Desulfurization and Kinetic Study of Diesel Fuel by Batch Adsorption on Activated Carbon

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Abstract

 The present research studied a batch adsorption desulfurization process for diesel fuel containing 580ppm sulfur, based on physical adsorption of refractory sulfur compounds on activated carbon (AC). The effects of time, temperature, diesel to AC ratio, AC particle size, mixing velocity, and initial sulfur concentration in commercial diesel fuel on the desulfurization efficiency were studied. The residual sulfur concentration in diesel fuel was decreased from 580 to 247ppm, corresponding to a desulfurization efficiency of 57%, at best conditions of 2.5 hours contact time, 50°C, 2ml diesel/gm AC, 0.8 mm AC particle size, and 1000 rpm mixing velocity. Different kinetic models were applied to fit the experimental data. The results showed that the pseudo-second order model has succeeded in predicting the equilibrium sorption capacity with correlation coefficient, $R^2=0.995$. The experimental adsorption isotherms were correlated by Langmuir and Freundlich models. The results indicated that Freundlich isotherm exhibits the best fits for the adsorptive desulfurization of diesel fuel ($R^2= 0.989$) as compared with the Langmuir model ($R^2 = 0.947$). The adsorption intensity as estimated from the Freundlich isotherm is larger than one which is indicative of physical adsorption.
Keyword: Sulfur Removal, Diesel Fuel Desulfurization, Adsorption Kinetic, Batch Adsorption, Sulfur Adsorption.

ازالة الكبريت ودراسة الحركية لوقود الديزل بعملية الامتزاز ذو الوجبة بأستخدام الكاربون المنشط

الخلاصة

 درس البحث عملية إزالة الكبريت بطريقة الوجبات من وقود الديزل ذو المحتوى الكبريتي 580 جزئ بالمليون , بالاعتماد على عملية الامتزاز الفيزيائي لمركبات الكبريت صعبة الإزالة على سطع الكربون المنشط. تم دراسة تأثير كل من الزمن , درجة الحرارة , نسبة وقود الديزل إلى الكربون المنشط , حجم دقائق الكربون , سرعة الخلط و التركيز الأولي للكبريت في وقود الديزل على كفاءة إزالة الكبريت . تم خفض تركيز الكبريت في وقود الديزل من 580 إلى 247 جزء بالمليون , والتي تقابل كفاءة إزالة 57% عند استخدام أفضل الظروف (2.5 ساعة , 50°م , 2 مل ديزل لكل غم من الكربون المنشط , 0.8 ملم حجم جسيمات الكربون المنشط و 1000 دورة بالدقيقة سرعة خلط) . نماذج حركية مختلفة تم تطبيقها لتتناسب مع البيانات التجريبية. لقد أظهرت نتائج التحليل الحركي أن تطبيق نظام شبه الدرجة الثانية نجح في التنبؤ عن قدرة التوازن لعملية الامتزاز(معامل ارتباط

0.995). تم تطبيق موديل لانجمير وفرندليتش على النتائج التجريبية و أشارت النتائج إلى أن موديل فرنديلتش عرض أفضل تطابق لعملية إزالة الكبريت من وقود الديزل بالإمتزاز بمعامل ارتباط مقداره 0.989 مقارنة بموديل لانجمير الذي اعطى معامل ارتباط مقداره 0.947. شدة الامتزاز كما اظهرها موديل فرنديلتش هي اكبر من واحد مما يدل على ان الامتزاز فيزيائي.
الكلمات الدالة: ازالة كبريت, ازالة الكبريت من وقود الديزل, حركية الامتزاز, امتزاز ذو الوجبة, امتزاز الكبريت.

