ADSORPTION STUDY OF DESULFURIZATION OF DIESEL OIL USING ACTIVATED CHARCOAL

by

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Abstract

This research investigates the use of adsorptive desulfurization for diesel oil using carbon-based adsorbents, and it evaluates the effect of the adsorptive desulfurization on the ignition quality of diesel fuel. Two of the adsorbents are commercial powdered activated carbons (PAC1 and PAC2); whereas, the third one is a granular activated carbon (GAC). The desulfurization process is investigated at different conditions of three factors: amount of sorbent material (3 wt. % - 10 wt. %), temperature (room temperature, 30, and 50 ^{o}C) and contact time (0.5 - 2 hrs). Equilibrium and kinetics studies of the adsorption process using the three adsorbents are considered. In addition, results from the experimental data found are analyzed using a two-level full factorial design and are correlated using artificial neural networks. This study shows that PAC1 and PAC2 have better sulfur removal affinity compared to the GAC. The adsorptive desulfurization of diesel fuel improved the ignition quality of the fuel significantly. The adsorption isotherms are determined using two isotherm models which are: Langmuir, and Freundlich. Results show that the adsorption behavior for both PAC1and PAC2 is described by Freundlich model at all temperatures. In the factorial experimental designs, two outputs are investigated: sulfur removal percentage and diesel index. According to the 2^2 and 2^3 designs, the amount of sorbent material shows a positive effect on the two response variables; whereas, the temperature has a varying effect on the two outputs. The predicted outputs are calculated using a regression model generated and compared with the actual experimental data. The predicted values show an excellent agreement with the experimental data. Finally, a feed-forward neural network with one hidden layers of size 15 is used to correlate the set of experimental data. Results show that the sulfur removal capacities for PAC1 and PAC2 can be correlated perfectly using Artificial Neural Networks (ANN).

Search Terms: adsorptive desulfurization, ignition quality, statistical analysis, factorial design, sulfur removal, diesel index, and neural networks.

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Nomenclature

Activated Carbon	AC
Atomic Emission Detector	AED
1-alkyl 3-methylimid-azolium	AMIM
Bio-desulfurization	BDS
butyl 3-methylimidazolium	BMIM
Benzothiophene	BT
Citric Acid	CA
Dibenzothiophene	DBT
Diesel Oxidation Catalysts	DOC
Dimethyl Sulfoxide	DMSO
4, 6-dimethyldibenzothiophene	4,6-DMDBT
ethyl 3-methylimidazolium	EMIM
Environmental Protection Agency	EPA
Fluid catalytic cracking	FCC
Flame Photometric Detector	FPD
Granular Activated Charcoal	GAC
Hydrocarbon	HC
Hydrodenitrogenation	HDN
Hydrodesulfurization	HDS
Ionic liquids	ILs
Light Cycle Oil	LCO
4-methyldibenzothiophene	4-MDBT
3-methylimidazolium	MIM
Oxidative Desulfurization	ODS
Powdered Activated Charcoal 1	PAC1
Powdered Activated Charcoal 2	PAC2
Pressure Controller	PC
Pulse Flame Photometric Detector	PFPD
Particulate Matter	PM

Chapter 1: Problem Statement and Introduction

1.1 Problem Statement

This research investigates the use of adsorptive desulfurization of diesel fuel using three types of carbon-based adsorbents. High percentages of the crude oil, including the diesel oil and gasoline, are used widely in different transportation applications. Such fuels contain high contents of sulfur compounds or sulfur impurities, mainly in the form of organic sulfur compounds. Reducing and/or eliminating such compounds is essential. This is due to the fact that the quality of fuel is significantly affected by the present impurities, such as the sulfur and nitrogen compounds. Moreover, sulfur emissions are a critical environmental issue that needs to be controlled through specifying the allowable sulfur content limits in the different types of fuels. This is required due to the negative effects of sulfur emissions on air quality. Diesel oil is composed mainly of complex mixtures of hydrocarbon compounds that have different boiling points and molecular weights.

Recently, various environmental or climate change issues, such as global warming, gain major importance among researchers. Greenhouse gases that are emitted directly to the atmosphere because of combusting the different petroleum products are the major causes of global warming. Currently, direct-injection diesel oil engines are utilized extensively. This is due to their high thermal efficiency and low emission rates compared to other types of diesel engines. However, reducing the emissions produced from these engines is still of critical necessity due to their harmful impacts on the environment. Furthermore, one of the main reasons for reducing such emissions is the stringent emission regulations initiated and imposed by several countries in order to protect the environment [1]. Reducing the exhaust emissions can be achieved through either improving the process of oil combustion or improving the properties of fuel that are directly related to its quality. Improving the quality of any fuel can be achieved by enhancing the ignition quality associated with that fuel, such as cetane number (CN), aromatic content, distillation temperature and viscosity [2, 3].

Hydrogen consuming catalytic process or hydrodesulfurization (HDS) is the catalytic process that is commonly used for reducing and/or removing organic sulfur compounds contained in hydrocarbons. However, this process is associated with the use of extremely harsh high temperature (up to 400 ^{o}C) and pressure (up to 100 bars) conditions, and extensive catalysts. Moreover, one of the main inefficient aspects in this process is its low effectiveness in removing some sulfur compounds, including the thiophenes and multi-ring aromatic compounds. This is due to the fact that such compounds necessitate high hydrogen consumption along with the harsh temperature and pressure operating conditions. Thus, due to the high cost and different limitations that are associated with HDS process, alternative or complementary technologies are increasingly selected in the petroleum industry. These include adsorptive desulfurization, extractive desulfurization, biological sulfur removal and oxidative desulfurization. The main goal of such technologies is to find an effective alternative for the desulfurization of the low reactive sterically hindered alkyl DBTs. Adsorptive desulfurization processes are among the best economically attractive and environmentally friendly techniques. This is due to their simple operating conditions, availability of economical and re-generable sorbent materials [3].

Since this study involves studying different operating conditions, an appropriate modeling tool is required. Modeling any set of experimental data is helpful in studying different factors for any process. This helps in applying better operating conditions in order to maximize the efficiency of the process. Thus, modeling the adsorptive desulfurization experimental data helps in recognizing the most appropriate amount of sorbent material, temperature, and contact time for the attainment of the best sulfur removal capacity and ignition quality improvement. In addition, in most research areas, the majority of experiments are designed in a way that allows researchers to study the effects of two or more factors on a certain response variable simultaneously. This technique is favored over studying the effect of an individual factor or using one factor at a time analysis approach. In adsorptive desulfurization processes, optimizing the operating conditions is needed due to its important role for improving such processes. Thus, a need for modeling techniques for the generated experimental data, such as factorial experimental designs, finds increasing interest among researchers. The importance of these techniques comes from their role in observing and examining the effects of multi factors and the interactions between the factors or variables. This is a beneficial test as it helps in minimizing the calculated errors.

In addition, artificial neural network (ANN) is a tool used for correlating the experimental data. This is achieved by deriving a meaning or a model from complex sets of data. After training the network by supplying part of the data, it shows the ability to learn how to complete new tasks by the experience gained from the earlier training step.

1.2 General Background

The production of hydrocarbon fuels with low sulfur contents and organic aromatics gains rising importance among researchers. Hydrocarbon fuels containing high contents of sulfur compounds have gained high interest not only from scientific societies, but also from governmental organizations [1, 2]. Sulfur (S) is an element that is contained naturally in crude oil. It is considered as a major source of particulates and/or impurities in diesel oil [3]. Currently, sulfur compounds that are contained in diesel oil play direct and indirect roles on environmental concerns and health problems. Generally, sulfur is found in the atmosphere in different forms and is utilized in different industries extensively. However, sulfur compounds are emitted directly to the atmosphere. This is due to the fact that only a limited destruction of the sulfur bonds can be achieved. Various types of diesel fuels having different specifications are used in several applications. It is used mainly as transportation fuels for high-way vehicles and non-highway transportation applications [4]. High percentage of sulfur compounds in the hydrocarbon fuels, particularly the ones that are contained in transportation fuels, are transformed directly to SO_x as soon as combusted in the engines. Accordingly, numerous problems are initiated in the environment; for instance, acid rain and higher contents of sulfuric oxides that are responsible for lowering the efficiency of the catalytic converters [5, 6]. Thus, a number of countries have initiated and applied a set of strict environmental regulations and laws to reduce the sulfur contents in diesel oil to ultra-low levels (given as 10-15 ppm). The main goal of applying such strict regulations is to minimize the harmful exhaust emissions, improve air quality and limit air pollution.

As mentioned earlier, petroleum products or petroleum distillates, including gasoline, diesel fuel, and jet fuel, are defined as complex mixtures of organic molecules or compounds. Such complex mixtures are classified according to their boiling point ranges. Variations in the boiling point ranges are controlled by the type of sulfur compounds or impurities mainly contained in the petroleum product. Diesel fuel is characterized by its highest boiling point range. This is due to the existence of the heaviest sulfur compounds or impurities, such as dibenzothiophene (DBT) and its alkyl derivatives.

However, gasoline is characterized by its lowest boiling point range due to the existence of impurities with lower boiling points, including thiophene and its alkyl derivatives [7]. Both diesel and gasoline fuels are favored due to several reasons; for example, high energy associated with them, their availability, and simple storage and safety issues that are easy to handle.

The main emissions associated with combusting diesel fuels are SO_x, NO_x, CO_2 and CO. Generally, these emissions can be reduced through the reduction and/or the elimination of the amount of sulfur compounds contained in the diesel fuel. This can be achieved either by utilizing different desulfurization processes for the fuel products, which is commonly carried out using the catalytic hydrogen processing approaches, or by removing sulfur compounds contained in stack gases [8]. BT and DBT compounds contained in diesel feeds compose around fifty percent of the total sulfur compounds available in most diesel fuels. However, the C2-DBT compounds, including 4, 6-dimethyldibenzothiophene (4, 6-DMDBT), compose most of the sulfur compounds in low sulfur diesel fuels which is the diesel oil produced after the HDS process [9]. The preferred limit of sulfur content in diesel fuels is around 0.1 ppm by weight [10] provided that the main sulfur compounds existing in most hydro-desulfurized diesel include the alkyl DBTs with alkyl groups at 4- or/and 6-positions [11]. Moreover, converting normal diesel oil to clean or ultra-deep de-sulfurized diesel oil is a complicated process that is controlled by several factors that have considerable effects on the desulfurization process. These factors include the type of the catalysts used, the selected operating conditions, feedstock source, reactivities of the contained sulfur compounds, influence of nitrogen compounds and other impurities contained in the diesel oil [3].

HDS is the conventional process used for the removal of sulfur compounds contained in diesel oil. However, this process has a number of limitations that forced the petroleum refineries to search for other processes [12]. Adsorptive desulfurization process is one of the suggested alternative processes for the HDS. Various adsorbents, such as reduced metals, metal oxides, activated charcoal, alumina, metal sulfides, zeolites and silica, are utilized in this process. Adsorptive desulfurization is simply performed by placing an active adsorbent on a porous and non-reactive substrate that tolerates a high surface area for the adsorption of sulfur compounds. This process is mainly utilized for the removal of some impurities contained in fuels such as aromatics from aliphatic and refractory sulfur compounds [11, 13].

1.2.1 The Need for sulfur compounds removal.

The major motives for the production of diesel oil with low sulfur content in petroleum products include the environmental hazards and human health problems that result from the direct emissions produced from combusting diesel oil in the diesel oil engines. As stated earlier, some of the direct emissions include: particulate matter (PM), NO_x, SO_x, CO_2 and CO. Moreover, the strict environmental legislations and standards for the specifications of the different types of fuels that were initiated by several countries play an important role in forcing the refineries to produce clean diesel oil. Several studies have illustrated the relation between the amount of SO_x and/or PM emitted, and the amount of sulfur compounds contained in the fuel. The different emissions produced from diesel powered vehicles and the organic sulfur compounds are converted mainly into SO_3. Unfortunately, this compound has the ability to dissolve easily in water vapor which may lead to the formation of sulfuric acid vapor. Sulfuric acid formed is then converted into fine particles that have the ability to penetrate into the human's lungs and cause lung cancer [14]. Reducing the harmful effects of sulfur emissions can be achieved through decreasing the emission rates of sulfur dioxide and sulfate PM, and/or enhancing or enabling the use of different emission control methods, such as Diesel Oxidation Catalysts (DOC) and PM filters [3].

Another important factor affecting the emissions produced from diesel oil powered vehicles or engines is the effect of other properties of diesel oil, such as the ignition quality [3]. The ignition quality is defined as a property of the fuel that is determined by the molecular composition of that fuel. The ignition quality of any fuel is associated directly with the ignition delay time which is defined as the time interval between the start of the injection and the start of the combustion processes of the fuel [15, 16]. Several studies [e.g., 17, 18] show that the ignition quality given as the calculated cetane number has a direct impact on the gaseous and particulate emissions produced.

Different studies show that there is a relation between the amount of sulfur contained in diesel oil, and the amount and type of pollutants present in the emissions. This means that as the amount of sulfur contained in diesel oil increases, the amount of emissions increases. Thus, a number of countries, such as the United States of America (USA), Japan and European countries imposed common specifications or standards for most fuels in order to reduce their levels. The Environmental Protection Agency (EPA) of the USA controlled the sulfur levels for the highway diesel levels to be around 15 ppmw by 2010. Moreover, the European Committee for Standardization developed standards to control the maximum sulfur content to be around 10 ppmw in 2009. These standards lead refineries to face key challenges to reach the new specifications of the allowed sulfur contents in diesel fuel [5, 19].

1.2.2 Challenges for the production of diesel oil with low sulfur content.

Reducing the sulfur content in diesel fuel to less than 15 ppm using the conventional catalytic HDS processes is considered a real challenge. This is due to the fact that some sulfur species contained in diesel oil have low reactivity and complicated removal mechanisms. However, researchers and experts are currently enhancing these processes. New HDS catalysts, improved reactors and optimized operating conditions were tested for the removal of certain sulfur compounds that are characterized by low reactivity. However, several issues still need to be considered in the HDS process. This is essential due to the fact that HDS processes may lead to changes in the properties of the diesel oil [3].

Deep desulfurization process may result in changing the properties of the diesel oil, such as reducing the lubricity. This may occur due to the elimination of some compounds that are responsible for lubricity of the diesel fuel. In addition, HDS may result in reducing the density of the produced diesel oil which is directly related to a reduction in the energy content by around 1%. Moreover, producing diesel oil with ultra-low sulfur content (ULSD) (15 ppm) has higher costs compared to producing low-sulfur content diesel oil (500 ppm). However, a significant reduction in the cost of producing diesel oil with sulfur content that is less than 15 ppm can be achieved by integrating the HDS units with a non-hydrogenation process, such as oxidative desulfurization (ODS) or adsorptive desulfurization units [3].

1.3 Specific Goals

This study focuses on the use of carbon-based adsorbents for diesel oil adsorptive desulfurization process. It also investigates the effects of the adsorptive desulfurization process on the ignition quality of diesel fuel. The main objectives of the present study are to:

1- Explore the adsorption capacity of different commercial carbon-based adsorbents for removal of sulfur compounds from commercial diesel oil.
2- Study the impacts of different operating conditions (amount of sorbent material, temperature and contact time) on the efficiency of the desulfurization process of the diesel oil.
3- Evaluate some of the physical and chemical properties of the produced diesel oil and the adsorbents before and after the adsorption process.
4- Apply two-stage adsorption process to maximize the sulfur removal capacity.
5- Examine the equilibrium and kinetics of sulfur adsorption using the three sorbents at different temperatures.
6- Study the improvement of ignition quality of diesel oil after the adsorption process and compare it with the untreated diesel oil.
7- Generate statistical models that fit the experimental data through the use of a factorial design analysis approach.
8- Use ANN to correlate the experimental data generated.

1.4 Thesis Organization

This thesis is structured in eight chapters. Chapter one is a brief introduction about the research topic. The problem statement, methodology, and objectives of the present study are defined clearly in this chapter. Details of the different statistical analysis methods used for the experimental data are illustrated in separate chapters.

Chapter two includes an extensive literature review about the currently used methods for sulfur removal from diesel oil, including the hydro-desulfurization, extraction, biological methods, and adsorption.

Chapter three addresses the experimental procedure followed in the lab to perform the adsorptive desulfurization experiments. This chapter summarizes the instruments used for analyzing the diesel oil and the sorbents before and after the adsorption process.

Chapter four examines the equilibrium and kinetics studies of sulfur adsorption using the three sorbents. Two kinetic models: pseudo first-order and pseudo second-order are tested to follow the adsorption processes. Furthermore, the adsorption isotherm study of sulfur compounds are presented. Two isotherm equations, Langmuir and Freundlich, are used.

Chapter five discusses the ignition quality improvements through the adsorptive desulfurization. The calculated diesel index, the major ignition quality measure, is studied at different temperatures and amounts of the sorbent materials using the three adsorbents. Afterward, diesel oil samples showing the best sulfur removal percentages are used to compare all other ignition quality measures using the three sorbents.

Chapter six examines the adsorptive desulfurization experimental data through two-level full factorial experimental designs. The background and methodology followed in this research are presented and described in this chapter. Then, the results and discussions of the experimental designs are compared and presented.

Chapter seven correlates the set of experimental data using a feed-forward ANN approach. The literature and the methodology followed for using ANN are illustrated in details. The results and discussion are also presented and compared.

Finally, chapter eight summarizes the results and findings of the thesis and provides recommendations and suggestions for future extensions.

Chapter 2: Literature Review

2.1 Sulfur Cycle

There are four main steps of the sulfur cycle in the atmosphere. This cycle is summarized as follows: mineralization of organic sulfur to its inorganic form which is hydrogen sulfide (H_2S), oxidation of sulfide, elemental sulfur and related compounds to sulfate, reduction of sulfate into sulfide, and microbial immobilization of the sulfur compounds [20]. Naturally, sulfur exists in the atmosphere from emissions of volcanoes, sea salt and biogenic emissions; whereas, it is removed either by dry or gaseous deposition, or by wet or aqueous deposition [21]. Combusting fossil fuel, such as coal and petroleum, is considered as the main source of the anthropogenic sulfur [22]. The combustion process generates sulfur emissions in the form of sulfur dioxide (SO_2), responsible for damaging the plants by chlorosis, and sulfur trioxide (SO_3). However, the concentration of SO_2 in the atmosphere is very low as its concentration in urban areas does not exceed 0.5 ppm; thus, its effects on human health are not clear [20]. Moreover, SO_2 is of little concern due to the fact that once it exists in the atmosphere, it is oxidized in gaseous and aqueous phases to form sulfate and sulfite. Most of the sulfur compounds in the gaseous phase react with the hydroxyl radicals through the following reaction, where around 15% of the sulfur is oxidized:

$$SO_2 + 2OH^{\cdot} \rightarrow H_2SO_4$$

In the aqueous phase, the oxidation process takes place in the water droplets and follows the set of reactions below.

$$SO_2 + H_2O \leftrightarrow SO_2.H_2O$$

$$SO_2.H_2O \leftrightarrow H^+ + HSO_3^-$$

$$HSO_3^- + O_3 + H^+ \leftrightarrow H_2SO_4 + O_2$$

Generally, the total amount of sulfur that exists in the atmosphere stays constant due to the high reaction rates. This leads to a quick removal via wet and dry deposition [23-24].

2.2 Sulfur Compounds in Diesel Oil

Complex mixtures of various sulfur compounds of different reactivities are contained in diesel oil. Reducing the sulfur content in diesel oil requires deep understanding of the sulfur compounds contained in diesel oil, their reaction pathways and reactivities. Sulfur compounds present in diesel blending streams can be analyzed and separated using several analytical techniques, including high resolution gas chromatography and sulfur selective detectors, such as FPD, SCD, PFPD and AED [3, 25].

Challenges of removing sulfur compounds are controlled by a number of factors, including the crude source, Fluid Catalytic Cracking (FCC) performance, the quantity of the Light Cycle Oil (LCO), and the end Point of the straight run and LCO [26]. The most common types of sulfur compounds that are contained in diesel fuels include middle distillate, light cycle oil (LCO), benzothiophenes (BT) including alkyl substituents containing 1–7 carbon atoms, and dibenzothiophene (DBT) including alkyl substituents containing 1–5 carbon atoms [27, 28]. The highest amounts of sulfur and aromatics that are contained in the LCO result from the FCC process. Moreover, LCO contains the highest amounts of refractory sulfur compounds mainly 4-methyldibenzothiophene (4-MDBT) and (4, 6-DMDBT) [29]. The relative reactivities of different sulfur compounds vary significantly. Comparing the relative reactivities of BTs and DBTs in HDS proves that the BTs and their alkyl derivatives can be de-sulfurized faster than the DBTs and their alkyl derivatives. Moreover, the alkyl DBTs that contain alky groups close to the sulfur atom, such as 4-MDBT, 4, 6-DMDBT, and 4, 6-MEDBT, have lower reactivity over the conventional alumina-supported Co/Mo and Ni/Mo catalysts compared to the reactivity of BTs. The relative reaction rates along with the boiling points of some sulfur compounds are presented in Figure 2.1 which shows that the substituted dibenzothiophenes having higher boiling points have lower reactivities [26, 30].

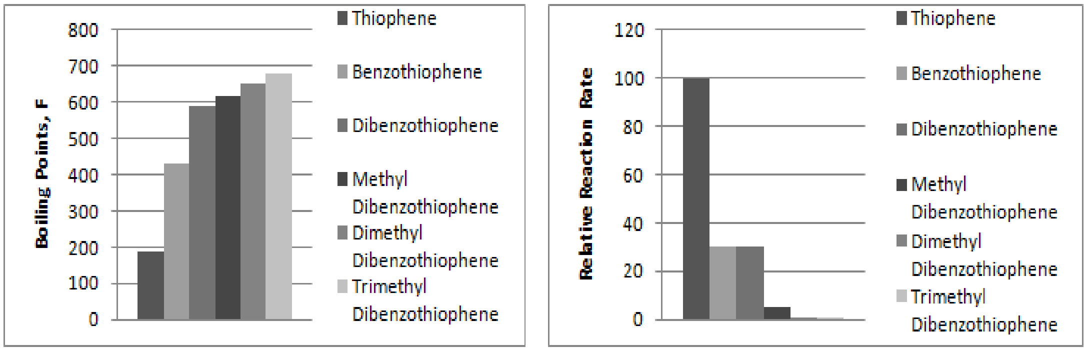


Figure 2.1: Relative Reaction Rates and Boiling Points of Some Sulfur Compounds [26] [30]

2.3 Ignition Quality

Controlling the ignition quality and the combustion process of diesel fuels is essential for having an efficient operation of a diesel engine. Ignition quality is a measure of the ease of the self-ignition of diesel fuel when the fuel is injected in hot compressed air into the engine cylinder. The ignition quality of diesel fuel is linked to the ignition delay time which is the time between the start of injection and the start of the combustion process. Cetane number is a diesel fuel combustion quality measure during the compression ignition. It is considered as one of the most significant measures of diesel fuel quality compared to the other measurements used for testing the diesel fuel quality. In general, a CN range of 40-55 indicates that the diesel engine is operating well. However, fuels having higher cetane number offer longer time for the fuel combustion process, and this is directly related to the amounts and types of emissions produced. High ignition quality of a certain fuel means short ignition delay, and vice versa, where a fuel of poor ignition quality produces long ignition delay time [15, 16]. A long ignition delay (i.e., low cetane number) in a diesel engine can affect the power output, exhaust emissions and the combustion efficiency [31]. Moreover, the ignition delay may result in rapid pressure rise that can cause undesirable audible knock and engine vibrations. Furthermore, the ignition delay is directly affected by the design of the engines and the operational conditions selected, as well as the properties of the fuel used [32, 33]. Exhaust emissions of diesel fuel combustion are directly affected by the aromatic content. This is due to the influence of aromatics on some physical and chemical properties, such as cetane number, viscosity, boiling range, chemical structure and density of diesel fuel. Changes on these properties have a direct impact on the combustion process. Moreover, the aromatic content in diesel fuel has direct effects on various aspects of the engine's operation other than the combustion chemistry, such as the combustion process timing and the air-fuel mixing process [34].

2.4 Existing Methods

Several processes have been suggested for the removal of sulfur compounds from light oil. The most widely used process is the HDS that utilizes high temperature and pressure in the presence of hydrogen [35]. The products of catalytic refining processes contain sulfur compounds, such as mercaptans, aliphatic and cyclic thioethers, and thiophenes and their derivatives are hydrodesulfirzed using catalytic systems [36]. Reducing the sulfur content in the petroleum distillate fuels can be achieved by two main approaches: hydrogen consuming methods (HDS) and non-hydrogen consuming methods. Nowadays, researchers are studying alternative processes for sulfur removal from diesel oil. As mentioned above, HDS is limited in removing some thiophenic compounds (TCs) such as benzothiophenes (BTs), and dibenzothiophenes (DBTs), especially DBTs having alkyl substituent on 4 or/and 6 positions due to the steric hindrance [37]. Moreover, increasing the efficiency of HDS is related to the use of severe temperature and pressure conditions, more expensive catalysts, larger reactors and longer contact-time. Thus, researchers are trying to explore and develop alternative or complementary processes for sulfur removal, especially refractory sulfur compounds under mild operating conditions [38]. A number of processes have been developed for the removal of the aforementioned compounds, such as adsorption, oxidation, extraction and bio-desulfurization.

2.4.1 Hydrogen consuming processes (Hydrodesulfurization).

Industrially, HDS is a catalytic chemical process that is used widely for the removal of impurities present in refined petroleum products, such as gasoline, jet fuel, diesel fuel and fuel oils. These contaminants or impurities include nitrogen, metals, oxygen, and sulfur compounds [39]. Keeping such contaminants may damage the refinery processing units which will have direct effects on the equipment and the quality of the products. HDS utilizes different catalysts, such as Mo/Al_2O_3, $Ni–Mo/Al_2O_3$ or $Ni–W/Al_2O_3$ that need to be replaced every two to three years [35]. In spite of the fact that most of the low-sulfur hydrocarbon fuels (HC) are produced through HDS, several limitations associated with the HDS still exist. The production of ultra-low-sulfur hydrocarbon fuel requires certain catalysts to be used during the reaction pathways for hydrotreating [40]. HDS is limited in treating some compounds, such as the thiophenic compounds (TC) including benzothiophenes (BTs) [37], and dibenzothiophenes (DBTs) especially the DBTs that are having alkyl substituent on 4 or/and 6 positions. This is due to the fact that the alkyl groups especially in the positions that are subjected to steric hindrance reduce the reactivity of the TC in HDS [41]. However, HDS is highly efficient for the removal of thiols, sulfides and thiophenes. Different studies show that increasing the removal rates of such sulfur compounds through the HDS process requires a threefold increase of the catalyst volume/reactor size which is directly related to the cost [5] [42]. Thus, different emerging techniques, other than the HDS, have been used in order to produce low-sulfur products.

In HDS, the removal of such molecules can be achieved through different suggested methods, such as replacing the used catalysts by other highly active catalysts, using higher temperatures and pressures, adjusting the end point of the feed, utilizing higher purity hydrogen, increasing the partial pressure of the hydrogen, increasing the volume of the reactor by adding one or more reactors, removing H_2S from the recycled gas, and finally improving the feed distribution to the trickle-bed reactor [43].

Industrially, hydrodesulfurization reaction takes place in a fixed-bed reactor at a temperature varying between 300 - 400 ^{o}C and pressure varying between 20 to 100 atms, in the presence of a catalyst. The liquid feed fuel is pumped to reach the desired pressure. This stream is mixed with a hydrogen-rich recycle gas stream. The produced stream consisting of liquid and gas mixture is then preheated using a heat exchanger. Then, this stream is sent to a fired heater to achieve complete vaporization where it reaches the desired temperature. Once this stream reaches the desired temperature, it is fed to the reactor where the hydrodesulfurization reaction takes place through a fixed bed of the catalyst. The products are then partially cooled through the use of a water-cooled heat exchanger. Then, the cooled stream flows through a pressure controller (PC), and its pressure is reduced to 3 to 5 atms approximately.

The resulting liquid-gas mixture enters a gas separator vessel at a temperature of 35 °C and a pressure of 3 to 5 atms. The hydrogen-rich gas stream leaving the gas separator is a recycled gas that is sent to an amine contactor for the H_2S removal reaction. The H_2S

free hydrogen-rich stream is recycled to the reactor for reuse. The liquid stream leaving the gas separator is sent to a re-boiled stripper distillation tower, where the bottom stream from the stripper is the desulfurized liquid product. The top steam from the stripper includes hydrogen, methane, ethane, hydrogen sulfide, propane and heavier components. This stream is sent to the gas processing plant for hydrogen sulfide removal in the amine gas treating unit, where it will be converted to elemental sulfur or sulfuric acid, along with a series of distillation towers for the recovery of propane, butane and heavier components [44].

The disadvantages of HDS process include the fact that these catalytic processes are operated at high temperatures (varying between 300 - 400 ^{o}C) and pressure (varying between 20-100 atms H_2). This raises safety concerns, low efficiency for the removal of the refractory sulfur compounds [45], production of low quality products due to the saturation of aromatics, and high consumption of hydrogen and catalysts [46].

Maintaining the HDS as the most practical option for oil desulfurization is related to the achievements of certain advancements in the performance of the catalyst. As mentioned earlier, combinations of Co/Mo and Ni/Mo catalysts are the conventional catalysts used. However, such catalysts are not efficient in desulfurizing diesel oil to reach ultra-low sulfur content under normal temperature and pressure, and they require harsh operating conditions, such as high temperature, low space velocity and high H_2 partial pressure. This leads to a faster catalyst deactivation. Producing enhanced hydrotreating catalysts is possible if a complete understanding of the catalysts' properties in term of the nature and the structure of the active sites, along with the effects of the different supports is attained [47-48].

2.4.1.1 Improvements in HDS catalysts.

Several HDS catalysts have been improved and introduced to the market by different companies and researchers [3]. For instance, an unsupported Ni-W-Mo catalyst with higher thiophene HDS activities has been prepared by a reflux method [49]. The new catalyst was prepared by using reflux method in presence of an organic additive. In a typical preparation, $(NH_4)6(Mo_7O_{24})\cdot4H_2O$, $(NH_4)6H_2W_{12}O_{40}$, $Ni(NO_3)_2\cdot6H_2O$ and tetrabutyl ammonium bromide were dissolved in water and then concentrated NH_4OH was added. The resulting mixture was refluxed and then cooled down to room temperature.

The characterization of the new unsupported catalyst showed higher surface area, pore volume and denser active phase. The performance of the prepared catalyst showed better HDS and Hydrodenitrogenation (HDN) performance than the traditional supported catalyst.

Cosmo oil developed a new highly active Co/Mo catalyst for the production of ULSD [50]. The new catalyst was prepared via impregnation method using a solution containing Cobalt (Co), Molybdenum (Mo), Phosphorous (P) and nitric acid (HNO_3) on a HY-Al_2O_3. The catalyst's activity was measured using a straight-run light gas oil feedstock under normal hydrotreating conditions. Compared to the performance of the conventional Co-Mo-P/Al_2O_3 catalyst, the new catalyst showed three folds higher HDS activity that enables less than 10 ppm sulfur content in diesel oil.

A series of Ni/W catalysts supported on –Al_2O_3–MB–TiO_2 denoted as AMBT composites was prepared [51]. For the preparation of the AMBT supports, the MB zeolite was prepared via in-situ crystallization process from minerals. The Ni/W catalyst was prepared via both co-impregnation and incipient-wetness impregnation techniques using a solution containing ammonium metatungstate hydrate [$(NH_4)6W_{12}O_{39}\cdot H2O$] and nickel nitratehexahydrate [Ni $(NO_3)_2\cdot 6H_2O$]. Results show that adding both MB zeolite and TiO_2 alterthe interactions between the tungsten species and the support and enhances the sulfidation degree of the active metals. The HDS efficiency of diesel oil reached 99.7%, and the specifications of the produced diesel oil met the Euro V fuel specifications of ultra clean diesel.

Valencia and his colleague [52] considered the influence of the chemical composition of Silica SBA-15 as well as the ZrO_2-containing SBA-15 support on both Ni/Mo and Co/Mo catalysts. The produced catalysts were used for the HDS of both DBT and 4,6-DMDBT compounds. It was found that the behavior of the Mo catalysts has been affected considerably because of the removal of the sterically hindered molecules, mainly the 4, 6-DMDBT.

