Adsorption Desulfurization of Actual Heavy Crude Oil Using Activated Carbon

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A B S T R A C T

The strict new regulations to reduce the sulfur content of fuel require new economical and efficient ways to remove the sulfur from the organic sulfur components. In the current work, sulfur was removed from the actual crude oil containing 2.5 wt.% from southern Iraq, specifically the Halfaya Oil Field was studied using adsorption desulfurization with activated carbon (AC). The effects of different operating conditions, including the dose of AC (0.2-1.0 gm), time (15–120 min) and temperature (30–50°C) were investigated. The best operating conditions were obtained as 0.8 gm AC, 90 minutes and 50℃, respectively. Langmuir, Freundlich and Temkin isotherm models were implemented. The steady data were best denoted via Temkin models with correlation coefficient (R^2= 0.974). The kinetics sulfur components on activated carbon were examined by using pseudo-first order, pseudo-second order kinetics models and Intra-Particle diffusion. The adsorption process can be well described by pseudo-first order adsorption kinetic model with correlation coefficient ($R^2 = 0.9552$). Thermodynamic parameters, which include Gibbs Free Energy (ΔG^o), Enthalpy (ΔH^o) and Entropy (ΔS^o), were determined in the present research and showed that the adsorption of sulfur components on activated carbon is spontaneous, endothermic and increases the randomness of the sulfur compounds on the surface of the adsorbent. The content of sulfur in the treated crude oil was reduced from 2.5% to 1.8% corresponding to a desulfurization efficiency of 28%.

1. Introduction

Through the fast economic evolution and the explosive growth of the population of world, people don't merely possess a rising demand for oil, but also become more and more conscious of the environmental fortification importance, consequently there are higher needs for the industry of oil [1]. Crude oil contains both organic and inorganic sulfur compounds, and the inorganic sulfur compounds (active sulfur) includes sulfur, hydrogen sulfide and light mercaptans which can react directly with the metal. Organic sulfur compounds (inactive sulfur) comprises sulfide, thiophene, thiols, carbon disulfide, substituted benzo- and dibenzothiophene (BTs and DBTs), benzonaphthothiophenes (BNT) and numerous significantly more intricate molecules which cannot react directly with the metal [2]. In which the condensed thiophene are the most common form [3-5]. Crude oil treatment techniques can remove the impurities and contaminants, especially sulfur contaminants that can be treated by conventional methods using a combination of physical, chemical and biological methods. Many refineries around the world use a diversity of procedures for reducing the sulfur concentration in the crude oil [6]. Adsorption desulfurization is considered one of the most promising desulfurization methods for many reasons, such as requiring mild operating conditions, good desulfurization effect and high selectivity to thiophenic compounds [7- 9]. It's the highly usual technique utilized for achieving the ultra-clean fuels [10]. Adsorption is a process of mass transfer, in which free-radical molecules get bound to a surface via inter-molecular forces. It's frequently used for removing the trace impurities, like the elimination of the aromatics trace amounts from the aliphatics [11]. It's active in the separation procedures that involve low concentrations of sorbate, and therefore a potential being to the elimination of the refractory sulfur compounds in the transportation fuels [12]. To remove the impurities from liquids, many solids are used as adsorbents which can be classified into two forms: natural and industrial. Natural adsorbents include zeolites, charcoal, clays and clay minerals. Industrial adsorbents comprise activated carbon, silica gel, activated alumina, molecular sieves, etc. [13]. Yu et al., [14] studied the desulfurization of a commercial diesel using activated carbons for dibenzothiophene (DBT). A diesel fuel (having 800 ppm sulfur) with hydrogen peroxide was studied in the existence of the formic acid and activated carbon. The sulfur was eliminated from the diesel oil with (82%) of oil recovery. Jabbar [15] investigated the crude oil desulfurization utilizing hydrogen peroxide, activated carbon, formic acid as oxidizing agent. The content of sulfur in the crude oil was reduced from (3.9 wt%) to (2.622 wt%) matching to a (32%) desulfurization efficiency. Al Zubaidi et al. [16] studied the sulfur components adsorption form commercial diesel oil on a Granular Activated Charcoal (GAC). Results showed that the content of sulfur was decreased by (20.9%) in comparison with the original specimen. The kinetic study manifested that the Langmuir isotherm is more concise. Ibrahim [17] investigated the desulfurization of commercial diesel fuel using activated carbon. The residual sulfur concentration in diesel fuel was decreased from (580) to (247) ppm, corresponding to a desulfurization efficiency of (57%). The kinetic analysis revealed that the pseudo-first order model was the best fits, the Freundlich isotherm exhibited the best fits, and the adsorption was physisorption. In the present study, the removal of sulfur from Al-Halfaya Oil Field (southern Iraq) was investigated by activated carbon (AC) as adsorption desulphurization. The effects of different operating conditions were inspected: the dose of AC (0.2-1.0 gm), time (15–120 min) and temperature (30–50°C). The sulfur removal process was outright in a batch reactor (autoclave), and three isotherm models were applied. The kinetics sulfur components on activated carbon were examined by using three types of kinetics and thermodynamic parameters studied which included Gibbs free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o).

