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Adsorptive Desulfurization of Iraqi Light Naphtha Using Calcite and Modified Calcite

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Abstract

This study used the adsorption method to remove sulfur compounds from light naphtha fuel by using calcite and modified calcite as adsorbents. The calcite was prepared from chicken eggshells by heating and activation methods. It was modified by mixing it with commercial activated carbon as a new adsorbent. XRD and FTIR were used to characterize the adsorbents. Light naphtha fuel from the Al-Diwaniyah refinery, with a sulfur concentration of 776 ppm, was used in batch adsorption studies. Various operation conditions that affect the adsorption process were studied such as temperature (20–40 °C), weight of the adsorbent (1-3 g), and contact time (15–45 min) at constant mixing speed (300 rpm). In this study, the Minitab Program-Box-Behnken design was used to design experiments in batch adsorption studies of light naphtha, which is considered more straightforward and accurate because it shows the effect of each dependent factor on the adsorption efficiency and removal ratio. Results and analysis showed that the increase in temperature, the amount of adsorbent, and contact time would increase the removal efficiency. The analysis of adsorption equilibrium isotherms shows that the experimental data follows the Freundlich isotherm model for adsorbents. According to the results of the study, the highest removal percentages of sulfur content of light naphtha using calcite and modified calcite were 61% and 79%, respectively.

Keywords: *Adsorption; desulfurization; naphtha; adsorption isotherm; activated carbon; calcite.*

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1- Introduction

Demand for crude oil as a source of energy is increasing as the global economy grows. Crude oil is either considered sweet (with a sulfur concentration of less than 0.5%) or sour (with a sulfur content of greater than 0.5%). The Location of a crude oil reservoir is a key factor in determining its sulfur concentration [1]. Market prices for crude oil are based mostly on its sulfur content and API, with a preference for crude oil with a low sulfur content [2]. There are still significant levels of sulfur compounds in the naphtha fraction (up to 1000 ppm), the kerosene fraction (at least 3000 ppm), and the diesel fuel fraction (up to 10000 ppm) of crude oil [3].When it comes to sulfur compounds in feedstock derivatives (fuels). Environmental Protection Agency (EPA) and other environmental protection organizations are constantly revising their requirements. Oil derivatives such as petrol, kerosene, and diesel oil contain sulfur compounds, which are among the most toxic elements impacting the environment due to their offensive odor, corrosive nature, and ability to poison chemical catalysts. To comply with strict environmental requirements, it is normal practice to keep the sulfur concentration as low as feasible [4, 5].

As a result, to comply with the extremely low levels of sulfur, which are less than 10 parts per million, worldwide rules have been mandated. A primary objective must continue to be the creation of a desulfurization technology that is both effective and economically feasible. Although hydrodesulfurization, also known as HDS, is commonly used in industry, it is not very effective in removing refractory sulfur compounds (such as dibenzothiophene (DBT) and alkyl-substituted DBTs), and it must be able to withstand difficult circumstances such as high temperature, high pressure, high hydrogen consumption, and so on. There have been, fortunately, developments in several other technologies, such as adsorption desulfurization, extractive desulfurization, oxidative desulfurization, bio desulfurization, and so on [6].

Adsorptive desulfurization (ADS) stands out among these approaches because of its many benefits, such as its efficiency, energy savings, low cost, environmental friendliness, and operational safety [7]. Numerous novel or composite adsorbents, such as carbon-based adsorbents, metal-organic frameworks (MOFs), metal oxides, activated alumina, mixed oxides, and zeolites, have been prepared and studied for ADS. The most essential aspect of this process is the selection of adsorbents, as the efficiency of adsorptive desulfurization is largely dependent on their textural properties. Most of these adsorbents are insufficient for deep desulfurization [8].

This work is done for sulfur removal from light naphtha by adsorptive desulfurization by calcite extracted from eggshell and modified this calcite. The process was done

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in batch mode. Calcite's adsorptive performance has been studied considering this, and the synthesis of calcite adsorbent with unique and useful modifications has been studied. The commercial activated carbon was used in the synthesis of these modifications by mixing with calcite. The results were analyzed and optimized for both adsorbents. The adsorption isotherm desulfurization was studied too.

2- Experimental Work

2.1. Materials

The chemicals used here were chicken eggshells used to extract the adsorbent. Hydrochloric acid (HCl 36.5%, CHD company:). Activated carbon was purchased from the local market, and deionized water (DW) was produced in the lab. The feedstock was light naphtha supplied from Al-Diwaniya refinery with sulfur content (776 ppm) as one of the atmospheric distillation fractions as listed in Table 1, which was tested in Al-Diwaniya refinery/Ministry of Oil.