INTRODUCTION

Production of clean hydrocarbon fuels with low sulfur and aromatic content has become one of the most important tasks of a modern petroleum refinery. The use of environmentally benign fuels requires the removal of organosulfur compounds present in various petroleum fractions because these compounds are known to contribute to air pollution and acid rain by sulfur oxides [1]. Removal of sulfur compounds from liquid fuels in refineries is for the most part carried out by hydrodesulfurization (HDS) based on cobalt- and nickel-based catalysts, and it is carried out at high temperatures and pressures with high consumption of hydrogen making HDS a very costly option for deep desulphurization. HDS process is highly efficient for the removal of sulfur compounds such as thiols, sulfides and thiophenes, but employing conventional HDS process for removing refractory sulfur compounds, such as benzothiophenes, dibenzothiophenes and their alkylated derivatives which are usually in large amounts present in diesel fuel, has met with high degree of difficulty due to their low reactivity in the HDS process [2,3]. This is why alternative, modern processes of desulfurization are being considered. Separation processes that are being applied to the desulfurization of different petroleum fractions include Oxidative Desulfurization (ODS) [4], Biodesulfurization (BDS) [5], Extractive desulfurization (EDS) [6], and adsorptive desulfurization (ADS) [7-9]. ADS has attracted much attention among other desulfurization technologies to produce ultra-low-sulfur diesel (ULSD) due to some advantages, such as low-energy consumption since it can be performed at ambient temperature and pressure without hydrogen or oxygen consumption. Also, adsorbents can be reused by the proper regeneration process [10]. Recently, there was a lot of interest in developing sorbents for selective adsorption of organosulfur compounds from liquid fuel. Various studies on the ADS process using different adsorbents such as activated alumina [11], zeolites [12], activated carbons [13] and mesoporous materials [14] were carried out. Salem and Hamid [15] examined ADS for diesel fuel using zeolite 13X, 5A and AC. The results indicate that zeolite 13X has a high capacity for sulfur in low concentration ranges less than 25ppm. When the concentration increases, the capacity of AC can be 3 times greater than that with zeolite. Muzic et al. [16] tested the efficiency of removing sulfur from diesel using ADS on AC and activated aluminium oxide. AC proved to be more efficient than aluminum oxide during the adsorption of sulfur compounds from diesel. Al Zubaidy et al. [17] examined the desulfurization of diesel oil containing 410ppm by adsorption process using commercial AC and carbonized date palm kernel powder at room temperature in batch process. The results showed a reduction in the amount of sulfur by more than half of the original amount of sulfur. It was demonstrated by Toida [18] that AC having a specific pore structure attains an efficient and selective removal of dibenzothiophenes (DBTs). Mesopores activated carbon is one of the most important characteristics in the liquid phase adsorption, owing to the high surface areas (ranging

from 164 to 1260 m^2/g) and pore volumes (up to 1.62 cm^3/g) [19]. For the refinery applications, one potential new option is to use a sulfur-selective adsorption unit for ultra-deep removal of organic sulfur following a conventional HDS unit, and such a combination could remove all of the sulfur from the liquid fuel products [20]. The aim of the present study is to investigate the effect of the main operating parameters on the desulfurization efficiency of locally available hydrotreated commercial diesel fuel and to study the kinetics of the desulfurization process by applying different kinetic models.

Experimental
Materials and methods
Feedstock:
Light commercial diesel fuel was used as feedstock for the desulfurization process; its properties as measured using MINISCAN IRXpert Gasoline and Diesel Analyzer (available at the Chem. Eng. Dept. / Univ. of Technology) are listed in ***Table (1)***. The sulfur content in diesel fuel was measured using energy dispersive X-ray fluorescence (EDXRF) method, which is an accurate, non-destructive, economical and yet quick method prescribed in ISO 8754 and ASTM D4294-03. Diesel samples of different initial sulfur concentrations (280, 380 and 480ppm sulfur) were obtained by blending the original feed stock with diesel fuel containing 180ppm sulfur in different proportions.

Table (1): Properties of Diesel Fuel

Property	Value
Sp.gr at 15.5 °C	0.832
Viscosity at 29 °C	5.5cst
°API	38.57
Sulfur content (wt%, ppm)	0.0580 ; 580
Cetane No. at 28 °C	20.9

Activated Carbon (AC)
Industrial grade granular and powder activated carbons (AC) supplied from local markets were used as an adsorbent. The carbon particles were sieved to get different particle sizes (d_P = 0.2, 0.45, 0.8, 1.09, and 1.44mm) and dried in an oven at 110°C for 4 hours before adsorption to remove any moisture. The physical properties of the different AC particle sizes as measured by BET Surface Area Analyzer (Model No. Qsurf 9600, product of Thermo Finnegan Co. USA, available at the Oil Research & Development center/ Ministry of Oil) is given in

Table (2). Table (2): Physical Properties of Different AC Particle Sizes

d_P (mm) / Test	1.4	0.8	0.5
Surface area (m^2/g)	300	930.1	1041.4
Pore volume (cm^3/g)	0.19	0.506	0.610
Real density(gm/cm^3)	——	1.86	1.81

Experimental Procedure

The experimental runs were carried out batch wise in a laboratory scale setup.30 ml of diesel fuel (initial sulfur content=580 ppm) was mixed with 5 gm AC (dp=0.8mm) at 30°C and 400 rpm. After one hour adsorption treatment, the contents were allowed to cool to room temperature and the mixture was transferred to a filtration paper where the activated carbon particles were separated from the fuel. The sulfur content in the treated diesel fuel phase was then measured using x-ray fluorescence (XRF) sulfur analyzer. Each experiment was repeated 2-3 times to make sure of the accuracy of the results.

