

ORIGINAL RESEARCH ARTICLE

Desulfurization of heavy naphtha with synthesized active carbon (DPAC) and impregnated (CuCl₂): Optimization, kinetic, and isotherm studies

Fatima K.Hamza*, Abbas K.Mohammad

College of Engineering, Department of Chemistry, University of Al-Qadisiyah, Al-Diwaniyah, Iraq

*Corresponding author: Fatima K.Hamza, fatima.kadum.humza@qu.edu.iq

ABSTRACT

This study investigates the adsorptive removal of sulfur compounds from heavy naphtha using phosphoric acid-activated date pit carbon (DPAC) and CuCl₂ impregnated phosphoric acid-activated date pit carbon (CuCl₂/DPAC). The adsorbent was optimized by Response Surface Methodology (RSM) using Box-Behnken Design to study the influence of temperature, contact time, and adsorbent dosage on the sulfur removal efficiency. The optimum conditions led to a maximum sulfur removal efficiency of 71% (31°C, 2.96 hr, and 0.0397 g/mL adsorbent). Kinetic studies revealed that sulfur adsorption followed the pseudo-second-order model, suggesting chemisorption as the adsorption mechanism, and equilibrium data were best fitted with the Freundlich model of adsorption isotherms based on temperature. The research confirms that low-cost biomass-based activated carbon impregnated with CuCl₂ is a viable and promising adsorbent to remove sulfur compounds from heavy naphtha, which helps in producing clean fuel and protects the environment.

Keywords: heavy naphtha; adsorptive desulfurization; DPAC; response surface methodology; kinetics; isotherm models; sulfur removal

1. Introduction

Petroleum fractions, particularly heavy naphtha, contain sulfur compounds that are significant environmental pollutants as they are oxidized to sulfur oxides (SO₂) during combustion, leading to acid rain, air pollution and catalyst poisoning^[1,2]. The world's increasingly stringent environmental regulations have increased the demand for ultra-deep desulfurization processes to supply cleaner fuels^[1,3]. While traditional hydrodesulphurization processes are commercially mature, they are typically associated with high costs, harsh operating conditions and low yields for recalcitrant sulfur compounds such as thiophenic compounds^[3]. Adsorptive desulfurization has gained popularity as an alternative method owing to its low energy consumption, ease-of-operation and selective removal of sulfur-containing compounds at mild conditions^[4]. Activated carbon is a promising adsorbent due to its high specific surface area, well-developed pore structure, chemical inertness, and low cost^[4]. In recent years, bio-based activated carbons have attracted special attention as environmentally-friendly adsorbents due to their use of renewable agricultural waste materials and low cost^[4]. Iraq and other Middle Eastern nations have a significant amount of date pits, an agricultural waste product, which is a cheap and sustainable raw material for the preparation of activated carbon due to its high carbon content.

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Activation with phosphoric acid can increase the carbon's porosity and surface functional groups, which boost the sulfur adsorption^[4]. Moreover, the impregnation of various metals (e.g. copper chloride) can improve adsorption capacity by creating more adsorption sites and enhancing the interactions with sulfur compounds^[5,6]. Design of experiments (DOE) using statistical methods such as Response Surface Methodology (RSM) and Box-Behnken Design are powerful methods to assess process variables and interactions with reduced experimental effort^[7,8]. Recent local investigations on Iraqi refinery streams demonstrated that adsorptive desulfurization with locally sourced adsorbents is feasible, highlighting the need for sustainable fuel purification systems^[9,10]

Hence, this study deals with the preparation, optimization, kinetic and thermodynamic studies of CuCl₂-loaded date pit activated carbon for the desulfurization of heavy naphtha, presenting an effective and sustainable method of preparing environmentally-friendly fuels locally.

2. Kinetic models

Kinetic models are used to find the effectiveness of the adsorbent and the time needed to attain equilibrium. The most common models are:

- Pseudo-First Order Model

This model was first introduced by Lagergren in 1898 and it suggests that the rate of adsorption is controlled by the availability of adsorption sites on the adsorbent's surface^[11].

Linear Equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Where: q_e and q_t Amount of adsorbate at equilibrium and at time t (mg/g).

k_1 -Pseudo-first order rate constant (min⁻¹).

- Pseudo-Second Order Model

This model assumes that the adsorption is chemisorption, meaning that there are valence forces through the sharing or exchange of electrons between the adsorbent and adsorbate^[12,13].

Linear Equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where: k_2 -Pseudo-second order rate constant (g/mg·min).