Mendoza-Nieto and his colleagues [53] prepared two series of tri-metallic Ni-Mo-W catalysts that are supported on pure silica and Al_2O_3 with and without the presence of citric acid (CA) in the impregnation solutions. The prepared catalysts were tested for the

HDS of two compounds: DBT and 4, 6-DMDBT. The alumina support was prepared via calcinations of Boehmite Catapal B; whereas, the silica support was prepared according to the procedure given in [54]. Results showed that the addition of CA does not modify the dispersion of both Mo and W species considerably compared to the catalyst prepared without the addition of CA. It was concluded that the impact of adding CA alters the behavior of the HDS catalysts according to the material used for the preparation of the support and its interaction with the metal species deposited.

Cecili and his colleagues [55] prepared Nickel phosphide (Ni_2P) catalysts that are supported on a mesoporous Silica via a novel method based on a technique called a temperature programmed reduction. The catalyst's preparation involved using Nickel (II) dihydrogenphosphite Ni $(HPO_3H)_2$ as a precursor salt. Results proved that the measured activity of HDS of DBT for the prepared catalyst was improved and showed good turn over frequencies at 400 C.

Trejo and his colleagues [56] prepared three catalyst supports using different ratios of magnesia-alumina. The prepared supports were impregnated with both Cobalt (Co) and Molybdenum (Mo) salts via incipient wetness method, where 1,2 cyclohexanediamine-tetraacetic acid was used as a chelating agent. The activity of the catalyst prepared was tested on the HDS of thiophene based on utilizing the chelating agent throughout the preparation of the catalyst and then a comparison between the activity of the uncalcined and calcined catalysts was conducted. Results showed that catalysts that were supported on the calcined $MgO–Al_2O_3$ had higher activity.

2.4.1.2 Improvements on the HDS technologies.

Desulfurizing sulfur compounds with the least reactivities is another important issue that requires researchers' attention when studying new improvements in the design and development of HDS process. One important enhancement in designing the HDS process is the utilization of two-stage process. This technology is considered as an efficient alternative that is able to significantly reduce both sulfur levels and aromatics present in diesel fuel. Conventional catalysts, such as $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$, are used in the first stage; whereas, types of sulfur resistant noble metal/zeolite catalysts are used in the second stage [57].

Another improvement in the utilization of HDS is the improvement of the SK – HDS process. The working principle of this process is to add an adsorptive desulfurization step prior to the HDS process in order to remove the nitrogen based polar compounds. This will help to reach the ultra-low sulfur content easier through the catalytic hydro-treating stage [58].

2.4.2 Oxidative desulfurization.

Oxidative desulfurization (ODS) has been considered as a new and efficient alternative for deep desulfurization of light oil [59]. This technique can reduce the sulfur content significantly as it involves the oxidation of the sulfur - containing compounds over certain oxidants in order to convert them to their related sulfoxides and sulfones. These compounds are highly polar and can be removed later by adsorption, extraction, decomposition or distillation techniques [60-61]. Different catalysts have been used in aqueous state along with their salt solutions. Other possible catalysts are the supported transition metals, such as Mo/Al_2O_3. Several oxidizing agents are currently utilized on the oxidative desulfurization processes, such as hydrogen peroxide (H_2O_2), t-butyl hypochlorite, ozone and t-butyl hydro-peroxide.

Organo-sulfur compounds have different reactivities to the oxidation process which can be determined according to the structure and the environment of the sulfur atom itself. According to the electrophilic addition mechanism for the oxidation of sulfur, it was found that 4, 6-DBT molecule has higher reactivity to the oxidation process than the BT molecule [3].

Different studies have investigated the utilization of ODS processes for desulfurizing both commercial and synthetic diesel oils [3]. Studies proved the ability of the oxidation processes to reduce the sulfur compounds contained in light oil to the preferred value 0.1 ppm_w and to recover them as organic sulfur compounds that have different industrial uses [62]. In [63], hydrogen peroxide-formic acid has been used as an oxidizing reagent for the sulfur compounds present in diesel oil with a total sulfur content of 500 ppm. Results showed that after oxidizing the sulfur contained in the oil with the aforementioned reagent, a complete conversion of the DBT into DBT-sulfones that can be removed easily by either extraction or adsorption can be attained. Another study [64] examined the effect of applying the ultrasound during the oxidation process. Results showed a good enhancement on the efficiency of oxidizing sulfur compounds into their sulfones.

Successful implementation of ODS can be achieved in refinery applications by integrating the ODS unit with the diesel hydro-treating unit [65]. When oxidative desulfurization is used as a second step after the HDS unit, it can take the produced low sulfur diesel (~500 ppm) down to ultra-low sulfur diesel (ULSD) (<10ppm). Nevertheless, even when applying this technology, the cost reduction is still limited due to the fact that the deep desulfurization through HDS process requires elevated temperature and pressure [65].

Moreover, a novel ODS process was utilized [66] by combining the ODS process in the presence of molecular oxygen and a catalytic component such as iron (III) salts with an adsorptive desulfurization using activated carbon (AC). Results showed that the use of Iron (III) salts is effective in converting the benzothiophenic compounds contained in the fuel to sulfones or sulfoxides. The catalytic oxidation of the sulfur compounds contained in the liquid hydrocarbon fuels to form sulfones and sulfoxides increased the adsorbtion of sulfur compounds significantly due to the fact that the ACs showed higher adsorption affinity for both sulfones and sulfoxides compared to thiophenic compounds [66].

It was shown that the advantages of the ODS process include the low temperature and pressure requirements for the reaction, as well as the absence of hydrogen. Moreover, the ability of converting the refractory-S-containing compounds by oxidation is another important feature of the ODS [40] [67-68].

2.4.3 Biological sulfur removal.

Another process for the sulfur removal from fossil fuel is through bio-desulfurization (BDS). BDS has been used significantly where organo-sulfur compounds are bio-transformed to the corresponding sulfones or sulfoxides by bio-catalytic activity. The basis for this process is the removal of organo-sulfur compounds present in the fuels while keeping the carbon structure unchanged.

Microorganisms need sulfur to fulfill both growth and biological activity as it forms around 1% of the dry weight of the bacterial cell. Some microorganisms have the ability to supply their needed sulfur from various sources due to the fact that sulfur exists in the structure of some enzymes cofactors, amino acids and proteins. Some microorganisms have the ability to consume sulfur in the thiophenic compounds and thus reduce the sulfur content in the fuel. This method is considered as an advantageous process as it can be conducted under mild conditions (room temperature and pressure) and requires biocatalysts or enzymes which make this process highly selective [69]. However, it is also characterized by a low bio-catalytic activity and low stability of the bio-catalysts afterward [40] [70]. It was illustrated that both aerobic and anaerobic microorganisms are effective in the desulfurization process while protecting the aliphatic and aromatic contents of the fuel.

The bio-desulfurization process has been conducted using R. sphaericus, Rhodococcuserythropolis, Arthrobactersp and R. rhodochrous under mesophilic conditions, i.e., under a temperature range of 25 to 40 ^oC, and using Paenibacillus sp. under thermophilic conditions, i.e., under a temperature higher than 50 ^oC [71-72]. However, the main challenge in the use of bio-desulfurization as an alternative industrial method for producing ultra-low sulfur content is the isolation or design of a microbial strain that is characterized by a higher efficiency.

Different studies have been considered on the use of BDS for the removal of sulfur compounds especially the least reactive ones in the HDS, such as the sterically hindered alkyl-DBTs [73] [74]. In the reference [75], it was found that Rhodococcus sp. has the ability to use DBT as a source of sulfur. Results proved that Rhodococcus sp. has the ability to transform DBT into sulfite and 2-hydroxybiphenyl that builds up in the medium.

Although some researchers are focusing on implementing the BDS processes on a large scale, the BDS rates are still low when compared to the HDS. This is due to the limitations that are faced in such processes. Main limitations include the need to enhance the thermal stability of desulfurization, the limited transport of the sulfur compounds from the oil to the membrane of the bacterial cell and the limited ability to recover the biocatalyst [76]. Most BDS processes are used currently as complementary steps for deep desulfurization, where the BDS is integrated with the existing HDS units. BDS can be used either before or after the HDS unit. Some researchers have suggested that the BDS should follow the HDS in order to achieve the removal of the remaining sulfur compounds that have the lowest reactivity with the HDS. Other researchers believe that employing the BDS before HDS is more efficient as a major part of the hydro-treating resistant compounds can be removed. This will result in less hydrogen consumption in the HDS unit [74].

2.4.4 Extractive desulfurization.

Extractive desulfurization has gained growing attention as an alternative for the production of ultra-low sulfur diesel oil. Nowadays, researchers consider the extractive desulfurization as a promising technology due to the significant cost reduction as no hydrogen is used, the mild conditions that are required (ambient temperature and pressure) and the wide range of fuels that can deal with including all kinds of middle distillates. In this process, the removal of sulfur compounds is achieved using selective solvents.

2.4.4.1 Conventional extractive desulfurization.

Conventional solvent extraction technique has been utilized for the removal of sulfur compounds from petroleum feeds. This process is based on the solvent's polarity. For this process to be efficient, solvents should show higher solubility of the organo-sulfur compounds contained in the fuel when compared with their solubilities in the hydrocarbons. Thus, increasing the efficiency of this process is related to the optimization of the operating conditions to maximize the sulfur extraction and the careful selection of the required extractant. Several solvents have been examined for the removal of sulfur compounds, such as acetone, carbon disulfide, ethanol, dimethyl sulfoxide (DMSO), n-butyl alcohol, methanol, lactones (i.e., gamma butyrolactone), N-containing solvents and water [37] [77-78]. Solvent polarity is not the only parameter that governs the process of selecting the appropriate solvent; other factors need to be considered carefully as they may affect the separation and recovery of the solvent. These factors include melting point, boiling point and surface tension. However, this process is characterized by a poor sulfur removal capacity that resulted from the slight difference of the polarity between the contained sulfur compounds and the aromatic hydrocarbons.

Different studies have investigated the use of extractive desulfurization for the removal of sulfur compounds. In [79], light oil was mixed with different organic solvents like DMSO, acetonitrile and tetramethylenesulfone at ambient conditions in order to examine the sulfur compounds and aromatics extractability. This study showed that the extraction equilibrium between the oil and the solvents was attained in about five minutes; whereas, the phase separation was attained in ten minutes or less. The main conclusion that was drawn from this study is that the most suitable solvent for light oils or distillates is the acetonitrile. Another study [80] utilized a two-stage extraction process with dimethylformamide as a solvent. Results showed that the sulfur content in diesel oil was reduced from 2.0 wt. % to around 0.33 wt. %.

In spite of the fact that ultra-low sulfur content cannot be attained using the aforementioned solvents, the polarity and the solubility of the sulfur compounds in the solvent can be improved by oxidizing the sulfur compounds before employing the extraction step.

2.4.4.2 Extraction using ionic liquids.

Ionic liquids (ILs) are defined as salt in the liquid state, salt whose melting points are below some arbitrary temperature like 100 °C. Currently, ILs are applied widely in the liquid-liquid extraction processes due to their flexibility in modulating their hydrophobic or hydrophilic nature by modifying the cations and anions [81]. ILs have been used in chemical industries, pharmaceuticals, algae processing, gas separation, nuclear fuel reprocessing, solar thermal energy, waste recycling and fuel desulfurization.

Some types of ILs, such as tetrafluoroborate, Chloroaluminate and hexafluorophosphateare, are efficient in the extraction of DBT derivatives contained in diesel oil [82]. The first study that was published related to the deep desulfurization of industrial diesel oil by extractive desulfurization using ionic liquids was conducted by Bösmann [82]. In this study, chloroaluminate ionic liquids were used, and results showed that by using a five-stage-extraction process operated at a temperature of 60 ◦C, around 80% of the available sulfur compounds can be removed successfully. However, hydrolytic instability was created, which make its use difficult. Afterward, a number of studies considered the extractive desulfurization of sulfur compounds from diesel oil using stable ILs. The main challenge that researchers faced is to find an efficient way to regenerate the ILs. This is due to the fact that regenerating the ILs using distillation or stripping was inefficient. This is mainly because of the significantly low vapor pressure of the sulfur compounds extracted and contained in the IL. A suggested solution was to apply the re-extraction procedures; however, significant amounts of solvents were required for the re-extraction. In [83], Holbery experienced the use of different ionic liquids with different cation classes, such as pyridinium and pyrrolidinium, and a set of anion classes for liquid-liquid extraction of DBT and dodecane. Results indicated that the partition ratio of DBT to the IL showed a clear variation with cation class when compared to the variation with anion class. It was found that the highest extraction potential is attained using a polyaromaticquinolinium-based ionic liquids. Another study [12] indicated that there is a direct proportionality between the absorption capacity of ILs and the number of alkyl groups. Results showed that using different ILs based on 3-methylimidazolium (MIM) such as 1-alkyl 3-methylimid-azolium (AMIM), butyl 3-methylimidazolium (BMIM) and ethyl 3-methylimidazolium (EMIM), increased the absorption capacity of thiophene to higher than 2-methylthiophene. Advances in liquid-liquid extraction technologies involve combining oxidative desulfurization and ILs [84]. This approach is capable of removing sulfur species from DBT model diesel oil by around 96.1%, which is much better than that of either using the conventional solvent extraction approach or the oxidative desulfurization.

2.4.5 Photochemical desulfurization.

In this process, organo-sulfur compounds are removed from fuel oil by liquid extraction as a first step, where a polar solvent such as water or acetonitrile is used. This is followed by a process called photochemical oxidation that is carried out in the solvent phase. This leads to the accumulation of sulfoxides and sulfones in the polar phase [12].

2.4.6 Adsorptive desulfurization.

Selective adsorption of sulfur compounds contained in diesel oil is an economically acceptable alternative for the attainment of diesel oil with low sulfur content [85]. Adsorptive desulfurization processes are considered among the most economically attractive techniques due to their simple operating conditions, availability of inexpensive and the re-generable adsorbents such as reduced metals, metal oxides, alumina, metal sulfides, zeolites, silica and activated carbon [11] [13]. This process occurs as the sulfur molecules attach to the adsorbent and stay there separate from the fuel [41]. The main part of any adsorption process is a porous solid medium as it offers high surface area or high micropore volume that is translated into high adsorption capacity. There are three different mechanisms for adsorption separation which are steric, equilibrium and kinetic mechanisms. Adsorption separation is called steric mechanism if the dimensions of the pores of the porous solid medium allow the small molecules to enter while prohibiting the large molecules. However, it is called equilibrium mechanism if the solid medium has different abilities to accommodate different species according the strength of the adsorbing species. Moreover, kinetic separation mechanism is based on the rate of diffusion of different species into the pores [86]. Adsorption process can be classified to two categories: physical adsorption (physisorption) or chemical adsorption (chemisorptions) according to the nature of the adsorbent-sorbate interaction.

The most important challenge in adsorptive desulfurization is in producing easily remunerable adsorbent that is characterized by high adsorption capacity and high selectivity for the removal of refractory aromatic sulfur compounds that are not removed through the HDS process. Most adsorbents are modified through different treatment techniques, such as metal impregnation and oxidation, in order to improve their affinities for the TC removal from liquid fuels. For example, activated carbon, alumina, silica and zeolites are impregnated with different transition metals, including copper, nickel, zinc, iron and lead in order to produce adsorbent with higher TC removal capacities for both model and commercial fuels [87-88]. The TC adsorption is controlled by different factors, such as the chemical interactions between the metals impregnated with the adsorbents and the thiophenic molecules, as well as the adsorbent pore geometry. Moreover, according to the fact that the diesel fuel contains sulfur compounds, nitrogen compounds, as well as a large number of aromatic compounds that have aromatic skeleton structure similar to the coexisting sulfur compounds, there is a great challenge in developing an effective adsorptive desulfurization process that is able to selectively adsorb the sulfur compounds.

2.4.6.1 Merits of adsorptive desulfurization.

Currently, adsorptive desulfurization appears as a promising alternative for HDS for several reasons. Adsorptive desulfurization is considered as an effective process for the separation processes that involve low sorbate concentrations; thus, it is a good candidate for the removal of the contained refractory sulfur compounds in the feed streams. Adsorptive desulfurization process requires mild conditions (i.e., low temperature and pressure) when compared with several other sulfur removal techniques, especially the HDS- which decrease the operating cost of the process. Most of the adsorbents used can be regenerated easily either by thermal processes, or by washing with a solvent. Most sorbent properties such as the adsorption capacity, surface area and selectively are directly affected by their structure and composition. These properties may be enhanced by modifying their preparation methods and conditions.

2.4.6.2 Adsorption at solid surfaces.

Sulfur molecules are adsorbed onto the solid surface through physical adsorption (physisorption) or chemical adsorption (chemisorptions). Generally, physical adsorption takes place due to Van der Waals forces and electrostatic forces in molecules with a permanent dipole moment. In physical adsorption, the forces that attract a molecule to the surface do not change the adsorbate molecule and are usually weak. However, in the chemical adsorption, chemical bonds are formed between the adsorbate molecule and the surface. This is a result of one or more free valences on the surface of an adsorbent material resulted from the broken covalent bonds between atoms at the surface. This causes an imbalance of forces at the surface as well as a net surface energy at the free valences. Chemical adsorption involves molecular interactions with these free valences, which leads to a monolayer coverage on the surface of the adsorbent. Chemical adsorption that involves dissociation of the adsorbed molecules is referred to as dissociative adsorption. However, molecules that are adsorbed chemically via pi-electrons and lone pair electrons do not necessarily go through dissociation, yet they participate in free valences via non-dissociative adsorption [89].

2.4.6.3 Adsorbents and their properties.

The porous solid medium for a certain adsorption process is usually considered as a critical variable. Performing a successful adsorption process depends on the performance of the solid medium in equilibria and kinetics. A solid medium that is characterized by acceptable adsorption capacity and slow kinetics is not efficient as it requires long time for the adsorbate molecules to reach the particle interior. In addition, a solid medium which is characterized by fast kinetics and low capacity is not efficient either as a large amount of adsorbent is required. Therefore, the solid medium should have high adsorption capacity and good kinetics which can be attained if the solid medium has reasonably high surface area or micropore volume and relatively large pore network for the transport of the molecules to the interior [86]. Adsorbents can be classified according to their physical, chemical and dynamic properties. The physical properties include surface area, particle size, pore volume as well as some mechanical properties. Chemical properties are related to the composition and structure of the adsorbents, acid and base properties, and electrostatic properties. The dynamic properties include the selectivity, capacity and re-generability of the adsorbents that need to be considered in selecting the adsorbent in order to achieve the required goals.

2.4.6.4 Materials used for adsorptive desulfurization.

Adsorptive desulfurization is based on removing the organo-sulfur compounds from the liquid hydrocarbon fuels while keeping the other compounds present in the fuel unchanged. Several materials have been developed and tested to improve the adsorptive desulfurization process. Generally, the performance of the sorbent material used is estimated by its dynamic properties, such as selectivity for sulfur compounds and the ease of re-generability [90].

2.4.6.4.1 Adsorption on Carbon Materials and Activated Carbon.

Activated carbons (AC) are characterized by their low cost, both thermal and chemical stability under anoxic conditions, high and tunable surface area that is widely affected by the precursors of carbonaceous materials and the preparation methods, modification receptivity, and high affinity to adsorption of both aromatic and refractory sulfur compounds. AC has been used and studied widely for the removal of TC from different fuels [91]. Moreover, the slit shape geometry of the pores of the activated carbon is suitable for the aromatic compounds adsorption in comparison with the cylindrical zeolite pores that are suitable for non-planer molecules adsorption [92]. Mostly, activated carbons were utilized for the adsorption of compounds that have weaker polarity from gas-phase or polar fluid-phase, such as the adsorption of organics in wastewater. Consequently, the major challenge of using adsorptive desulfurization for liquid hydrocarbon fuels is to selectively separate the sulfur compounds with low polarity from a non-polar fluid phase [93]. In general, AC is mainly a micro-porous solid; however, besides micro-pores, it may contain meso-and macropores. The gas- adsorbing carbons typically have more micropores; whereas, the liquid-adsorbing carbons have significant mesopores that are important because of the larger size of liquid molecules [94-95].

Several studies have explored the adsorption of different sulfur compounds, including BT, DBT and 4,6-DMDBT, from both model and commercial fuels using various types of activated carbon. Song and his colleagues have performed a set of experiments [96-98] on adsorptive desulfurization for various types of fuels using different adsorbents, such as transition metals that are supported on different porous materials, activated carbon, zeolites and metal oxides. Such studies helped researchers to propose a new process that consists of three main stages which are the selective adsorption for sulfur removal, the recovery of the concentrated sulfur compounds and finally hydro-desulfurization of the concentrated sulfur compounds. Another study [99] investigated the effects of certain modification approaches, such as the use of steam and concentrated H_2SO_4, on the adsorption capacity. The adsorption experiments of DBT removal on the modified ACs were conducted using a fixed-bed flow reactor under ambient temperature and pressure. A model diesel fuel used contained DBT in heptane with a total sulfur content of 220 mg/dm^3. Five different samples of commercial activated carbons have been utilized donated as AC, AC_{W900} (AC sample treated by steam at 900 C for 25 min), AC_{S250} (AC sample treated by concentrated H_2SO_4 (96%) at 250 C for 4 h), AC_{WS} (a combination treatment by steam and H_2SO_4) and AC_{WSN} (AC_{WS} was heated at a rate of 10 C/min under flowing nitrogen from room temperature to 900 C and was kept at 900 C for 12 h). Results showed that AC_{W900} and AC_{S250} have an enhanced adsorption performance when compared with the unmodified AC.

In [1], granular activated carbon (GAC) that was produced from dates' stones through chemical activation using $ZnCl_2$ as an activator was used as a sorbent for sulfur compounds removal. The particle size chosen for the GAC preparation was 1.71 mm. Moreover, model diesel oil that is composed of n-$C_{10}H_{34}$ and dibenzothiophene (DBT) as sulfur containing compound was prepared. Results showed that approximately 86% of the DBT was adsorbed during the first three hours. Sulfur adsorption increased gradually to reach a value of around 92.6% in 48 hours and no more sulfur was removed after that.

Mochida and his colleagues on their work in the area of adsorptive desulfurization found that activated carbons are capable of removing both nitrogen compounds and refractory sulfur compounds simultaneously. These studies showed that at a temperature of 30 ˚C, the adsorption capacity for sulfur compounds was around 0.098 gram sulfur; whereas, it was around 0.039 gram nitrogen per 1 gram of activated carbon. The same group of researchers proposed a two-step adsorption process for achieving ultra-low sulfur diesel (ULSD). In the first stage, both nitrogen and refractory sulfur compounds contained in the feed stream were removed via adsorptive desulfurization using activated carbon fiber; then, the treated stream was hydro-desulfurized under mild conditions. [100-101].

In [102], Qin studied the performance of Polystyrene-based activated carbon spheres (PACS) in the adsorption of sulfur-containing dibenzothiophene (DBT). The activated carbon was produced from polystyrene ion exchange resin spheres by carbonization and steam activation and has a surface area of 1672 m^2/g and total pore volume of 1.63 cm^3/g. The fuel oil used was prepared by dissolving DBT in n-heptane with initial concentration of DBT solution varying from 0.882 g/L to 0.0882 g/L. Results showed a maximum DBT adsorption capacity of 109.36 mg/g of the PACS.

In [103], Selvavathi examined the adsorptive desulfurization process for the removal of the refractory sulfur compounds. Diesel oil used contained mainly dibenzothiophene (DBT), 4 methylbenzothiophene (4MDBT) and 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) with a total sulfur compounds of 290 ppm. In this study, two commercial activated carbons A and B, modified forms of the aforementioned activated carbon, nickel loaded on modified activated carbons, alumina, silica and Y-zeolite samples were utilized for the adsorption process. Results showed that the maximum value of sulfur removal was around 90.7 %.

Moreover, in [104], different types of commercial activated carbon from different sources (Pitch, Apricot, Coconut and wood) with surface areas that vary between 713 to 1403 m^2 /g were used. The particle size chosen for the activated carbon used varied between 400-800 µm. The adsorption process was carried out using both real diesel oil with a sulfur content of 398 ppmw (Singapore Refinery Co. Ltd.) and model diesel oil with a sulfur content of 400 ppmw (prepared by adding sulfur compounds, such as 4,6-dimethyldibenzothiophene, and various mono-aromatic, di-aromatic and tri-aromatic compounds to hexadecane) diesel oil in batch and fixed-bed adsorption systems. This study proved that various factors play an important role for an effective adsorption process. First the pore size should be at least larger than the critical diameter of the adsorbate. Second, it should also be sufficiently large in order to reduce diffusional resistance during adsorption. The sulfur removal percent reaches a maximum value of around 96%. This study also concluded that the adsorption selectivity increases as follows: naphthalene< dibenzothiophene< 4,6-dimethyl dibenzothiopheneanthracene < phenanthrene.

In addition, Zhang and Liu [105] reported that the use of oxygen plasma to enhance the ACs greatly increased the carbon surface oxygen-containing groups. This enhanced the adsorption capacities of DBT significantly. Moreover, this technology helped in minimizing the mass loss of the ACs as it keeps it within a narrow range of ±2%, unlike the conventional thermal oxidation treatment that resulted in 31.7–91.4% mass loss. AC particles with a surface area of 1187 m^2/g were modified by oxygen plasma for 30, 60 and 120 min. Results showed that the working adsorption capacities of AC_{30}, AC_{60} and AC_{120} increased by 35.1%, 44.7% and 49.1% respectively when compared to the original AC.

In [106], Mykola studied the use of polymer-derived carbons with incorporated heteroatom of oxygen, sulfur and phosphorus as adsorbents for sulfur compounds from diesel oil. Model fuel contained the same molar concentrations of dibenzothiophene, 4,6 DMDBT, naphthalene and 1-methylnaphthalene in mixture of decane and hexadecane. Results showed that incorporating the phosphorous to the carbon matrix has a positive effect on the adsorption process according to the fact that phosphorus species have a strong acidity. This enhanced the attraction of slightly basic dibenzothiophenes.

In [107], Kumar performed a study in which response surface methodology was employed for sulfur removal from model oil (dibenzothiophene; DBT dissolved in iso-octane) using commercial activated carbon (CAC) as a sorbent material. Experiments were performed with four input parameters which are the initial concentration (C_0: 100–900mg/L), adsorbent dosage (m: 2–22 g/L), time of adsorption (t: 15–735min) and temperature (T: 10–508^oC). Results showed that the highest removal of sulfur by CAC was obtained with m=20 g/L, t=6hr and T=308 ^oC.

In [108], Al-Zubaidy studied the adsorptive desulfurization process using commercial activated carbon and carbonized date palm kernel powder at room temperature. Diesel oil used had a total sulfur content of 410 ppmw. Results showed that the use of used activated carbon reduced the sulfur content by more than 54%; whereas, the carbonized date palm kernel powder showed lower sulfur removal efficiency.

In another study [109], Pengpanich investigated the adsorptive desulfurization process for the removal of DBT from n-octane using sewage sludge-derived activated carbon under ambient conditions. The effect of different operating conditions, such as the type of activating agent – $ZnCl_2$, HNO_3 and KOH-, activating agent: char weight ratio, carbonization temperature and time- on the adsorption capacity and physicochemical properties were studied. Results showed that varying all parameters has a direct effect on both surface chemistry and physicochemical properties. Varying the type of the activating agent has a clear effect on the textural properties, surface chemistry and the iodine number of the produced activated carbon. Moreover, char weight ratio, the activating agent, did not show any effect on both physicochemical properties and surface chemistry of the produced activated carbon with the exception of the activation of KOH, char weight ratio of 6. Furthermore, it was found that the adsorption capacity of DBT increased as the oxygen containing-groups increased. AC activated using KOH showed the highest adsorption capacity as it removes about 70.6 % of the DBT contained in the diesel oil which is higher than that attained by the commercial activated carbon by 1.28 fold.

Another research group studied the adsorption isotherms of low sulfur diesel oil (72 ppmw) using four different types of commercial activated carbons having a surface area of more than 1000 m^2/g. These activated carbons were produced from bituminous coal and lignite by a Dutch company. Results showed that after the adsorption process, the sulfur content in the diesel oil was around 15 ppmw. This experiment was carried out in a batch system at 30 ^{o}C and atmospheric pressure over 18 hr [110].

Sano [111] utilized the activated carbon for the desulfurization of the straight run gas oil (SRGO) as a pre-treatment step for the HDS in order to achieve ultra-deep desulfurization under normal operating conditions. Results showed a high adsorption saturation capacity of around 0.098 g of sulfur/g of activated carbon.

2.4.6.4.2 Other Adsorbents.

Different adsorbents are used in the adsorptive desulfurization processes. A study [112] showed that Cu^+ and Ag^+ zeolite Y are efficient in adsorbing sulfur compounds contained in industrial diesel fuel. Results indicated that the sulfur compounds contained in diesel oil were reduced from 430 ppmw to 0.2 ppmw. Another study conducted by Yang [113] utilized nickel (II)-exchanged zeolites as an adsorbent for the desulfurization of diesel oil containing initially around 297 ppmw sulfur content. This experiment was conducted at ambient temperature and pressure in a fixed-bed adsorber. The best adsorbent used was (alumina)/Ni (II)-Y which is a 25 wt% activated alumni followed by nickel (II)-exchanged zeolite-Y, which produced diesel oil with 0.22 ppmw sulfur content. Another study [13] proved that sodium-Y type zeolite is efficient in removing thiophenic sulfur compounds from model oils. Moreover, metal sulfides are also used for the adsorptive desulfurization of refractory sulfur compounds from different fuels. These adsorbents are useful under ambient temperature and pressure [114].

Chapter 3: Experimental Work

3.1 Introduction

In the present study, three different commercial carbon-based adsorbents are used to test their efficiencies in removing the sulfur compounds contained in commercial hydro-desulfurized diesel oil. Sulfur compounds contained in diesel oil are those that were not removed through the HDS process. The produced diesel oil samples after the adsorptive desulfurization process are then used to evaluate the improvements in the ignition quality of diesel oil.

3.2 Materials

3.2.1 Diesel oil.

The diesel fuel used in this study was supplied from a petrol station located in Sharjah, United Arab Emirates (UAE). The diesel oil is hydro-desulfurized, and the total sulfur content present initially is 398 ppm. The properties and trace metal percentages of the used diesel oil are listed on Tables 3.1-3.2.

3.2.2 Carbon materials.

Three commercial activated charcoals were used as adsorbents in this study. The first adsorbent (PAC1) is a powdered activated charcoal that was supplied from Scott Science and Healthcare Ltd. The second adsorbent (PAC2) is also a powdered activated charcoal that was supplied from NORIT and purchased from Sigma Aldrich (product number C3445). PAC2 particles are of mesh sizes that range between 100 and 400 mesh (37 to 149 micron). The third adsorbent used is a granular activated charcoal (GAC) and was supplied from a local chemical supply in the UAE.

Table 3.1: Physical Properties of Diesel Oil

Property	ASTM Number	Diesel oil
Specific gravity @15/15°C	D98	0.819
Water content, vol. %	D96	Nil
Water and sediment,vol. %	D1796	Nil
Conradson Carbon residue, wt. %	D189–97	0.100
Ash content, wt. %	D482	0.099
Kinematic viscosity @ 40 °C, cSt	D445	9.030
Flash point, CCPM, °C	D 93	81.20
Aniline point, °C	D 611	75.00
Diesel index	D611	69.10
Cetane index	[115]	59.70
Calorific value, J/g	D 240	46,000
Sulfur content, ppm	D7220-06	398.3

Table 3.2: Percentage Trace Elements in Diesel Oil

Symbol	Diesel Oil
Magnesium (Mg)	32.19
Aluminum (Al)	13.04
Silicon (Si)	33.31
Phosphorous (P)	1.456
Chlorine (Cl)	5.709
Potassium (K)	0.618
Calcium (Ca)	7.091
Vanadium (V)	0.105
Chromium (Cr)	0.293
Manganese (Mn)	2.304
Iron (Fe)	2.629
Nickel (Ni)	0.105
Copper (Cu)	0.492
Zinc (Zn)	0.241
Molybdenum (Mo)	0.105
Barium (Ba)	0.314

3.3 Instruments for Analysis

- **Energy Dispersive X-ray Fluorescence Spectrophotometer (ED-XRF):** used to determine the sulfur content and the amount of heavy metals present in diesel oil.
- **Scanning Electron Microscopy Instrument (SEM: Tescan VEGA3 SEM, Czech Republic):** used to analyze the morphology and the structural heterogeneity of the surface of the different sorbent materials and to determine the surface metals of the different sorbent materials.
- **SEM/EDAX (Oxford instruments INCA X-act, UK) and Inductively Coupled Plasma (ICP) Analysis**: SEM/EDAX technique was used to investigate the level of surface chemical heterogeneity and surface contamination. The metal content in the three adsorbent was done using Varian Liberty AX sequential inductively-coupled plasma–optical emission spectroscopy (ICP-OES) analysis.
- **Nitrogen Adsorption analysis using Autosorb iQ from Quantachrome:** used to determine the Brunauer, Emmett and Teller (BET) surface areas for the different adsorbents.