2. Materials and Methods

I. Chemicals

Crude oil was obtained for testing from Al-Halfaya Oil Field. The chemicals that were used include Formic acid (CH_2O_2, 95% purity), Hydrogen peroxide (H_2O_2, 93% purity) and distilled water (H_2O), and Activated carbon (AC) supplied from the local markets. All chemicals were used without any processing and were taken from Sigma Aldrich.

II. Characterization of activated carbon
    1. Scanning Electron Microscope (SEM) analysis
SEM was utilized for analyzing the AC chemical compounds by using back scattered electron (BSE) and secondary electron (SE) at a voltage acceleration of 20 kV.

2. Fourier transforms infra-red spectroscopy

FTIR spectra are used for the AC devices as well as the range of some frequency groups can be seen. The range that shows the extended vibrations can also be assigned to chemical bonds.

3. Measurement of surface area and pore volume

The measurements of (BET) surface area, pore volumes, and real density of samples were conducted. Before the measurement, the (AC) was dried in an oven at (110°C) for (4 hrs.) for removing the moisture that presents in it.

III. Method of Analysis

The measurement of the content of sulfur in the processed and unprocessed samples of crude oil was carried out via the analysis of X-ray as per (ASTM D-4294) from Horiba Ltd., Japan. Such apparatus being armed with the spectra of membrane that is normally backing the superfine films of a frame mount material that works as holder.

The percentage of removal of sulfur components is obtained as the ratio of the sulfur that is reduced (or removed) to those in the crude oil as given in eq. (1).

$$Re\% = \frac{c_i - c_0}{c_i} * 100 \quad \ldots\ldots\ldots (1)$$

IV. Desulfurization procedures

The activated carbon (AC) with the mean particle size of (0.8 mm) was utilized. The AC was first dried in an oven at 110°C for (4 hrs.) for removing the moisture that presents in it. The procedure was carried out by mixing 50 ml of processed oil in the first stage with (3 mL) Hydrogen peroxide, (4 mL) formic acid, (5 ml) distilled water and (0.2, 0.4, 0.6, 0.8 and 1 gm) activated carbon at (500) rpm and temperature (30, 35, 40, 45 and 50°C) for the time (15, 30, 60, 90 and 120 min), respectively using a hot plate stirrer placed in a water bath to control the desired temperature. Then, the mixture was allowed for cooling at the room temperature. The reaction mixture was then transferred to a centrifuge for separating the molecules of AC from this mixture, in which the content of sulfur content was measured. Experiments were conducted in the laboratory of the Department of Chemical Engineering. The treated results were processed by X-ray fluorescence that corresponds to (ASTM D-4294) and manufactured via Horbia Ltd., Japan. The ranges of the investigated experimental variables are listed in the Table 1.

Table 1. The ranges of the investigated experimental variables

Variables	Range
Time (min)	15-120
Temperature (°C)	30-50
Sorbent dose of AC (gm)	0.2-1
Formic acid & Hydrogen peroxide (ml)	4 & 3

3. Results and Discussion

I. Analysis of the heavy crude oil

The actual crude oil sample used in this work was tested at the Halfaya Oil field Laboratory, as mentioned in the previous study [18].

II. Characterization of the activated carbon

1. Scanning Electron Microscope (SEM) analysis

Morphology analysis of AC was performed using SEM instrument (Type: VEGA 3 LM, Origin: Germany) to know the surface texture and porosity of the sample. Figure 1 manifests the surface structure of the activated carbon. Closer scoping upon the AC surface exhibited the existence of mesoporous channels having a uniform size with a spherical shape, swollen or puffy structures and smooth surfaces within a range of (500 nm in dia.). Such swollen structures are suitable for the sulfuric components absorption.
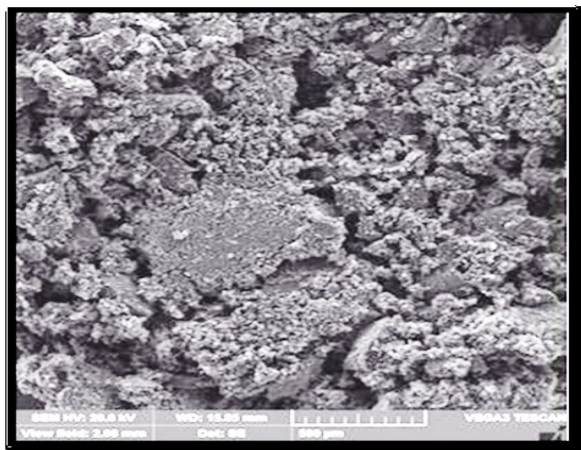
Figure 1: Surface structure for AC.