In most liquid phase adsorption studies, this model has a very high correlation coefficient (R^2).

3. Isotherm models

These models refer to the equilibrium relationship between the concentration of the substance in solution and its amount on the adsorbent at a constant temperature^[14].

- Langmuir Isotherm

Model This is based on the adsorption of a single layer of molecules on a uniform surface, with no interaction between adsorbed molecules^[15].

Linear Equation:

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

Where: C_e : Concentration of the substance at equilibrium (mg/L).

q_m : Maximum monolayer adsorption capacity (mg/g).

K_L : Langmuir constant (related to energy of adsorption).

- Freundlich Isotherm

Model This empirical model is used to describe the adsorption on a heterogeneous surface and allows formation of multilayers^[16].

Linear Equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

Where: K_F : Freundlich constant related to the capacity of adsorption.

$1/n$: Factor related to the intensity of adsorption and the heterogeneity of the surface.

4. Experimental

4.1. Materials and methods

The date pits used in this research were sourced from the date pit (DPAC) located on local farms in Diwaniyah, Iraq. The samples were thoroughly washed with distilled water to remove any remaining impurities, then sun-dried for three days, followed by oven-baking at 110°C for three hours. The dried material was then ground and sieved for particle size between 150 and 300 μm which is appropriate for mass transfer and pressure drop during adsorption as mentioned in previous works^[17].

A type of adsorbent, acid-activated carbon (DPAC), was synthesized. For carbonization, 100 grams of the produced PD date pits were heated at 280°C for 90 minutes. Under a continuous nitrogen flow rate of 3 L min^{-1} to provide an inert atmosphere and prevent oxidation during carbonization^[17].

The pre-carbonized material was impregnated with a 4 M phosphoric acid solution to improve the pore development since the use of 300 mL of 4 M phosphoric acid per 45 g of pre-carbonized material (carbon-to-solution ratio 1:6.7 w/v) is reported as the most efficient condition for the development of carbon pores during chemical activation^[17]. The mixture was stirred for 30 min to ensure uniform contact between the activating agent and the carbon precursor^[17] and then left to infuse for 24 hours before drying. The impregnated samples were activated at 600 °C for 2 h under a continuous nitrogen flow (3 L min^{-1}). The temperature was increased at a heating rate of 5 °C min^{-1} until the desired activation temperature was reached to ensure controlled pore development and prevent thermal damage to the carbon structure^[18], then rinsed with deionized water to neutral pH and dried at 110 °C for 6 hours.

The activated carbon was impregnated with copper(II) chloride solution, CuCl_2 was chosen because it has a high affinity for sulfur compounds, and is known to improve the adsorption performance of activated carbon^[19], prepared by dissolving 0.3 g of CuCl_2 in 40 mL of distilled water per 5 g of activated carbon. The impregnation ratio was 6 wt% (CuCl_2 /carbon). The mixture was stirred at 60 °C for 5 hours to ensure uniform distribution of the metallic precursor across the entire carbon network^[16]. The suspension was then filtered, and the resulting solid precipitate was dried at 100 °C and calcined for 2 hours in a nitrogen atmosphere to prepare mineral-loaded activated carbon. Adsorption experiments were conducted using heavy naphtha produced at the Diwaniyah refinery, which had an initial sulfur content of 1200 ppm. The mineral-loaded activated carbon was the adsorbent used in the batch adsorption tests as show in **Figure 1**. Quantities of adsorbent (2, 3, and 4 grams) were added to 100 mL of naphtha, and the mixtures were analyzed at different temperatures (20, 30, and 40 °C). The mixtures were mixed under controlled conditions, and liquid samples were withdrawn at specified time intervals. The amount of residual sulfur was determined to measure the desulfurization efficiency. To ensure the accuracy of elemental measurements, the sulfur content after

adsorption was determined using X-ray fluorescence spectroscopy (XRF). The adsorption kinetics were analyzed using pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models to explain the adsorption mechanism and identify the phases controlling its rate. The kinetic parameters were determined using the linear formulas of the different models and evaluated using correlation coefficients (R^2).

The experimental data were fitted to the Langmuir and Freundlich isotherm models to describe the equilibrium adsorption phenomenon. The parameters of the models were determined from linear plots and correlation coefficients (R^2).