Data Analysis

The desulfurization efficiency (η%) was calculated as:

$$\eta\ (\%) = \frac{(Co - C)}{Co} * 100 \qquad \ldots\ldots\ (1)$$

The total amount of sulfur adsorbed on AC (mg/g) was calculated as:

$$q = \frac{(Co - C)\ *\ \rho * V}{W} \qquad \ldots\ (2)$$

Where:

Co   Sulfur content of untreated diesel (ppm)

C   Sulfur content of treated diesel (ppm)

q   Amount of the sulfur compounds adsorbed $(\frac{mg}{g})$.

ρ   Diesel density $(\frac{gm}{cm^3})$

V   Volume of diesel fuel (cm^3)

W   Sorbent mass (gm)

Results and Discussion

Effect of Operating Parameters

The effect of the main operating variables namely: contact time (t), operating temperature (T), sorbent dose (D/AC), AC particle size (d_P), mixing speed (R), and initial sulfur concentration (Co) on the residual sulfur content and/or desulfurization efficiency were investigated.

Effect of Contact Time

The effect of contact time on the desulfurization efficiency is presented in *Figure (1)*. The results indicate that the rate of sulfur removal was rapid in the beginning but it gradually decreased with time and at some point in time (2.5 h) it almost reaches a constant value beyond which no more sulfur is further removed from the solution. At this point dynamic equilibrium is reached and the amount of sulfur adsorbed indicated the adsorption capacity. The obtained results agree fairly well with the findings of Al- Zubaidy et al. who obtained a sulfur reduction from 410 to 251ppm after 2 hours contact time [17].
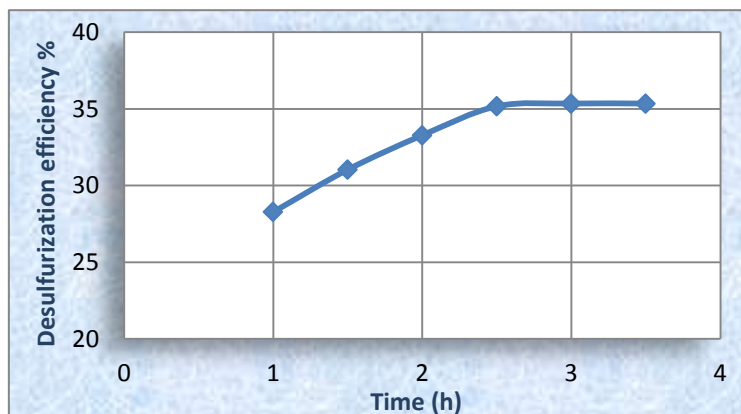
Figure (1): Effect of Contact Time on Desulfurization Efficiency
(T= 40°C, D/AC, 6ml/gm, d_P = 0.8mm, R=400 rpm, Co = 580ppm)

Effect of Temperature

The effect of temperature on the desulfurization efficiency ($\eta\%$) was investigated at 2.5hr contact time. The results as shown in *Figure (2)* indicate an enhancement in the desulfurization efficiency on increasing adsorption temperature. Sharp increase in desulfurization efficiency occurs by increasing the treatment temperature from30℃ to 50℃. However, by increasing the adsorption temperature from 50℃ to 70℃ only slight improvement in the desulfurization efficiency was obtained. It is a well-known fact that diesel fuel, after hydrodesulfurization and with less than 500ppm sulfur contains mainly the refractory sulfur compounds.
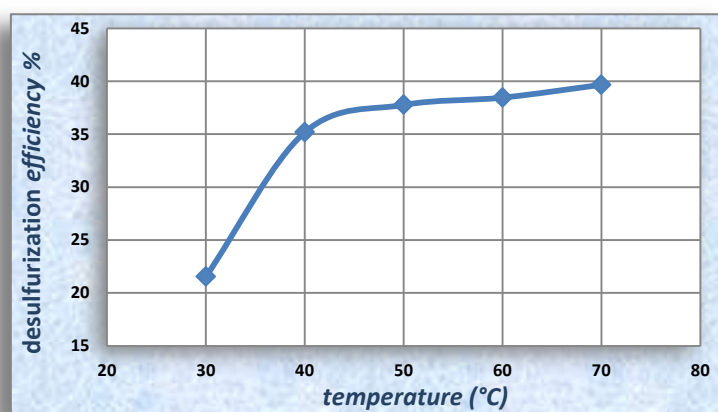

Figure (2): Effect of Temperature on Desulfurization Efficiency
(t=2.5h, D/AC= 6ml/gm, d_P = 0.8mm, R=400 rpm, Co = 580ppm)

The increase in the amount of sulfur compounds (mainly DBT) adsorbed with temperature can be attributed to an increase in mobility of the adsorbate molecules in solution and within the sorbent porous structure overcoming the activation energy barrier [21]. Sano et al. [22] and Muzic et al.[23] show that although in general the adsorption effectiveness drops with the increase in temperature, the refractory sulfur

species, such as 4,6- dimethyl dibenzothiphenes, were found to be more selectively removed at 50°C.