3.4 Experimental Procedure

3.4.1 Desulfurization process.

The desulfurization process using the three adsorbents was investigated at different levels of the amount of sorbent material used (3 wt. % - 10 wt. %), operating temperatures (room temperature, 30 ^{o}C, and 50 ^{o}C) and contact times (0.5 hr - 2 hrs) according to the following procedure:

1- Before starting the experiments, all three adsorbents (PAC1, PAC2 and GAC) were dried at a temperature of 110 ^{o}C for 2 hours.
2- 20 grams of the commercial diesel oil were mixed with the adsorbents and shaken using a flask shaker oscillating at 300 oscillations/min.
3- The resulting mixtures were then filtered to separate the solid adsorbents from the filtrate.
4- The sulfur and metal contents were then analyzed in the diesel fuel samples using Energy Dispersive X-ray Fluorescence Spectrophotometer.

To study the ignition quality, the physical properties of the diesel fuel were calculated in order to conduct a comparison between the ignition quality before and after the desulfurization process. This was conducted by finding the aniline points for diesel oil samples that showed the best sulfur removal efficiencies (10 wt. % PAC1, PAC2 and GAC at room temperature). This was conducted by mixing 5 ml of Aniline with 5 ml of each diesel oil sample. Two layers were formed and the mixture was heated in a water bath at a controlled heat rate. The temperature at which only one phase was attained was recorded as the aniline point for that sample. Moreover, 10 wt. % of the three adsorbents were mixed by 20 grams diesel oil at room temperature for different time intervals that ranged from 0.5-3 hrs. The equilibrium time for the maximum sulfur removal was found to be 1 hr.

3.4.2 Determination of sulfur removal percentage.

The sulfur removal percentage was calculated as the ratio of the sulfur concentration that was adsorbed by the sorbents to the sulfur concentration present initially in diesel oil according to the following equation:

$$Sulfur\ Removal\ percentage = \frac{S_{initial} - S_{final}}{S_{initial}} * 100 \tag{3.1}$$

Where, $S_{initial}$ and S_{final} refer to the sulfur content in the feed diesel fuel and the sulfur content in the diesel fuel at equilibrium, respectively.

3.4.3 Determination of diesel indices for diesel oil samples.

Diesel indices were calculated for all desulfurized diesel oil samples. Generally, calculating the diesel index for a certain sample requires determining both the density and the aniline point. These properties are then used to calculate the diesel index using the following formula:

$$Diesel\ Index = \frac{Aniline\ Point\ (F)\ *\ API\ gravity}{100} \qquad (3.2)$$

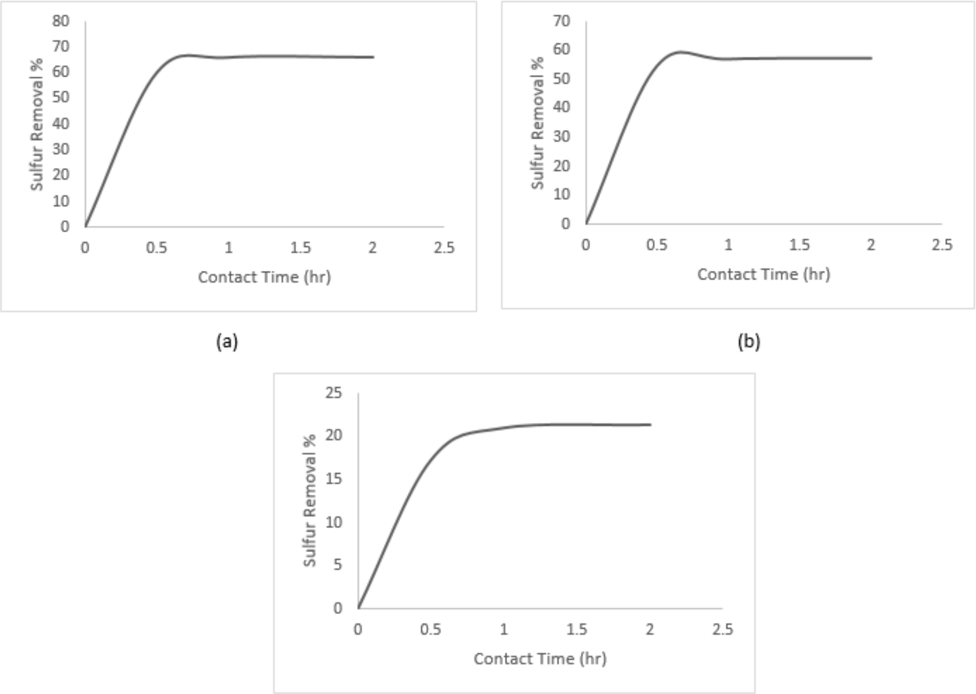
Chapter 4: Results and Discussion - Adsorption Equilibrium and Kinetics of Sulfur Compounds on the Sorbent Materials

4.1 Introduction

The main goals of the present work are: to study the sulfur removal efficiencies of three carbon-based adsorbents for the adsorptive desulfurization process of commercial diesel oil and investigate the improvement of the ignition quality of diesel oil after the adsorption process. The sulfur removal capacity for the three sorbent materials are compared, and following this step, the diesel oil samples showing the best sulfur removal percentages are used to study the improvement in the ignition quality. In this chapter, the equilibrium and kinetics of sulfur adsorption on the different sorbents are examined. Mainly, two kinetic model equations (pseudo first-order and pseudo second-order) are tested to determine the adsorption kinetics. Moreover, the adsorption isotherm of sulfur on PAC1 and PAC2 are determined and correlated using two isotherm equations (Langmuir, and Freundlich).

4.2 Desulfurization of Diesel Oil

The results for the sulfur removal percentages and the calculated diesel indices after the adsorption process using the three adsorbents at different conditions are given in Table A.1 in Appendix A. The equilibrium sulfur removal percentages using a 10 wt. % of the three adsorbents were determined, where the optimum contact time required to reach equilibrium was found to be 1 hr. (Figure 4.1). When 10 wt. % of PAC1, PAC2 and GAC was mixed with diesel oil at room temperature, the sulfur content in diesel oil was reduced by 66.2%, 57.9% and 20.91%, respectively. As shown in Table 4.1, some of the physical properties of diesel oil after the adsorption process were evaluated and compared with those for the untreated diesel oil samples. Results show low values of carbon residue and ash content as expected. For the un-desulfurized diesel oil sample, the calculated diesel indices, and accordingly the cetane numbers showed good ignition quality that can be improved further by the adsorption process. Moreover, results show an improvement in the properties of diesel oil caused by removing heavy metals and some aromatic compounds from diesel oil samples.



(a)

(b)

(c)

Figure 4.1: Sulfur Removal with Contact Time Using 10 wt. % (a) PAC1, (b) PAC2, and (c) GAC

Table 4.1: Physical Properties of Untreated and De-sulfurized Diesel Oil

Property	ASTM Number	Diesel Oil	DS Diesel Oil (PAC1)	DS diesel oil (PAC2)	DS Diesel Oil (GAC)
Specific gravity @15/15°C	D 98	0.819	0.810	0.812	0.817
Water content, vol. %	D 96	Nil	Nil	Nil	Nil
Water and sediment, vol. %	D1796	Nil	Nil	Nil	Nil
Conradson Carbon residue, wt. %	D189–97	0.100	0.017	0.120	0.035
Ash content, wt. %	D 482	0.099	0.088	0.009	0.062
Kinematic viscosity @ 40 °C, cSt	D 445	9.030	8.760	8.920	8.920
Flash point, CCPM, °C	D 93	81.20	81.00	81.00	81.00
Aniline point, °C	D 611	75.00	79.00	76.00	77.00
Diesel index	D 611	69.10	75.20	72.10	71.30
Cetane index	[115]	59.70	64.10	61.90	61.30
Calorific value, J/g	D 240	46,000	~46,000	~46,000	~46,000
Sulfur content, ppm	D 7220-06	398.3	135.0	168.0	315.0

Trace element percentages in diesel oil samples were determined using Energy Dispersive X-ray Fluorescence Spectrophotometer (ED-XRF). The ED-XRF results, given as percentages, provide a qualitative indication about the behavior of the trace elements in the untreated and desulfurized diesel oil samples (Table 4.2). Results show that the amount of chlorine present in diesel oil samples dropped significantly using PAC1, PAC2, and GAC, which means a corresponding reduction in corrosion rates. Results in Table 4.2 also show reduction in the amounts of aluminum, vanadium, iron, and zinc metals in the diesel oil samples treated using PAC1, and a decrease in the amounts of aluminum, and iron metals in diesel oil samples treated using PAC2. In addition, diesel oil sample treated using GAC show a decrease in magnesium, aluminum, and iron.

Table 4.2: Percentage Trace Elements in Untreated and Desulfurized Diesel Oil

Symbol	Diesel Oil	Treated Oil (PAC1)	Treated Oil (PAC2)	Treated Oil (GAC)
Magnesium (Mg)	32.19	35.62	35.11	29.96
Aluminum (Al)	13.04	12.95	12.63	11.42
Silicon (Si)	33.31	33.86	34.60	37.18
Phosphorous (P)	1.456	1.302	1.230	1.372
Chlorine (Cl)	5.709	4.422	4.720	4.714
Potassium (K)	0.618	0.383	0.906	0.786
Calcium (Ca)	7.091	6.840	7.013	6.526
Vanadium (V)	0.105	0.044	0.123	0.105
Chromium (Cr)	0.293	1.094	0.257	0.293
Manganese (Mn)	2.304	2.079	1.633	2.189
Iron (Fe)	2.629	0.339	0.324	0.388
Nickel (Ni)	0.105	0.109	0.112	0.105
Copper (Cu)	0.492	0.427	0.671	0.419
Zinc (Zn)	0.241	0.088	0.224	0.230
Molybdenum (Mo)	0.105	0.109	0.112	0.105
Barium (Ba)	0.314	0.328	0.336	0.314

4.3 Adsorption Kinetics Models

Results show that most of the adsorption capacity of sulfur compounds using the three adsorbents is attained during the first 60 minutes. The adsorption capacity of the sorbent materials increases slowly after 60 minutes. The rate constants of the adsorption processes were found using the pseudo first-order equation or model. This model is given by:

$$ln(q_e - q_t) = \ln(q_e) - k_1 t \tag{4.1}$$

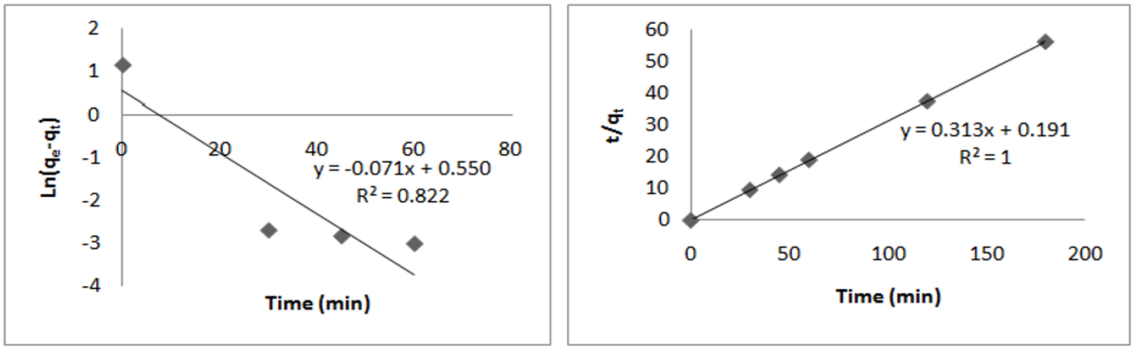
where $q_e$and q_t are the amounts of sulfur adsorbed (mg/g) at equilibrium and at time t (min) respectively, and k_1 is the rate constant for adsorption (min^{-1}). The values of k_1 were calculated from the plots of $ln(q_e - q_t)$ versus t for each sorbent material (see

Figures 4.2 (a), 4.3 (a), and 4.4 (a)). As shown in Table 4.3, results show that the values of q_e that were found experimentally do not agree with the calculated values for all adsorbents. Thus, this proves that the adsorption kinetics of sulfur compounds using the three adsorbents do not follow the first order kinetics model.

Alternatively, a pseudo second-order model equation is used. The pseudo second-order model equation is given by:

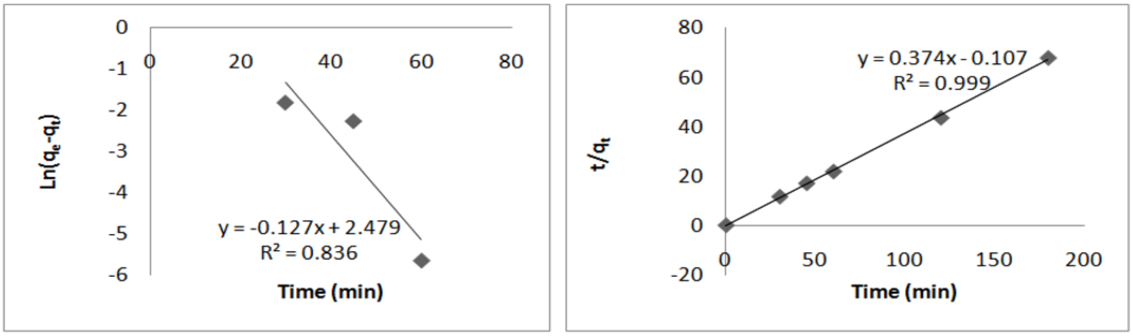
$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{t}{q_e} \tag{4.2}$$

where, k_2 is the equilibrium rate constant of the pseudo second order adsorption in (g/mg.min). The q_e values calculated should match the equilibrium capacity values obtained experimentally for this model to be valid. Similarly, values for q_e and k_2 can be determined from the slope and intercept of the plot of $\frac{t}{q_t}$ versus t. The linear plots (see Figures 4.2 (b), 4.3 (b), and 4.4 (b)) show good agreement between experimental and calculated q_e values for all adsorbents. The correlation coefficients for the second-order kinetic model were also calculated showing the applicability of this kinetic model equation and the second-order nature of the adsorption process. The sum of error squares (SE %) were also calculated for the three adsorbents (Table 4.3). The small values for the calculated SE % proved the applicability of the pseudo second-order model.



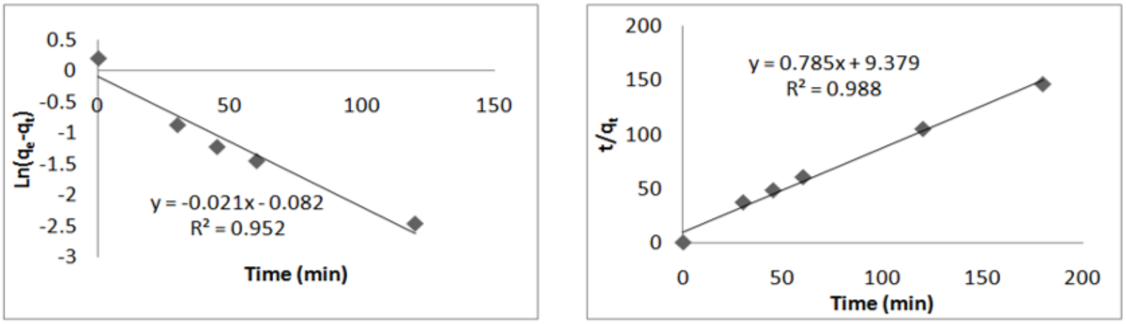
(a) (b)

Figure 4.2: Pseudo First Order (a) and Second Order (b) Kinetics for Adsorption of Sulfur Using 10 wt. % PAC1



(a) **(b)**

Figure 4.3: Pseudo First Order (a) and Second Order (b) Kinetics for Adsorption of Sulfur Using 10 wt. % PAC2



(a) **(b)**

Figure 4.4: Pseudo First Order (a) and Second Order (b) Kinetics for Adsorption of Sulfur Using 10 wt. % GAC

Table 4.3: Comparison of the Pseudo First- and Second-Order Adsorption Rate Constants using 10 wt. % of the Different Adsorbents.

PAC1								
C_0 (mg/L)	$q_{e,exp}$ (mg/g)	First-order kinetics model			Second order kinetics model			
		k_1(min^{-1})	$q_{e,cal.}$ (mg/g)	R	k_2 [g (mg min^{-1})]	$q_{e,cal.}$ (mg/g)	R	SE %
398.3	3.184	0.071	1.733	0.822	0.513	3.195	1.000	0.427
PAC2								
C_0 (mg/L)	$q_{e,exp}$ (mg/g)	First-order kinetics model			Second order kinetics model			
		k_1 (min^{-1})	$q_{e,cal.}$ (mg/g)	R	k_2 [g (mg min^{-1})]	$q_{e,cal.}$ (mg/g)	R	SE %
398.3	2.650	0.127	11.93	0.836	1.307	2.674	0.999	1.111
GAC								
C_0 (mg/L)	$q_{e,exp}$ (mg/g)	First-order kinetics model			Second order kinetics model			
		k_1 (min^{-1})	$q_{e,cal.}$ (mg/g)	R	k_2 [g (mg min^{-1})]	$q_{e,cal.}$ (mg/g)	R	SE %
398.3	1.226	0.021	0.921	0.952	0.066	1.274	0.988	1.967

4.4 Adsorption Isotherm Models

The adsorption isotherm analysis was conducted using two of the most well-known isotherm equations which are: Langmuir, and Freundlich. The main assumptions considered in Langmuir isotherm model include: the monolayer adsorption on a surface that contains a finite number of homogeneous adsorption sites and the absence of transmigration of adsorbate on the plane of surface. For Freundlich model, the main assumption is the heterogeneous surface energies [116]. Non-linear regression tool such as SOLVER in excel is required to find the Langmuir and Freundlich isotherm constants. The applicability of each isotherm model can be judged by comparing the calculated sum of squared errors.

4.4.1 Langmuir isotherm.

The Langmuir's isotherm model is given by the following equation:

$$q_e = \frac{q_m K_L \, C_e}{1 + K_L C_e} \tag{4.3}$$

where C_e is the equilibrium concentration of sulfur given in (mg/L), q_e is equilibrium amount of sulfur adsorbed per unit mass of the adsorbate given in (mg/g), q_m is the maximum amount of sulfur adsorbed per unit mass of the adsorbate given in (mg/g), and K_L is the Langmuir constant which is related to the rate of adsorption.

The Langmuir adsorption isotherms for PAC1, and PAC2 were studied at room temperature, 30 ^{o}C and 50 ^{o}C (Figures 4.5-4.7). The Langmuir isotherm constants and the sum of squared errors (SSE) were determined by non-linear regression and are shown in Table 4.4.

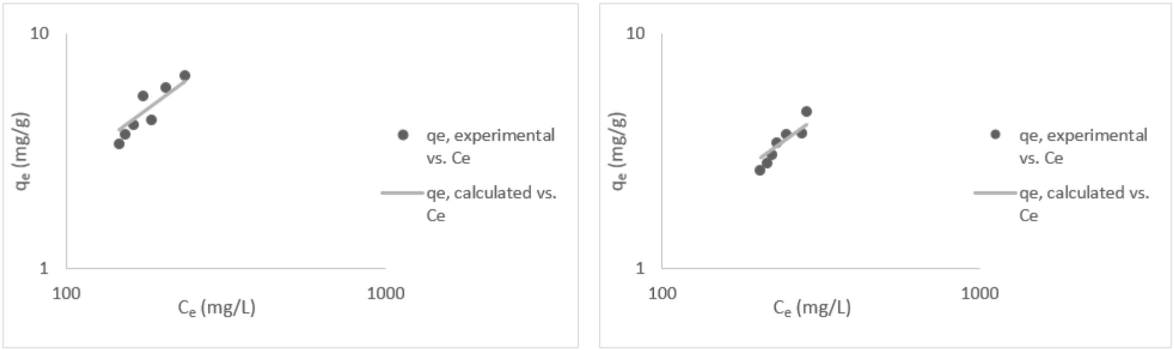
4.4.2 Freundlich isotherm.

The exponential form of Freundlich isotherm model is given by the following equation:

$$q_e = K_f (C_e)^{\frac{1}{n}} \tag{4.4}$$

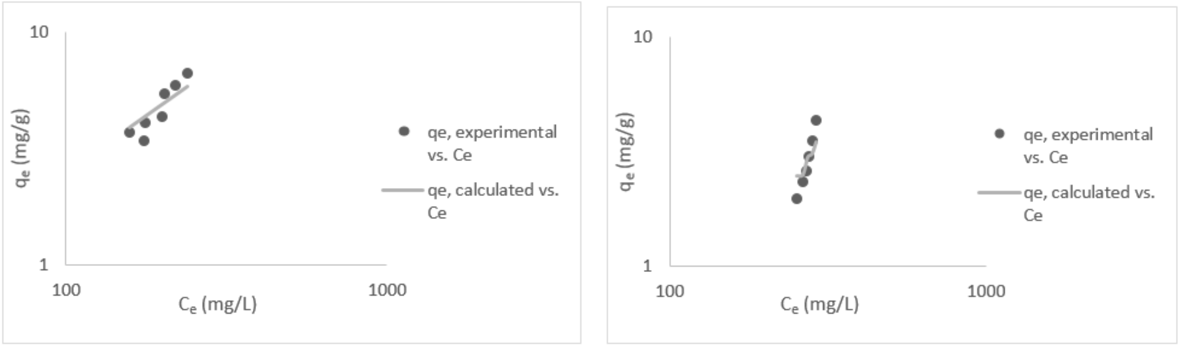
where, K_f and n are the Freundlich constants.

The Freundlich adsorption isotherms for PAC1, and PAC2 were also generated at room temperature, 30 ^{o}C and 50 ^{o}C (Figures 4.8-4.10). The Freundlich isotherm constants and the sum of squared errors (SSE) were determined by non-linear regression and are shown in Table 4.5. Results showed that for both PAC1 and PAC2, the adsorption behavior is described by Freundlich model for all temperatures. The results are verified by the calculated sum of squared errors (SSE) between the experimental and the calculated q_e values for the two models considered. Fitting of the adsorption parameters for the Langmuir is poor compared to the Freundlich model according to the calculated SSE values. Using Freundlich isotherm model, results showed that for PAC1 the calculated SSE were 1.323, 0.973, and 0.934 at room temperature, 30 ^{o}C, and 50 ^{o}C respectively. Also, for PAC2 the calculated SSE values were 0.362, 0.456, and 0.324 at room temperature, 30 ^{o}C, and 50 ^{o}C respectively. Results for the nonlinear regression for both Langmuir and Freundlich Isotherm models are shown in Appendix B.



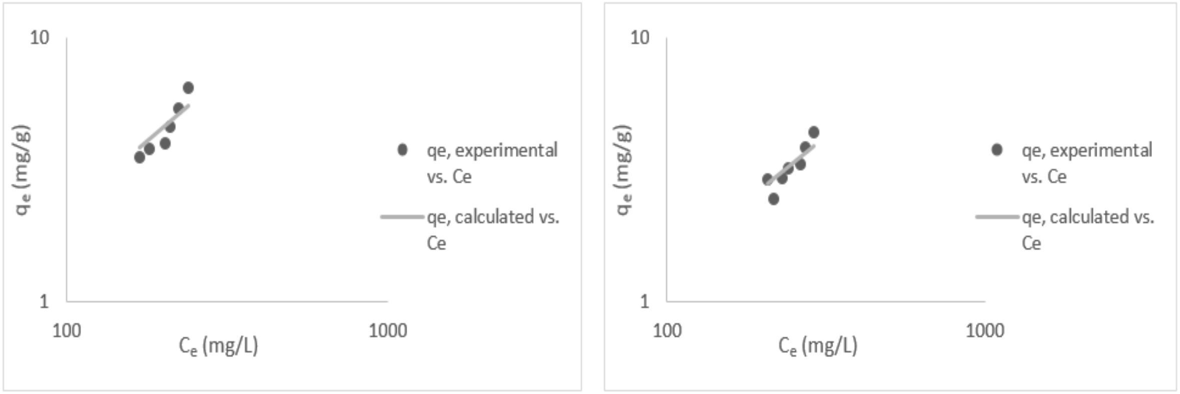
(a) (b)

Figure 4.5: Fitting of Langmuir Adsorption Isotherms on (a) PAC1, and (b) PAC2 at Room Temperature



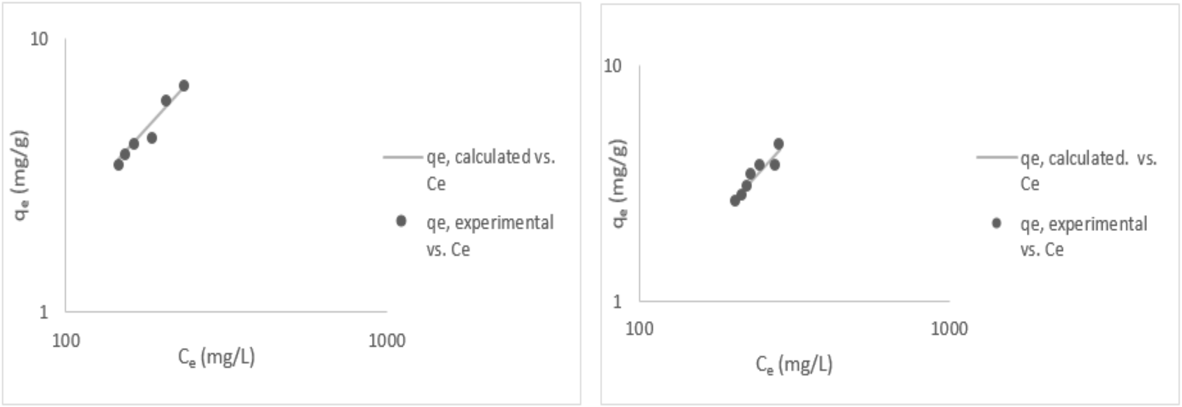
(a) (b)

Figure 4.6: Fitting of Langmuir Adsorption Isotherms on (a) PAC1, and (b) PAC2 at 30 ^{o}C



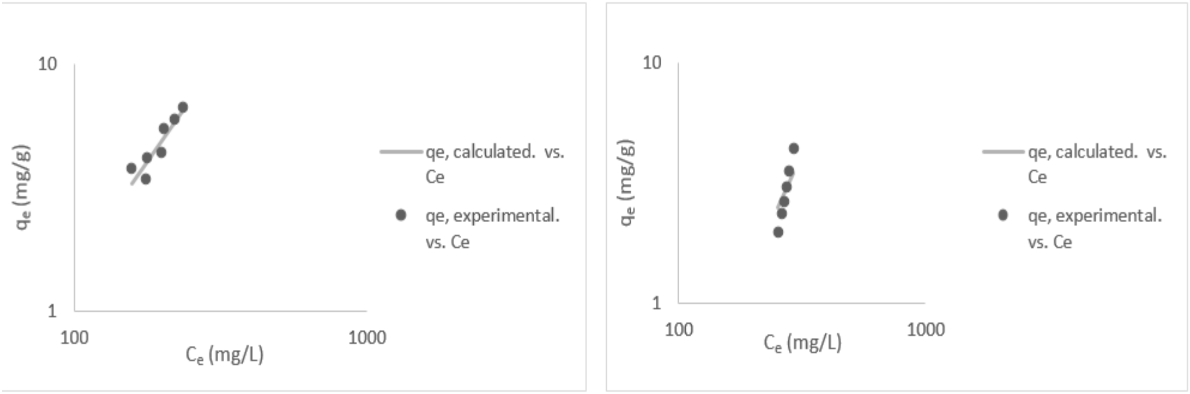
(a) (b)

Figure 4.7: Fitting of Langmuir Adsorption Isotherms on (a) PAC1, and (b) PAC2 at 50 ºC



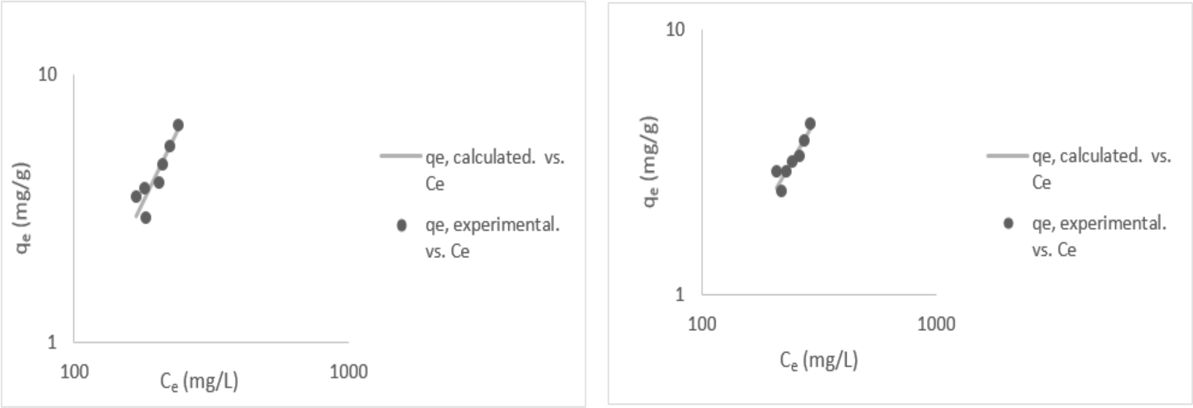
(a) (b)

Figure 4.8: Fitting of Freundlich Adsorption Isotherms on (a) PAC1, and (b) PAC2 at Room Temperature.



(a) (b)

Figure 4.9: Fitting of Freundlich Adsorption Isotherms on (a) PAC1, and (b) PAC2 at 30 ºC



(a) (b)

Figure 4.10: Fitting of Freundlich Adsorption Isotherms on (a) PAC1, and (b) PAC2 at 50 ºC

Table 4.4: Langmuir Adsorption Parameters

Sorbent	**PAC1**			**PAC2**		
Parameter	$q_m(\frac{mg}{g})$	$K_L(\frac{L}{mg})$	**SSE**	$q_m(\frac{mg}{g})$	$K_L(\frac{L}{mg})$	**SSE**
Room Temperature	481.6	5.613E-5	1.784	484	3.019E-5	0.604
30 ºC	298.8	8.424E-5	2.312	2468	4.448E-6	1.193
50 ºC	384.4	5.819E-5	3.1	247.6	5.52E-5	0.574

Table 4.5: Freundlich Adsorption Parameters

Sorbent	**PAC1**			**PAC2**		
Parameter	K_f	n	**SSE**	K_f	n	**SSE**
Room Temperature	0.005	0.759	1.323	0.001	0.694	0.362
30 ºC	0.001	0.599	0.973	4.480E-6	0.420	0.456
50 ºC	6.18E-5	0.476	0.934	0.001	0.666	0.324

4.5 Two-Stage Adsorption

The amount of sulfur contained in diesel oil was reduced further by adding a second adsorption stage. The diesel oil produced from the first adsorption stage using 10 wt. % of each of PAC1 and PAC2 were used as a feed for the second adsorption stage. 10 wt. % of each of fresh PAC1 and PAC2 were used for the second stage of the adsorption process. The second stage adsorption process was carried out under similar operating conditions used in the first adsorption stage (room temperature for 1 hr). For PAC1, results showed that the total sulfur content was reduced by 84.7 % where the sulfur content in the diesel oil produced from the second stage was 61 ppm. However, for PAC2, results showed that the total sulfur content was reduced by 81.0 % where the sulfur content in the diesel oil produced from the second stage was 75.7 ppm. Again, ED-XRF was used to determine the trace element percentages in the desulfurized diesel oil samples after the second stage, and the results are given in Table 4.6.