The equipment used in this work was a magnetic hot plate, Alfa Company, speed range 100–1800 rpm with a temperature range of 30-300 °C, a drying oven (Heraeus Company, maximum temperature 220 °C), a digital electronic balance (maximum weight 220 g with 0.0001 g accuracy), a pH meter (HANNA Instruments), an industrial grinder, a 200-mesh sieve, and some other class laboratory equipment.

Two adsorbents were used for adsorptive desulfurization: calcite and modified calcite. The preparation process of calcite from eggshells as an adsorbent following a similar procedure by previous researchers [9, 10] was as follows: Eggshells were washed in water until they were free of dirt and debris. They were then sun-dried for 24 h and mashed in an industrial grinder. Sieving was used to achieve a grain size that was small enough to pass through a sieve with a mesh size of 200. After being sieved, they were heated for 15 min at 110 °C, followed by activation with a solution of 0.1 M HCl for 48 h. After being filtered and cleaned with deionized water until the pH level reached 7, the adsorbents were activated in an oven heated to 150 °C for 30 min. The modified calcite (eggshell-activated carbon composite) was made by mixing the calcite that had already been made with commercial activated carbon in equal weight ratios using a planetary ball mill machine. Fig. 1 shows the calcite before and after modification.

Table 1. Properties of the Light Naphtha

Property	API	Initial boiling point, (°C)	Final boiling point, (°C)	Reid vapor pressure at 37.8 °C	Sulfur content, (ppm)
Value	71	42	130	8.5	776

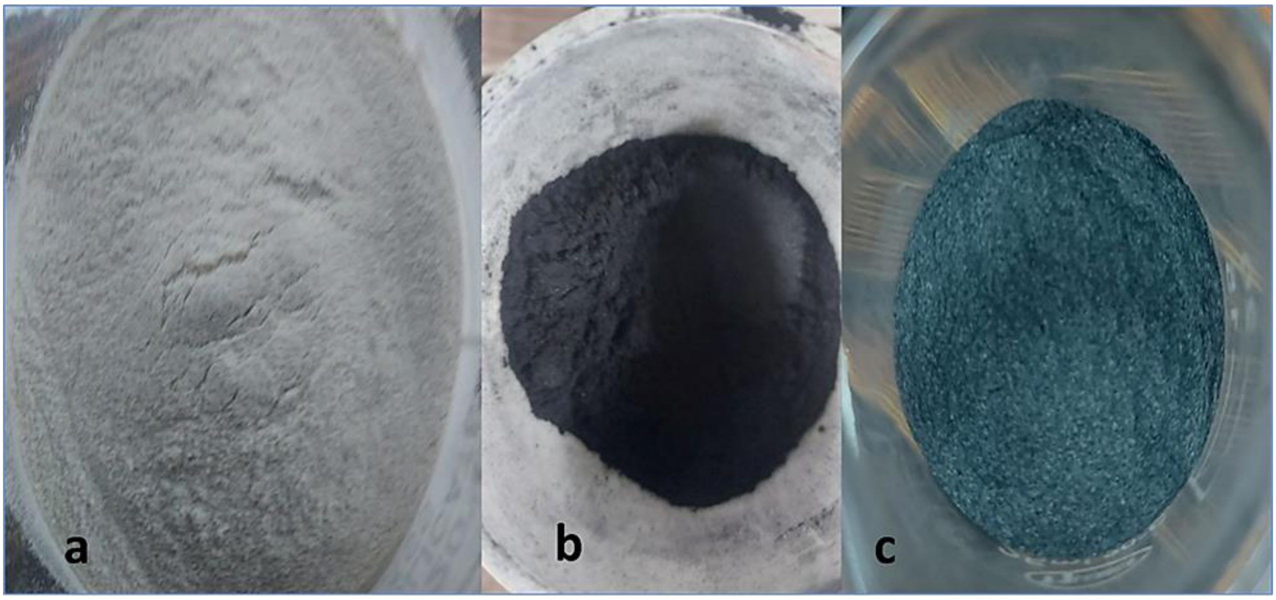

Fig. 1. (a) Calcite, (b) Commercial Activated Carbon, and (c) Eggshell-Activated Carbon Composite (Modified Calcite)

2.2. Materials Using Box-Behnken experiment design with response surface methodology RSM

Response surface methodology (RSM) is a statistical method used to evaluate the association between actual experimental results (response) and studied variables (control variables); this is typically accomplished by combining RSM with factorial design methodologies like central-composite design (CCD) and Box-Behnken design (BBD). When compared with alternative factorial design methods, the BBD approach was able to reduce the necessary number of experiments while maintaining a high level of accuracy in the optimization. Following BBD, the minimum number of experiments needed to account for the variables in the study was:

$$N = 2k(k-1) + r \qquad (1)$$

Where K is the number of studied variables, N is the number of experiments, and r is the number of central points which usually (3-6).