Effect of Sorbent Dose

   Figure (3) shows the effect of D/AC ratio on the desulfurization efficiency using a constant volume of diesel (D=30ml), t=2.5 h and T=50°C. The results indicate clearly a strong dependence of the desulfurization efficiency on D/AC ratio. The desulfurization efficiency for constant diesel fuel volume increases in direct relationship with the increase in sorbent dose due to the increase in surface area, and hence more active sites are available for the adsorption of sulfur [24][25]. But any additional decrease in D/AC ratio above 2ml/gm is impractical for batch system. Beyond this ratio the system tends to be a slurry and more difficult to be treated.
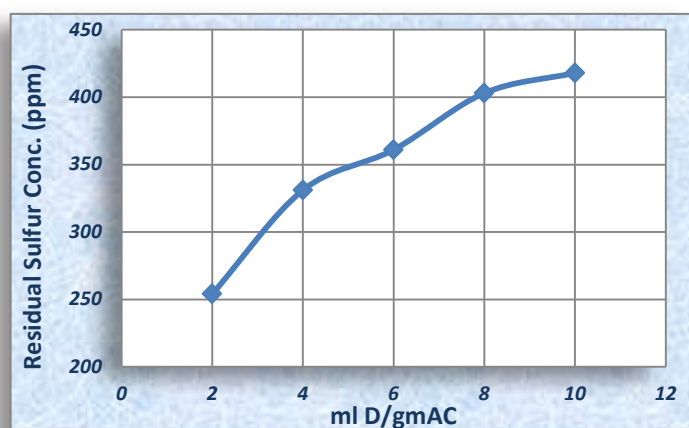

Figure (3): Effect of D/AC Ratio on Residual Sulfur Conc.
(t =2.5h, T = 50°C, d_P = 0.8mm, R= 400rpm,Co =580ppm)

Effect of AC Particle Size

   As the sorbent particle size was decreased from 1.4mm to 0.8mm, *Figure (4)* shows that the removal efficiency increased sharply from about 14% to 56% at which maximum removal efficiency was reached. As presented in Table (2) the surface area and pore volume increases from 300 to 930m²/g and from about 0.19 to 0.5cm³/g respectively when the sorbent particle size decreased from 1.4mm to 0.8mm. However beyond 0.8mm, any additional decrease in the sorbent particle size showed a slight decrease in desulfurization efficiency. The desulfurization efficiency decreased from 56% to 52% when the AC particle size decreased from 0.8mm to 0.2mm. Although a slight increase in both surface are and pore volume was obtained but the agglomerations of the small size AC particles impose this increase and reduces the actual contact area and closes the path of sulfur components to the active centers. Thus 0.8mm can be chosen as the best sorbent particle size.
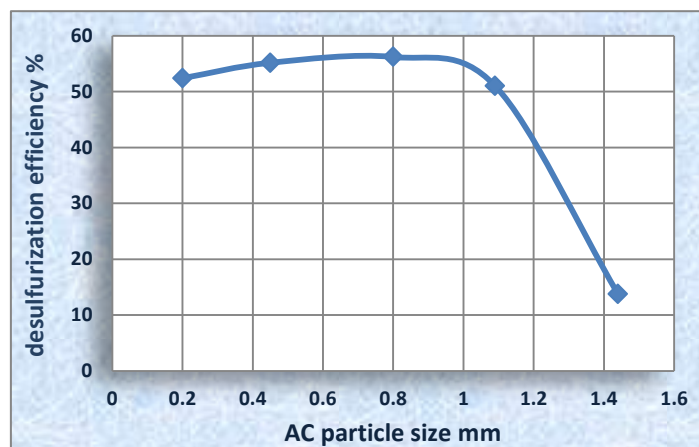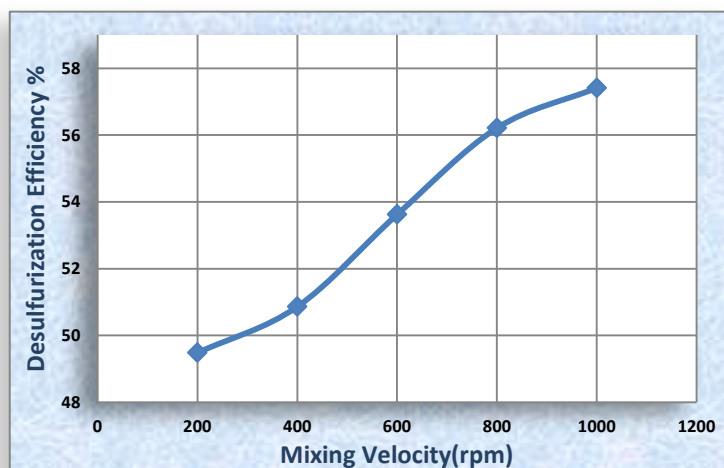
**Figure (4): Effect of AC Partice Size on Desulfurization Efficiency
(t = 2.5 h, T= 50°C, D/AC =2ml/gm, R=400 rpm, Co = 580ppm)**