Table 4.6: Percentage Trace Elements in Untreated and Desulfurized Diesel Oil

Symbol	Diesel Oil	PAC1		PAC2	
		Treated Oil (Stage 1)	**Treated Oil (Stage 2)**	**Treated Oil (Stage 1)**	**Treated Oil (Stage 2)**
Magnesium (Mg)	32.19	35.62	35.13	35.11	34.27
Aluminum (Al)	13.04	12.95	12.64	12.63	13.42
Silicon (Si)	33.31	33.86	34.57	34.60	34.50
Phosphorous (P)	1.456	1.302	1.231	1.230	1.274
Chlorine (Cl)	5.709	4.422	4.721	4.720	4.532
Potassium (K)	0.618	0.383	0.906	0.906	1.116
Calcium (Ca)	7.091	6.840	7.014	7.013	7.328
Vanadium (V)	0.105	0.044	0.123	0.123	0.023
Chromium (Cr)	0.293	1.094	0.257	0.257	0.113
Manganese (Mn)	2.304	2.079	1.633	1.633	1.545
Iron (Fe)	2.629	0.339	0.324	0.324	0.372
Nickel (Ni)	0.105	0.109	0.112	0.112	0.113
Copper (Cu)	0.492	0.427	0.671	0.671	0.496
Zinc (Zn)	0.241	0.088	0.224	0.224	0.451
Molybdenum (Mo)	0.105	0.109	0.112	0.112	0.113
Barium (Ba)	0.314	0.328	0.336	0.336	0.338

4.6 Sorbent Surface Characterization

Nitrogen Adsorption analysis was used to determine the Brunauer, Emmett, and Teller (BET) surface areas for the different adsorbents. The BET surface areas for PAC1 and PAC2 were found to be 1104 and 2210 m^2/g, respectively. Moreover, the amount of trace metals in the sorbents before and after the adsorption process was determined using the ICP analysis, and the results are shown in Table 4.7. The difference in the amount of the trace metals in the surface of the sorbent material provides an indication about the amount of metals leached into the diesel oil from the sorbent materials, which is most likely due to the process used to prepare the commercial sorbent materials. Results showed a decrease in the amount of Aluminum, Chromium, Iron and Nickel on the surface of all of the adsorbents. However, PAC1 showed an increase in the amount of both Cobalt and Lead; whereas, PAC2 and GAC showed a slight decrease in the amount of these metals. Scanning Electron Microscopy (SEM) instrument was used to study the structure of the surface of the sorbent materials before and after the adsorption process. The results are shown in Figure 4.11. The SEM images of fresh activated carbon and granular carbon illustrate that the sorbent materials have smooth surface with compact structure (see Figures 4.11 a, c and e). After adsorption, results showed that sulfur is homogenously adsorbed on the surfaces of the sorbent materials (see Figures 4.11 b, d and f) which proves the validity of using both activated carbon and granular carbon for the adsorption of sulfur from diesel oil. SEM was used also to determine the metals present on the surface of each sorbent material before and after the adsorption process (Table 4.8).

Table 4.7: Heavy Metals in ppm for the Different Sorbents

Sorbent Material	Aluminum	Cobalt	Chromium	Copper	Iron	Nickel	Lead
PAC1 (fresh)	281	0.00	19.2	9.90	145	10.3	4.45
PAC1 (after adsorption)	172	1.87	6.27	13.4	66.1	8.48	5.05
PAC2 (fresh)	101	1.42	3.74	11.1	104	4.03	5.46
PAC2 (after adsorption)	82.1	1.35	1.19	9.90	40.3	4.12	5.36
Granular Carbon (fresh)	1203	0.58	149	15.1	915	579	7.69
Granular Carbon (after adsorption)	30.4	0.38	1.37	4.94	13.1	6.59	0.42

Table 4.8: SEM/EDS Surface Metals of the Different Sorbent Materials before and after the Adsorption Process in ppm

Element	PAC1		PAC2		GAC	
	Before DS	After DS	Before DS	After DS	Before DS	After DS
Na	0.13	0.19	0.21	0.06	0.24	0.08
Mg	0.00	0.02	0.00	0.00	1.03	0.34
Al	0.18	0.11	0.00	0.00	0.28	1.38
Si	0.45	0.18	0.24	0.07	0.27	0.47
P	1.91	0.93	4.08	3.34	0.32	0.16
S	0.24	0.25	0.07	0.21	0.58	0.17
Ca	0.05	0.18	0.13	0.01	1.10	0.73
Cr	0.00	0.03	0.00	0.01	0.02	0.00
Mn	0.00	0.00	0.16	0.03	0.00	0.05
Fe	0.00	0.01	0.00	0.00	0.11	0.32
Ni	0.01	0.29	0.01	0.00	0.02	0.10
Cu	0.00	0.07	0.08	0.00	0.12	0.00
Zn	0.24	0.21	0.09	0.00	0.00	0.01
Sr	0.23	0.00	0.00	0.30	0.17	0.07
Pb	0.00	0.00	0.54	0.00	0.42	0.00

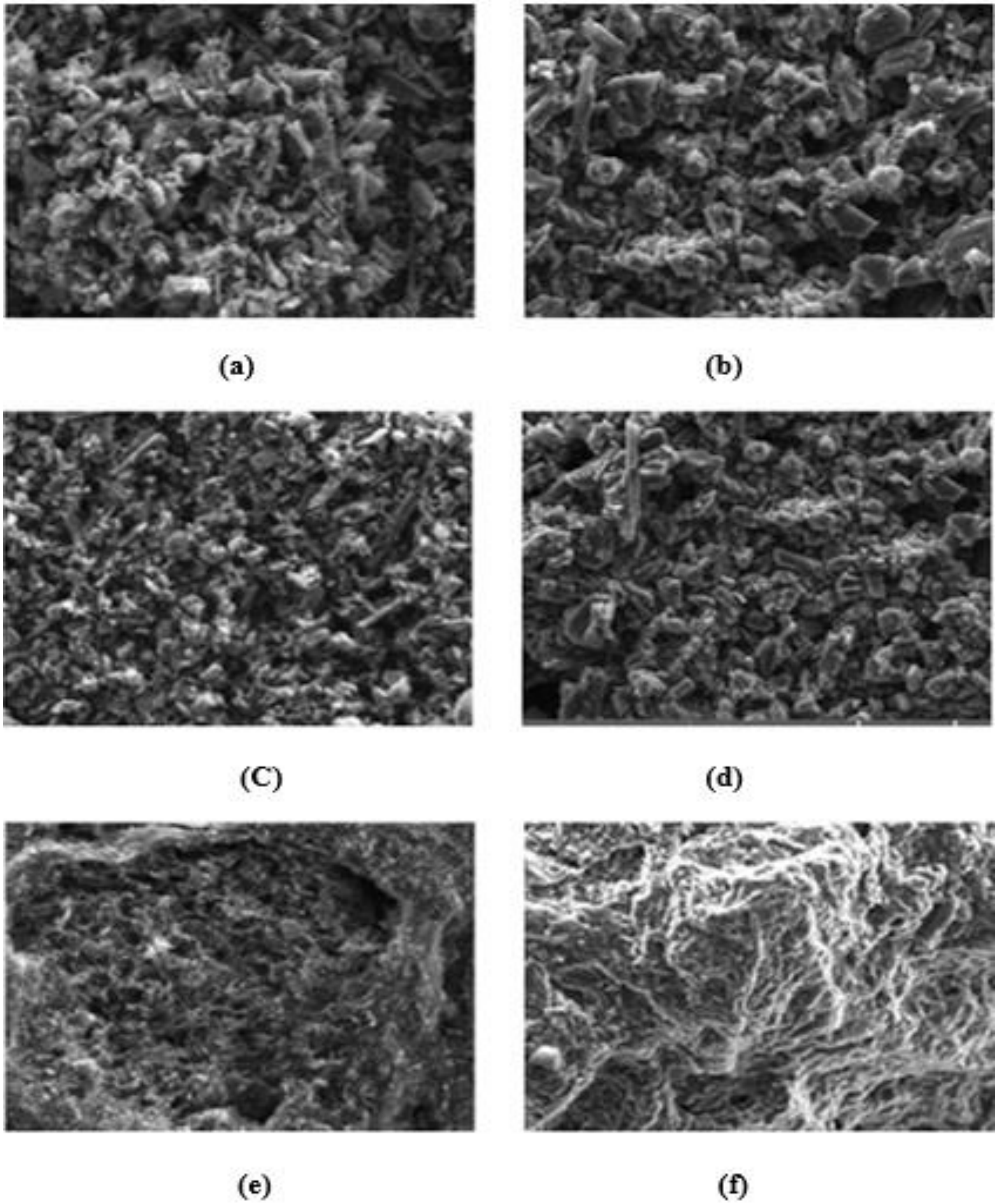


Figure 4.11: Scanning Electron Micrographs of the Sorbent Materials. PAC1 (a) before and (b) after the adsorption, PAC2 (C) before and (d) after the adsorption, and GAC (e) before and (f) after the adsorption

4.7 Conclusions

Adsorptive desulfurization of diesel oil was performed using three different commercial sorbents (PAC1, PAC2 and GAC). Sulfur removal capacity, adsorption kinetics and adsorption isotherms were studied. The present study show that the sorbents used can remove sulfur compounds effectively. Both PAC1 and PAC2 showed better sulfur removal affinity compared with the GAC. Results show that for both PAC1 and PAC2, the adsorption behavior is described better by Freundlich isotherm model. This is concluded from the calculated SSE at all temperature considered. Using Freundlich isotherm model, results showed that for PAC1 the SSE values were 1.323, 0.973, and 0.934 at room temperature, 30 ^{o}C, and 50 ^{o}C respectively, whereas for PAC2 the SSE values were 0.362, 0.456, and 0.324 at room temperature, 30 ^{o}C, and 50 ^{o}C respectively. Kinetic data for the three adsorbents follows a pseudo second-order model. Results indicate that sulfur adsorption kinetic study prove the applicability of the pseudo-second order model where the calculated sum of error squares was 0.427 %, 1.11% and 1.967 % for PAC1, PAC2 and GAC, respectively. Using a two-stage adsorption process, the total sulfur content in diesel oil was reduced by 84.7% and 81% using PAC1 and PAC2, respectively. Moreover, results showed a reduction in the amounts of aluminum, vanadium, iron, and zinc metals in the diesel oil samples treated using PAC1, and a decrease in the amounts of aluminum, and iron metals in diesel oil samples treated using PAC2. In addition, diesel oil sample treated using GAC show a decrease in magnesium, aluminum, and iron. The increase in the metal contents depends on the equilibrium concentration of each metal in the system.

Chapter 5: Results and Discussion - Improvement of the Ignition Quality of the Diesel Fuel through Adsorption Desulfurization Process

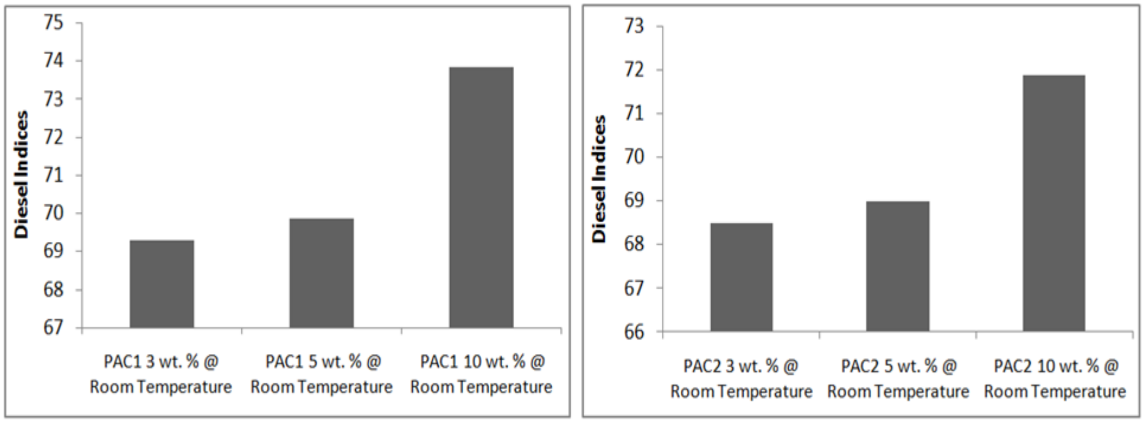
5.1 Introduction

Ignition quality is a measure of the ease of the self-ignition of diesel fuel when the fuel is injected in hot compressed air into the engine cylinder. The ignition quality of diesel fuel is linked to the ignition delay time, which is the time between the start of injection and the start of combustion. Several properties of diesel fuel, such as aromatics content, cetane number, distillation temperature (T_{90}%) and density, have a direct impact on the type of emissions produced. Reducing the emissions associated with combusting diesel oil can be achieved either by removing sulfur from stack gas or by improving the ignition quality. In this chapter, the improvement of the ignition quality of diesel fuel through adsorptive desulfurization process is studied. The ignition quality measure (calculated diesel index) is studied at different temperatures and amounts of the sorbent materials using the three adsorbents considered. Then, diesel oil samples showing the best sulfur removal percentages (10 wt. % of PAC1, PAC2 and GAC at room temperature) are used to compare all other ignition quality measures (carbon residue, aniline points, cetane number, cetane index, diesel index, calculated carbon aromaticity index (CCAI) and the combustion ignition index (CII)).

5.2 Improvement of the Ignition Quality of Diesel Oil

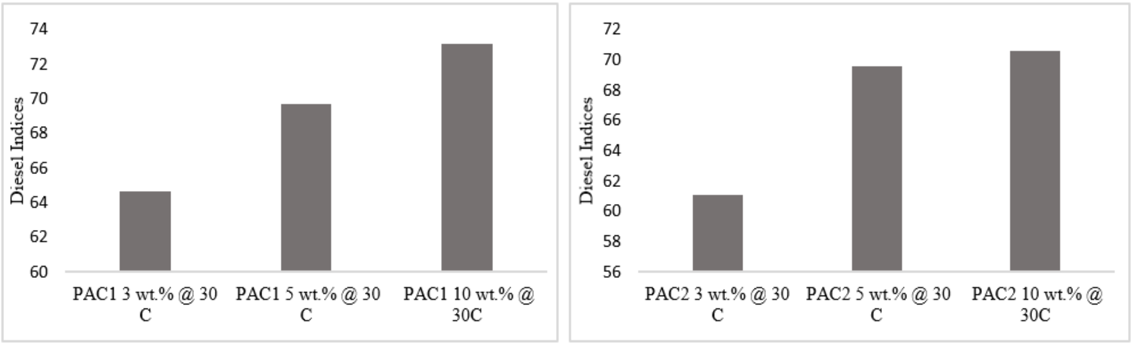
5.2.1 The effects of the amount of sorbent materials and the temperature.

Diesel indices were calculated for diesel oil samples produced after the adsorption process. Three different amounts of sorbent materials (3 wt. %, 5 wt. % and 10 wt. %) and three operating temperatures (room temperature (24 ^oC), 30 ^oC, and 50 ^oC) were considered in this study. The contact time for all adsorption experiments was selected as 1 hr as no significant sulfur removal was observed after 1 hr, and accordingly, the calculated diesel indices will not change significantly. Results show that the calculated diesel indices for diesel oil samples showed a positive increase as the amount of sorbent material used is increased. This behavior was the same at all temperatures considered using the three adsorbents (Figures 5.1 -5.3). The best values for the calculated diesel indices were found using 10 wt. % of PAC1 and PAC2 at room temperature and are given as 73.83 and 71.88, respectively. Diesel indices calculated for diesel oil samples produced after the adsorption process using GAC are not shown as all samples showed similar behavior at the different temperatures examined. However, the best value for the calculated diesel index using 10 wt. % GAC at room temperature was found to be 71.24.



(a) (b)

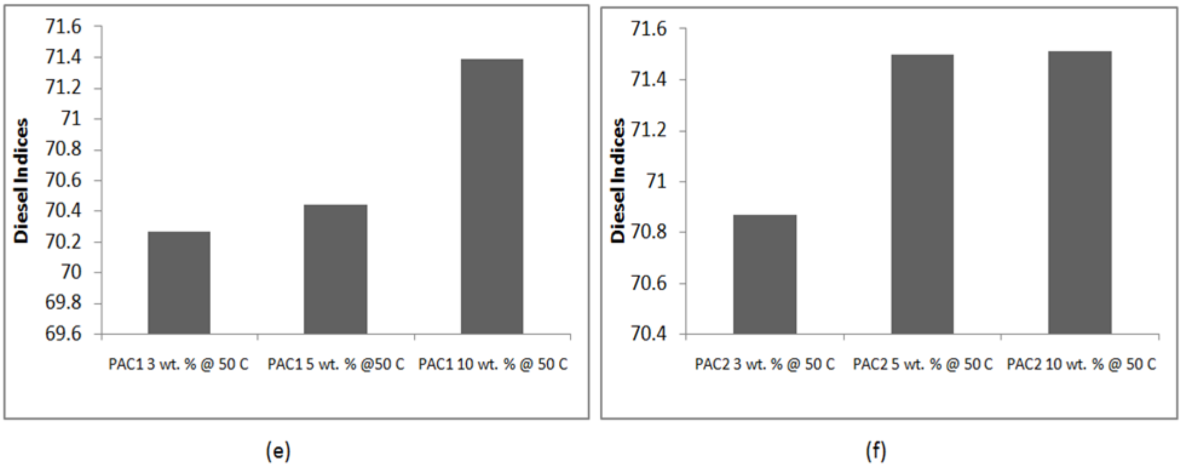
Figure 5.1: Calculated Diesel Indices at Room Temperature using Different Amounts of (a) PAC1 and (b) PAC2



(C) (d)

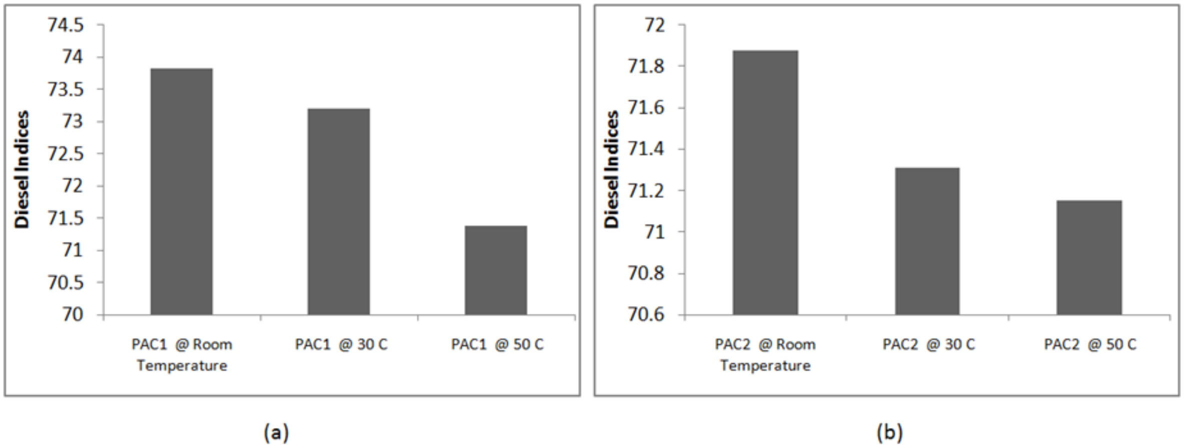
Figure 5.2: Calculated Diesel Indices at 30 ºC Using Different Amounts of (C) PAC1 and (d) PAC2

Diesel oil samples showing the best calculated diesel indices were found to be after the adsorption using 10 wt. % of PAC1 and PAC2 at the three different temperatures. These samples were used to study the effect of temperature while keeping the amount of sorbent material constant (taken as 10 wt. % of PAC1 and PAC2). As shown in Figure 5.4, results showed that the calculated diesel indices decreases as the operating temperature increases, as expected. This is justified by the fact that the amount of sulfur removal also decreases at elevated temperatures. Diesel oil samples that showed the best values for the calculated diesel indices were then used to study the other ignition quality measures (section 5.2.2).



(e) (f)

Figure 5.3: Calculated Diesel Indices at 50 ºC Using Different Amounts of (e) PAC1 and (f) PAC2



(a) (b)

Figure 5.4: Calculated Diesel Indices of Diesel Oil Samples at Different Temperatures Using (a) PAC1 and (b) PAC2

5.2.2 Ignition quality measures.

Generally, different tests have been used for the evaluation of the ignition quality, such as carbon residue, aniline point, diesel index, cetane index and cetane number. Results showed a significant reduction in the Conradson carbon residue of the diesel oil after the removal of sulfur using PAC1 and GAC as shown in Figure 5.5. This can be justified by the removal of certain aromatics through the adsorption process. However, results showed a slight increase only in the carbon residue of the diesel oil treated using PAC2 (0.12% of carbon residue) compared to that for the diesel oil treated using PAC1 and GAC (0.017% and 0.035%, respectively).

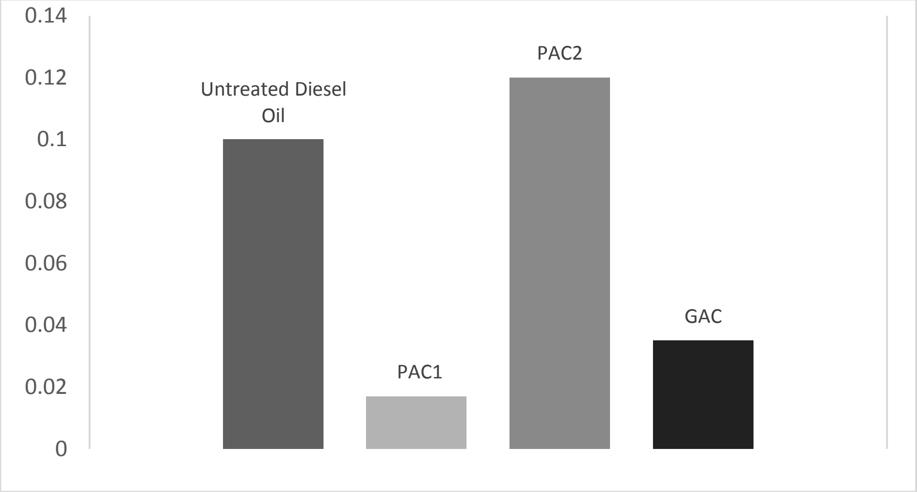


Figure 5.5: Carbon Residue for Diesel Oil

The aniline points were also found for the diesel oil samples in order to understand the ignition behavior of a diesel fuel after the adsorption process. The aniline points give an indication about the content of aromatic compounds in diesel fuel. As the aniline point decreases, the content of aromatic compounds in the oil increases. Moreover, the higher the aromatics content is, the lower the cetane number of the diesel fuel is. For aromatic oil having 75% aromatic content, the aniline point would be between 32-49 ^{o}C. For the naphthenic type of oil containing 40% aromatic structures, the aniline point would be between 65.5-76.5 ^{o}C. However, for paraffinic oil with 15% aromatic content, the aniline point would be between 93-126 ^{o}C. Results showed that the aniline points of the desulfurized diesel fuels were increased due to aromatic removal (Figure 5.6).

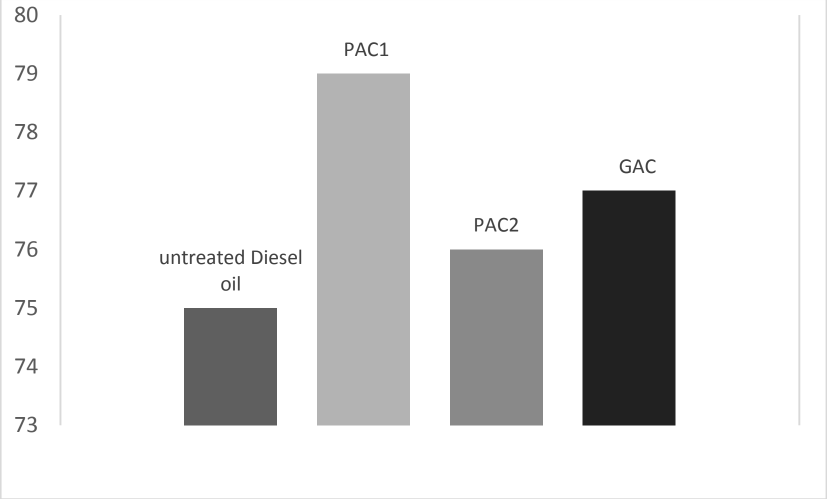


Figure 5.6: Aniline Points for Diesel Oil

The diesel indices were also measured for the treated samples. The calculation of diesel indices are related to the aniline points calculated earlier. The diesel indices are calculated using the following formula:

$$Diesel\ Index = \frac{Aniline\ Point,\ (F) * API\ gravity}{100} \tag{5.1}$$

High quality fuel has high diesel index. It has been found that the diesel index of diesel fuel is approximately equal to its cetane number. Therefore, a lower aromatic content in diesel fuel is desirable to prevent auto-ignition in diesel engines [23]. The diesel index of the desulfurized diesel fuel using PAC1 showed the highest value compared to the other two sorbents. This is due to higher sulfur removal from diesel fuel using PAC1 (Figure 5.7).

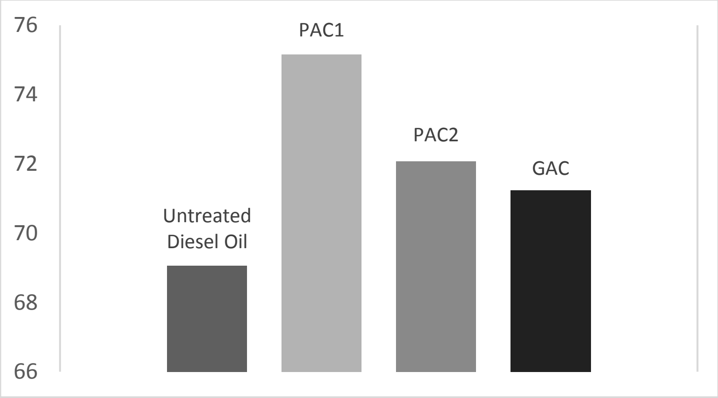


Figure 5.7: Diesel indices for Diesel Oil

The calculated cetane index is also a measure of the fuel ignition quality. Diesel indices were used to calculate the cetane indices using the following formula:

$$Cetane\ Index = (0.72 * Diesel\ Index) + 10 \tag{5.2}$$

The cetane index for the untreated diesel oil was found to be around 59.7. Similarly, results showed an increase in the cetane indices for all treated diesel oil samples. The highest value was found for the diesel oil treated using PAC1 having a value of around 64, followed by the diesel oil treated using PAC2 having a value of 61.8 and finally diesel oil treated using granular carbon having a value of 61.3 (Figure 5.8). These high values of cetane indices indicate a shorter ignition delay time and a more complete combustion of the fuel. This is translated into smoother running, better performing engine with more power and fewer harmful emissions.

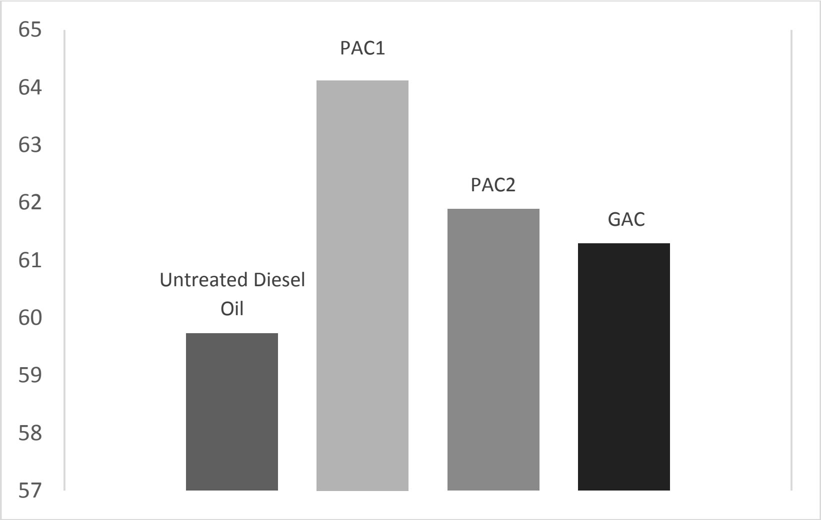


Figure 5.8: Cetane Indices for Diesel Oil

The cetane number (CN) is defined as a measure of the ignition delay of fuel and the time interval between the injection and the ignition of it. In diesel engines, higher CN fuels have shorter ignition delay periods compared with lower CN fuels. This reduces the amount of fuel burned in the premixed phase and accordingly lower peak combustion pressures and temperatures will be attained. The calculated CN is related to the diesel index according to the following equation [115]:

$$Cetane\ Number(CN) = Diesel\ Index - 3 \tag{5.3}$$

The CN for diesel fuel treated using PAC1 was found to be around 72 which is the highest compared to the other sorbents used (Figure 5.9).

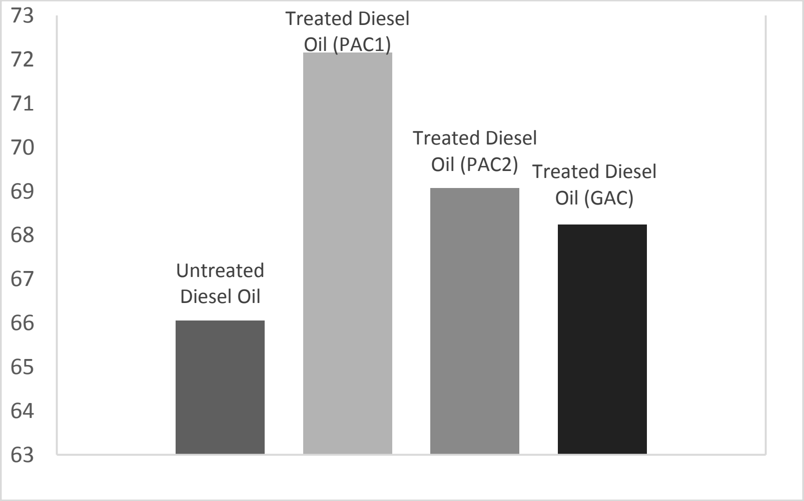


Figure 5.9: Calculated Cetane Numbers

For heavy fuel oil, two measures for the ignition quality are used which are: the CCAI and the CII. CCAI is recognized as a reliable indicator for the ignition properties of fuel oil. Generally, the low values of CCAI lead to a better ignition quality. However, CCAI values that exceed 880 cause problems to engines due to induced poor ignition quality. CCAI can be calculated using properties such as viscosity and density of diesel fuel according to the following formula [115]:

$$CCAI = D - 141 \log * [\log(V + 0.85)] - 483 * \log\left[\frac{T + 273}{323}\right] \tag{5.4}$$

Whereas the CII is calculated according to the following formula:

$$CII = (270.795 + 0.1038t) - (0.254565D + 23.708 \log(V + 0.7) \tag{5.5}$$

Where D is the density of diesel fuel at 15 ^{o}C, ($\frac{Kg}{m^3}$) and V is the kinematic Viscosity of diesel fuel, (cS), t is the operating viscosity temperature, (^{o}C).

The CCAI for the untreated diesel oil was found to be around 803.9. Results showed an increase in the CCAI for all diesel oil treated samples as shown in Figure 5.10. The highest value was found for the diesel oil treated using Granular Carbon having a value of 810.7, followed by the diesel oil treated using PAC2 having a value of 806.32, and finally the treated diesel oil treated using PAC1 having a value of 804.67. The calculated CII also increased for all samples after fuel desulfurization process as shown in Figure 5.11.

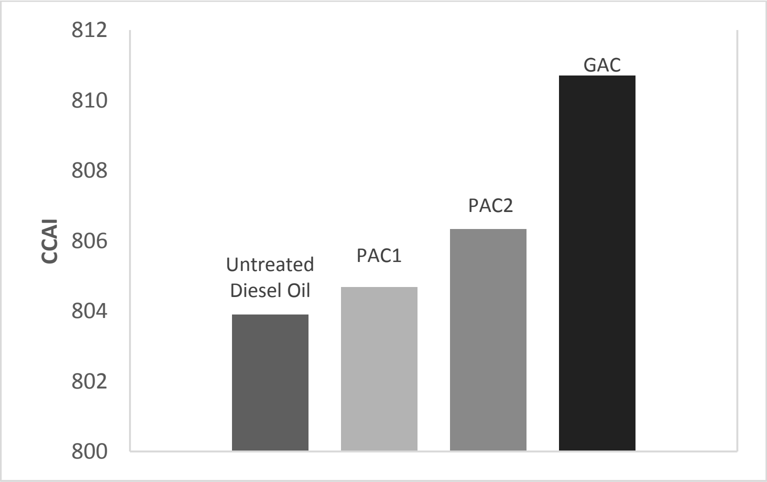


Figure 5.10: Calculated Carbon Aromaticity Indices for Diesel Oil

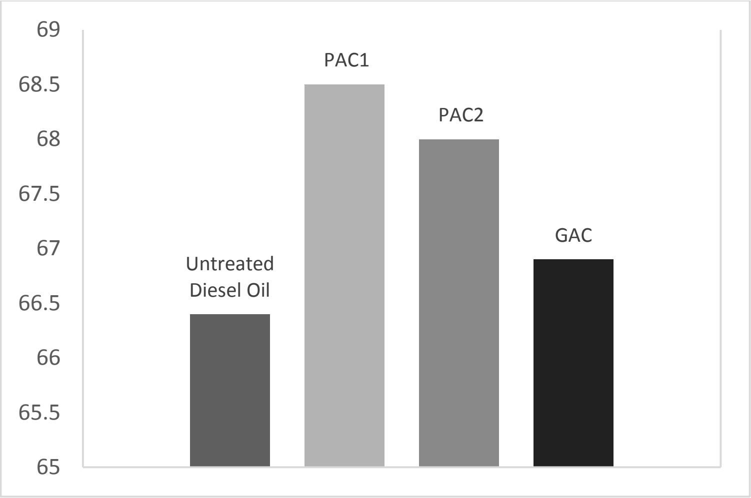


Figure 5.11: Calculated Combustion Ignition Indices of Diesel Oil

5.3 Conclusions

In this chapter, the improvements in the ignition quality for diesel oil samples were examined. In the first part of this study, a major ignition quality measure given as the calculated diesel index was studied at different temperatures and amounts of the sorbent materials using the three adsorbents (PAC1, PAC2 and GAC). Results showed that there is a positive increase in the calculated diesel indices as the amount of sorbent material used is increased. This behavior was the same at all temperatures considered. The best values of the calculated diesel indices were found using 10 wt. % of PAC1, PAC2 and GAC at room temperature and are given as 73.83, 71.88 and 71.24, respectively. The effect of temperature in the calculated diesel indices was clear for diesel oil samples produced after the adsorption process using PAC1 and PAC2. Results showed that the calculated diesel index decreases as the operating temperature increases. However, diesel indices calculated for diesel oil samples produced after the adsorption process using GAC showed similar behavior with all of the operating temperatures examined.