According to BBD, only three values (-1,0,1) were allowed for the variables in the analysis, with the distance between each level having equal values. This means that the number of experiments for three variables with three levels was between fifteen and eighteen, dependent on the parameter r (replicates) in the formula. The chosen studied variables were temperature, adsorbent dosage, and contact time with ranges 20-40 °C, 1-3 g, and 15-45 min respectively to investigate the activity of adsorbent in light naphtha ADS process as listed in Table 2**,** the experimental design by Minitab version 17 as shown in Table 3.

Table 2. Independent (Controllable) Variables and their Levels

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

Table 3. Box-Behnken Design BBD Matrixes

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

An equation for estimating predicted values and optimizing the system may be obtained by fitting the results of experiments for the impacts on temperature (x_1), the amount of adsorbent (x_2), and time of contact (x_3) on ADS as the second-order polynomial [10]:

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

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

2.3. ADS activity investigation

The ranges of 20-40 °C, 1-3 g, and 15-45 min were chosen as the experimental parameters for batch adsorption studies for adsorbent activity investigation. Box-Behnken's experimental design was used to determine the effect of the variables under study. This design indicates that 15 experiments must be carried out for a three-variable system, as indicated in Table 3. The desulfurization experiments for light naphtha were conducted to study the effect of three variables in batch mode. The experiments were designed according to Box-Behnken experimental design to study the impact of temperature, adsorbent dosage, and adsorption time with the following ranges: 20-40 °C, 1-3 g, and 15-45 min respectively. 100 ml of light naphtha was put into a glass flask equipped condenser which was put on a marantic hot plate heater and started heating with continued stirring (300 rpm). While the temperature was adjusted according to the Box-Behnken experimental design matrix. As the temperature reached the adjusted value, the specified adsorbent dosage was poured into the conical flask, and the process was stopped at the end of the required time. The mixture was filtered to separate the adsorbent from the low sulfur-content light naphtha. After each experiment, the total sulfur content was measured by X-ray fluorescence made by Oxford Company according to ASTM D-4294. Finally, the sulfur removal percent was calculated according to Equation 3.

$$R\% = \frac{S_o - S_f}{S_0} \qquad (3)$$

Where: S_0 is the initial sulfur content in fuel (ppm) and here is equal to 776 ppm, while the S_f is the final sulfur content in fuel (ppm).

3- Result and Discussion

3.1. Adsorbents characterization

3.1.1. X-Ray Diffraction XRD spectrum

As shown in Fig. 2, the XRD spectrum for both calcite and modified calcite, where the pattern showed many peaks at 2θ 29.3, 31.4,39.4,47.1,48.5, 56.6 57.4 60.6, and 64.7 ° which are corresponding to the presence of $CaCO_3$ [11]. The XRD pattern for modified calcite exhibited three sharp peaks at about 2θ equal to 25°, 40°, and 50° respectively that revealed crystalline carbonaceous structure [12], and other peaks were the corresponding presence of calcite [11].

3.1.2. FTIR

Fig. 3 illustrates the FTIR spectra for prepared calcite ($CaCO_3$) from eggshell only (red curve), activated carbon only (aqua curve), and mixed of them (green), in which the spectra analysis shows an apparent peak at 711, 872, 2516 cm $^{-1}$. At 1487 cm^{-1}, there is a very strong absorption peak from eggshell particles, which is likely due to the presence of carbonate minerals in the eggshell matrix.

The existence of a hydroxyl (-OH) group or an acidic hydrogen (-OH) group may be indicated by the presence of peaks 3400 and 2516 cm -1. The two peaks which were noted clearly at about 712, and 872 cm^{-1}, respectively indicated the presence of calcium carbonate [13,14, 15]. The spectra analysis for calcite prepared from eggshell (red curve) shows an apparent peak at 711,872, 2516 cm^{-1}. At 1487 cm^{-1}, there is a strong peak of eggshell particles, which is highly linked to the presence of carbonate minerals in the eggshell matrix. The hydroxyl (-OH) group and the acidic hydrogen (-OH) group can be seen in peaks at 3400 and 2516 cm^{-1}. The two peaks which are noted clearly at about 712 and 875 cm^{-1} indicate the presence of calcium carbonate [16,17]. The FTIR spectra of M-calcite (aqua curve) have the parks closed to the origin calcite, and this represents an improvement in the understanding of complex interferences and interactions between $CaCo_3$ and activated carbon.