Effect of Mixing Speed

   Figure (5) illustrates the effect of mixing velocity on the desulfurization efficiency. It can be noticed that the desulfurization efficiency increases with increasing mixing velocity. The overall sulfur removal rate is limited by the mass transfer between phases. For this reason, an increase in the mass transfer clearly improves the overall sulfur removal rate. Agitation affects reaction rate by increasing the amount of collisions the atoms make with one another, therefore speeding up the reaction rate.

**Figure(5): Effect of Mixing Speed on Desulfurization Efficiency
(t = 2.5 h, T= 50°C, D/AC = 2ml/gm, dp = 0.8 mm, Co = 580 ppm)**

Effect of Initial Sulfur Concentration

   The effect of initial sulfur concentration (Co) in commercial diesel fuel on the desulfurization efficiency is illustrated in **Figure (6)**. The results indicate that the removal efficiency decreases when the initial sulfur concentration in the diesel fuel

increased for constant sorbent dose. This is due to the fact that for a fixed sorbent dose, the total available adsorption sites are limited, thereby adsorbing almost the same amount of sulfur.
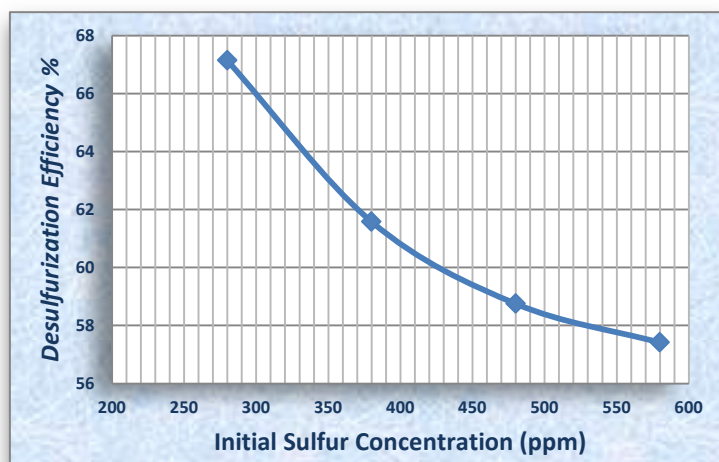

Figure (6): Effect of Initial Sulfur Concentration on Desulfurization Efficiency (t = 3 h, T=50°C, D/AC = 2ml/gm, dp =0.8mm, R=1000 rpm)

Kinetic Analysis

Kinetic experiments were carried out in order to gain a better understanding of the adsorption process, and evaluate the applicability of activated carbon for the adsorptive desulfurization of diesel fuel. The time dependency of sulfur compounds adsorption onto AC is shown in *Figure (7)*. It can be seen that the rate of adsorption was very fast during the first 30 min and equilibrium was approximately achieved after 2.5h with an equilibrium sorption capacity of 0.554mg/g. This indicates that the adsorption process has a two-stage kinetic behavior; rapid initial adsorption followed by a second stage with a constant adsorption rate. The reason for this behavior is the large number of vacant surface sites (small mesopores) that are available for adsorption of sulfur during the initial stage of adsorption. During the later period of adsorption, the sulfur molecules have to traverse further and deeper into the pores encountering much larger resistance, which results in slowing down of the adsorption process [26].

Various kinetic models were used to test the experimental data. Pseudo-first order (PFO), pseudo-second order (PSO) and intraparticle diffusion models were used for this purpose under the assumptions that the organosulfur components in diesel fuel, due to their very low individual concentrations, can be represented by sulfur concentration as a single component and measured sulfur concentrations are equal to surface concentrations [27].
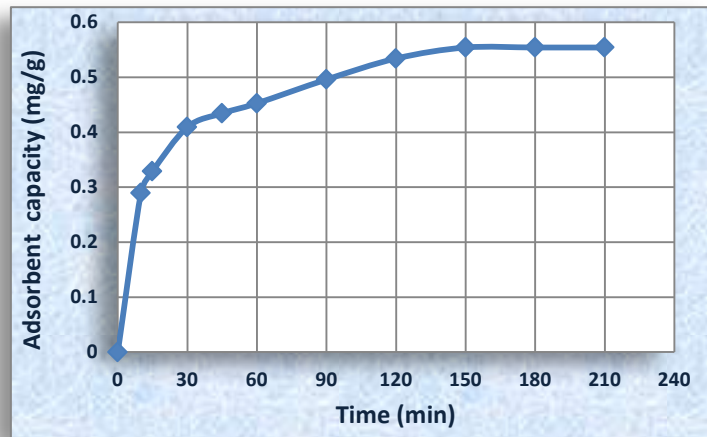
Figure (7): Adsorbent Capacity (mg/g) vs. Time
(T= 50°C, D/AC =2 ml/gm, d_P = 0.8, R=1000 rpm, C_o =580ppm)