In the second part of this study, diesel oil samples that showed the best sulfur removal percentages (10 wt.% of PAC1, PAC2 and GAC) were used to compare all other ignition quality measures (carbon residue, aniline points, cetane number, cetane index, diesel index, CCAI and CII) among the three adsorbents. Results showed that there is an improvement in all ignition quality measures using the three adsorbents used. The best results were obtained using the diesel oil samples produced using PAC1.

Chapter 6: Results and Discussion - The Use of Factorial Design in the Analysis of Adsorptive Desulfurization Data

6.1 Introduction

Design of experiments (DOE) is defined as a statistical technique or approach that is used for the design and the analysis of experiments. The use of DOE is required in designing experiments in order to draw valid and accurate conclusions about any set of experiments. In DOE, a series of tests are made where certain changes are imposed to the input factors, so that the causes of the main changes in the output or response are identified. DOE is a statistical tool used to explore new processes and gain understanding of the existing processes. This helps researchers to optimize such processes. DOE is about following a particular pattern of experiments in order to generate a great deal of information about a certain process while using the absolute minimum of actual experiments or runs needed to get this information [117].

In most research areas, the majority of experiments are designed by studying the effects of two or more inputs on the output or the response variable rather than the effect of the individual factors. A full factorial design study is about studying the effect of each of the selected factors on the desired response variable or output. Typically, two levels (high and low) of k inputs or factors are selected in the analysis. This results in 2^k factorial experimental designs. For example, in 2^2 factorial designs, two levels (high and low) of each factor are studied. This results in four different combinations of treatments or runs [118]. The use of factorial design is more advantageous than studying the effects of individual factors or the one-factor-at-a-time analysis approach [119] [120].

In adsorptive desulfurization processes, the need to optimize the operating conditions is of extreme importance for improving these processes. Accordingly, factorial experimental designs find growing interest among researchers. For instance, M. Muzic et al. [121] used a DOE method to study the adsorptive desulfurization of diesel oil (27 mg/kg) using certain activated carbon as an adsorbent material. The DOE method used was a full factorial design with three factors which are the time, initial sulfur concentration and adsorbent mass or amount on two levels (low, and high) for two output variables (output sulfur concentration and sorption capacity) and five center points. This results in a 2^3 full factorial design. The effects of the individual factors as well as their interactions on the two response variables were investigated and then followed by developing a statistical or regression model of the process. Results showed that the sulfur concentration is affected directly by all factors and interactions between the initial sulfur concentration and the adsorbent mass or amount. However, the sorption capacity is affected by all factors as well as the interaction between the initial sulfur concentration and adsorbent mass, and the interaction effect between time and initial sulfur concentration.

In this chapter, the sets of experimental data that were generated on adsorptive desulfurization study are examined using 2^2 and 2^3 factorial designs. This statistical approach is used to determine the most important operating conditions on the sulfur removal percentage and the calculated diesel index for each diesel oil sample. For the 2^2 factorial designs, two designs are considered. For the first design, two levels (high and low) of two factors (amount of sorbent material used wt. % and temperature ^{o}C) are considered to study the effects on the sulfur removal percentage and the calculated diesel index using two different sources of activated charcoals (PAC1 and PAC2) on the adsorptive desulfurization process. Whereas, for the second design, again two levels (high and low) are selected to determine the effects of the amount of sorbent material and the contact time on the same response variables. However, for the 2^3 factorial design, two levels (high and low) of three factors (amount of sorbent material used wt. %, contact time and temperature ^{o}C) are considered to study the main effects and interactions on the same response variables. The main objective of this study is to investigate the effects and the interactions between the studied factors, so that invalid and inaccurate conclusions can be avoided about the process. Results found are also verified by studying and generating the analysis of variance or ANOVA tables for the three studies considered.

6.2 Factorial Design Methodology

6.2.1 2^k Factorial designs.

Factorial designs are used extensively in experimental works that involve studying several factors simultaneously here it is important to study the mutual effects of the factors on the response variable. If k factors need to be studied each at two levels, the complete set of treatments or runs of such design require 2^k observations that are called a 2^k Factorial Designs. The 2^k factorial designs are helpful in understanding the results of the early stages of any experimental work as several factors require testing and investigation. In these designs, the two levels of analysis are referred to as high and low, or +1 and -1. The main effect of a certain factor is defined as a change in the average output or response produced by the average change in the levels of that factor. This can be explained by studying a simple 2^2 factorial design in which two factors (X and Y) are studied at two levels (high and low). The main effect of factor X is given as the difference between the average output or response at the low and high levels of factor X. Moreover, in a 2^2 designs, the symbols – (1), a, b, and ab – are used to represent the total number of the replicates taken at the treatment combinations as shown in Figure 6.1

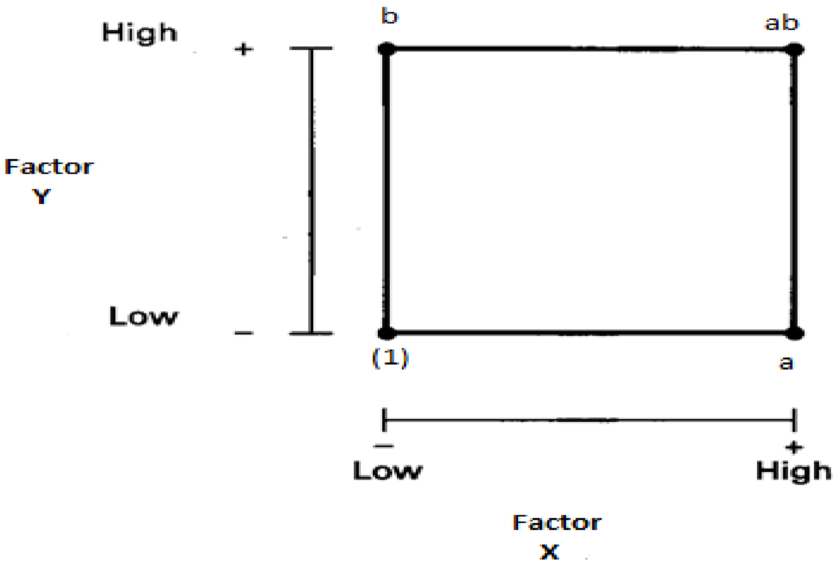


Figure 6.1: Treatment or Run Combinations in 2^2 Designs

If the difference in the output values between the levels of a certain factor is strongly dependent on the levels of another factor or input, i.e., if it is a function of the levels of that factor, there is an interaction between the different factors. For the 2^2 factorial designs, the interactions between factors can be described graphically as shown in Figure 6.2 below. Getting parallel lines represent the absence of interactions between the considered factors; whereas, crossed or un-parallel lines represent the presence of interaction between X and Y.

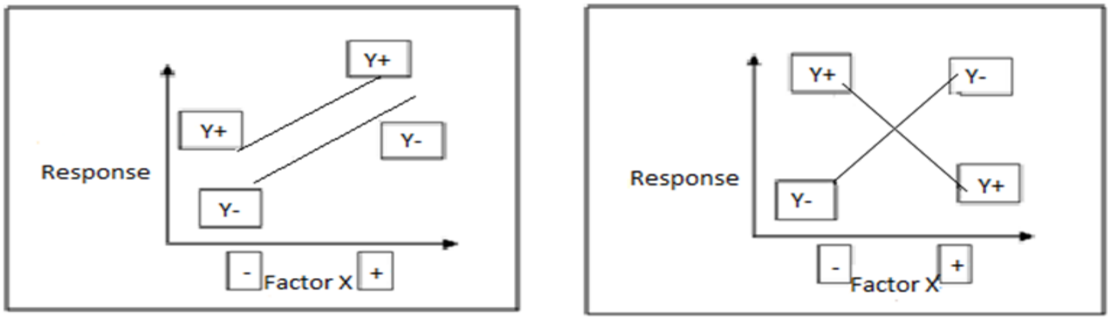
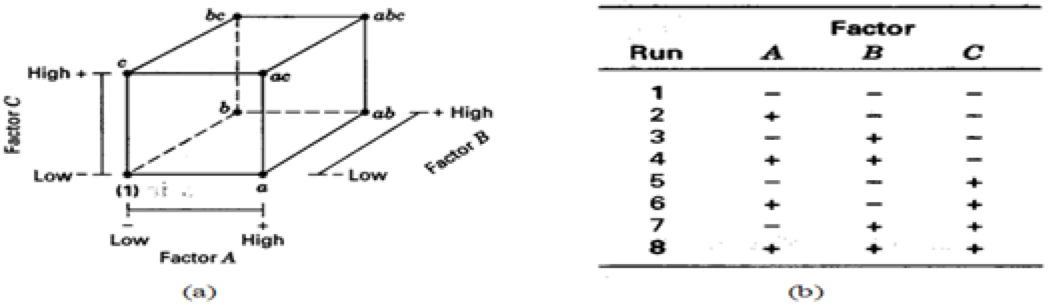


Figure 6.2: Factorial Design without and with Interaction

In addition, if three factors A, B and C, each at two levels, are to be examined in a certain experiment, the design is called a 2^3 factorial design, and the resulting eight treatments are arranged in a cube (see Figure 6.3 (a)). Using the "- and + " symbols to signify the low and high levels, respectively, the resulting eight treatments are represented by the design matrix shown in Figure 6.3 (b). As mentioned earlier, the symbols (1), a, b, ab, c, ac, bc and abc are used to represent the total number of replicates for all of the treatment or run combinations for a 2^3 designs.



(a)

	Factor		
Run	A	B	C
1	−	−	−
2	+	−	−
3	−	+	−
4	+	+	−
5	−	−	+
6	+	−	+
7	−	+	+
8	+	+	+

(b)

Figure 6.3: The Geometric View (a) and the Design Matrix (b) of 2^3 Factorial Design

One way to understand and represent the interactions between the tested factors is through generating their related predictive regression models. The regression model for a 2^2 factorial experiment is expressed as:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \varepsilon \qquad (6.1)$$

Whereas, the regression model for a 2^3 factorial experiment is expressed as:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3 + \varepsilon \qquad (6.2)$$

where y is the output response variable, x 's are the coded variables, ε is the calculated error and $\beta's$ are the regression parameters which indicates the corresponding effects. As the value of β increases, the corresponding effect becomes more significant.

In the factorial designs considered in this study, i.e., 2^2 and 2^3, the methodology followed includes the following procedures [118]:

1- Calculating all of the main effects of the involved factors and their corresponding interactions.
2- Constructing the ANOVA tables for each of the experimental designs.
3- Generating the corresponding regression models and response surfaces.

For the 2^3 factorial designs, the equation used for calculating the effect of factor A can be developed through its calculated contrast C_j which is given as:

$$C_j = \sum_{i=1}^{i=8} Sign_{ij}\ in\ the\ design\ matrix * y_i \tag{6.3}$$

where the $Sign_{ij}\ in\ the\ design\ matrix$ corresponds to the sign in the design matrix for effect "j", and y_i is the output or the response value [117]. The main effect E_j, taking into account the effect of blocking (2 blocks), is then calculated as:

$$E_j = \frac{C_j}{(\frac{2^k}{2})} \tag{6.4}$$

The regression coefficients $\beta's$ mentioned earlier are calcultated by dividing each effect by 2 except the β_o which is defined as the grand arithmetic average of all treatments.

Analysis of variance or ANOVA tables are also generated according to the overall sum of squared deviations (SS_T) into the individual sum of squares (SS_j) [120]. In the case of 2^2 designs, taking into account the effect of blocking (2 blocks), and the total sum of squares is given as:

$$SS_T = SS_A + SS_B + SS_{AB} + SS_{blocks} + SS_{error} \tag{6.5}$$

Whereas, in the case of 2^3 factorial designs, it is given as:

$$SS_T = SS_A + SS_B + SS_C + SS_{AB} + SS_{AC} + SS_{BC} + SS_{ABC} + SS_{blocks} + SS_{error} \qquad (6.6)$$

In the 2^k Factorial designs, the SS_j is calculated using the following equation:

$$SS_j = \frac{C_j^2}{(2^k * 2)} \qquad (6.7)$$

Whereas, the sum of squares for the blocks SS_{blocks} is given by:

$$SS_{blocks} = 4 * (\overline{y_1} - \beta_o)^2 + 4 * (\overline{y_2} - \beta_o)^2 \qquad (6.8)$$

The total sum of squares SS_T is given by:

$$SS_T = \sum_{i=1}^{2^k} (y_{i,1} - \overline{y_1})^2 + (y_{i,2} - \overline{y_2})^2 \qquad (6.9)$$

where $y_{i,1}$'s are the response values in block 1, $y_{i,2}$'s are the response values in block 2, $\overline{y_1}$ is the average of the response values in block 1 and $\overline{y_2}$ is the average of the response values in block 2.

The mean sum of squared deviations or MS_j is defined as the sum of squares SS_j divided by the associated DOF. Finally, the F-distribution is given by dividing a certain MS_i by another. The complete analyses of the two response variables (sulfur removal percentage and diesel index, respectively) are summarized in Tables 6.1 - 6.4 for 2^2 factorial designs and in Tables 6.5 and 6.6 for 2^3 factorial designs. All of the figures shown in this this chapter are generated using Design-Expert 9.0.4.1 software [122].

6.3 Results and Discussions

6.3.1 2^2 Two-level factorial designs – study 1.

In the 2^2 factorial design, four different experiments were conducted for each source of the sorbent materials (PAC1 and PAC2). Two 2^2 facorial design studies were conducted. For the first study, the two factors selected were the amount of sorbent material in wt% (A) and the operating temperature in °C (B) each at two levels (- and +) or (high and low). However, for the second 2^2 facorial design study, the two factors selected were the amount of sorbent material in wt. % (A) and the contact time in hrs (B) each at two levels (- and +) or (high and low). The first response variable considered is sulfur removal percentage; whereas, the second response variable is the calculated diesel index for each of the produced diesel oil sample. Tables 6.1-6.2 show the factorial design results for the first 2^2 factorial design study for the two response variables. The tables include: the design matrix, the main effects and interactions among the considered factors, the generated regression models as well as the ANOVA tables. It is noticed from the tables that the absolute effect of the amount of sorbent material used (A) is greater than the effect of tempretaure (B) on the two response variables. This result is also confirmed in the ANOVA analysis given by the p-value. The p-values for factor A are 0.0001 and 0.0009 (Tables 6.1-6.2). This indicates that these model terms are significant as both are less than 0.050. However, the p-values for factor B are 0.2660 and 0.2998 (Tables 6.1-6.2). This shows that these model terms are insignificant. Thus, results show that the amount of sorbent material used is more important than the operating temperature using the two sources of sorbent material (PAC1 and PAC2). Moreover, for the two response varaibles considered (sulfur removal percentage and calculated diesel index), the effect of A is positive; whereas, the effect of B is negative, both of which physically expected. However, the effect of the amount of sorbent material is more significant in the two cases. This can also be verified by the calculated p-value.

A part of this study is also to generate a regression model that fits the experimental data. Using the results of the 2^2 factorial experimental design study, the predictive capability of the generated regression model was also studied (Figures 6.4-6.5). For the two response variables considered, good agreement between the experimental and predicted values was observed. The differences between the experimental and the predicted values for the two responses were also determined and are shown in Figures 6.6-6.7. In addition, 3-D surface plots and contour plots for the two response variables were also generated and are shown in Figures 6.8-6.11.These graphs show that for the first response variable (sulfur removal percentage), there is a slight interaction between the two factors. Whereas, for the second response variable (diesel indices), the interaction between the two factors is significant, indicating that the two factors are dependant.

Table 6.1: Analysis of Sulfur Removal Percentage (Response Variable 1) Data as a 2^2 Factorial Design – Study 1.

Factors				**Low (-1)**			**High (+)**		
A=Amount of Sorbent Material Used, wt %				3			10		
B= Temperature, °C				25			50		
				PAC1	**PAC2**				
Treatments	A	B	AB	y1	y2	Total	Contrast A×y	Contrast B×y	Contrast AB×y
[1]	-	-	+	40.95	28.47	69.42	-69.42	-69.42	69.42
a	+	-	-	66.16	57.95	124.1	124.1	-124.1	-124.1
b	-	+	-	39.82	29.43	69.24	-69.24	69.24	-69.24
ab	+	+	+	63.85	55.16	119.0	119.0	119.0	119.0
				$\overline{y_1}$	$\overline{y_2}$	β_o			
Effects	26.11	-1.318	-1.230	52.69	42.75	47.72			
Regression Model	$47.72+13.06x_1-0.659x_2-0.615x_1x_2$								
ANOVA									

Source of Variations	**Sum of Squares (SS_i)**	**Degrees of Freedom (DOF)**	**Mean Squares (MS_i)**	**F-values**	**P-values**
A	1364	1	1364	729.7	0.0001
B	3.475	1	3.475	1.860	0.2660
AB	3.027	1	3.027	1.620	0.2928
Blocks	197.7	1	197.7	105.8	
Error	5.606	3	1.869		
Total	1573	7			
Model	**1370**	**3**	**456.7**	**244.4**	**0.0004 → Significant**

Table 6.2: Analysis of Diesel Indices (Response Variable 2) Data as a 2^2 Factorial Design – Study 1.

Factors				**Low (-1)**			**High (+)**		
A=Amount of Sorbent Material Used, wt %				3			10		
B= Temperature, °C				25			50		
				PAC1	**PAC2**				
Treatments	A	B	AB	y1	y2	Total y	Contrast A×y	Contrast B×y	Contrast AB×y
[1]	-	-	+	69.28	68.50	137.8	-137.8	-137.8	137.8
a	+	-	-	73.83	73.03	146.9	146.9	-146.9	-146.9
b	-	+	-	71.03	70.87	141.9	-141.9	141.9	-141.9
ab	+	+	+	71.39	70.49	141.9	141.9	141.9	141.9
				$\overline{y_1}$	$\overline{y_2}$	β_o			
Effects	2.267	-0.212	-2.275	71.38	70.72	71.05			
Regression Model	$71.05+1.134x_1-0.1062x_2-1.138x_1x_2$								
ANOVA									

Source of Variations	**Sum of Squares (SS_i)**	**Degrees of Freedom (DOF)**	**Mean Squares (MS_i)**	**F-values**	**P-values**
A	10.28	1	10.28	178.0	0.0009
B	0.090	1	0.090	1.563	0.2998
AB	10.36	1	10.36	179.3	0.0009
Blocks	0.867	1	0.867	15.02	
Error	0.173	3	0.058		
Total	21.77	7			
Model	**20.73**	**3**	**6.910**	**119.6**	**0.0013→ Significant**

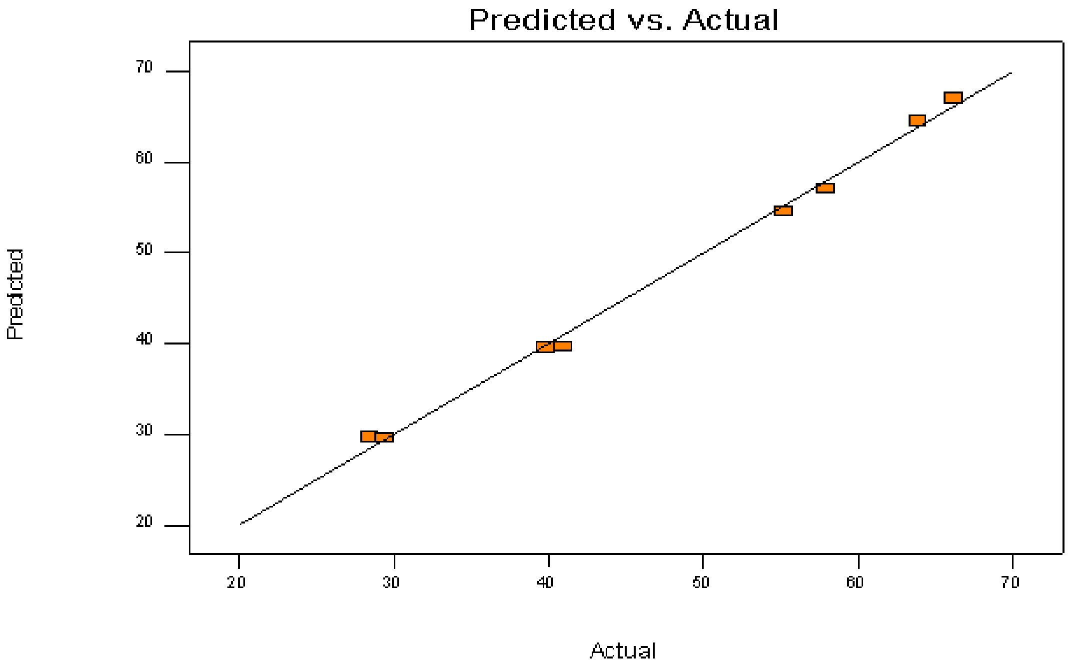


Figure 6.4: The Sulfur Removal Percentage (Experimental and Predicted) for 2^2 Factorial Design – Study 1

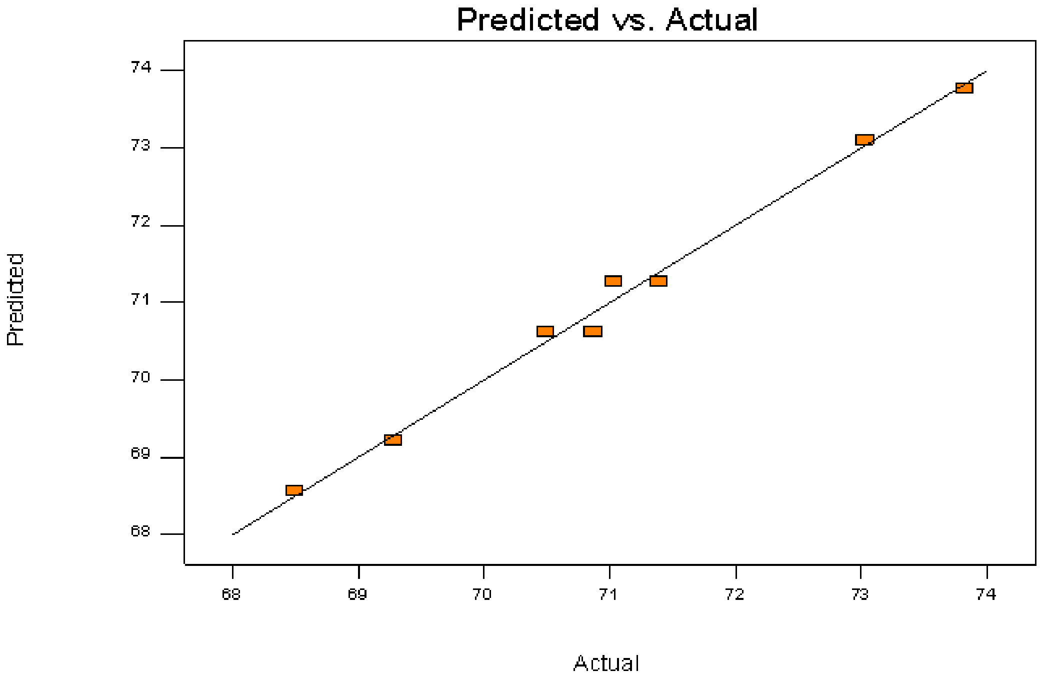


Figure 6.5: Diesel Index (Experimental and Predicted) for 2^2 Factorial Design – Study 1

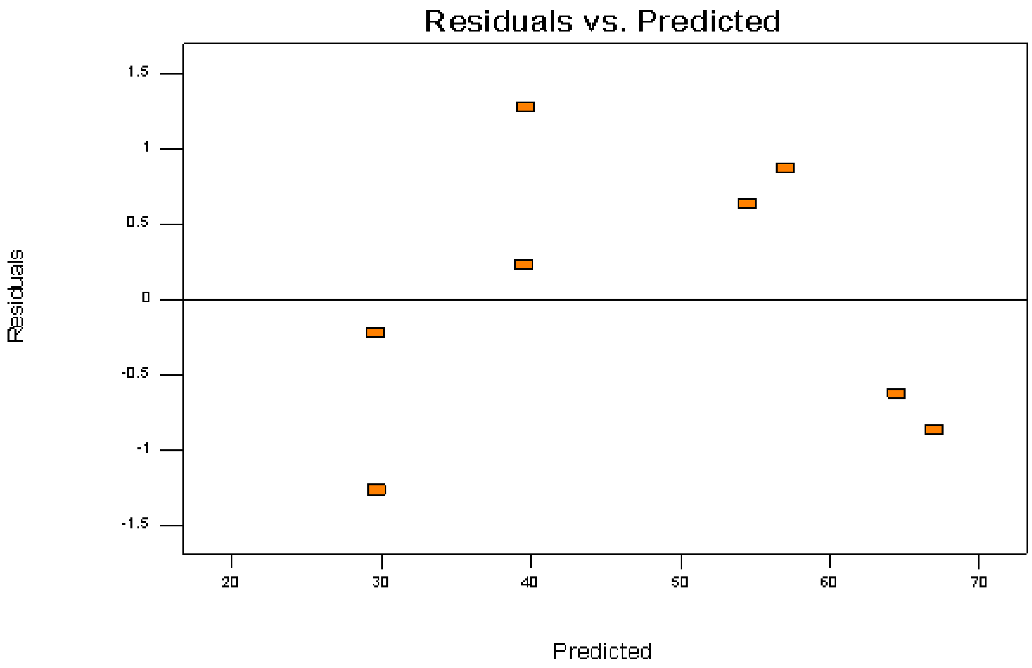


Figure 6.6: Residuals vs. Predicted Values for Sulfur Removal Percentage for 2^2 Factorial Design - Study 1

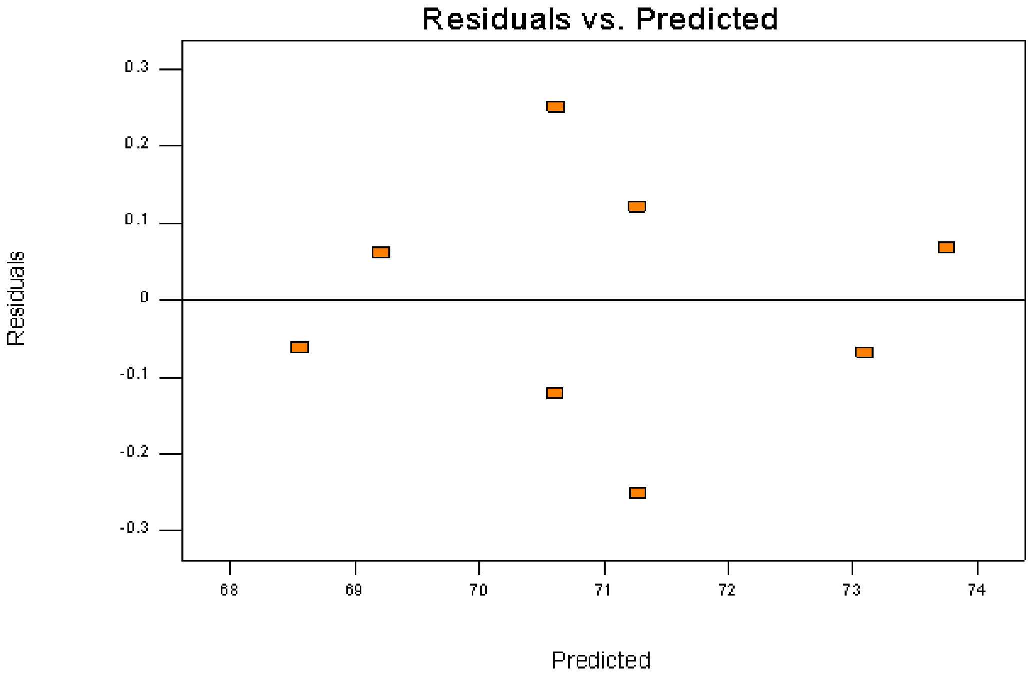


Figure 6.7: Residuals vs. Predicted Values for the Calculated Diesel Indices for 2^2 Factorial Design – Study 1

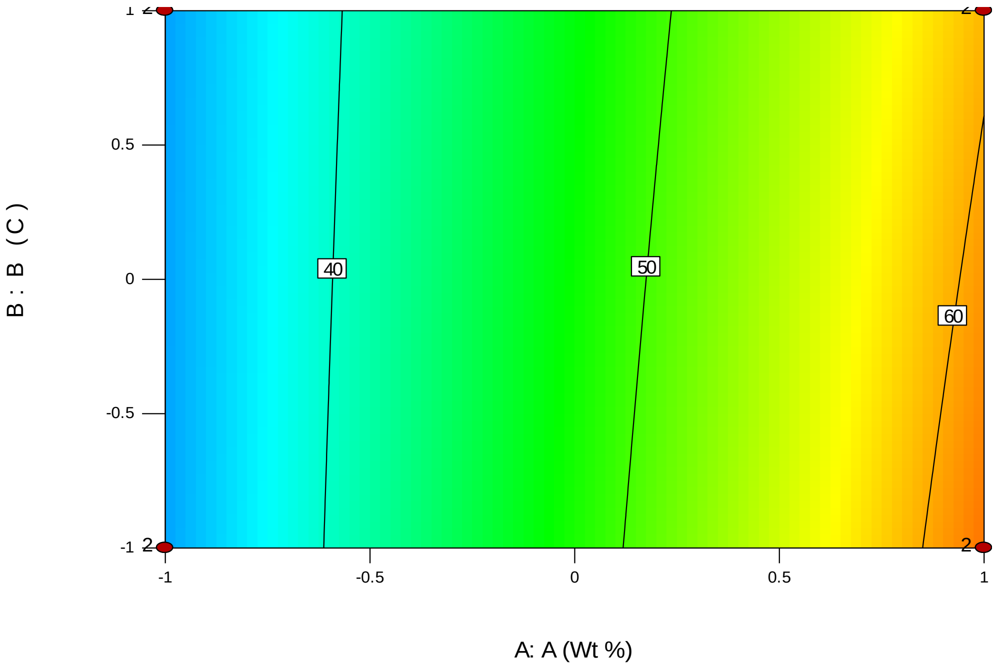


Figure 6.8: Contour Plot for Sulfur Removal Percentage for 2^2 Factorial Design – Study 1

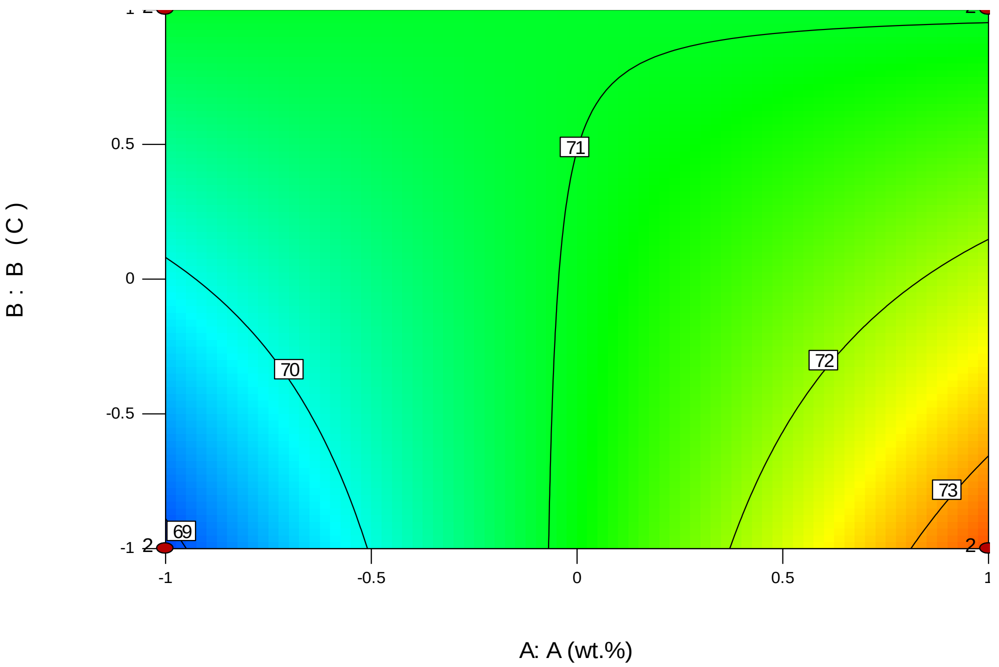


Figure 6.9: Contour Plot for Diesel Index for 2^2 Factorial Design – Study 1

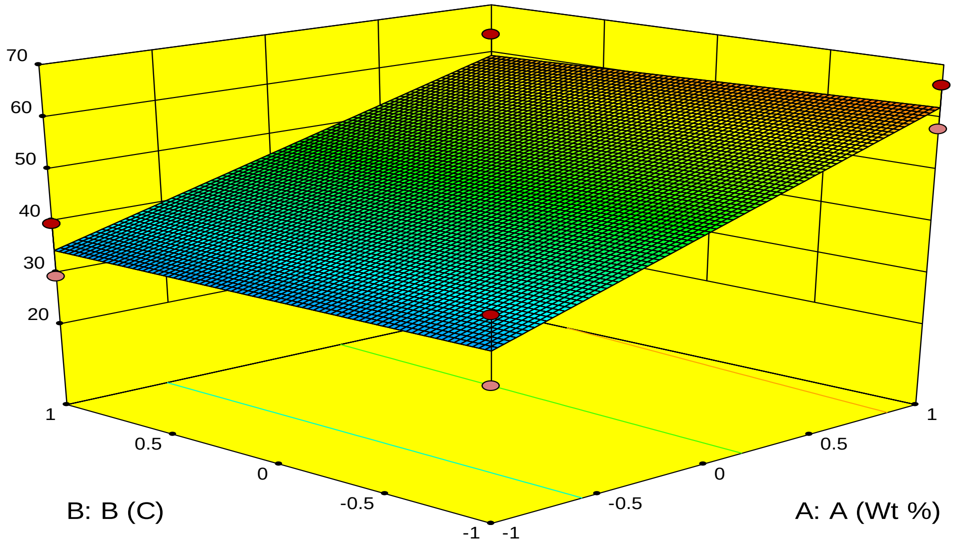


Figure 6.10: 3-D Plot for Sulfur Removal Percentage for 2^2 Factorial Design – Study 1

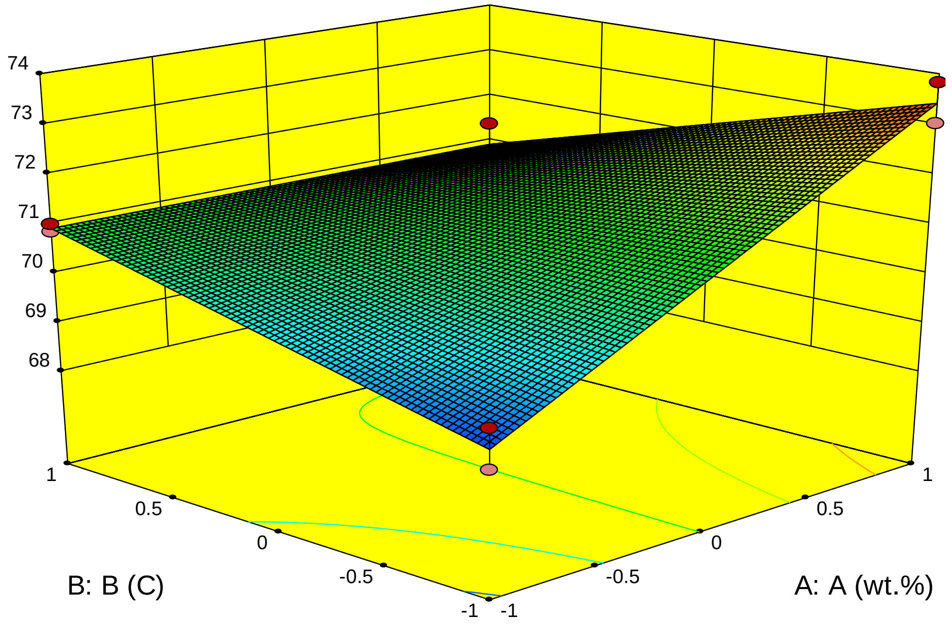


Figure 6.11: 3-D Plot for Diesel Index for 2^2 Factorial Design – Study 1

6.3.2 2^2 Two-level factorial designs – study 2.