2. Fourier transforms infrared spectroscopy

The FTIR spectrum of the activated carbon is illustrated in Figure 2. The range of some frequency groups can be seen, and the band that appears around 3700 cm⁻1 can be assigned to the stretching vibrations of N-H bonds. Also, the stretching modes of O-H bonds can be noticed around 3100-3500 cm⁻1. The absorption bands at 2920 cm⁻1 correspond to the CH_2 bending vibration. The broad peak around 1300 to 1500 cm⁻1 is for N=O, and the C=O bending peaks are at 1500 cm⁻1. Stretching of ether and carboxylate structures can be attributed to the C–O bands at about 1200 cm⁻1. These functional groups play an important role in the absorption of sulfuric contaminants [19].
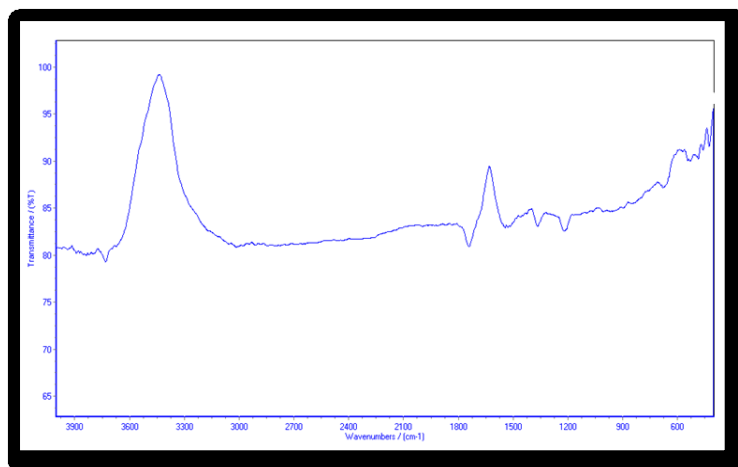

Figure 2: FTIR spectrum of AC.

3. Physical Properties of the Activated Carbon

The AC physical properties are listed in the Table 2. The measurements of surface area, porosity, and real density were carried out in the catalyst laboratory at the Centre of Petroleum Research and Development.

Table 2. AC physical properties

Test	Result	Method
Surface area (m^2/g)	519.4	ISO- 9277-2010
Pore volume (cm^3/g)	0.36	ISO- 9277-2010
Real density (g/cm^3)	2.84	ASTM D 5550

III. Effect of variables

1. Effect of Dose

The removal of the content of sulfur raises in a gradual way in a straight relation with the increment in the sorbent dose from 0.2 to 0.8 gm, and that the efficiency of removal increased from 3.6 to 23.2%, while by raising the sorbent dose from 0.8 to 1 gm, the removal is almost constant. The increment in the adsorption of sulfur components with the rising of adsorbent dose may be ascribed to the rising obtainability and availability of the surface area and the sites of adsorption for the sulfur components adsorption from the heavy crude oil [20, 21]. As well as, the increase in the removal with concurrent increase in sorbent dose is essentially due to the verity that the AC catalyses the Hydrogen peroxide decomposition for producing hydroxyl radicals by a series of free radical reactions that work as vigorous oxidizing agents. Sulfur compounds are thought to be converted to SO_4^{-2} to be removed into the aqueous phase [14, 22], as elucidated in Figure 3.
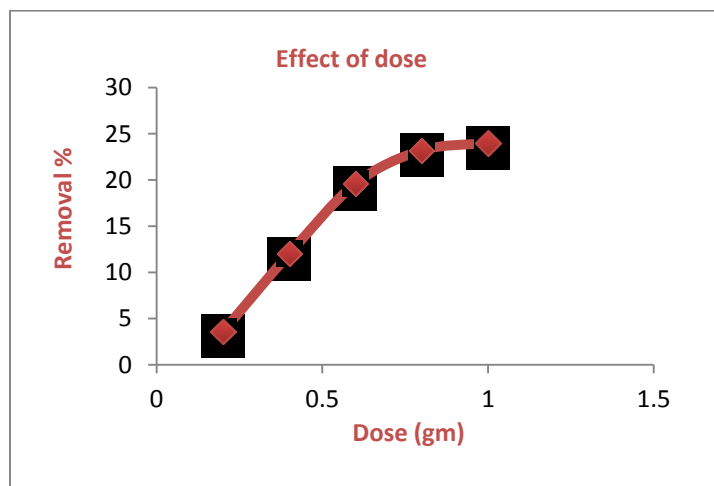