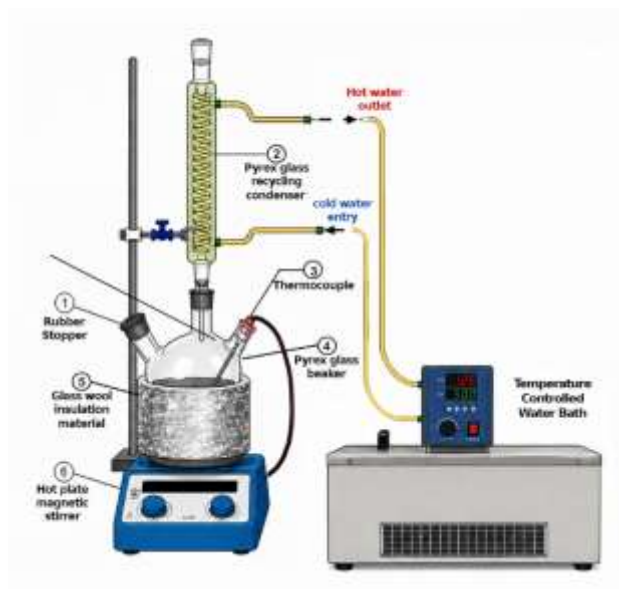


Figure 1. The adsorption process apparatus.

The prepared adsorbent was characterized with Brunauer–Emmett–Teller (BET) analysis, to obtain the specific surface area, pore volume and average pore diameter. Scanning Electron Microscopy (SEM) was used to study the surface morphology and Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the surface functional groups before and after the impregnation with CuCl_2 .

4.2. Process parameter optimization

In order to investigate the influence of process variables and their interaction in the process of adsorptive desulfurization, a series of experiments was performed, varied the key operating variables; temperature, contact time and adsorbent dosage. The sulfur content of the feed was maintained at 1200 ppm using heavy naphtha from Al-Diwaniyah refinery. The Box-Behnken Design (BBD) experimental design involved 15 experiments with three independent variables (temperature (A), contact time (B), adsorbent loading (C)) Three levels (low, medium and high) of the variables were investigated: 20–40 °C, 1–3 hours and 0.02–0.04 g mL⁻¹, for temperature, contact time and adsorbent dosage, respectively. The design in **Table 1** is a combination of factorial and repeated center points (runs 2, 6 and 13) and is used to estimate experimental error and the reproducibility of the model. The central point (30 °C, 2 h, 0.03 g mL⁻¹) is the center point and represents the average of all variables and it is used to check the curvature of the response surface.

Table 1. Experimental design of adsorption of sulfur.

Std	Run	Factor 1	Factor 2	Factor 3
		A:Temp.	B:Time	C:Conc.
		C	hour	gm/ml
3	1	20	3	0.03
14	2	30	2	0.03
8	3	40	2	0.04
11	4	30	1	0.04
2	5	40	1	0.03
15	6	30	2	0.03
1	7	20	1	0.03
12	8	30	3	0.04
9	9	30	1	0.02
6	10	40	2	0.02
7	11	20	2	0.04
4	12	40	3	0.03
13	13	30	2	0.03
10	14	30	3	0.02
5	15	20	2	0.02

Varying the experimental conditions helps assess the main and interaction effects of the variables. Runs 10 and 15 assess the effect of temperature at constant contact time and adsorbent dosage, while runs 3 and 11 assess the interaction effect of extreme temperatures and dosage at constant contact time. This systematic design allows the development of a quadratic model for the adsorption-desulfurization process and in the determination of optimum conditions with lesser number of experiments than the full factor design^[20].

5. Result and discussion

5.1. Characterization of the prepared adsorbent

5.1.1. BET analysis

BET analysis was conducted to evaluate the textural properties of the H₃PO₄-activated carbon (DPAC) before and after CuCl₂ impregnation. The specific surface area of activated carbon was 765 m²/g, which confirmed a porous structure achieved with the activation process using phosphoric acid^[17]. It is believed that the well-developed pore network will facilitate diffusion and adsorption of sulfur-containing compounds during desulfurization process. The BET surface area of the impregnated CuCl₂ was found to be 690 m²/g after impregnation which can be explained by the impregnated copper species occupying part of the pore channel^[21]. This decrease did not significantly reduce the surface area of the adsorbent, indicating that the porous structure was largely retained^[22]. This synergy of the developed pore structure and presence of copper active sites is anticipated to enhance the adsorption capacity for sulfur compounds. The results are similar to those reported in earlier research of Cu impregnated activated carbons.

