of the resulting sulfur with this bituminous material due to its tendency to dissolve with this substance. For this reason, it was necessary to follow purification methods that differ from the traditional. purification methods used in the production of sulfur.

A surface area of Activated Carbon (AC) ($531.250 \text{ m}^2/\text{g}$), from Al-Mishraq Sulfur Solid Waste (Foam), has been successfully exploited, as a potential and priceless feedstock for AC and prepared through a thermal activation method. The as-created AC was influential in the ADS of DBT with an efficiency of 56.95% at relatively mild conditions of 0.25 g AC dose, a contact period of 60 minutes at 20°C . The ADS data fitted well to the Freundlich adsorption isotherm due to its higher R^2 value ($R^2 = 0.9971$) than other models, suggesting the heterogeneity and porosity of the as-prepared adsorbent. The present investigation offers a cheap and potential feedstock to create AC as an adsorbent for model gasoline fuel desulphurization.

Dedication and acknowledgment

I dedicate this work and give special thanks to my family for being there for me throughout the entire process and I would like to thank my supervisors, Dr. Marwa and Dr. Ahmed for their guidance throughout my research project. They consistently allowed this paper to be my own work, but steered me in the right direction whenever they thought I needed it.

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