Figure 3: Sulfur content against sorbent dose at blending speed 500 rpm, 30°C and 120 min

2. Effect of Reaction Time

The increasing of the time of reaction enabled more reduction of sulfur components so as the removal up to 23% was observed after 90 min compared to 1.6% after 15 min, as shown in Figure 4. Also, the increase of the time of blending raises the contact between the phases (sulfur compounds in crude oil and adsorbents) with 500 rpm speed. This figure shows that no important variation in the efficiency of desulfurization is determined after 1.5 hr because of the adsorption of alkyl-substituted sulfoxides and sulfones, which are produced during the oxidation process upon the AC surface, therefore suppressing the process of adsorption. The results obtained are agreed fairly well in line with the findings of [15].
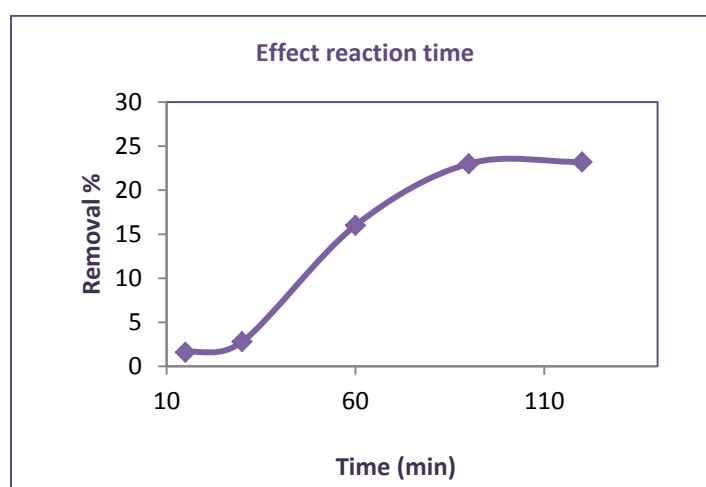

Figure 4: Sulfur content versus Time at 500 rpm mixing speed, 30°C and 0.8 gm sorbent dose.

3. Influence of Reaction Temperature

Removal of sulfur components increases from 22.4 % to 28 % by increasing the temperature range from 30 to 50°C, as shown in Figure 5. The high temperature (50°C) leads to the increased sulfur components adsorption capacity from crude oil, as well due to its anticipated influence to reduce the viscosity of the highly viscous crude oil, thus allowing the better diffusion of sulfur molecules and therefore enhancing the oxidation [23]. Several publications [24, 25 and 26] concentrated upon the temperature influence on the (ODS) reaction with adsorption. In the majority of investigations, the increase of temperature from (30°C) to (50°C) improves the reduction of sulfur components but beyond (50°C), increasing the temperature had an opposite influence chiefly because of the used oxidant degradation as well as the asphaltenes and resins formation [24].
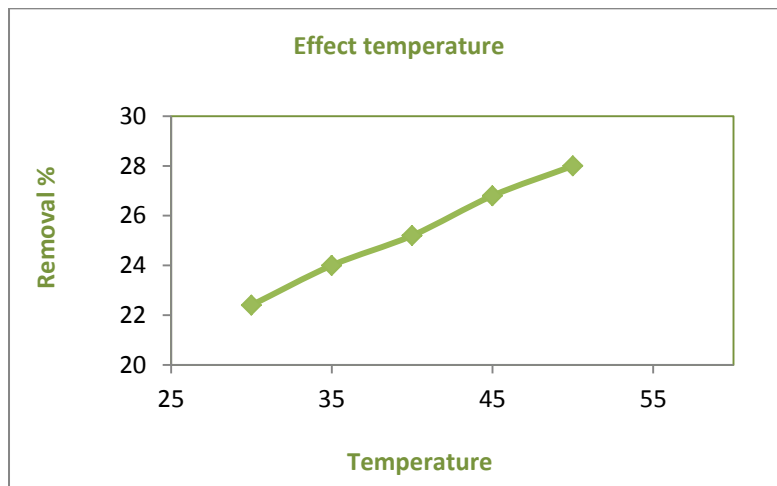
Effect temperature

Figure 5: Sulfur content versus Temperature at 500 rpm mixing speed, 90 min and 0.8 gm sorbent dose.