5.1.2. SEM analysis

Surface morphology of the prepared H₃PO₄-Activated Carbon before and after impregnation with CuCl₂ was studied by SEM analysis. The surface of the activated carbon was irregular and porous as can be seen in **Figure 2** and has a number of cavities and interconnected pores formed during the phosphoric acid activation. This porous morphology offers a huge number of adsorption sites and allows the infiltration of compounds containing sulfur into the structure of the adsorbent. Some similar observations have been made with biomass-derived carbons activated with H₃PO₄^[23, 24]. CuCl₂ impregnation caused changes in the morphology with fine

particles visible on the carbon surface and some pore openings being partially filled. The changes indicate impregnation of the activated carbon and the maintenance of the majority of the porous framework, and this is expected to benefit the adsorption process of sulfur compounds. Metal impregnated activated carbons^[25] have similar morphological characteristics.

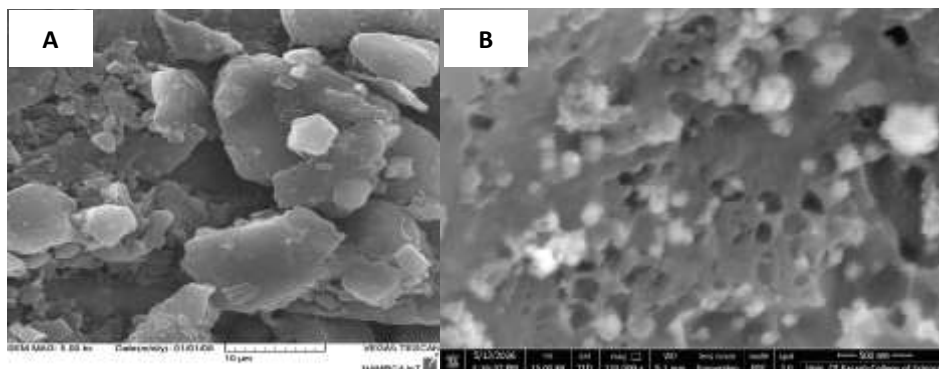


Figure 2. SEM micrographs of H₃PO₄-activated carbon (DPAC): A- before CuCl₂ impregnation and B-after impregnation.

5.1.3. FTIR analysis

The FTIR spectra of the H₃PO₄ activated carbon (H₃PO₄-AC) before and after impregnation with CuCl₂ are given in **Figure 3**. The absorption bands of O–H stretching (~3430 cm⁻¹), aliphatic C–H stretching (2935 and 2855 cm⁻¹), C=O stretching (~1742 cm⁻¹) and aromatic C=C vibrations (~1632 cm⁻¹) were observed in the activated carbon. Further, bands in the region corresponding to the phosphate vibrations (980–1207 cm⁻¹) were observed, which further indicated the effect of activation of H₃PO₄ on the surface chemistry of the adsorbent. The presence of these functional groups with phosphate as the functional group favours enhanced surface polarity and may lead to increased interaction between the functional group and the polar sulfur compounds found in heavy naphtha, as previously reported^[17]. After CuCl₂ impregnation, it was observed that the transmittance decreased, and the intensity of several absorption bands slightly changed, which indicated the interaction between CuCl₂ and the functional groups on the surface of the activated carbon. The principal functional groups were still present following impregnation, indicating that the overall carbon framework was preserved to a large extent and it also contained extra active sites for sulfur adsorption. This FTIR behavior is observed for the Cu-loaded activated carbon adsorbents as well^[19,26].

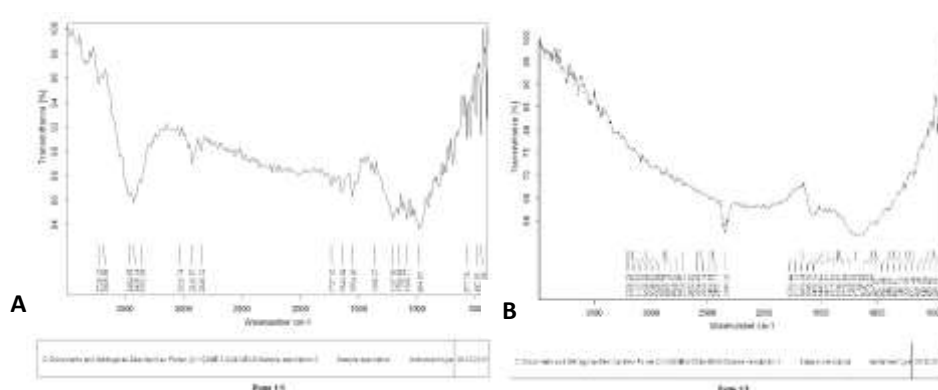


Figure 3. FTIR spectra of H₃PO₄-activated carbon (DPAC): (A) Prior to CuCl₂ impregnation and (B) post CuCl₂ impregnation.