From the previous study, by comparing the main effects of the two factors considered for the two response variables, it is noticed that the absolute effect of factor (A) is considerably larger than that of factor (B) (shown in Tables 6.1 and 6.2). This is due to the wide range of the amount of sorbent material used (3 wt. %- 10 wt. %). Thus, for the second 2^2 and the 2^3 factorial designs, different levels were selected for the amount of sorbent materials. Tables 6.3-6.4 show the factorial design results for the second 2^2 factorial design study for the two response variables. From the analysis shown below, the absolute effect of the amount of sorbent material used (A) is greater than the absolute effect of the contact time (B) on the two response variables. This result is also shown in the ANOVA analysis given as the p-value. The p-values for factor A are 0.0012 and 0.0292 (Tables 6.3-6.4). This proves that these model terms are significant as both are less than 0.050. However, the p-values for factor B are 0.0275 and 0.5378 (Tables 6.3-6.4). This shows that this term is significant for the first response variable only. Thus, results show that the amount of sorbent material used is more important than the contact time using PAC1 and PAC2. Moreover, for the two response varaibles considered (sulfur removal percentage, and calculated diesel index), the effects of the two factors (A and B) are positive which proves that as the amount of sorbent material used and the contact time increase, the sulfur removal percentage increases which is physically expected. However, the effect of the amount of sorbent material is more significant in the two cases.

The predictive capability of the generated regression model was also studied (Figures 6.12-6.13). Again, for the two response variables considered, good agreement between both the experimental and predicted values was observed. The differences between the experimental and the predicted values for the two responses were also determined and are shown in Figures 6.14-615. Moreover, 3-D surface plots and contour plots for the two response variables were also generated and are shown in Figures 6.16-6.19. These graphs show that for the first response variable (sulfur removal percentage), there is a slight interaction between the two factors. Whereas, for the second response variable (diesel indices), the interaction between the two factors is significant, indicating that the two factors are dependant.

Table 6.3: Analysis of Sulfur Removal Percentage (Response Variable 1) Data as a 2^2 Factorial Design - Study 2.

Factors				**Low (-1)**			**High (+)**		
A=Amount of Sorbent Material Used, wt %				5			10		
B= Contact Time, hr				0.5			1		
				PAC1	**PAC2**				
Treatments	A	B	AB	y1	y2	Total y	Contrast A×y	Contrast B×y	Contrast AB×y
[1]	-	-	+	51.49	43.01	94.50	-94.50	-94.50	94.50
a	+	-	-	65.78	54.61	120.4	120.4	-120.4	-120.4
b	-	+	-	56.16	49.39	105.5	-105.5	105.5	-105.5
ab	+	+	+	66.16	57.95	124.1	124.1	124.1	124.1
				$\overline{y_1}$	$\overline{y_2}$	β_o			
Effects	11.10	3.690	-1.830	59.90	51.24	55.57			
Regression Model	$55.57+5.555x_1-1.845x_2-0.916x_1x_2$								
ANOVA									

Source of Variations	**Sum of Squares (SS_i)**	**Degrees of Freedom (DOF)**	**Mean Squares (MS_i)**	**F-values**	**P-values**
A	246.8	1	246.8	146.8	0.0012
B	27.24	1	27.24	16.20	0.0275
AB	6.720	1	6.720	3.998	0.1394
Blocks	150.1	1	150.1	89.28	
Error	5.043	3	1.681		
Total	435.9	7			
Model	**280.8**	**3**	**93.60**	**55.68**	**0.004 → Significant**

Table 6.4: Analysis of Diesel Indices (Response Variable 2) Data as a 2^2 Factorial Design – Study 2.

Factors				**Low (-1)**			**High (+)**		
A=Amount of Sorbent Material Used, wt %				5			10		
B= Contact Time, hr				0.5			1		
				PAC1	**PAC2**				
Treatments	A	B	AB	y1	y2	Total y	Contrast A×y	Contrast B×y	Contrast AB×y
[1]	-	-	+	70.84	70.89	141.7	-141.7	-141.7	141.7
a	+	-	-	71.35	70.91	142.3	142.3	-142.3	-142.3
b	-	+	-	70.25	69.23	139.5	-139.5	139.5	-139.5
ab	+	+	+	73.83	71.88	145.7	145.7	145.7	145.7
				$\overline{y_1}$	$\overline{y_2}$	β_o			
Effects	1.691	0.298	1.426	71.56	70.73	71.15			
Regression Model	$71.\ 15+0.8455x_1+0.1489x_2+0.7129x_1x_2$								
ANOVA									

Source of Variations	**Sum of Squares (SS_i)**	**Degrees of Freedom (DOF)**	**Mean Squares (MS_i)**	**F-values**	**P-values**
A	5.720	1	5.720	15.50	0.0292
B	0.178	1	0.178	0.481	0.5378
AB	4.066	1	4.066	11.02	0.0451
Blocks	1.405	1	1.405	3.809	
Error	1.107	3	0.369		
Total	12.48	7			
Model	**9.960**	**3**	**3.320**	**9.000**	**0.0520→ not Significant**

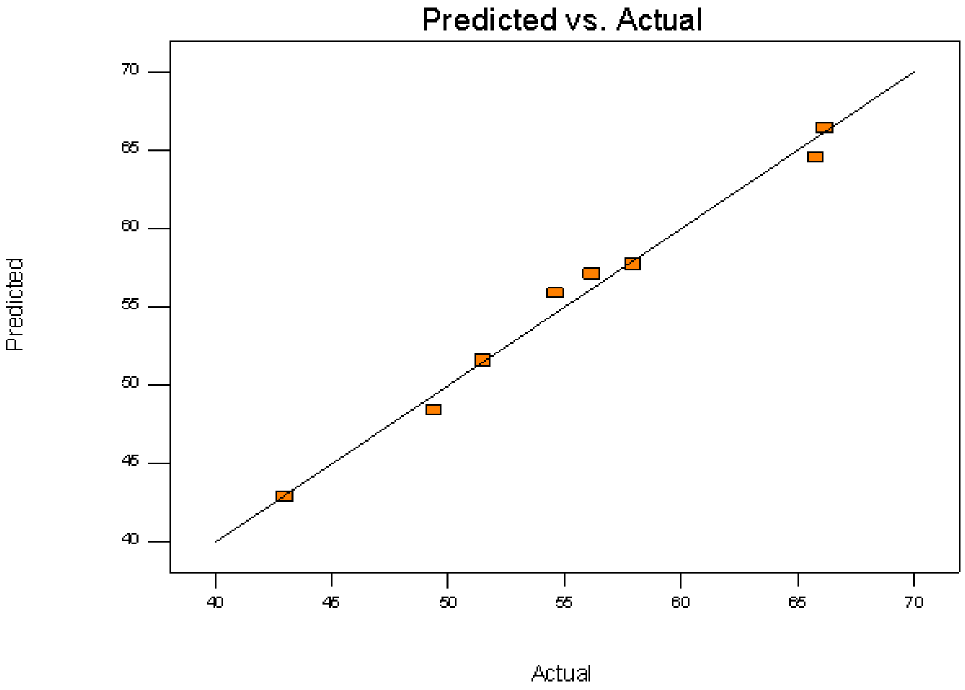


Figure 6.12: The Sulfur Removal Percentage (Experimental and Predicted) for 2^2 Factorial Design – Study 2

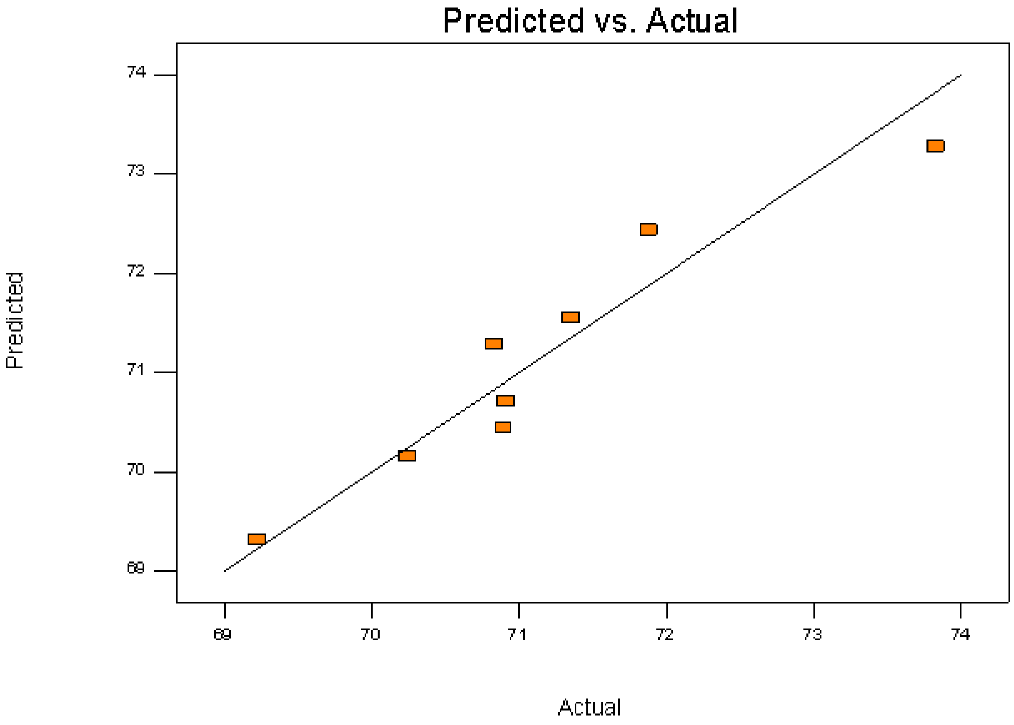


Figure 6.13: Diesel Index (Experimental and Predicted) for 2^2 Factorial Design – Study 2

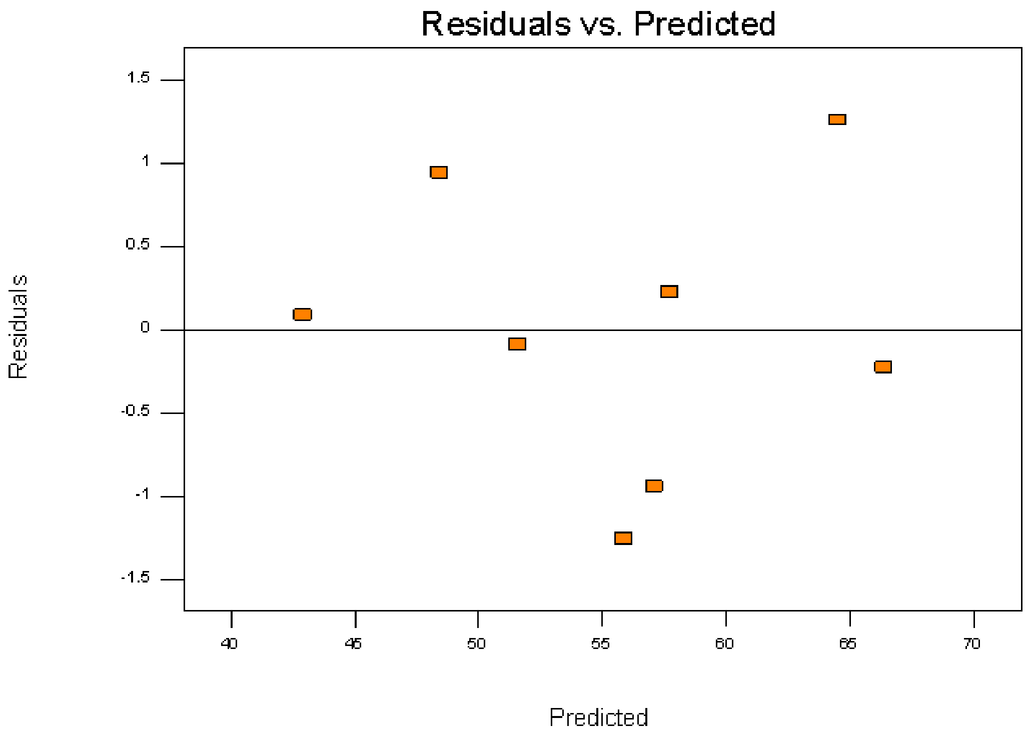


Figure 6.14: Residuals vs. Predicted Values for Sulfur Removal Percentage for 2^2 Factorial Design - Study 2

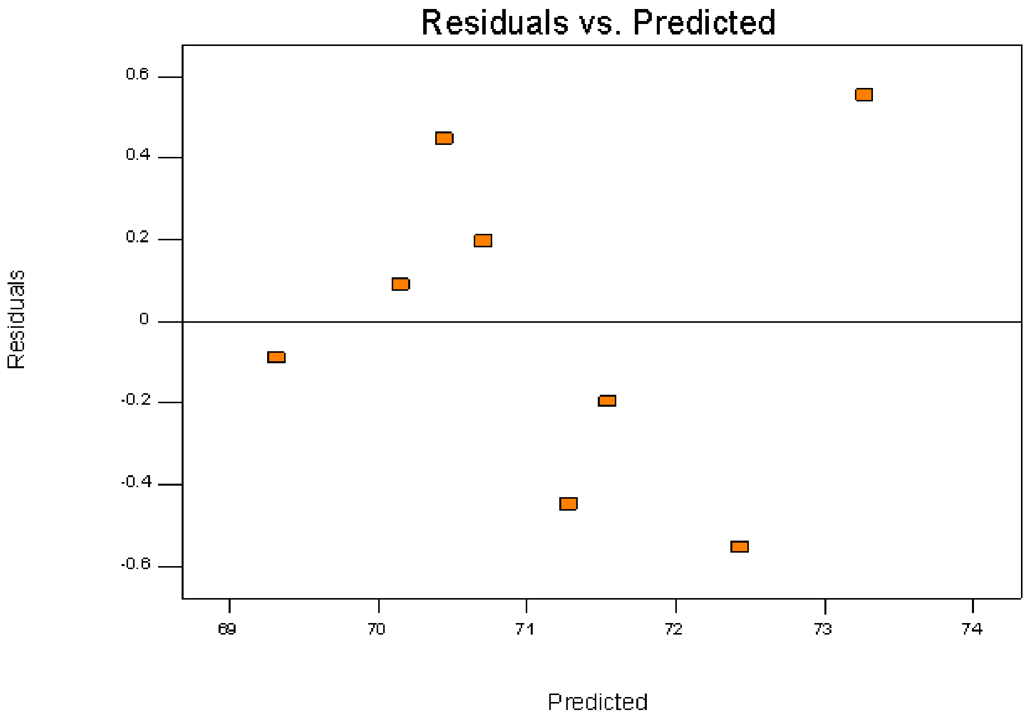


Figure 6.15: Residuals vs. Predicted Values for the Calculated Diesel Indices for 2^2 Factorial Design – Study 2

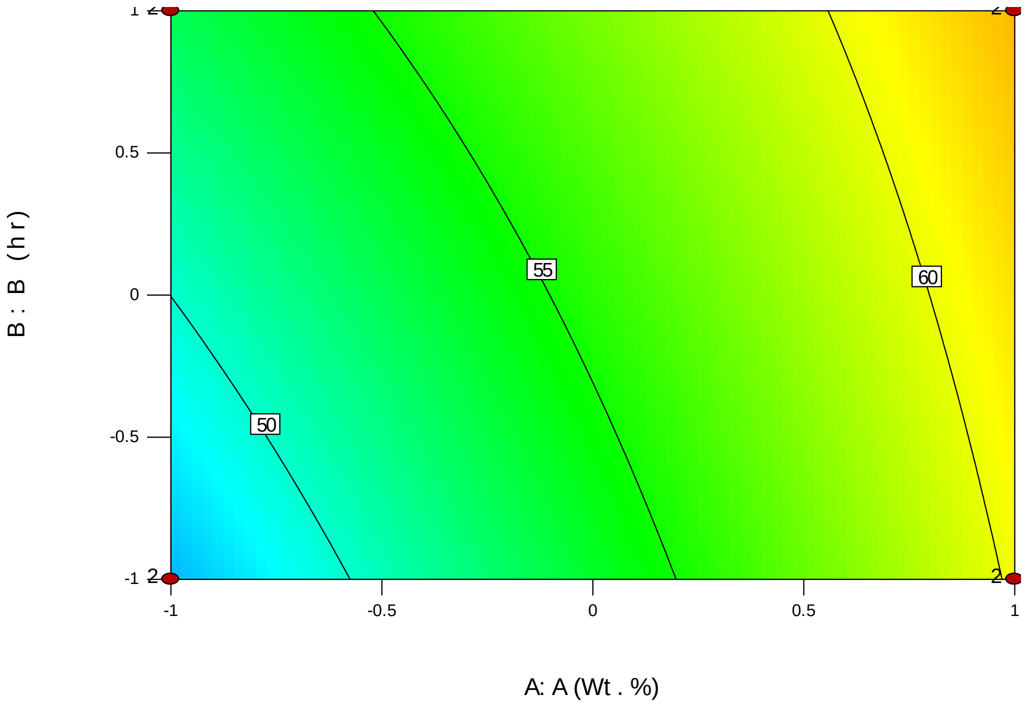


Figure 6.16: Contour Plot for Sulfur Removal Percentage for 2^2 Factorial Design – Study 2

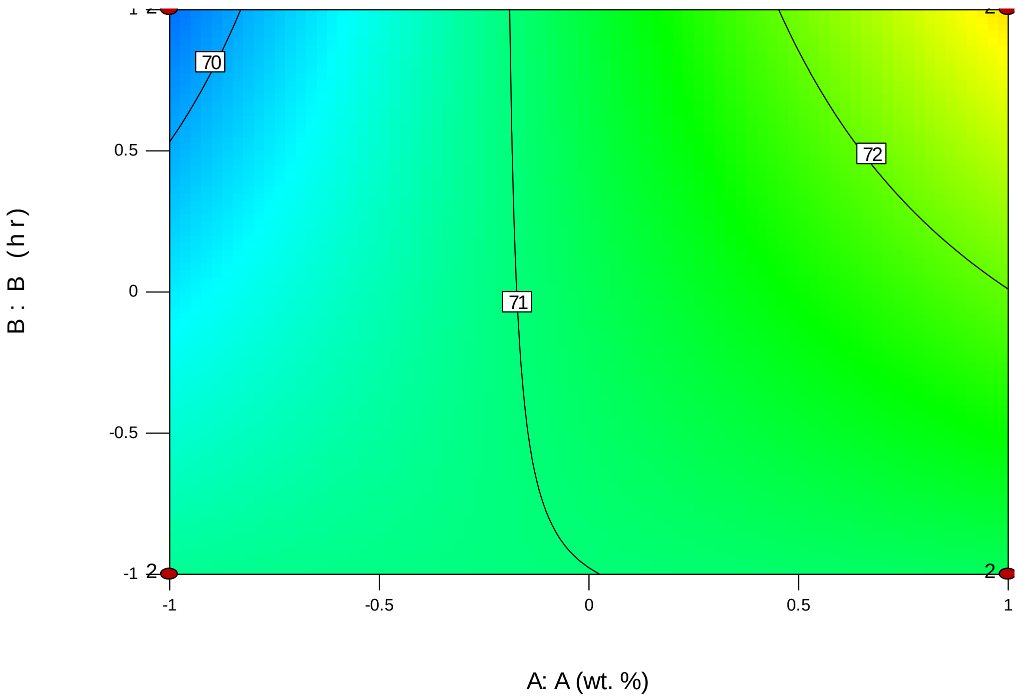


Figure 6.17: Contour Plot for Diesel Index for 2^2 Factorial Design – Study 2

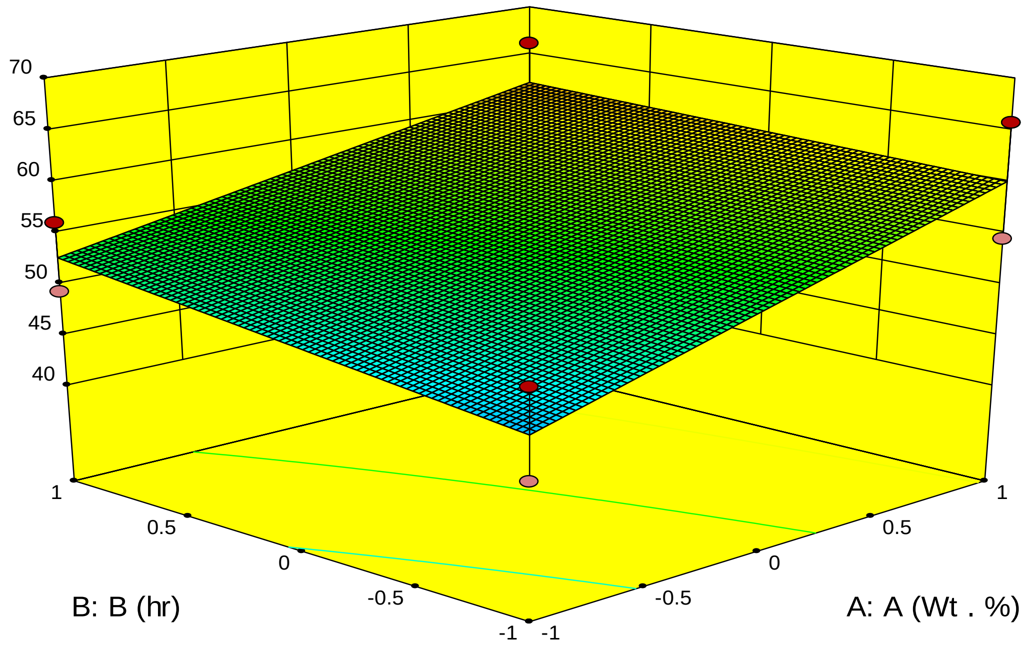


Figure 6.18: 3-D Plot for Sulfur Removal Percentage for 2^2 Factorial Design – Study 2

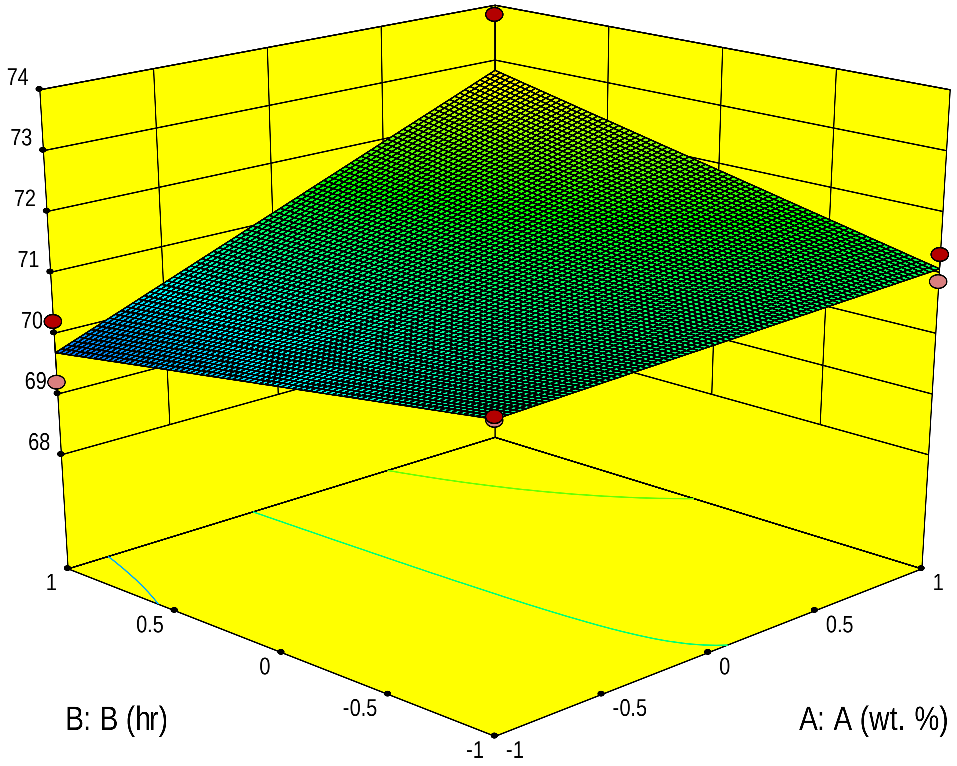


Figure 6.19: 3-D Plot for Diesel Index for 2^2 Factorial Design – Study 2

6.3.3 2^3 Factorial designs.

In the 2^3 factorial design considered, eight runs were conducted for each source of the sorbent materials (PAC1 and PAC2) where three factors each at two levels (high and low) were studied. The two response variables considered are similar to those considered in the previous studies, which are the sulfur removal percentage and the calculated diesel index. The three factors considered were: amount of sorbent material (A), temperature (B) and contact time (C). In comparison with the previous study, the two levels of the amount of sorbent material (A) were: 5 wt. % and 10 wt. % instead of 3 wt. % and 10 wt. %. This is due to the fact that the wide interval selected previously gives a high value for the main effect of factor (A) compared to the main effect of the temperature (B) and the interaction between the two factors (AB). The two levels for the operating temperature were similar to those considered in the previous study: 25 ^oC and 50 ^oC, and the two levels for the contact time (C) were 0.5 hr and 1 hr.

Tables 6.5 and 6.6 represent the design matrix, main effects, and interactions between factors, the generated regression models and the ANOVA analysis. Results in Table 6.5 show a significant (positive) effect of the amount of sorbent material used (factor A), a marginal (negative) effect of the temperature (factor B) and a moderate (positive) effect of the contact time (factor C) on the sulfur removal percentage. These results prove that the amount of sorbent material used is still of major importance in selecting the optimum operating conditions for the adsorptive desulfurization process. The interactions A×B and A×B×C are considered moderate compared with the interactions A×C and B×C. High values of A×C and B×C interactions imply that the effect of amount of sorbent material and the temperature are highly dependent on the contact time. The ANOVA analysis that is shown in the lower part of Table 6.5 confirms the results discussed above at a confidence level of 95%. The regression model generated for the 2^3 factorial designs is also given in Table 6.5. The agreement between the experimental and the predicted values is excellent, which means that there is a linear relationship between the sulfur removal percentage and the considered factors. The predictive capability of this model is explained in Figures 6.20 and 6.22. Moreover, the 3-D surface plots and contour plots were also generated and are shown in Figures 6.24 and 6.26.

Different results were obtained for the second response variable. Results show that changing the low level of factor (A) has a significant impact on the calculated diesel indices. Results in Table 6.6 illustrate the main effects of the three factors considered on the calculated diesel indices, which are: a positive effect of the amount of sorbent material used (factor A), a significant (negative) effect of the temperature (factor B) and again a positive effect of the contact time (factor C). However, results show that the main effects of factors A and C are comparable. Besides, the analysis shows that the operating temperature is of major importance as it shows the highest absolute impact on the calculated diesel indices. The interactions A×B and A×B×C are considered moderate compared with the interaction A×C. High values of A×C interactions indicate an effect of amount of sorbent material that is highly dependent on the contact time. However, the interactions between the operating temperature and the contact time are weak.

The ANOVA analysis shown in the lower part of Table 6.6 proves the results discussed above at a confidence level of 95%. The regression model generated for the 2^3 factorial designs using the eight runs conducted using each sorbent material is also given in Table 6.6. As shown in Figure 6.21, the agreement between the experimental and the predicted values is excellent. This indicates that there is a linear relationship between the calculated diesel indices and the three factors considered. Figure 6.23 shows the residuals calculated for each run, which proves the ability of the generated model to represent the data. 3-D surface plots and contour plots for the second response variable were also generated and are shown in Figures 6.25 and 6.27. These graphs prove the validity of conclusions presented earlier regarding the interactions between the three factors.

Table 6.5: Analysis of Sulfur Removal Percentage (Response Variable 1) Data as a 2^3 Factorial Design.