IV. Adsorption Isotherm Model

1. Langmuir isotherm

The model of Langmuir isotherm is the monolayer adsorption on the surface of adsorbent with a restricted no. of the sites of adsorption. The model is based on the assumption that there's no adsorbate transmigration in the plane of surface and that there are homogenous adsorption energies upon the surface as well as there is no lateral interaction among the adsorbed molecules [27]. The nonlinear Langmuir model is given in **eq. (2).**

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b\,q_{max}} \qquad ………. (2)$$

Where:
q_{max}: The maximum monolayer capacity (mg/g)
b: The constant of Langmuir constant representing to the adsorption energy (L/mg)

The values of q_{max}, and b that can be determined from eq. (2) via the slope and the intercepts of the plot of (Ce_q/q_e) against (Ce_q) are given in Table 3 and Figure 6.a.

R_L is a dimensionless equilibrium parameter and refers to that the isotherm is favorable ($R_L<1$), unfavorable ($R_L>1$) and irreversible ($R_L=1$), and it can be expressed by **eq. (3)**:

$$R_L = \frac{1}{1 + b\,C_i} \qquad ………. (3)$$

Where, Ci is the initial sulfur concentration (mg/L).

2. Freundlich isotherm

It is describing the heterogeneous (not homogeneous) process or multilayer adsorption [28], with a non-homogeneous distribution for the heat and the affinity of adsorption. Stronger bonding sites are assumed to be initially occupied and the energy of adsorption reduces with the increase of site occupancy [29, 30]. The linear form is expressed by **eq. (4)**:

$$ln\,q_e \;=\; ln\,K_f + \left(\frac{1}{n}\right) ln\,C_e \quad \cdots\cdots\cdots (4)$$

Where, q_e is the number of analyses upon the surface of absorbent (mg/g), K_f is the constant related to adsorption capacity of the sorbent (mg/g), 1/n is the value that gives the favorability indication of the process of adsorption and it's a measure of adsorption intensity and surface heterogeneity, that refers to the value of 1/n is (0.1-1), and it represents the favorable sorption.

Figure 6.b depicts the Freundlich isotherm plot, and the Freundlich constants are given in Table 3. 1/n and K_f can be determined from the slope and the intercept of the plot of $ln\,q_e$ against $ln\,C_e$. The comparatively high values of (R^2) remark the experimental data fitness with the model of Freundlich isotherms.

3. Temkin isotherm

Temkin isotherm assumes that the adsorption heat in the layer decreases linearly with the coverage of all adsorbate molecules because of the inter actions of adsorbent and adsorbate, and that the absorption is eminent by a uniform energy distribution [31]. Such model differs from the model of Langmuir, which includes a clear factor for the sorbent species and sorbent interactions [32]. This model is given in **eq. (5)**:

$$q_e \;=\; B\,ln\,C_e + B\,ln\,K_t \cdots\cdots\cdots (5)$$

Where, K_t is the equilibrium binding constant (L/g) corresponding to the maximum binding energy, B is the constant of Tempkin (J/kJ) and can be expressed by **eq. (6):**

$$B \;=\; \frac{RT}{b_t} \quad \cdots\cdots\cdots (6)$$

Where, R is the universal gas constant (8.314 J/mol.K), T is the absolute temperature (K), and b_t is the heat of adsorption (kJ/mol).

The Temkin isotherm model provided the best fit to the experimental data, and the higher correlation coefficient ($R^2 = 0.974$). K_t and b_t were determined from the intercept and the slope of the linear plot of q_e versus $ln\,C_e$, as shown in Figure 6c. The b_t negative value refers to that the process is an endothermic [33]. The value of ($R_L = 0.38 < 1$) indicates that the isotherm is favorable, and the R^2 value (0.974) suggests that the model of Temkin to characterize the sulfur components adsorption on the AC adsorbent is better than Langmuir and Freundlich isotherm models. The Temkin constants are given in Table 3.