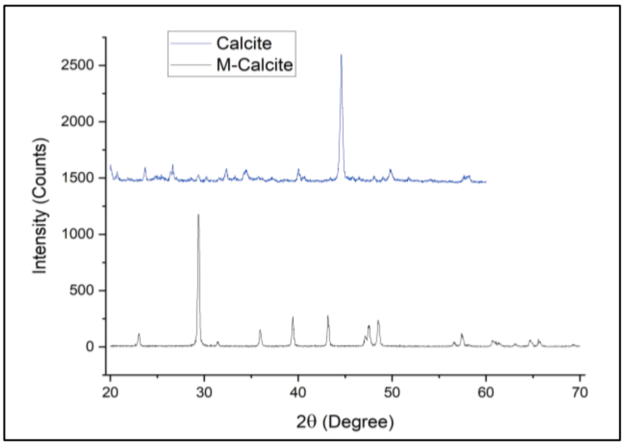

Fig. 2. XRD Pattern for Calcite and Modified Calcite (M-Calcite)

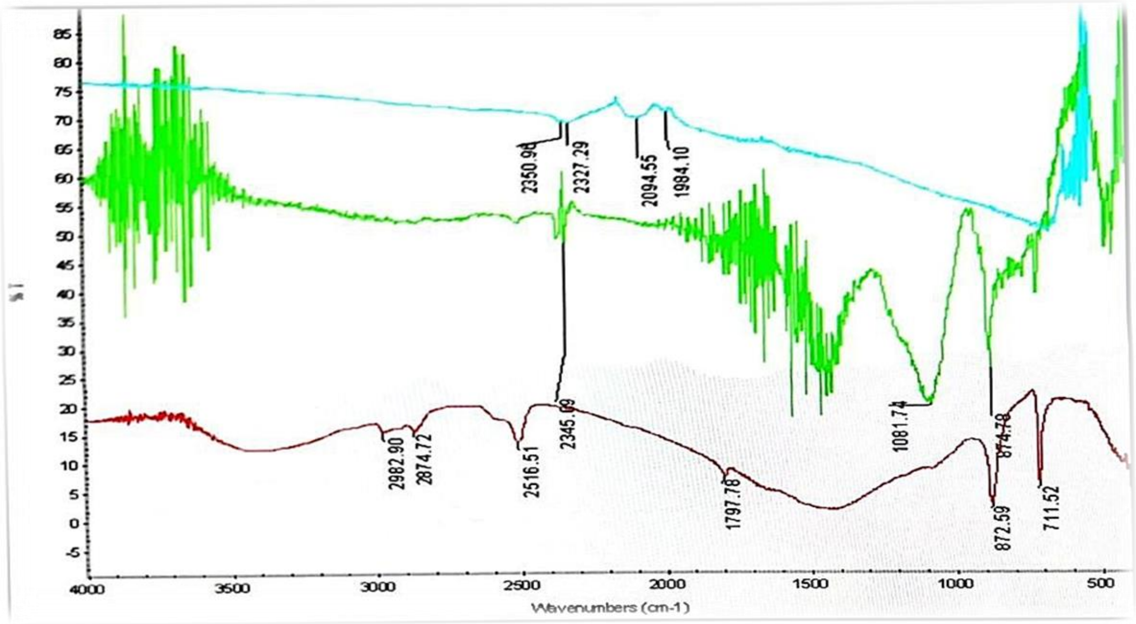

Fig. 3. FTIR for Calcite, Modified Calcite and AC

3.2. Adsorptive desulfurization results for calcite

Table 4 shows the adsorptive desulfurization (ADS) by prepared calcite adsorbent for all experiments designed according to BBD. Minitab 17 was used to fit the experimental batch results to a second-order polynomial (quadratic model) with BBD, and the sulfur removal effectiveness was found to be in the 45-60% range. The fitting product shows that a regression equation in uncoded variables for using $CaCo_3$ adsorbent is:

$$R\% = 32.6 + 0.688\ X1 - 1.08\ X2 - 0.014\ X3 - 0.00167\ X12 + 0.583\ X22 - 0.00074\ X32 - 0.0250\ X1\ X2 - 0.00000\ X1\ X3 + 0.0500\ X2\ X3 \quad (4)$$

Table 4. Experimental (Actual) Value for Sulfur Removal Efficiency

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

As noted from ANOVA presented in Table 5, the F-value was 11.19 for regression and it was greater than the tabulated value for Fisher`s (F=4.77). The high R^2 (0.9527) with high values of the adjusted R^2 (0.8676) refers to that the model's assumptions are reasonably consistent with the data. Moreover, based on the actual results and ANOVA, the temperature has the highest effect on sulfur adsorption, whereas other parameters effect is ordered as follows; adsorbent dosage and adsorption time via their F-value 86.13, 11.93, and 1.16 for temperature, weight, and contact time, respectively. The sulfur removal efficiency by ADS increased as temperature, adsorbent weight, and contact time increased. The results analysis shows the optimum sulfur removal efficiency was (61%) at the following operation conditions; 40 °C, 3 grams, and 45 min for temperature, adsorbent dosage, and adsorption time respectively as shown in Fig. 4.