On applying the Pseudo-first order (PFO) model, the amount of sulfur that can be adsorbed at equilibrium (q_e) and the rate constant (K_1) are estimated from ***Equation (3)*** by plotting $\ln(q_e$-$q_t)$ vs. t, as shown in Figure (8) where qt is the amount of sulfur compounds adsorbed at time t.

$$\ln(q_e - q_t) = (\ln q_e - K_1 t) \qquad \qquad \dots (3)$$

Figure (9) shows a plot of t/q vs. t for the pseudo second order rate (PSO) model ***Equation (4)***.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e{}^2} + \frac{1}{q_e} t \qquad \qquad \dots(4)$$
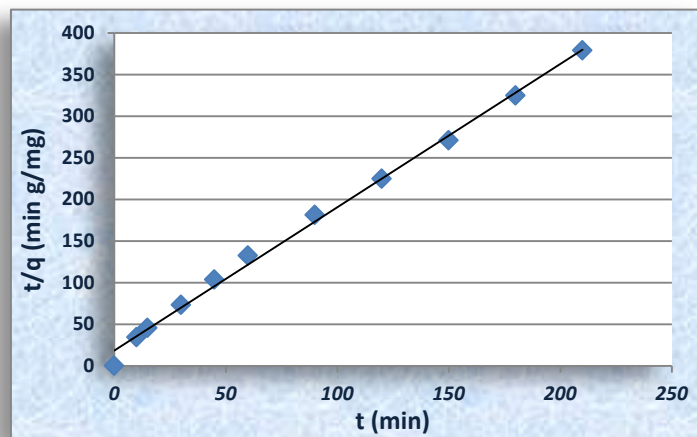

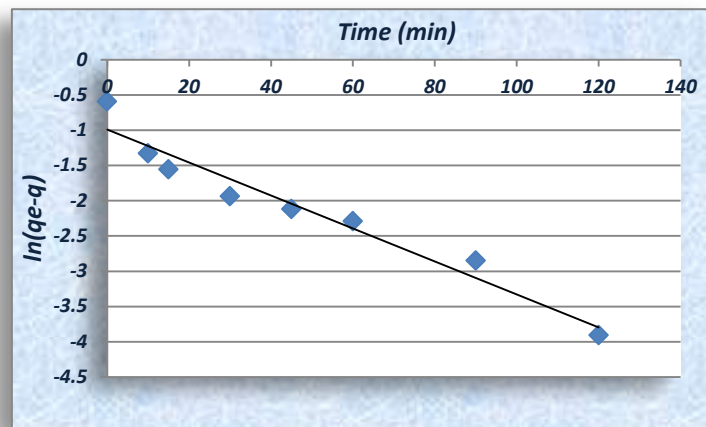**Figure (8): Pseudo-First Order Model**

Figure (9): Pseudo-Second Order Model

It can be noticed from the plot that for the application of this model the value of qe does not need to be estimated from the experimental data. The same is true for the intraparticle diffusion model. The intraparticle diffusion model constants are estimated by plotting q vs. $t^{0.5}$ **Equation (5)** as shown in Figure (10).

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$$q_t = K_i \, t^{\frac{1}{2}} + C \qquad \qquad \dots (5)$$
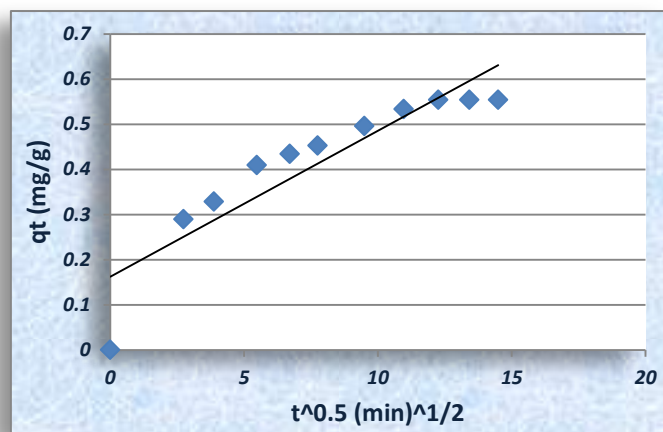

Figure (10): Intraparticle Diffusion Model

Table (2) presents the correlation coefficients of the various kinetic models. The results of the kinetic analysis and the correlation coefficients of these models as presented in Table (3) show that the pseudo-second order model succeeded to predict the equilibrium sorption capacity with correlation coefficient, $R2 = 0.995$. Typically, various mechanisms control the adsorption kinetic; the most limiting are the diffusion mechanisms, including external diffusion, boundary layer diffusion and intraparticle diffusion. Hence, the intraparticle diffusion model was utilized to determine the rate-limiting step of the adsorption process.