Table 3. Parameters of isotherm models for the desulfurization by AC

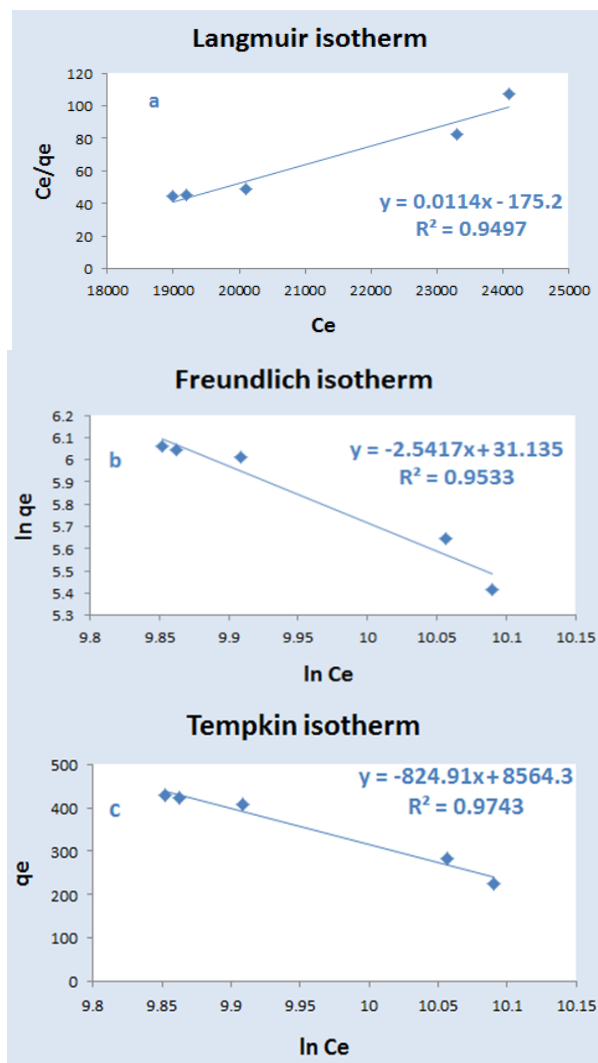|	q_{max} (mg/g)	R_L	b (L/mg)	R^2
Langmuir	87.71	0.38	$6.5*10^{-5}$	0.94
Freundlich	K_f (mg/g)	1/n	R^2	-
	$3.32*10^{13}$	0.41	0.953	-
Temkin	b_t (KJ/mol)	K_t (L/mg)	R^2	-
	-00.003	$3.098*10^{-5}$	0.974	-

Figure 6: (a) Langmuir, (b) Freundlich and (c) Temkin isotherms.

V. Adsorption kinetics

1. First order kinetic

The kinetic data was treated with the pseudo-first order kinetic model. The linear form of the model is given in **eq. (7)** [34, 30]:

$$\log(q_e - q_t) = \log(q_e) - (\frac{K_1}{2.303} t) \ldots\ldots (7)$$

Where:

q_e: The sulfur adsorbed amount at the equilibrium, mg/g

q_t: The sulfur absorbed amount at the time (t), mg/g

K_1: The constant equilibrium rate of the pseudo-first model, min^{-1}

The rate constant K_1, the adsorbed amount at the equilibrium (q_e) and the values of R^2 can be obtained from the slope and the intercept of the linear plot manifested in Table 4 and Figure 7a. The value of R^2 was equal to 0.955, which is higher than the other kinetics. Therefore, this means that the process of adsorption was a pseudo-first-order model. The resulted data in Table 4 indicate that the AC simultaneous adsorption performance was comparable to some of the preceding findings via other investigators [35].

2. Second order kinetic

The kinetic interaction of the pseudo- second order is represented in **eq. (8)** [36]:

$$\frac{t}{q_t} = \frac{1}{K_2 \, q_e^2} + \frac{t}{q_e} \ldots\ldots\ldots (8)$$

Where, K_2 is the rate constant of pseudo second-order for sorption (g/mg.min). In Figure 7b, (t/q_t) was plotted against the time to obtain K_2 and qe for the pseudo-second-order kinetic model. The summary of the computed values for the pseudo-second- order kinetics is given in Table 5. The values of R^2 were less compared with the pseudo-first-order kinetic that it was equal to (0.870).

3. Intra-Particle diffusion

The possibility of intra-particle diffusion is represented by the use of this model, as shown in the **eq. (9)** [37]:

$$q_t = K_P \, t^{0.5} + I \ldots\ldots\ldots (9)$$

Where, K_P is the constant of intra-particle diffusion rate (0.5 mg/g.min), and I is the constant of intra-particle diffusion.

Figure 7.c evinces that the regression lines do not pass through the origin (all points do not apply to the regression line) and this indicates that the intra-particle diffusion cannot be the merely rate determining step, and thus other processes might be involved. The Intra-particle diffusion constants are given in Table 4.