5.2. RSM statistical analysis and results of the experiment

Response Surface Methodology (RSM) is a widely adopted statistical and mathematical method that is designed to model, analyze and optimize processes influenced by multiple variables and their interactions ^[8]. In this study, RSM was used to study the influence of the process parameters on the desulfurization efficiency of heavy naphtha and to reduce the significant number of experimental runs^[7]. The desulfurization of heavy

naphtha was performed in two stages by 15 batch tests. of different process parameters. These are presented in **Table 2**. The desulfurization efficiencies were determined with actual and predicted values. There was a good level of agreement between the actual and estimated results as shown in **Figure 4**. Desulfurization efficiencies were calculated by Design-Expert 13 software^[27]. to determine the relationship between the percent desulfurization and the process parameters. The final quadratic equations which were the results of analysis are as follows:

$$R1\% = 62.17 + 0.5125A + 4.05B + 6.56C + 1.83AB - 0.85AC + 0.025BC - 2.83A^2 - 0.6583B^2 - 0.9833C^2 \quad (5)$$

In which, R1% represents the desulfurization efficiency of heavy naphtha and (A, B, C) represent, respectively: A, B and C represent the temperature, time and amount of adsorbent used per 100 ml of heavy naphtha, respectively. The interaction effects of the model parameters are represented by AB, AC, and BC, and A2, B2 and C2 represent the quadratic constraints of the process parameters. The signs of the coefficients in Equation (5) suggest the direction of the effect of each process parameter. A positive coefficient represents a positive or additive effect, while a negative coefficient represents a negative or subtractive effect. The influence of each variable is determined by the overall effect of its linear, interaction and quadratic components^[8].

Table 2. Experimental design values of response variables for the removal percentage of predicted and actual values.

Std	Run	Factor 1	Factor 2	Factor 3	Removal %	
		A:Temp.	B:Time	C:Conc.	Actual Value	Predicted Value
		C	hour	gm/ml		
3	1	20	3	0.03	59.8	60.39
14	2	30	2	0.03	62.5	62.17
8	3	40	2	0.04	64	64.58
11	4	30	1	0.04	63	63.01
2	5	40	1	0.03	53.9	53.31
15	6	30	2	0.03	61.7	62.17
1	7	20	1	0.03	55.2	55.94
12	8	30	3	0.04	71	71.16
9	9	30	1	0.02	50.1	49.94
6	10	40	2	0.02	52.4	53.15
7	11	20	2	0.04	66	65.25
4	12	40	3	0.03	65.8	65.06
13	13	30	2	0.03	62.3	62.17
10	14	30	3	0.02	58	57.99
5	15	20	2	0.02	51	50.43

5.3. Analysis of variance

Variance partitioning with sources of variance allowed an assessment of the suitability of the Box-Benkhen design^[28]. Fisher's F-test was used to analyze variance (ANOVA) to determine the significance of the coefficients^[7]. The F-values and P-values for sulfur adsorption are shown in **Table 3**. The table shows the degrees of freedom, sum of squares, mean squares, F-value (Fisher's) and P-value. The P-test is carried out to check the F-value is high enough to affirm the statistical significance between the different statistical variables. The significance of the coefficient usually increases with decreasing P-value, but the significance of a factor increases with increasing F-value^[8]. The model boundaries were considered significant if P-values were less than 0.05 and non-significant if P-values were greater than 0.1^[7].

Table 3 presents the ANOVA model for heavy naphtha desulfurization. The analysis of variance (ANOVA) model demonstrates a statistical significance with an F-value of 73.78 and a p-value below 0.0001. As seen in **Table 4**, The standard deviation is 0.8904. The R^2 value is 0.9925, the adjusted R^2 value is 0.9791, and the coefficient of variation (CV) is 1.49%, signifying an appropriate accuracy of 29.1946.