Table (3): Correlation Coefficients of the Various Kinetics Models

pseudo-first order		
K_1 (min^{-1})	$q_{ecal.}$ (mg/g)	R^2
0.023	0.372	0.948
pseudo-second order		
K_2(g/mg.min)	$q_{ecal.}$ (mg/g)	R^2
0.16	0.581	0.995
intraparticle diffusion		
K_i(mg/g. min$^{0.5}$)	C,(mg/g)	R^2
0.032	0.162	0.826

If the regression of q versus $t^{0.5}$ is linear and passes through the origin, then intraparticle diffusion is the proper rate-limiting step. As it can be clearly seen from *Figure (10)*, the regression is not linear and it did not pass through the origin, suggesting that the adsorption is not influenced by the intraparticle diffusion and that it was not the rate controlling step [28].

Adsorption Isotherms

The effect of initial sulfur concentration in the range of 280 to 580ppm on the extent of its adsorption onto AC is shown in *Figure (11)*. As it can be seen from this figure, the equilibrium adsorption amount is dependent on the initial sulfur concentration. the equilibrium uptake has been increased with the increase in the adsorbate concentration. The increase in sulfur adsorption with respect to its initial concentration is a result of the increase in mass transfer driving force due to concentration gradient developed between the bulk solution and surface of the adsorbent [27].
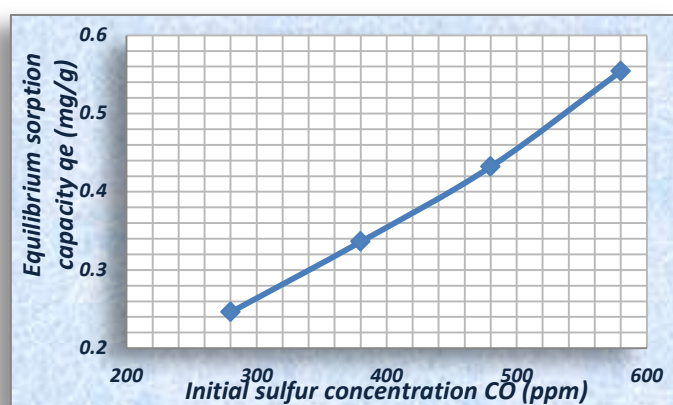

Figure (11): Adsorption Equilibrium Isotherm
(t = 3 hr , T= 50°C, D/AC= 2 ml/gm, d_P =0.8, R=1000 rpm)

The experimental adsorption isotherms were correlated by Langmuir and Freundlich models *Equations (6)* and *(7)*. Correlating equilibrium adsorption data to these models is not only important in the design and operation of adsorption systems but in this particular case also to further strengthen the assumptions made regarding the treatment of adsorptive desulfurization of diesel fuel as single component adsorption process.

$$q_e = q_m \frac{K_l C_e}{1 + K_l C_e} \qquad \qquad \dots (6)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m K_l} + \frac{C_e}{q_m} \qquad \qquad \dots (7)$$