Table 5. ANOVA Results for the Calcite Quadratic

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

3.3. Effect of studied variables on ADS by calcite adsorbent

According to Fig. 4**,** the optimal desulfurization efficiency was achieved when the adsorbent weight levels were raised while keeping all other variables constant. High weight of Calcite's means more available adsorption surface area. So, the adsorption capacity of the adsorbent was improved because of the increasing number of active sites on its surface. The sulfur removal efficiency from naphtha increased steadily with temperature increasing compared with the increase in the sulfur removal efficiency resulting from increasing the adsorbent dosage. High temperatures accelerate light naphtha spread across the external borders and internal pores within the adsorbent material. Therefore, increasing temperature increases the mobility and reduces the viscosity of large OSCs molecules thereby producing a swelling effect with the internal structure of the adsorbent [18], or the pores enlarging by breaking chemical bonds or oxidizing molecules on the surface during the heating step in preparation. Consequently, they run into adjustments in physical properties, leading to a rise in surface area and a resulting enhancement in adsorption [19]. The desulfurization efficiency improved as a function of increased processing time. This is likely the result of longer reaction times between the liquid reactants which leads to a great chance of adhesion of sulfur compounds to the surface adsorbent [20].

3.4. Adsorption Isotherm for calcite

The interaction between adsorbate with adsorbent was described as adsorption isotherms, and they are important to optimize the usage of any adsorbent. The profile of isotherm provides information about the stability of the interaction and on adsorption convergence of molecules. Some of these adsorption isotherms may be characterized in many mathematical forms which are based on the streamlined physical behavior of adsorption, whereas the others are empirical and correlated experimental results [21], [22]. The Langmuir and Freundlich isotherm were verified for batch results in which the Langmuir and Freundlich models are used to explain adsorption for equilibrium. The adsorbent capacity was calculated as follows:

$$q = \frac{(C_0 - C_e)V}{w} \tag{5}$$

Where q (mg/g): amount adsorbate that adsorbed (mg)/amount of adsorbent (g), C_e and C_0: equilibrium and initial concentrations of SOCs (ppm); V: volume solution (Liter), w: adsorbent weight (grams). The weight of SOCs that adsorbed, qe (mg/g) per gram of adsorbent was studied. The adsorption isotherm can explain the adsorption capacity at different equilibrium concentrations. Adsorption isotherms of SOCs on calcite at different temperatures (20, 30, and 40 °C), As well know Langmuir and Freundlich isotherms are two models that can be used to describe the adsorption process. Fig. 5 shows the Langmuir isotherm at different temperatures, the Langmuir isotherm postulates that no more adsorptions can occur at that site if SOCs occupy the sites on the adsorbent surface, mathematically the Langmuir equation can express as follows [23]:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_l C_e} \tag{6}$$

In the linear form is:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \tag{7}$$

Here q_{max} is the amount of adsorbate in case of complete monolayer coverage (mg/g), K_L: adsorption constant of

Langmuir (L/mg). The constants K_L and q_{max} can be estimated from intercepts and slop of straight lines in plots C_e /qe versus C_e.

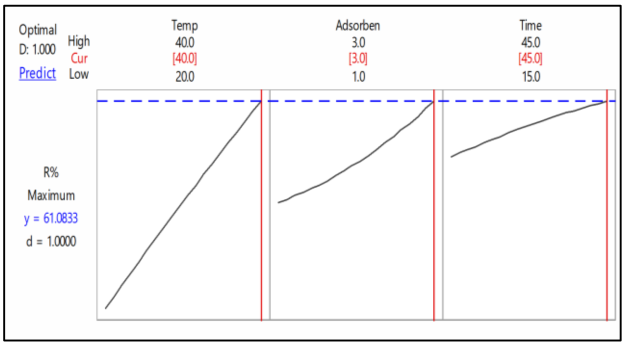

Fig. 4. General Effect of Studied Variables for Calcite on Sulfur Removal Efficiency Increases as Temperature, Adsorbent Dosage, and Adsorption Time Increase at Optimum Conditions

Freundlich isotherm can be seen in Fig. 6 where the Freundlich model is described as an experimental equation with the following form [24]:

$$q_e = K_F C_e^{1/n} \tag{8}$$

In the linear form is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{9}$$

q_e: adsorbate for concentration equilibrium with unit (mg/g), Ce: liquid phases for concentration equilibrium (mg/L), K_F: constant for Freundlich (mg/g)(L/mg)$^{1/n}$),{1/n}: heterogeneity factor. The constants K_f and exponent of (1/n) may be determined from intercepts and slop of straight lines in plots in Fig. 6.