Factors	Low (-1)	High (1)
A = amount of sorbent material used wt.%	5	10
B = temperature °C	25	50
C = contact time (hr)	0.5	1

Run	A	B	C	PAC1	PAC2	Total	A×y	B×y	C×y	(A×B) ×y	(A×C) ×y	(B×C) ×y	(A×B ×C)×y
				y_1	y_2								
[1]	-	-	-	51.49	38.87	90.36	-90.36	-90.36	-90.36	90.36	90.36	90.36	-90.36
a	+	-	-	65.78	54.61	120.4	120.4	-120.4	-120.4	-120.4	-120.4	120.4	120.4
b	-	+	-	51.27	43.01	94.28	-94.28	94.28	-94.28	-94.28	94.28	-94.28	94.28
ab	+	+	-	63.07	55.64	118.7	118.7	118.7	-118.7	118.7	-118.7	-118.7	-118.7
c	-	-	+	56.16	49.39	105.6	-105.6	-105.6	105.6	105.6	-105.6	-105.6	105.6
ac	+	-	+	66.16	57.95	124.1	124.1	-124.1	124.1	-124.1	124.1	-124.1	-124.1
bc	-	+	+	52.37	48.28	100.7	-100.7	100.7	100.7	-100.7	-100.7	100.7	-100.7
abc	+	+	+	63.85	55.16	119.0	119.0	119.0	119.0	119.0	119.0	119.0	119.0
Average				58.77	50.36	54.57							

Effects

A	B	C	AB	AC	BC	ABC
11.42	-0.969	3.198	-0.725	-2.194	-1.529	0.675

Regression Model

$$54.57+25.71x_1-0.480x_2+1.600x_3-0.360x_1x_2-1.100x_1x_3-0.760x_2x_3+0.340x_1x_2x_3$$

ANOVA

Source of Variation	Sum of Squares (SS)	Degrees of freedom (DF)	Mean Squares (MS)	F-value	p-value
A	521.7	1	521.7	152.7	<0.0001
B	3.762	1	3.762	1.101	0.329
C	40.91	1	40.91	11.97	0.011
AB	2.102	1	2.102	0.615	0.459
AC	19.25	1	19.25	5.635	0.049
BC	9.344	1	9.344	2.735	0.142
ABC	1.821	1	1.821	0.533	0.489
Blocks	282.8	1	282.8	82.77	
Error	23.91	7	3.416		
Total	905.6	15			

Table 6.6: Analysis of Calculated Diesel Indices (Response Variable 2) Data as a 2^3 Factorial Design.

Factors	Low (-1)	High (1)
A = amount of sorbent material used wt.%	5	10
B = temperature ºC	25	50
C = contact time (hr)	0.5	1

Run	**A**	**B**	**C**	**PAC1** y1	**PAC 2** y2	**Total** y	**A×y**	**B×y**	**C×y**	**(A×B) ×y**	**(A×C)× y**	**(B×C) ×y**	**(A×B ×C)×y**
[1]	-	-	-	70.84	70.89	141.7	-141.7	-141.7	-141.7	141.7	141.7	141.7	-141.7
a	+	-	-	71.35	70.91	142.3	142.3	-142.3	-142.3	-142.3	-142.3	142.3	142.3
b	-	+	-	69.10	68.48	137.6	-137.6	137.6	-137.6	-137.6	137.6	-137.6	137.6
ab	+	+	-	69.73	68.96	138.7	138.7	138.7	-138.7	138.7	-138.7	-138.7	-138.7
c	-	-	+	71.25	70.77	142.0	-142.0	-142.0	142.0	142.0	-142.0	-142.0	142.0
ac	+	-	+	73.83	71.88	145.7	145.7	-145.7	145.7	-145.7	145.7	-145.7	-145.7
bc	-	+	+	70.44	69.07	139.5	-139.5	139.5	139.5	-139.5	-139.5	139.5	-139.5
abc	+	+	+	71.39	70.49	141.9	141.9	141.9	141.9	141.9	141.9	141.9	141.9
Average				70.99	70.18	70.59							

Effects

A	B	C	AB	AC	BC	ABC
0.963	-1.760	1.110	-0.091	0.552	0.173	-0.238

Regression Model

$$70.59+0.482x_1-0.878x_2+0.553x_3-0.046x_1x_2+0.276x_1x_3+0.086x_2x_3-0.119x_1x_2x_3$$

ANOVA

Source of Variation	**Sum of Squares (SS)**	**Degrees of freedom (DF)**	**Mean Squares (MS)**	**F-value**	**p-value**
A	3.713	1	3.713	19.69	0.003
B	12.34	1	12.34	65.42	<0.0001
C	4.900	1	4.900	25.99	0.0014
AB	0.034	1	0.034	0.178	0.686
AC	1.219	1	1.219	6.465	0.039
BC	0.120	1	0.120	0.634	0.452
ABC	0.226	1	0.226	1.198	0.310
Blocks	2.626	1	2.626	13.92	
Error	1.320	7	0.189		
Total	26.49	15			
Model	**22.55**	**7**	**3.220**	**17.08**	**0.0007**

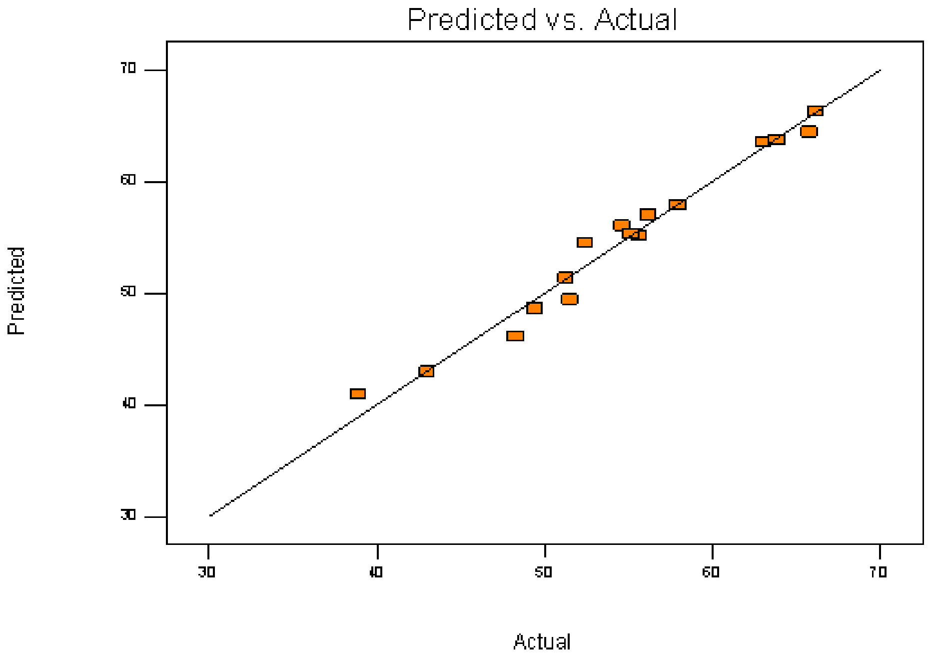


Figure 6.20: Sulfur Removal Percentage (Actual and Predicted) for 2^3 Factorial Design

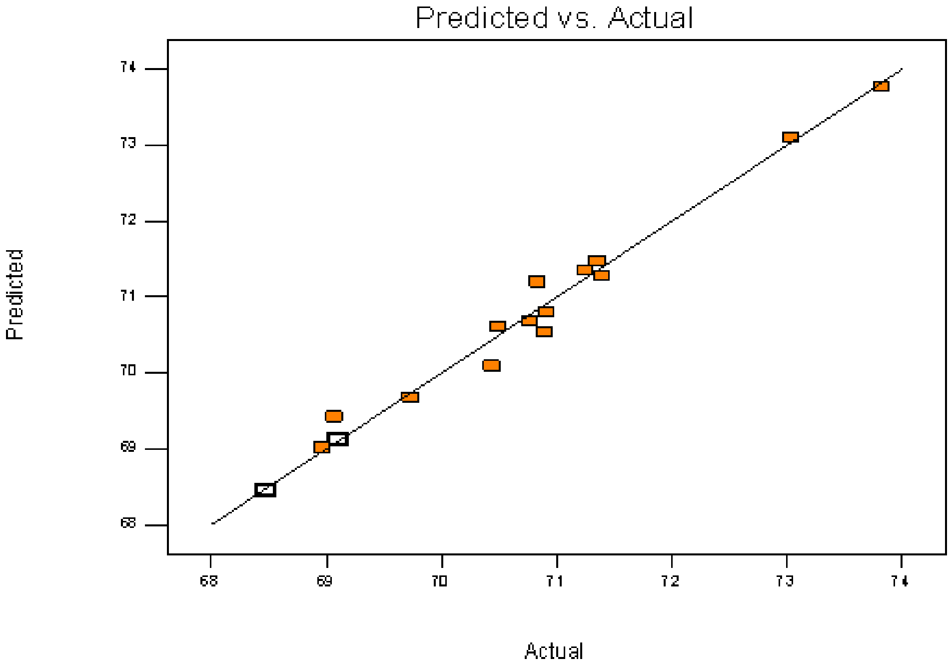


Figure 6.21: Diesel Indices (Actual and Predicted) for 2^3 Factorial Design

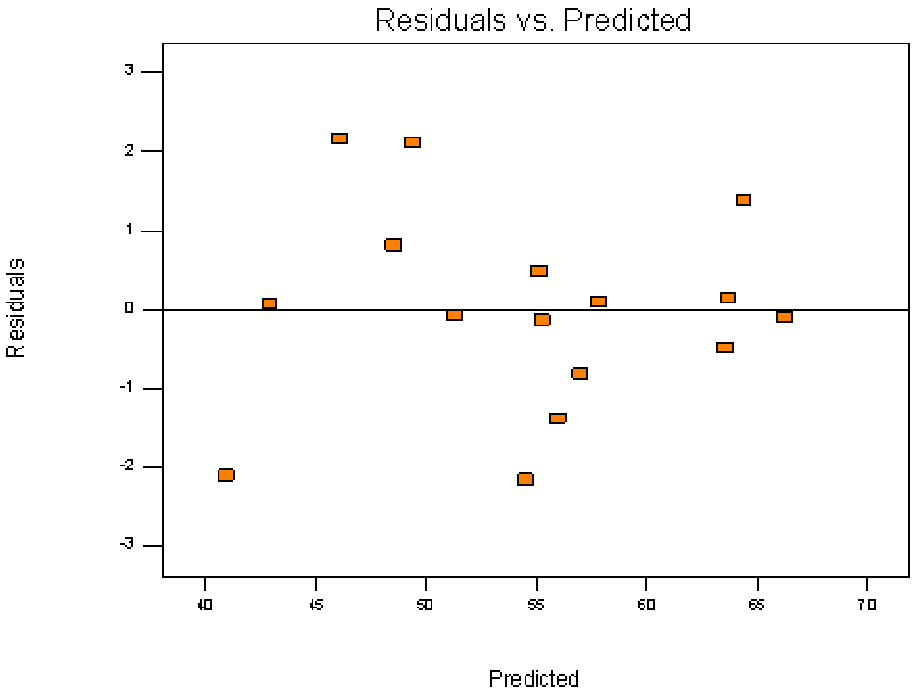


Figure 6.22: Residuals vs. Predicted Values for Sulfur Removal Percentage for 2^3 Factorial Design

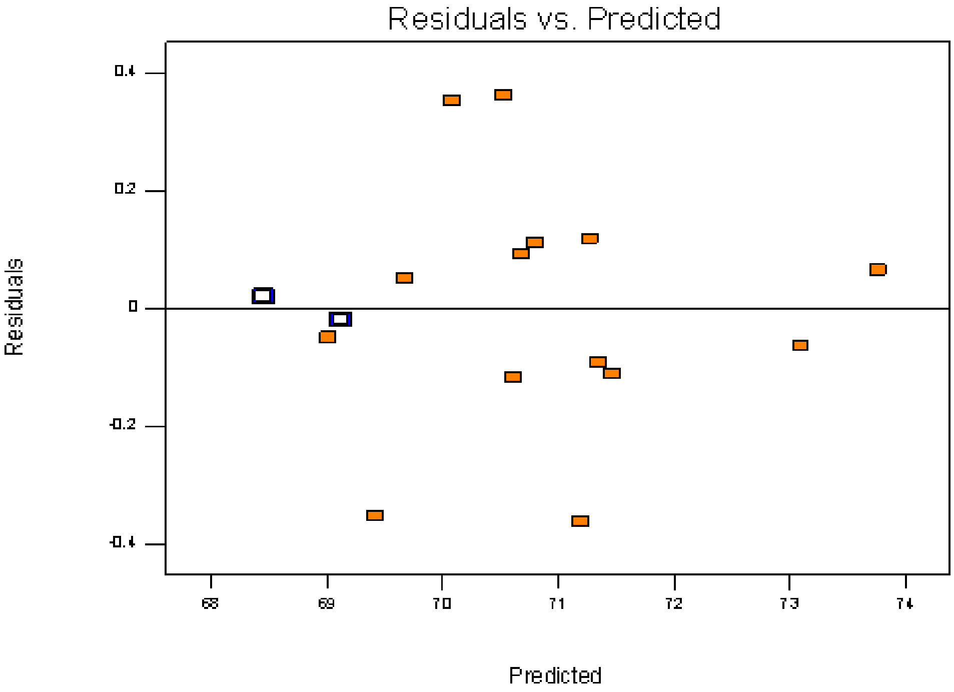


Figure 6.23: Residuals vs. Predicted Values for Calculated Diesel Indices for 2^3 Factorial Design

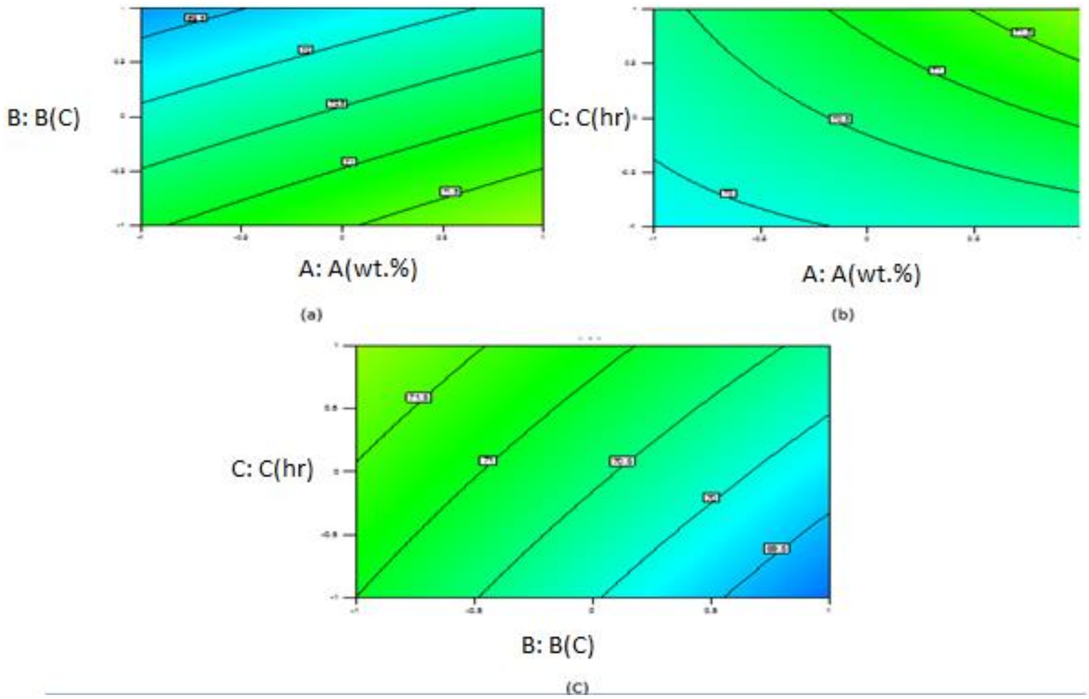


Figure 6.24: Contour Plots for Calculated Diesel Indices for 2^3 Factorial Design, (a) AB, (b) AC, and (c) BC

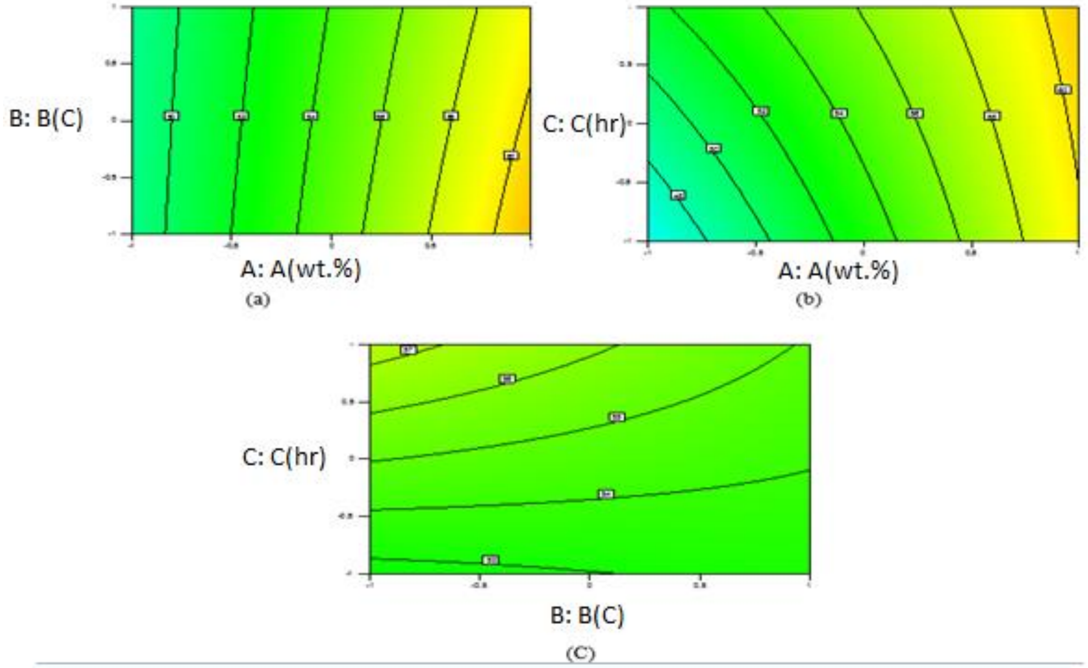
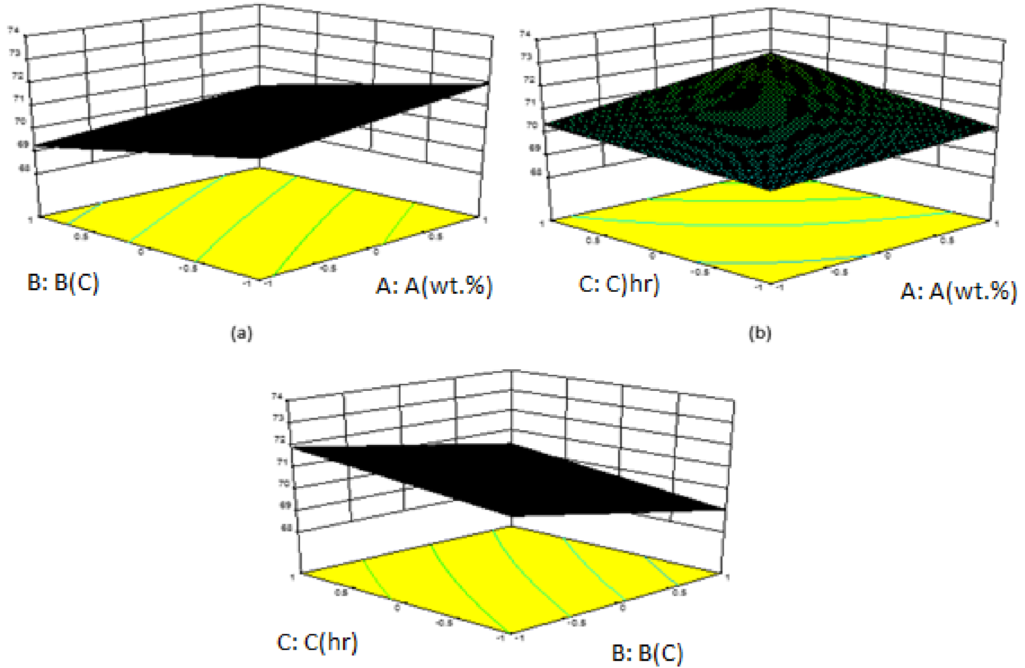


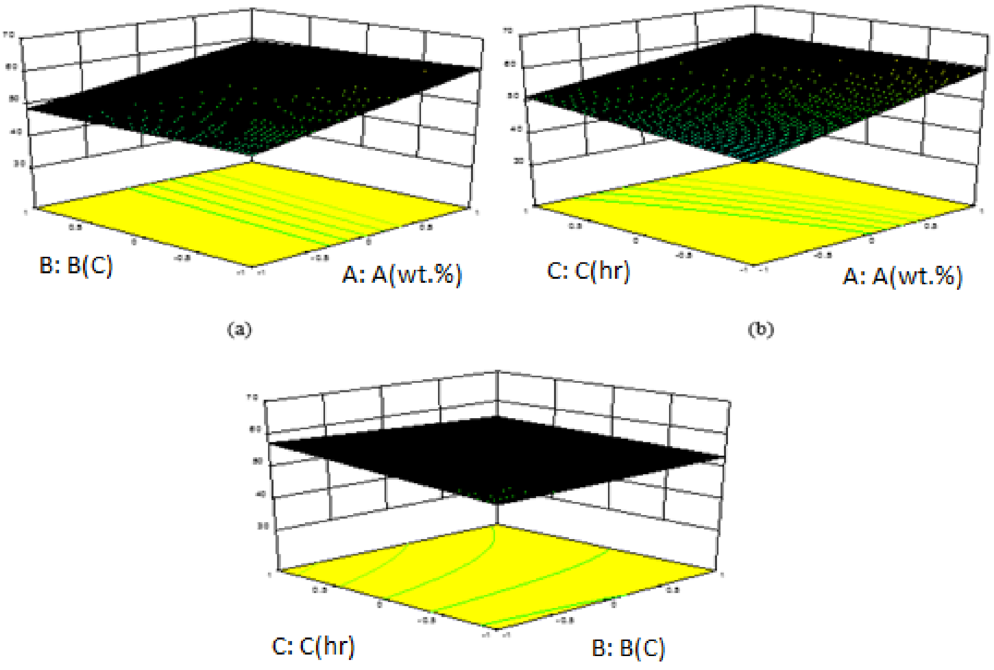
Figure 6.25: Contour Plots for Sulfur Removal Percentages for 2^3 Factorial Design, (a) AB, (b) AC, and (c) BC



(a) (b)

(c)

Figure 6.26: 3-D Plots for Diesel Indices for 2^3 Factorial Design



(a) (b)

(C)

Figure 6.27: 3-D Plots for Sulfur Removal Percentages for 2^3 Factorial Design

6.4 Conclusions

Applying a factorial design analysis helped in identifying the most significant factors affecting the sulfur removal percentages and the calculated diesel indices after the adsorptive desulfurization process of diesel oil. A set of experimental data on the adsorptive desulfurization was analyzed using two 2^2 and one 2^3 factorial designs. For the 2^2 factorial designs, results show that the absolute effect of the amount of sorbent material used (A) is greater than the effect temperature and contact time has on the two response variables considered. For the first 2^2 factorial design study, factor A showed a positive effect on both response variables, showing a direct positive relation between the amount of adsorbent material used and sulfur removal percentage, and the calculated diesel index. However, the effect of factor B was negative with respect to the first response variable, indicating an inverse negative relation between the temperature and sulfur removal percentage, and a positive effect for the calculated diesel indices showing a direct positive relation between the temperature and the calculated diesel index. Furthermore, results show that significant interactions between the two factors were found for the second response variable. For the second 2^2 factorial design study, the effects of the two factors considered showed positive values for the two response variables. Significant interactions between the factors were observed for the two response variables.

In 2^3 factorial design, results showed different results for each response variable. For the first response variable (sulfur removal percentage), results showed that the effect of the amount of sorbent material (factor A) is of major importance. The effect of the contact time is also important as it showed a moderate positive effect; however, the temperature (factor B) showed a weak inverse effect, as expected. The main interactions between the factors considered were A×C and B×C interactions. This indicates that the effect of amount of sorbent material and the temperature depend highly on the contact time. On the other hand, for the second response variable (calculated diesel indices), results showed the following effects: a moderate positive effect of the amount of sorbent material, a significant negative effect of the temperature and a moderate positive effect of the contact time. The main interaction between the factors was between the amount of sorbent material and the contact time (A×C), which means that the amount of sorbent material is highly dependent on the choice of the contact time.

Chapter 7: Results and Discussion - Correlation of Adsorptive Desulfurization Data Using Artificial Neural Networks (ANN)

7.1 Introduction

In this chapter, the set of experimental data generated on adsorptive desulfurization process is correlated and analyzed by ANN. The sulfur removal percentage is correlated with respect to the amount of sorbent material (wt. %) and temperature (^{o}C) using two types of sorbent materials (PAC1 and PAC2). Two input variables and one output variable are considered in this study. Feed-forward ANN in which data is accepted in one direction only will be used with one hidden layer of size 15 for both PAC1 and PAC2. For these studies, the set of data used should be divided into three groups or subsets which are: training, validation and testing subsets. The major part of the experimental data is used in the training step which is conducted usually using trainlm as a training function, where Levenberg-Marquardt optimization tool is used to update results due to its good performance and high efficiency. The ANN is used to generate prediction models to test the agreement between the experimental and the predicted results.

7.2 General Background

ANN is defined as a computational technique that is developed by mimicking the learning skills and the processing methods of human brain and biological cells. Generally, the artificial neurons are organized in a known number of layers and connected by known connections or nodes, so that the information path is recognized. The best number (size) of these hidden layers and connecting nodes should be determined for any set of data in order to improve the capacities and abilities of the network. ANN is described by having a huge number of processing elements that mimic the real human neurons (Figure 7.1). Usually, the connecting nodes have different values which make some of these nodes play more important roles than others. Thus, if a certain node is connected to a number of inputs, the system shows the ability to decide which one is more significant according to the connection weight [123].

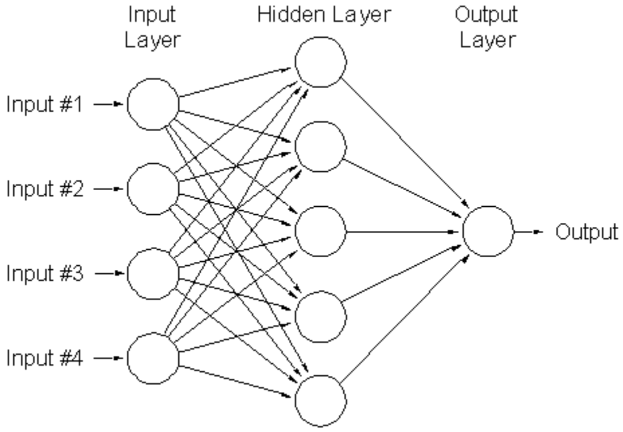


Figure 7.1: Neural Network Diagram [124]

ANN has several architectures, such as feed-forward network, feed-back network, and multilayer feed-forward or (MFF) network; however, the feed-forward ANNs is the most widely used architecture. In this type of ANNs, the information moves from the input to the output layers passing through hidden layers that are composed mainly of neurons. The functions associated with the hidden layers are used to map a certain input to a certain output. The typical transfer function used between the neurons is the sigmoid equation, which is similar to a step function. One useful property of this transfer function is the simplicity of finding its derivative. For the feed-forward ANNs, the inputs are nonlinear functions that can be represented by neurons that are connected in a way that allows a forward flow only (from inputs to outputs) [125].

The steps followed for ANNs modeling are:

- Collecting the inputs (independent variables) and the outputs (dependent variables).
- Selecting the neural network design or architecture.
- Designing the network which includes dividing the available data into three groups: training, validation and testing, and selecting the number of hidden layers.

The numerous applications of ANNs in different research areas led to plenty of important and influential contributions. ANNs are used in different areas, such as: pattern recognition, data fitting, nondestructive testing, forecasting and process control and modeling. ANNs have several advantages in comparison to the other modeling tools, such as regression or empirical modeling tools. This is due to the ability of ANNs as a correlative tool to deal with complex and nonlinear data and to recognize non-numeric inputs or variables [120] [125].

In this chapter, the set of experimental data given in Tables D.1.1 and D.1.2 in Appendix D is correlated using a feed-forward ANN design. Sulfur removal percentages as a function of amount of sorbent material and the temperature are correlated using ANN. This will help in finding prediction models that fit the experimental data using an easy technique in compression with the other polynomial correlation methods.

7.3 ANN Methodology

ANNs are characterized by the node weights and the activation functions selected between the input and the output variables. The ANN error is calculated by comparing the outputs or targets determined from the network with the actual or desired outputs. Initially, the calculated error indicates a great difference between the two calculated outputs. Accordingly, the system minimizes the error by adjusting the nodes weights. This occurs using the back-propagation method where the nodes weights are adjusted based on the information given from the output nodes to the hidden layers.

7.3.1 ANN modeling.

The main units or elements for ANN modeling include:

1- Inputs given as **1, 2,..*I***, which give an input model vector **$x=(x_1, x_2, \ldots x_I)$**.
2- Node connections where the strength of each node is given by its weight and bias. This gives a set of nodes weights **$w= (w_1, w_2 \ldots w_I)$** and biases **$b= (b_1, b_2, \ldots b_I)$.**
3- The activation or transfer function σ which is used for relating the input and the output of the neuron, i.e., such nonlinear transfer functions are used to transform the total or net inputs to the outputs.

The net input (u) to the neuron is related to the weight vector and is given by:

$$u = \sum_{i=1}^{I} w_i x_i + b_i \qquad (7.1)$$

Whereas, the output function y is given by:

$$y = \sigma(u) \tag{7.2}$$

The ANN composed of layers of several neurons that are interconnected with each other. Each ANN is characterized by the inputs model, the design type, number of nodes and hidden layers, the way of connecting the nodes and the transfer function used [126].

7.3.2 Back-propagation algorithm.

As mentioned earlier, part of the experimental data is assigned for the training step. The role of this step is to adjust both the weights and the biases of each node to generate the desired output activation based on each set of inputs. ANN training process can follow either supervised or un-supervised patterns. In the supervised training, there are correct outputs given for each input model externally where these correct outputs are assigned as targets for the ANN. This type of ANN training is the most widely used algorithm. However, for the un-supervised training process, there are no correct outputs or targets. In this case, the network adapts itself to certain behaviors in the system based on the implicit rules.

Network training is concerned with minimizing the error or the sum of squares associated with the models produced for the set of experimental data generated. The sigmoid transfer function (Figure 7.2) and its derivative are given by:

$$\sigma(\mathrm{x}) = \frac{1}{1+e^{-x}} \tag{7.3}$$

$$\frac{d}{dx}\sigma(\mathrm{x}) = \frac{d}{dx}(\frac{1}{1+e^{-x}}) \tag{7.4}$$

$$\frac{d}{dx}\sigma(\mathrm{x}) = -\left(\frac{-e^{-x}}{(1+e^{-x})^2}\right) \tag{7.5}$$

$$\frac{d}{dx}\sigma(\mathrm{x}) = \left(\frac{e^{-x}}{(1+e^{-x})^2}\right) \tag{7.6}$$

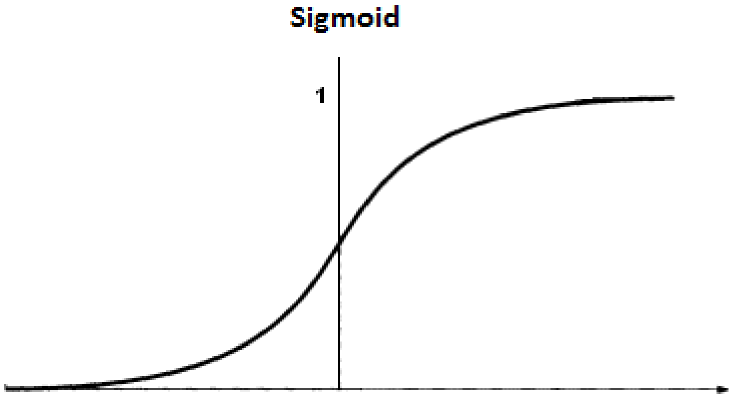


Figure 7.2: Sigmoid Transfer Function

The sum of squares is given by:

$$SSE = \sum_{i=1}^{I} \left(Q_i - \widehat{Q_\iota}\right)^2 \tag{7.7}$$

$$\widehat{Q_\iota} = \sigma_2\left[\sum w\sigma_{\mathrm{i}}\left(\sum wx + b\right) + b\right] \tag{7.8}$$

where Q_i is the observed output or target $\widehat{Q_\iota}$ is the calculated output or target from the generated model and σ_i is the activation or transfer function.

Subscripts 1 and 2 are the activation functions associated with the hidden and outer layers [127].

7.4 Results and Discussion

In this study, the ANN architecture was selected as a feed-forward ANN with fifteen hidden layers. The two input variables considered are the amount of sorbent material wt. % and the temperature °C, and the output variable is the sulfur removal percentage. Figure 7.3 below shows the neural network function used in this study that was generated using MATLAB©. As mentioned earlier, the set of experimental data was divided into three groups. Around 70% of the experimental data was used for the training step. The training function selected for this step is known as trainlm. Trainlm is a good and widely used training function as it updates the results according to Levenberg-Marquardt optimization method.