Table 4: Parameters of kinetic models for the desulfurization by AC

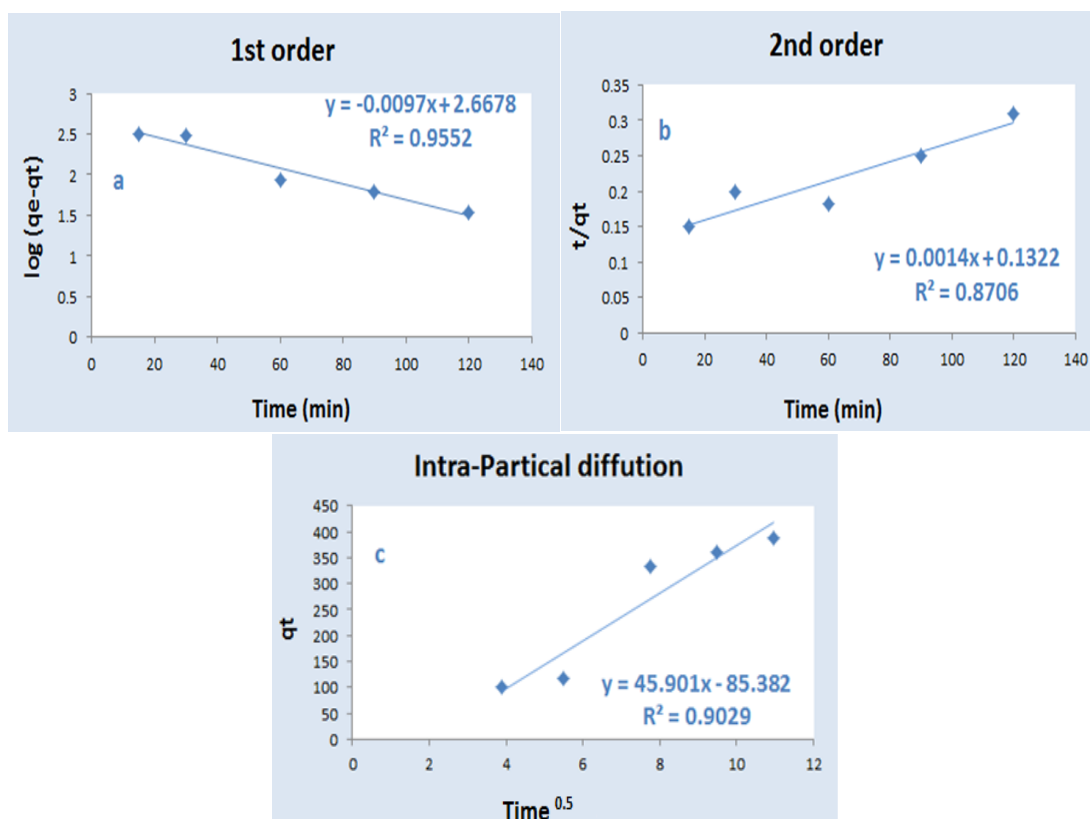| Pseudo-first order	q_e (mg/g)	K_1 (min^{-1})	R^2
	457	0.0223	0.955
Pseudo-second order	q_e (mg/g)	K_2 (gmg^{1}min^{-1})	R^2
	714.28	1.48*10-5	0.870
Intra-particle diffusion	I	K_p (mg/g.min$^{0.5}$)	R^2
	85.38	45.901	0.902

Figure 7: (a) First order, (b) Second order and (c) Intra-Particle diffusion kinetics.

VI. Adsorption Thermodynamics

The thermo-dynamics study is based on the temperature change because it is an important factor affecting adsorption capacity. The change in the enthalpy (ΔH°), entropy (ΔS°) and Gibbs free energy (ΔG°) as the parameters of thermodynamics which can calculate the process naturalness and viability. These parameters can be computed from the equation of Van't Hoff by using **eqs. (10, 11 and 12)** [38]:

$$\Delta G° = -RTlnK_C \ldots\ldots\ldots (10)$$

$$KC = \frac{q_e}{C_e} \qquad \ldots\ldots\ldots (11)$$

$$ln\,K_C = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad \ldots\ldots\ldots (12)$$

Where, ΔS° and ΔH° (J/mol) were obtained from the slope and intercept of Van't Hoff scheme of ln K_C versus 1/T, in **eq. (12).** (ΔH°) and (ΔS°) were determined from the intercepts and the slopes of ln K_C versus 1/T, as revealed in Table 5 and Figure 8.