The isotherm model parameters values for Langmuir and Freundlich can be found in Table 6.

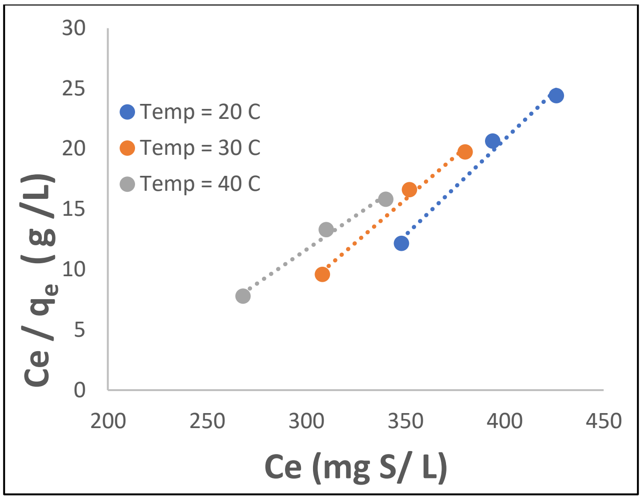

Fig. 5. The Langmuir Isotherm for OSCs Adsorption onto Calcite Adsorbent at Different Temperatures

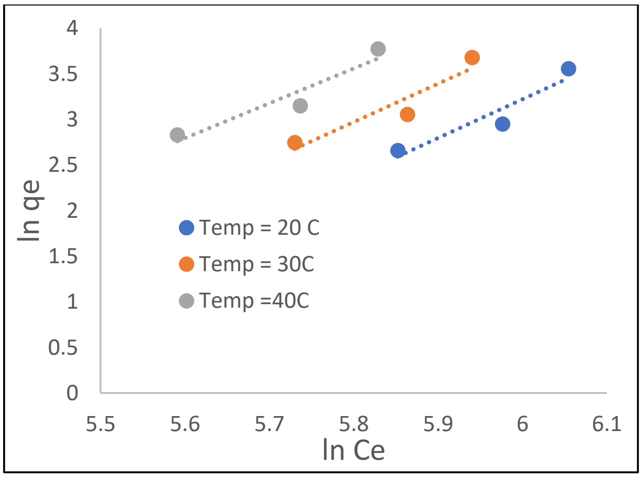

Fig. 6. The Freundlich Isotherm for OSCs Adsorption onto Calcite Adsorbent at Different Temperatures

Table 6. Langmuir and Freundlich Model Parameters for Calcite

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

Table 6 displays that the Langmuir model's fit to experimental data on the adsorption of sulfur compounds onto calcite as adsorbent yields a negative slope. This can happen if the constants are determined in an experimental part that is too steep. Although the correlation coefficient for the Langmuir model is the closest to 1, the adsorption behavior of the studied systems is inconsistent with this assumption, and the Freundlich isotherm is more appropriate for describing the adsorption of SOCs within the given concentration range [24]. These figures showed that the experimental data fit the Freundlich isotherm. This result indicates that the adsorption of sulfur compounds on adsorbent occurred on heterogeneous surface area and multi-layered.

3.5. Adsorptive desulfurization studies by modified calcite adsorbent

Table 7 shows the adsorptive desulfurization (ADS) by preparing a modified calcite adsorbent for all experiments designed according to BBD. Minitab 17 was used to fit the experimental batch results to a second-order polynomial (quadratic model) with BBD, and the sulfur removal effectiveness was found to be in the 46-79% range. The fitting product showed that a regression equation in the uncoded variables when $CaCO_3$ adsorbent was used is:

Regression Equation in Uncoded Units

$$R\% = 40.1 - 0.666\ X1 + 4.34\ X2 + 0.585\ X3 + 0.01065\ X1^2 + 0.839\ X2^2 - 0.00529\ X3^2 + 0.1224\ X1\ X2 - 0.00150\ X1\ X3 - 0.0000\ X2\ X3 \tag{10}$$

Table 7. Experimental (Actual) Value for Sulfur Removing Efficiency for All Runs

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

The analysis of ANOVA shown in Table 8 demonstrates that the F-value was 37.02 for regression and it was more than the tabulated value for Fisher`s (F=4.77). The high R^2 (0.9852) and large values of the adjusted R^2 (0.9586) referred to the fact that the model's assumptions are reasonably consistent with the data. Moreover, based on the actual results and ANOVA the weight has the highest effect on sulfur adsorption, whereas other parameters effect is ordered as follows; time and temperature via their F-value 295.55, .25.41, and 6.79 for adsorbent weight, adsorption time, and temperature respectively. The sulfur removal efficiency by ADS increased as adsorbent weight, time, and temperature increased. The results analysis showed the optimum sulfur removal efficiency was 79% at 40 °C, 3 g, and 45 min, respectively as shown in Fig. 7.