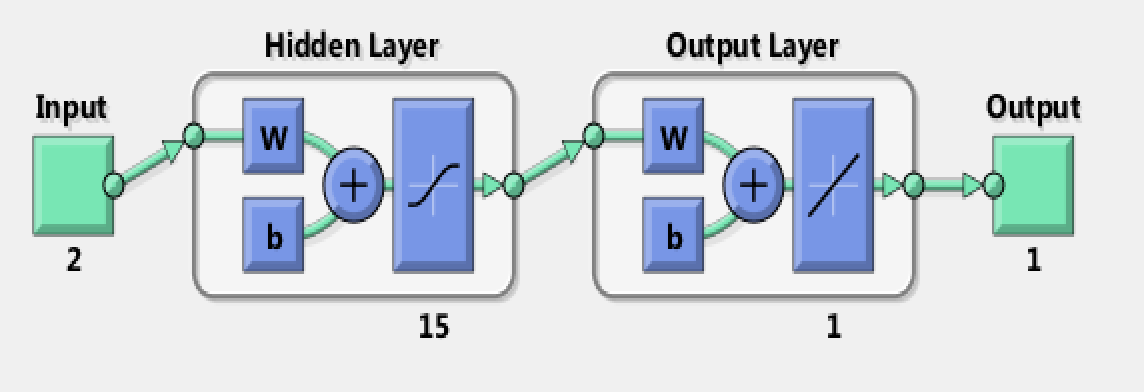
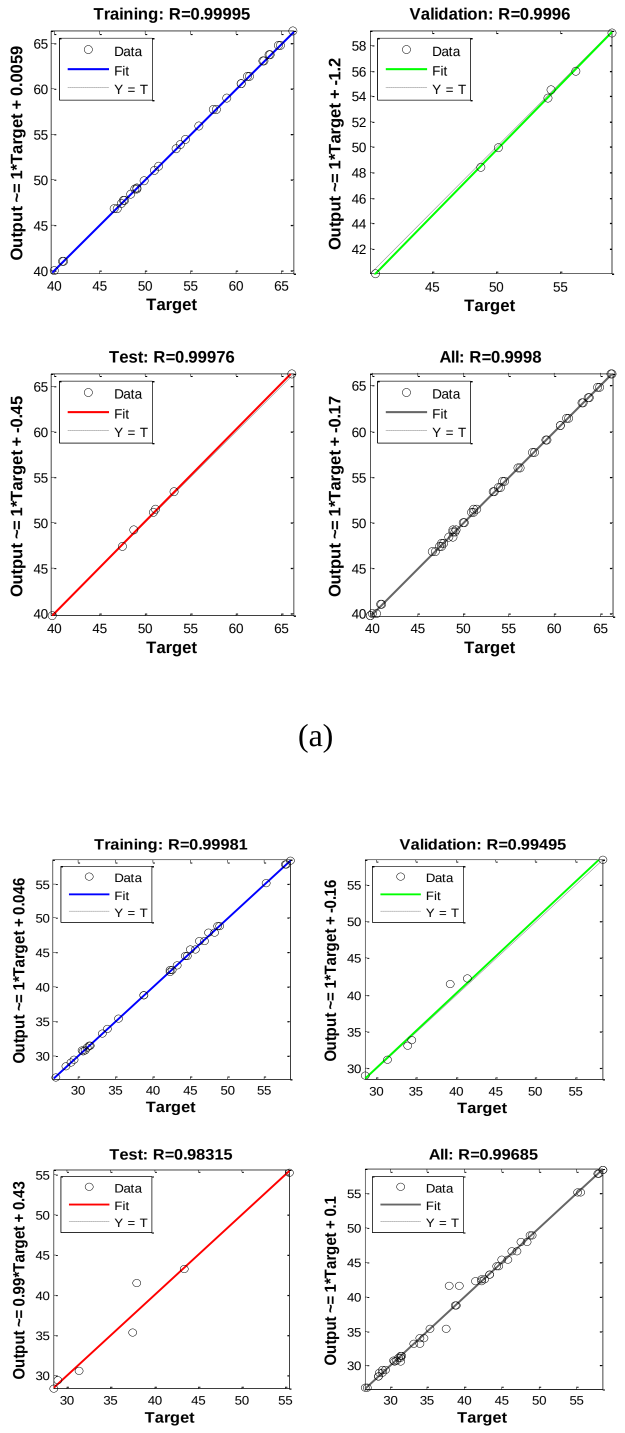


Figure 7.3: Artificial Neural Network Function (Feed-Forward ANN) of the Sulfur Removal Percentage

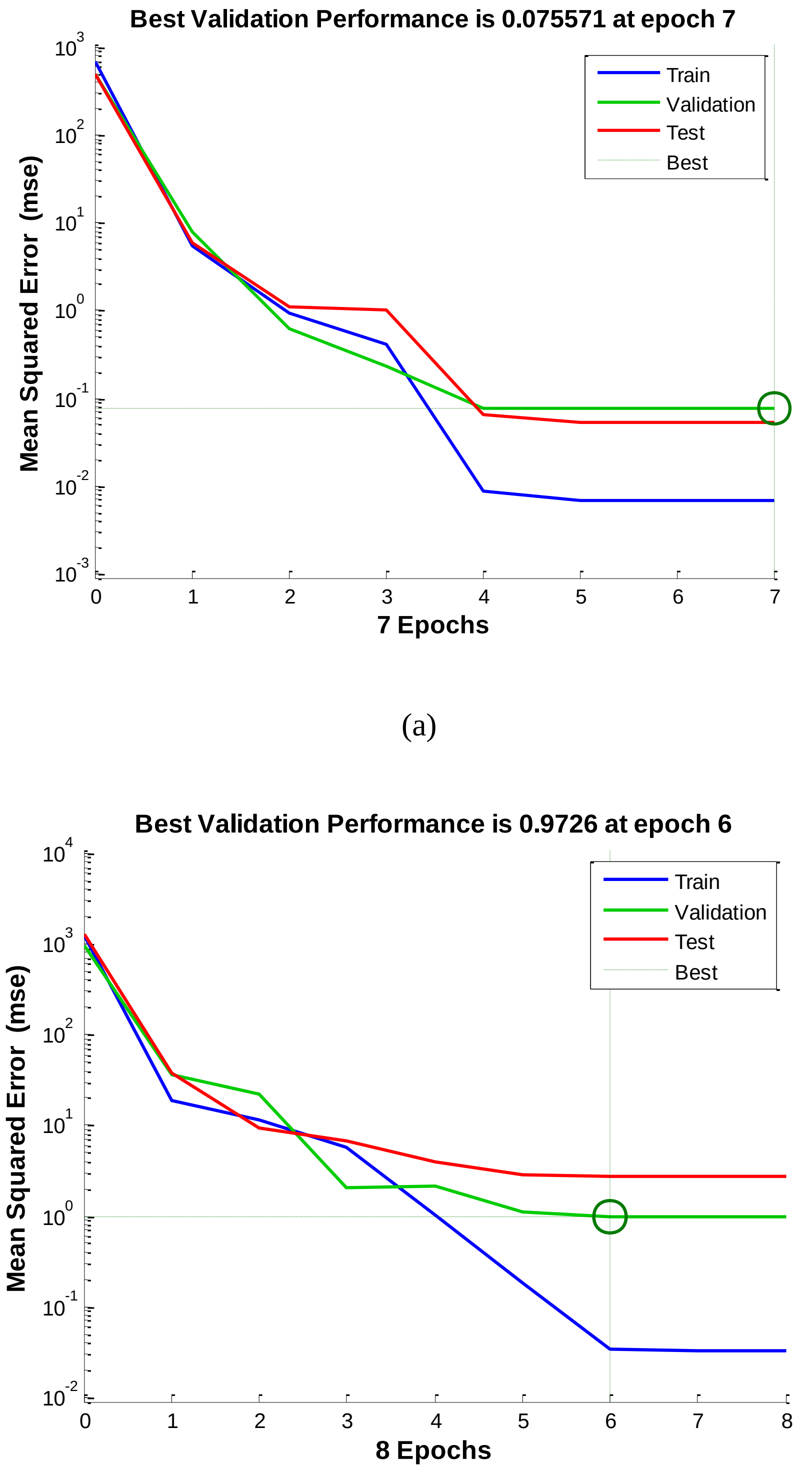
The differences between the experimental and the predicted values were obtained by choosing the sum of squares as a performance function. The main objective of determining the sum of squares is to verify the strength of the correlation generated. Smaller values for the sum of squares represent a strong correlation. The major goal of this study is to test the validity of the generated network. This was achieved by generating the regression plots as shown in Figure 7.4. The two lines on each graph represent the perfectly matching results (dashed line) and the regression model results (solid line). The extent of agreement between the experimental and the predicted values is determined by the correlation coefficients given at the top of each graph. Results show that an excellent fit was attained for the sulfur removal percentage using both PAC1 and PAC2 where the correlation coefficients found are 0.9998 and 0.99658 using PAC1 and PAC2, respectively (Figure 7.4). Moreover, the performance of the ANN for the two cases is shown in Figure 7.5. Results show that the correlations associated with both PAC1 and PAC2 are strong and can represent the experimental data. This is proved by the low values for the performance function which represent a strong correlation.



(a)

(b)

Figure 7.4: Regression Plots for Sulfur Removal Percentages for (a) PAC1 and (b) PAC2 Using Artificial Neural Network



(a)

(b)

Figure 7.5: Artificial Neural Network (ANN) Performance Function for (a) PAC1 and (b) PAC2

7.5 Conclusions

The set of experimental data generated on adsorptive desulfurization process was correlated using ANN. The sulfur removal percentages found using the two sorbent materials (PAC1 and PAC2) were correlated using a feed-forward ANN with a hidden layer of size 15. ANN showed excellent agreement between the experimental and the predicted values of sulfur removal percentages using both PAC1 and PAC2. This was proved by the correlation coefficients of 0.9998 and 0.99658 using PAC1 and PAC2, respectively.

Chapter 8: Findings and Recommendations

8.1 Findings

- For the adsorptive desulfurization process considered, the two powdered activated carbon (PAC1and PAC2) showed a better affinity for sulfur removal compared to the granular activated carbon (GAC).
- The adsorption isotherms for PAC1 and PAC2 were determined using two isotherm models: Langmuir, and Freundlich. Results showed that for both PAC1and PAC2 the adsorption behavior is described better by Freundlich isotherm model at all temperatures considered.
- Kinetic data for the three adsorbents follows a pseudo second-order model. Results indicated that sulfur adsorption kinetic study proved the applicability of the pseudo-second order model. This is confirmed by both the calculated correlation coefficients and the calculated sum of squared errors.
- Adsorptive desulfurization of diesel fuel using activated charcoals showed good performance for sulfur removal and improved the ignition quality of fuel significantly.
- Comparing the ignition quality measure (diesel index) before and after the adsorption process showed a direct increase between the calculated diesel indices and the amounts of sorbent material used. This result was attained at the three temperatures considered. Furthermore, this study showed an inverse effect of the temperature in the calculated diesel indices i.e as the temperature increases, the calculated diesel index decreases.
- The 2^2 factorial design results showed that the effect of the amount of sorbent material used is greater than the effect of the temperature and the contact time on the two response variables considered. This result is also confirmed in the ANOVA analysis given by the p-value. For the two response variables studied using the regression models generated, good agreement between the experimental and predicted values was observed.
- In the 2^3 factorial design, results showed that for the first response variable, the effect of the amount of sorbent material is of major importance. Whereas, for the second response variable, the effect of the operating temperature is the major factor.

- A feed-forward artificial neural network analysis showed an excellent agreement between the experimental values and the predicted values for PAC1and PAC2 using the correlation generated.

8.2 Recommendations

- Based on the results obtained in this work for commercial diesel oil, it is recommended to explore the adsorption capacity of the carbon-based adsorbents for the removal of sulfur compounds from synthetic oil. This will provide essential data for modeling the physical adsorption process.
- Developing an appropriate regeneration method for the spent sorbent materials is worth studying. Considering the adsorption capacity loss of the spent sorbent materials after several adsorption-regeneration cycles is also recommended. This study will help in understanding the main causes of deterioration of the sorbent capacity, as well as optimizing the overall sulfur removal process.

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Appendix A

Adsorptive Desulfurization Results

Table A.1: Results of the Adsorption Process

Run #	Sorbent Material	Amount of Sorbent Material (wt. %)	Temperature ^0C	Contact Time (hr)	Sulfur Concentration	% Sulfur Removal	Diesel Indices
PAC1							
1	PAC1	3	25	1	235.4	40.95	69.28
2	PAC1	4	25	1	205.5	48.41	-
3	PAC1	5	25	1	174.6	56.16	70.25
4	PAC1	6	25	1	185.6	53.40	-
5	PAC1	7	25	1	163.3	59.00	-
6	PAC1	8	25	1	153.2	61.54	-
7	PAC1	9	25	1	146.7	63.17	-
8	PAC1	10	25	1	134.8	66.16	73.83
9	PAC1	3	50	1	239.7	39.82	71.03
10	PAC1	5	50	1	189.7	52.37	70.44
11	PAC1	10	50	1	144.0	63.85	71.39
12	PAC1	3	25	2	227.5	42.88	70.74
13	PAC1	5	25	2	162.2	59.28	69.86
14	PAC1	10	25	2	130.7	67.19	74.04
15	PAC1	3	50	2	254.3	36.15	69.33
16	PAC1	5	50	2	179.0	55.06	69.86
17	PAC1	10	50	2	169.6	57.42	71.52
18	PAC1	3	30	1	238.8	40.05	64.63
19	PAC1	5	30	1	200.2	49.74	69.72
20	PAC1	10	30	1	140.7	64.68	73.21
21	PAC1	5	25	0.5	193.2	51.49	70.84
22	PAC1	5	50	0.5	194.1	51.27	69.10
23	PAC1	10	25	0.5	136.3	65.78	71.35
24	PAC1	10	50	0.5	147.1	63.07	69.73
PAC2							
1	PAC2	3	25	1	284.9	28.47	68.49
2	PAC2	4	25	1	275.0	30.48	-

3	PAC2	5	25	1	201.6	49.39	69.23
4	PAC2	6	25	1	228.8	42.63	-
5	PAC2	7	25	1	222.9	44.29	-
6	PAC2	8	25	1	213.8	46.32	-
7	PAC2	9	25	1	204.3	48.71	-
8	PAC2	10	25	1	167.5	57.95	71.88
9	PAC2	3	50	1	281.1	29.43	70.87
10	PAC2	5	50	1	206.0	48.28	69.07
11	PAC2	10	50	1	178.6	55.16	70.49
12	PAC2	3	25	2	287.8	27.74	69.74
13	PAC2	5	25	2	213.2	46.47	68.45
14	PAC2	10	25	2	167.2	58.02	70.51
15	PAC2	3	50	2	291.9	26.72	70.50
16	PAC2	5	50	2	211.4	47.02	70.62
17	PAC2	10	50	2	200.7	49.61	70.42
18	PAC2	3	30	1	292.3	26.61	64.08
19	PAC2	5	30	1	248.4	37.64	69.60
20	PAC2	10	30	1	165.6	58.42	70.57
21	PAC2	5	25	0.5	227.0	43.01	70.89
22	PAC2	5	50	0.5	243.5	38.87	68.48
23	PAC2	10	25	0.5	180.8	54.61	70.91
24	PAC2	10	50	0.5	176.7	55.64	68.96
GAC							
1	GAC	3	25	1	366.0	8.1094	70.56
2	GAC	4	25	1	354.0	11.12	-
3	GAC	5	25	1	349.0	12.38	-
4	GAC	6	25	1	341.0	14.39	-
5	GAC	7	25	1	323.0	18.91	-
6	GAC	8	25	1	322.0	19.16	-
7	GAC	9	25	1	314.9	20.94	-
8	GAC	10	25	1	315.0	20.91	71.24

Appendix B

B.1. Non-linear langmuir isotherm parameters.

Table B.1.1: Non-Linear Langmuir Isotherm Results for PAC1, and PAC2 at Room Temperature

PAC1		**PAC2**	
$q_{e,exp.}$	$q_{e,calc.}$	$q_{e,exp.}$	$q_{e,calc.}$
3.741	4.105	2.816	3.104
3.413	3.933	2.636	2.962
4.099	4.374	3.072	3.225
4.328	4.965	3.449	3.32
5.463	4.673	3.744	3.553
5.885	5.491	3.764	3.985
6.630	6.279	4.652	4.114
q_m	481.6	q_m	484.0
K_L	5.613E-05	K_L	3.019E-05
Sum of Absolute errors	1.784	Sum of Absolute errors	0.604

Table B.1.2: Non-Linear Langmuir Isotherm Results for PAC1, and PAC2 at 30 °C

PAC1		**PAC2**	
$q_{e,exp.}$	$q_{e,calc.}$	$q_{e,exp.}$	$q_{e,calc.}$
3.151	3.910	1.968	2.776
3.677	4.348	2.339	2.896
3.861	4.389	2.606	2.962
4.763	4.925	3.017	3.012
5.45	5.030	3.510	3.105
6.526	5.431	4.345	3.196
4.470	5.872	1.968	2.776
q_m	298.8	q_m	2468
K_L	8.424E-05	K_L	4.448E-06
Sum of Absolute errors	2.312	Sum of Absolute errors	1.193

Table B.1.3: Non-Linear Langmuir Isotherm Results for PAC1 and PAC2 at 50 °C

PAC1		PAC2	
$q_{e,exp.}$	$q_{e,calc.}$	$q_{e,exp.}$	$q_{e,calc.}$
3.509	3.721	2.911	2.801
2.938	4.013	2.453	2.934
3.783	4.005	2.939	3.097
3.967	4.484	3.191	3.253
4.617	4.612	3.326	3.527
5.368	4.9	3.826	3.67
6.447	5.279	4.389	3.902
q_m	383.4	q_m	247.6
K_L	5.819E-05	K_L	5.512E-05
Sum of Absolute errors	3.1	Sum of Absolute errors	0.574

B.2. Non-linear freundlich isotherm parameters.

Table B.2.1: Non-Linear Freundlich Isotherm Results for PAC1, and PAC2 at Room Temperature

PAC1		**PAC2**	
$q_{e,exp.}$	$q_{e,calc.}$	$q_{e,exp.}$	$q_{e,calc.}$
3.741	3.838	2.816	2.924
3.413	3.625	2.636	2.733
4.099	4.175	3.072	3.091
4.328	4.941	3.449	3.224
5.463	4.559	3.744	3.558
5.885	5.651	3.764	4.202
6.630	6.758	4.652	4.402
K_f	0.005	K_f	0.001
n	0.759	n	0.694
Sum of Absolute errors	1.323	Sum of Absolute errors	0.362

Table B.2.2: Non-Linear Freundlich Isotherm Results for PAC1, and PAC2 at 30 ºC

PAC1		**PAC2**	
$q_{e,exp.}$	$q_{e,calc.}$	$q_{e,exp.}$	$q_{e,calc.}$
3.741	3.279	1.968	2.498
3.413	3.936	2.339	2.761
4.099	3.999	2.606	2.913
4.328	4.878	3.017	3.029
5.463	5.058	3.510	3.257
5.885	5.775	4.345	3.487
K_f	0.001	K_f	4.480E-06
n	0.599	n	0.420
Sum of Absolute errors	0.973	Sum of Absolute errors	0.456

Table B.2.3: Non-Linear Freundlich Isotherm Results for PAC1 and PAC2 at 50 ºC

PAC1		PAC2	
$q_{e,exp.}$	$q_{e,calc.}$	$q_{e,exp.}$	$q_{e,calc.}$
3.509	2.966	2.911	2.536
2.938	3.482	2.453	2.721
3.783	3.468	2.939	2.955
3.967	4.410	3.191	3.184
4.617	4.683	3.326	3.601
5.368	5.326	3.826	3.827
6.447	6.242	4.390	4.201
K_f	6.180E-05	K_f	0.001
n	0.476	n	0.666
Sum of Absolute errors	0.934	Sum of Absolute errors	0.324

Appendix C

Regression Models for Sulfur Removal Percentage and Diesel Index (Hand Calculations)

For the two response variables (sulfur removal percentages, diesel indices), regression models were generated by determining the effects and interactions between the two factors studied.

C.1 Sulfur removal percentage (Blocking).

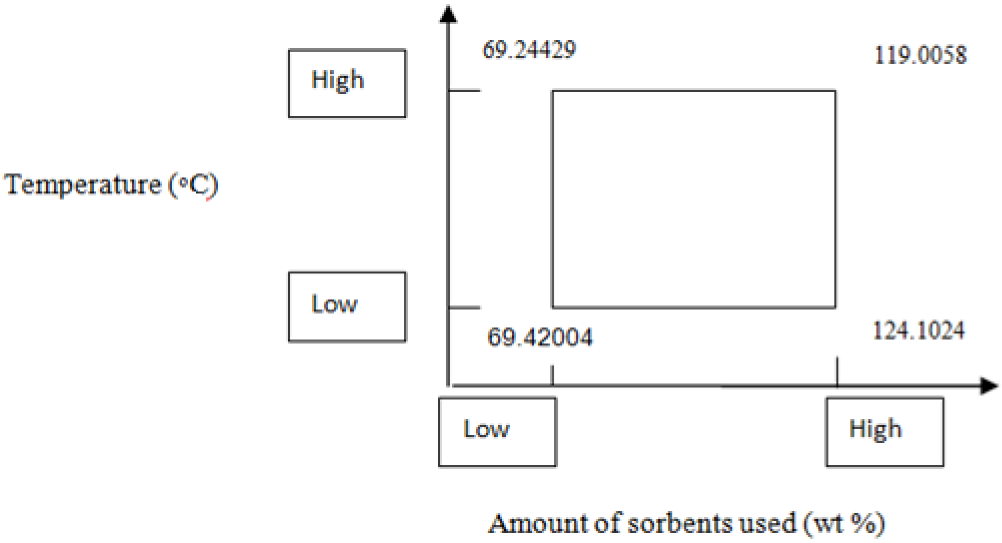

Figure C.1.1: Sulfur Removal Percentage

- **Contrast Calculations**

$$\boldsymbol{C_j = \sum_{i=1}^{i=4} Sign_{ij} in\ the\ design\ matrix \times y_i}$$

C_A =(-69.42)+ (124.10) + (-69.24) + (119.01) =104.45

C_B =(-69.42)+ (-124.10) + (69.24) + (119.01) =-5.272

C_{AB} =(69.42)+ (-124.10) + (-69.24) + (119.01) =-4.921

- **Main Effects Calculations**

$$E_j = \frac{C_j}{(\frac{2^k}{2} * 2)}$$

$$E_A = \frac{104.45}{(\frac{2^2}{2}*2)}=26.11$$

$$E_B = \frac{-5.272}{(\frac{2^2}{2}*2)} =-1.318$$

$$E_{AB} = \frac{-4.921}{(\frac{2^2}{2}*2)} =-1.230$$

Results showed a slight interaction between the two factors.

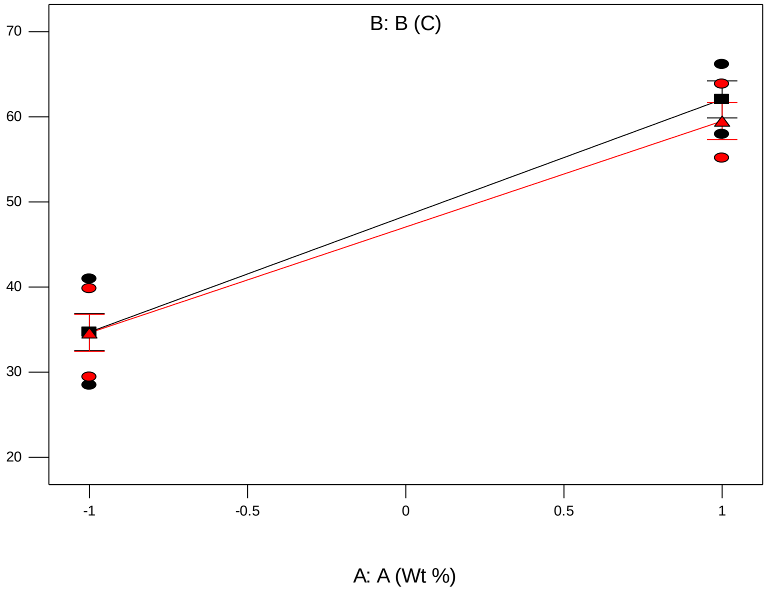

Figure C.1.2: Interaction Effects - Sulfur Removal Percentage

Where A: Amount of Sorbents used (wt. %)

B: Temperature (^{o}C)

- **Regression Models**

$$\beta_1 = \frac{26.11}{2} =13.06$$

$$\beta_2 = \frac{-1.318}{2}=-0.659$$

$$\beta_{12} = \frac{-1.230}{2} =-0.615$$

$$\beta_0 = \frac{\overline{y_1}+\overline{y_2}}{2}=\frac{52.69+42.75}{2}=47.72$$

$y=47.72+13.06x_1-0.659x_2-0.615x_1x_2$

C.2 Diesel indices (Blocking).

- **Contrast Calculations**

$$\boldsymbol{C_j = \sum_{i=1}^{i=4} Sign_{ij}\ in\ the\ design\ matrix \times y_i}$$

C_A =(-137.8)+ (146.9) + (-141.9) + (141.9) = 9.0699

C_B =(-137.8)+ (-146.9) + (141.9) + (141.9) = -0.8499

C_{AB} =(137.8)+ (-146.9) + (-141.9) + (141.9) = -9.1018

- **Main Effects Calculations**

$$E_j = \frac{C_j}{(\frac{2^k}{2} * 2)}$$

$E_A = \frac{9.0699}{(\frac{2^2}{2}*2)}$= 2.268

$E_B = \frac{-0.8499}{(\frac{2^2}{2}*2)}$ = -0.213

$E_{AB} = \frac{-9.1018}{(\frac{2^2}{2}*2)}$ = -2.276

Results showed that an interaction exists between the two factors. Thus, the two factors studied are dependent on each other.

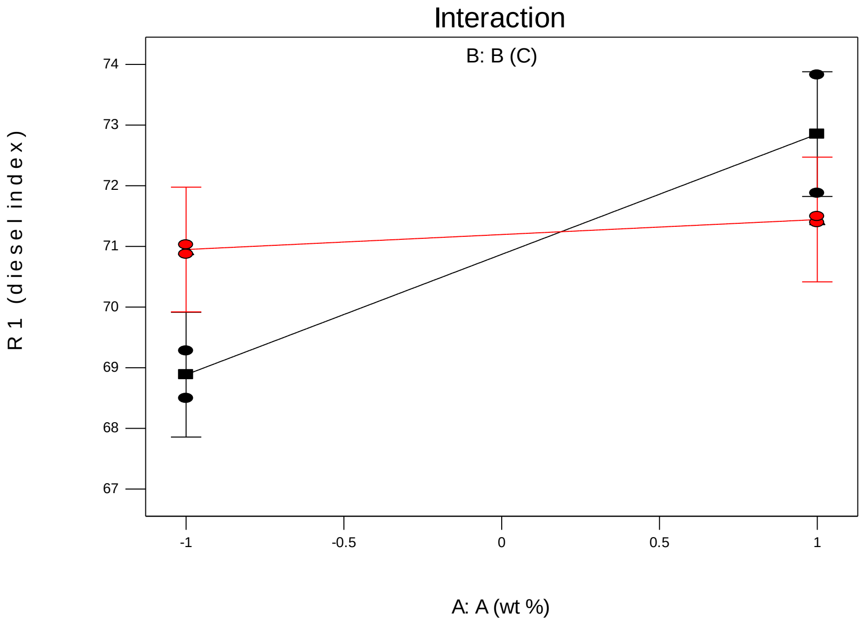

Figure C.2.1: Interaction Effects - Diesel Indices

Where A: Amount of Sorbents used (wt. %)

B: Temperature (^{o}C)

- **Regression Models**

$\beta_1 = \frac{2.2675}{2} = 1.134$

$\beta_2 = \frac{-0.8499}{2}$= -0.106

$\beta_{12} = \frac{2.2755}{2}$ = -1.138

$\beta_0 = \frac{\overline{y_1}+\overline{y_2}}{2}$=$\frac{(71.38+70.721}{2}$= 71.05

y=71.05+1.134x_1-0.106x_2-1.138x_1x_2

Appendix D

D.1 Artificial neural network data

Table D.1.1: Sulfur Content (ppm) Experimental Data for ANN (PAC1)

Temperature ($_{o}$C)	Amount of PAC1 (wt. %)							
	3	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Room Temperature	235.4	205.5	174.6	185.6	163.6	146.7	153.2	134.8
30	237.9	219.8	203.3	198.9	176.9	175.3	157.4	140.3
50	239.9	222.5	209.3	203.4	181.4	181.8	168.4	144.4

Table D.1.2: Sulfur Content (ppm) Experimental Data for ANN (PAC2)

Temperature (^{o}C)	Amount of PAC2 (wt. %)							
	3	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Room Temperature	284.0	275.1	245.0	228.0	222.2	204.0	213.8	167.5
30	291.6	283.3	274.8	270.3	264.2	253.3	244.6	165.5
50	290.5	273.0	262.1	241.5	229.8	217.5	207.6	177.9

D.2 Artificial neural network input-output script files

```
% Neural Network (ANN) for adsorptive desulfurization experimental data
                              %using PAC1

% Y (Sulfur removal percentage): response variable 1
Y = [40.95 48.41 50.89 53.40 40.47 47.80 48.81 50.14 39.82 46.95 47.38
48.83 59.13 61.26 63.04 66.36 54.03 56.24 60.63 64.67 51.14 54.48 57.85
63.65 41.05 48.81 51.09 53.23 40.05 47.63 49.13 49.96 39.72 46.62 47.55
49.06 59.00 61.54 63.17 66.16 53.85 55.99 60.58 64.90 51.49 54.26 57.59
63.85];
% C (Temperature): input variable 1
C = [25 25 25 25 30 30 30 30 50 50 50 50 25 25 25 25 30 30 30 30 50 50
50 50 25 25 25 25 30 30 30 30 50 50 50 50 25 25 25 25 30 30 30 30 50 50
50 50];
% A (Amount of sorbent material used): input variable 2
A = [3 4 5 6 3 4 5 6 3 4 5 6 7 8 9 10 7 8 9 10 7 8 9 10 3 4 5 6 3 4 5 6
3 4 5 6 7 8 9 10 7 8 9 10 7 8 9 10];
% I (Temperature and amount of sorbent material used), or the input
design matrix
IN= [C; A];
Input-variables = IN;
Output-variables = Y;


% Neural Network (ANN) for adsorptive desulfurization experimental data
                              %using PAC2

% Y2 (Sulfur removal percentage): response variable 1
y2 = [28.47 30.48 38.84 42.63 26.99 28.97 31.41 31.18 29.43 31.51 33.92
41.48 44.61 46.92 49.03 57.76 33.14 35.32 37.91 58.42 43.26 44.99 47.53
55.54 28.37 30.93 38.71 42.28 26.61 28.52 30.63 31.36 28.95 31.43 34.47
42.28 44.29 46.32 48.71 57.95 33.94 37.51 39.27 58.42 43.36 45.77 48.28
55.16];
% C2 (Temperature): input variable 1
```

```
C2 = [25 25 25 25 30 30 30 30 50 50 50 50 25 25 25 25 30 30 30 30 50 50
50 50 25 25 25 25 30 30 30 30 50 50 50 50 25 25 25 25 30 30 30 30 50 50
50 50];
% A2 (Amount of sorbent material used): input variable 2
A2 = [3 4 5 6 3 4 5 6 3 4 5 6 7 8 9 10 7 8 9 10 7 8 9 10 3 4 5 6 3 4 5
6 3 4 5 6 7 8 9 10 7 8 9 10 7 8 9 10];
% IN2 (Temperature and amount of sorbent material used), or the input
design matrix
IN2= [C2;A2];
Input-variables = IN2;
Output-variables = y2;
```

VITA

Noora Darwish was born on March 15th, 1990, in Oklahoma, USA. After completing her schoolwork at Ashbal Al-Quds Private School in Abu Dhabi, UAE (2008), Noora joined the Bachelor of Science program in Chemical Engineering at the AUS. She received a bachelor degree of Chemical Engineering and graduated with a cum laude honor in June, 2013. She worked as a research assistant at Masdar Institute of Science and Technology between September, 2013–January, 2014. Noora joined the Master of Science program of Chemical Engineering at the AUS in February, 2014. She has been working as a Graduate teaching assistant in the Chemical Engineering Department at the AUS from 2014 to 2015.