Table 5: Thermodynamic parameters for the desulfurization by AC

Temperature (K°)	ΔH° (kJ/mol)	ΔG° (J/mol)	ΔS° (J/mol.K)
303	3.255	-1939.73	17.098
308		-2022.96	
313		-2040.50	
318		-2194.39	
323		-2282.60	

The positive values of ΔH° display that the adsorptive desulphurization process is endothermic in nature. The positive value of ΔS° confirms the raised randomness of the molecules of sulfur upon the solid surface than in the solution [21]. The sulfur components adsorption from the treated oil was spontaneous at the whole investigated temperatures, as pointed out from the ΔG° negative values. The enthalpy change (ΔH°) indicates that a physisorption or chemisorption, if less than 20 KJ/mol, is physical. If it was more than 40 KJ/mol it is chemisorption. As illustrated in Table 5, it is physisorption that based on the interaction of the forces of Vander Waals.
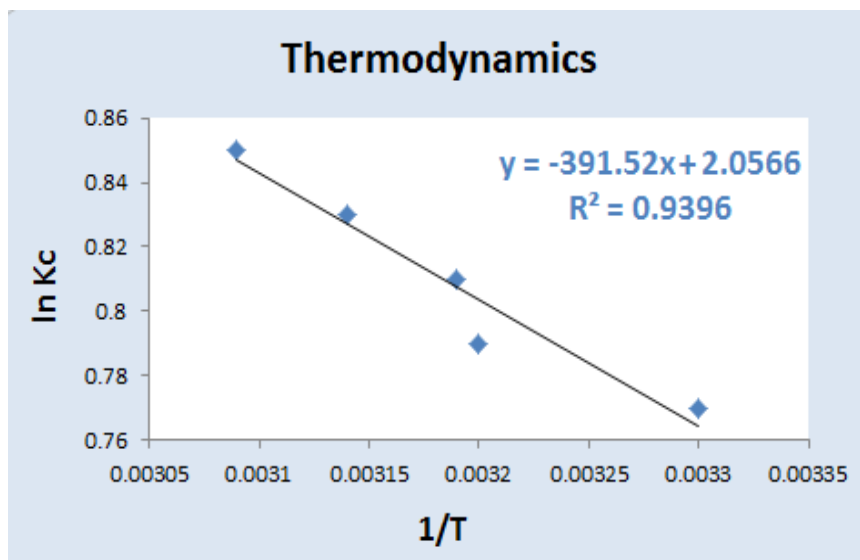
Figure 8: Thermodynamic for the desulfurization by AC

VII. The role of activated carbon in the removal of sulfur using Adsorptive Desulfurization

The activated carbon in sulfur oxidation is used as a catalyst for oxidation reaction and elucidates a good activity and selectivity. At the same time, it is easy to separate and recycle the renewable materials, so it has received more concern. In this study, the sulfur content can be reduced from 2.5 wt.% to 1.8 wt.%, as shown in Figure 9. The adsorption desulfurization is effective for removing the sulfur components, and the efficiency of desulfurization is about 28%.
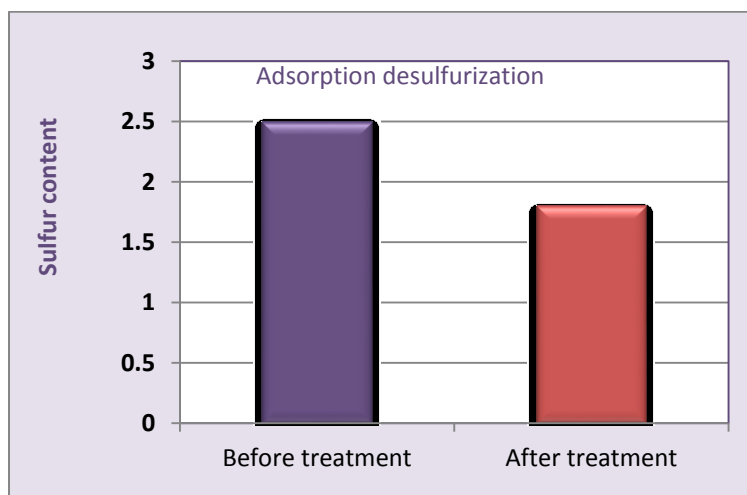

Figure 9: Sulfur content before and after treatment.

4. Conclusion

Based on the present experimental study and the results obtained from using the adsorption desulfurization of heavy crude oil from Halafaya oilfield, the desulfurization efficiency was found to be increasing with increasing time, temperature and adsorbent dose. The adsorption isotherms for the treated oil have confirmed that the desulfurization can be well fit by the Temkin isotherm model as the best fit with a higher correlation coefficient (0.974). The kinetic study also manifested that the best fit for a straight line of experimental data was achieved for the pseudo-first order model on the adsorption desulfurization with a higher correlation coefficient (0.955).

Thermodynamic parameters, which includes (ΔG^o), (ΔH^o) and (ΔS^o), were obtained in this study and elucidated that the sulfur components adsorption on the AC is spontaneous and endothermic as well as increases the randomness of the sulfur compounds on the adsorbent surface. The sulfur content was reduced to 1.8 wt% under the best operating conditions of 1.5 hr., 50°C and 0.8 gm of AC. The efficiency of sulfur removal was 28%.

Acknowledgement

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