Table 8. ANOVA Results for the M- Calcite Quadratic

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

3.6. Effect of studied variables on ADS for M-calcite

Fig. 7 shows that when the adsorbent weight quantities were increased, the percentage desulfurization efficiency also increased, assuming all other variables remained constant. The increased weight of calcite indicates an increase in the adsorbent's surface area and increased the number of active sites on the surface of the adsorbent, thereby enhancing its adsorption capacity [25]. The results demonstrated that when the system temperature was increased, the percentage desulfurization efficiency also increased, assuming all other variables remained at their optimal levels**.** High temperatures accelerate light naphtha spread across the external borders and internal pores within the adsorbent material. So, increasing temperature increased the mobility and reduced the viscosity of large OSC molecules thereby producing a swelling effect within the internal structure of the adsorbent [18]. Holding all other factors constant, the percentage desulfurization efficiency improved as the desulfurization time of sulfur in light naphtha increased. This could be because it is common knowledge that the sulfur content of a solution is better thermally treated or has long contact with the adsorbent surface. If the time of desulfurization is increased relative to the time spent desulfurizing the solution is decreased. Therefore, the adsorbent has a large capacity for sulfur conversion or adsorption, and so the efficiency of the light naphtha desulfurization will be increased [26].

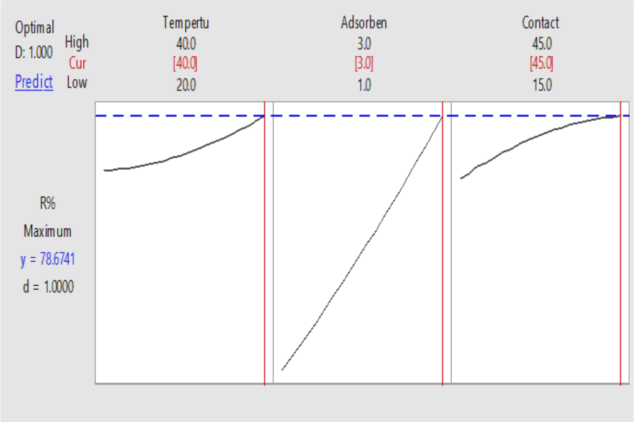

Fig. 7. General Effect of Studied Variables for Modified Calcite on Sulfur Removal Efficiency Increases as Temperature, Adsorbent Dosage, and Adsorption Time Increase at Optimum Conditions

3.7. Adsorption Isotherm by M-calcite

Adsorption isotherm for SOCs on the modified calcite was studied at different temperatures (20, 30, and 40 °C), Both the Langmuir and Freundlich were used to characterize the adsorption process. Fig. 8 shows the Langmuir isotherm and Fig. 9 shows the Freundlich isotherm at different temperatures. The isotherm model parameter values for the Langmuir and Freundlich are presented in Table 9.

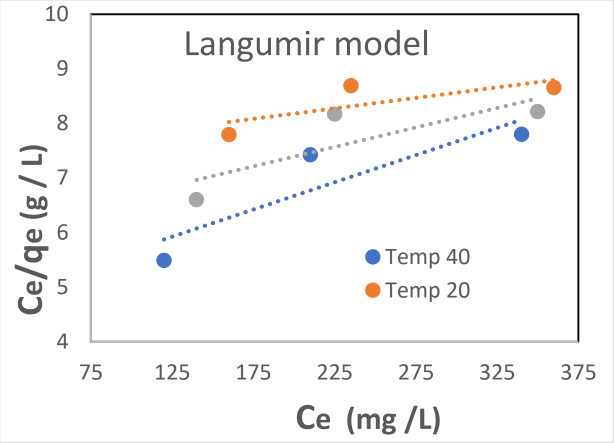

Fig. 8. Langmuir Isotherm for OSCs Adsorption by Modified Calcite Adsorbent at Different Temperatures