The results are graphically depicted in *Figures (12)* and *(13)* and are tabulated in *Table (4)*. The results indicate that Freundlich model gives better fit to the adsorption isotherms of adsorptive desulfurization of diesel fuel. The adsorption intensity (n) as estimated from the Freundlich Isotherm is larger than one which is indicative of physical adsorption. These results are in line with generally accepted notions that adsorption process on activated carbon is in most cases of physical nature, when chemical bond is not formed. In addition, the Freundlich isotherm is the simplest and the best way to describe physical adsorption, Music et al.[28].
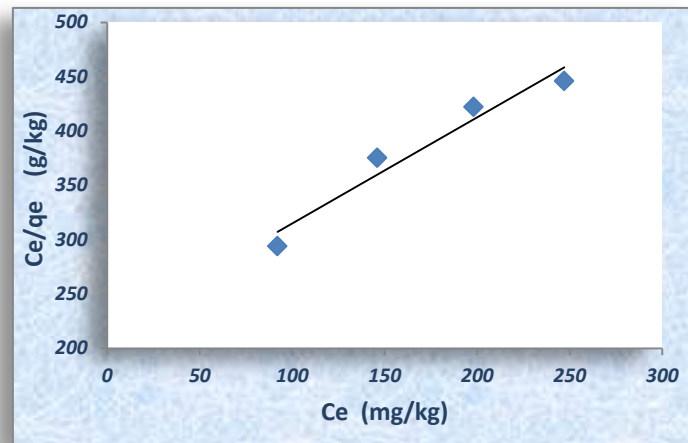
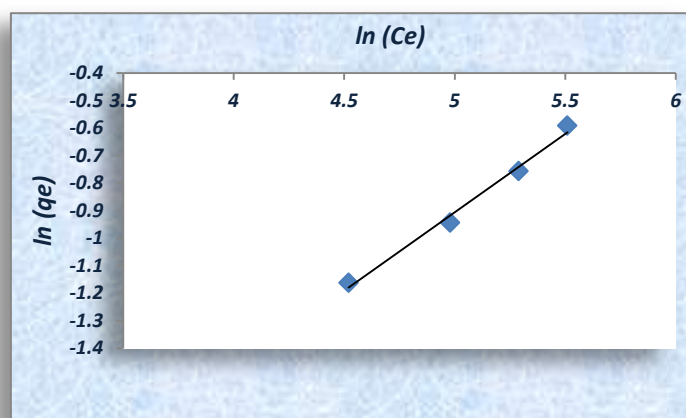**Figure(12): Langmuir Isotherm Model**

Figure (13): Freundlich Isotherm

Table (4): Constants of Langmuir and Freundlich Models and Correlation Coefficients

Langmuir isotherm model		
K_l (kg/mg)	q_m (mg/g)	R^2
0.00449	1.025	0.947
Freundlich isotherm model		
K_f (mg/g)(kg/mg) $^{1/n}$	n	R^2
0.0234	1.757	0.989

Effect of Adsorption Desulfurization on the Diesel Fuel Characteristics

Tables (4) and Figure (14) show the characteristics and the color, of the diesel fuel before and after adsorption desulfurization, respectively for the best operating conditions. These results clarify that the reduction in sulfur concentration in diesel fuel from 580 to 247 ppm, on applying the adsorption desulfurization treating method, leads to an improvement in the Cetane No. by about 40% while the color changes from straw to colorless. On the other hand, the specific gravity and viscosity show minor decrease which prove that the AC adsorbent has an impressive selectivity for organosulfur compound. Similar findings were obtained by and Xu et al. [24], Selvavathi et al. [29].

Table (4): Characteristics of the Diesel Fuel

Characteristics	Before Treatment	After Treatment
Sp.gr	0.832	0.830
Cetane No. at 28°C	20.9	29.3
Viscosity, cSt at 29°C	5.5	5.48
Total sulfur, ppm	580	247

Figure (14): Left (Original Diesel Fuel); Right (Treated Diesel Fuel)

Conclusions

Based on the present research work and the results of treating 580ppm diesel by adsorptive desulfurization, the following conclusions are drawn:

1.   The desulfurization efficiency was found to be increasing on increasing time, temperature, sorbent dose, mixing velocity, and reducing the initial sulfur concentration in diesel fuel.

2.   The highest desulfurization efficiency obtained was 57% at the best operating conditions of 2.5h, 50°C, 2ml/gm D/AC, 0.8mm AC particle size, and 1000rpm.

3.   Kinetic study has shown that the best fit to a straight line for the experimental data is achieved when

The pseudo-second order model was applied to the adsorptive desulfurization results indicating that the adsorption of organic sulfur compounds closely follows the second order reaction path.

4.   The equilibrium adsorption data is better described by Freundlich model indicating a physical adsorption.

5.   An improvement in the Cetane No. by about 40% with a minor decrease in specific gravity and viscosity has been noticed associated with adsorption desulfurization treating method.

Notation:

C	Residual sulfur concentration	ppm
C_o	Initial sulfur concentration	ppm
d_p	Mean partical diameter	mm
K	constant for Nitrogen	m^{-1}
K_1	PFO rate constant	min^{-1}
K_2	PSO rate constant	g/mg.min
K_f	Freundlich constant	$(mg/g)(kg/mg)^{1/n}$
K_i	Intraparticle diffusion rate constant	$mg/g.min^2$

K_l	Langmuir constant	kg/mg
n	Adsorption intensity	[-]
q_e	Amount of the sulfur compounds adsorbed at equilibrium	mg/g
q_m	Maximum adsorption capacity	(mg/g)
q_t	Amount of the sulfur compounds adsorbed at time t	mg/g
R^2	Correlation Coefficient	[m-]
V	Volume of diesel fuel	cm^3
W	Sorbent mass	g

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