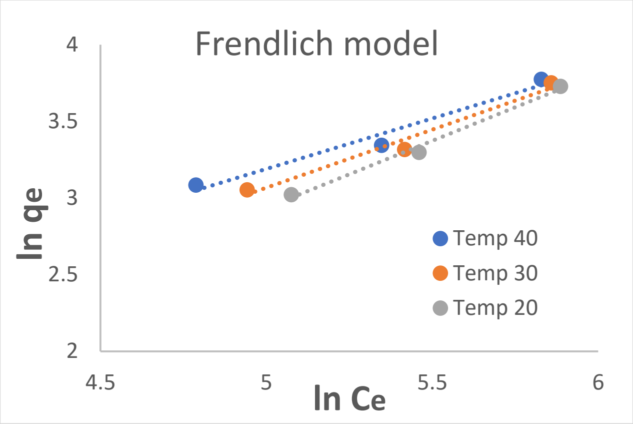

Fig. 9. Freundlich Isotherm for OSCs Adsorption by Modified Calcite Adsorbent at Different Temperatures

The experimental data provided here closely fits the Freundlich isotherm. This demonstrates that SOC adsorption occurred on a surface that was both heterogeneous and multilayered. If n is above 1, it suggests physical adsorption; if it's less than 2, it suggests moderate adsorption.

Table 9. The Langmuir and Freundlich Model Parameters for M-Calcite

	Langmuir constants			Freundlich constants		
Temp.(°C)	**q_m (mgS/g)**	**K_L (L/mg S)**	**R^2**	**K_F [(mgS/g) (L/mg S) $^{1/n}$]**	**n**	**R^2**
20	263	5.12×10^{-4}	0.60	0.24	1.14	0.97
30	140	1.2×10^{-3}	0.70	0.48	1.31	0.97
40	100	2.14×10^{-3}	0.80	0.90	1.5	0.99

4- Conclusion

The adsorptive desulfurization of light naphtha was studied by calcite and modified calcite, where the study showed that calcite and modified calcite gave promising results. The sulfur removal efficiency ranged between 46-60 % in the case of using calcite adsorbent, while it ranged between 46-79 % in the case of using modified calcite adsorbent. The optimum removal percentages of sulfur content of light naphtha using calcite and modified calcite were 61% and 79%, respectively. These results demonstrate the superior performance of the calcite and modified calcite adsorbents compared to other reported adsorptive desulfurization. This study provides valuable insights into the adsorptive desulfurization process and offers a foundation for the advancement of highly efficient adsorbents for sulfur removal in the petroleum industry. The adsorption equilibrium isotherms study shows that the experimental data follows the Freundlich isotherm model for adsorbents.

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إزالة الكبريت بالامتزاز للنفثا الخفيفة العراقية باستخدام الكالسيت والكالسيت المطور

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الخلاصة

في هذه الدراسة استخدمت تقنية الامتزاز لإزالة مركبات الكبريت من وقود النفثا الخفيفة باستخدام الكالسيت والكالسيت المطور كمواد مازة، حيث تم تحضير الكالسيت من قشور البيض بطريقة التسخين والتفعيل بعد ذلك تم تطويره من خلال خلطه مع الكاربون المفعل التجاري كمادة مازة جديدة رخيصة حيث تم الحصول على خصائص المواد المازة المحضرة من خلال فحص حيود الأشعة السينية (XRD) ومطياف الاشعة تحت الحمراء (FTIR). استخدم وقود النفثا الخفيفة بتركيز كبريتي ٧٧٦ جزء في المليون من مصفى الديوانية في دراسات دفعية (batch studies) حيث تمت دراسة ظروف التشغيل المختلفة التي تؤثر على عملية الامتزاز، مثل درجة الحرارة (٢٠–٤٠ درجة مئوية)، ووزن المادة المازة (١–٣ غم)، وزمن التلامس (١٥–٤٥ دقيقة) بسرعة خلط ثابتة (٣٠٠ دورة في الدقيقة)، في هذه الدراسة، تم استخدام تصميم برنامج Minitab–Box–Behnken لتصميم التجارب، والذي يعتبر أكثر وضوحًا ودقة لأنه يوضح تأثير كل عامل معتمد على كفاءة الازالة ونسبة الإزالة حيث تظهر النتائج والتحليل أن الزيادة في درجة الحرارة وكمية المادة المازة ووقت التلامس تؤدي الى زيادة في كفاءة الإزالة. كذلك يوضح تحليل مساواة توازن الامتزاز (adsorption isotherm) للدراسات الدفعية للمواد المازة بانها تتبع موديل (Freundlich). وفقًا لنتائج الدراسة، فإن النسب المثلى لإزالة محتوى الكبريت من النفثا الخفيفة باستخدام الكالسيت والكالسيت المطور كممتزات تساوي ٦١٪ و٧٩٪ على التوالي.

الكلمات الدالة: الامتزاز، إزالة الكبريت، النفثا، توازن الامتزاز، الكاربون المنشط، الكالسيت.