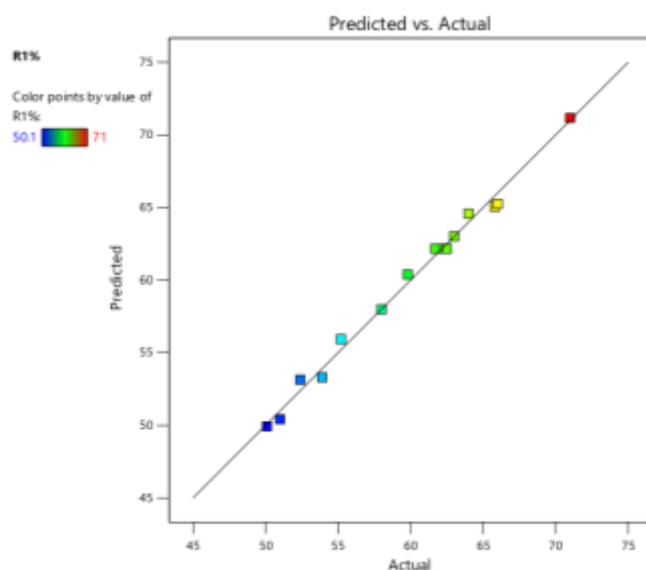


Figure 4. Plot of predicted vs. actual for % sulfur removal.

Table 3. ANOVA of response surface quadratic model for % sulfur removal.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	526.44	9	58.49	73.78	< 0.0001
A-Temp.	2.1	1	2.1	2.65	0.1645
B-Time	131.22	1	131.22	165.51	< 0.0001
C-Conc.	344.53	1	344.53	434.56	< 0.0001
AB	13.32	1	13.32	16.8	0.0094
AC	2.89	1	2.89	3.65	0.1145
BC	0.0025	1	0.0025	0.0032	0.9574
A ²	29.64	1	29.64	37.39	0.0017
B ²	1.6	1	1.6	2.02	0.2146
C ²	3.57	1	3.57	4.5	0.0873
Residual	3.96	5	0.7928		
Lack of Fit	3.62	3	1.21	6.96	0.1283
Pure Error	0.3467	2	0.1733		
Cor Total	530.4	14			

Table 4. Summary of regression values for % sulfur removal.

Std. Dev.	Mean	C.V. %	PRESS	R ²	Adjusted R ²	Predicted R ²	Adeq Precision
0.8904	59.78	1.49	58.66	0.9925	0.9791	0.8894	29.1946

5.4. Response surface and contour plots for desulfurization of heavy naphtha

The presented 3D response surface and 2D contour plots that demonstrate the influence of various parameters on the desulfurization efficiency (R1%) of heavy naphtha^[9]. Such graphs are critical towards understanding conditions of ideal functioning^[8].

In **Figure 5**, the desulfurization efficiency (R1%) of heavy naphtha was considerably improved by increasing the reaction temperature and time, resulting in a greater than 71% removal of sulfur. The response surface and contour plots demonstrate a synergistic effect between temperature and time, where maximum sulfur removal occurs at moderate temperatures and longer times. This trend can be explained by the enhanced mass transfer and kinetics at optimum operating conditions. This observation was also made by^[29], who showed that temperature and contact time are important factors for enhancing deep desulfurization of fuel streams. Similarly,^[3] report that improved reaction conditions also enhance sulfur removal from heavy streams. In addition,^[1] highlighted that Response Surface Methodology (RSM) is a powerful statistical technique to determine and optimize desulfurization.

The interaction of temperature (A) and adsorbent concentration (C) on the sulfur removal (R1%) of heavy naphtha are shown in **Figure 6**. The response surface and contour plots show that the optimal increase in both temperature and adsorbent concentration had a profound effect on sulfur removal efficiency, such that R1% improved from almost 50% to over 71%. Increasing adsorbent concentration increased the number of active sites, and increasing the temperature improved mass transfer and reaction rates, leading to better desulfurization. Nearly complete sulfur removal was achieved at medium-to-high temperature and maximum concentration^[29,3,1].

The response surface plot and contour plot in **Figure 7** illustrates the interaction between reaction time (B) and adsorbent concentration (C) on the desulfurization efficiency (R1%) of heavy naphtha. It was found that higher reaction time and adsorbent concentration significantly enhanced sulfur removal, with R1% increasing from almost 50% at the low levels to more than 71% at the high levels. Increasing reaction time allowed more time for sulfur compounds to interact with the active sites of the adsorbent, and increasing adsorbent concentration provided a larger surface area for the sulfur species to adsorb. The high positive interaction between these factors suggests that increasing both of them is critical to maximize sulfur removal efficiency^[29,3,1].

The competitive adsorption of aromatic and olefinic compounds in heavy naphtha may also influence the adsorption performance, as they may occupy part of the active sites, thus decreasing the sulfur selectivity.

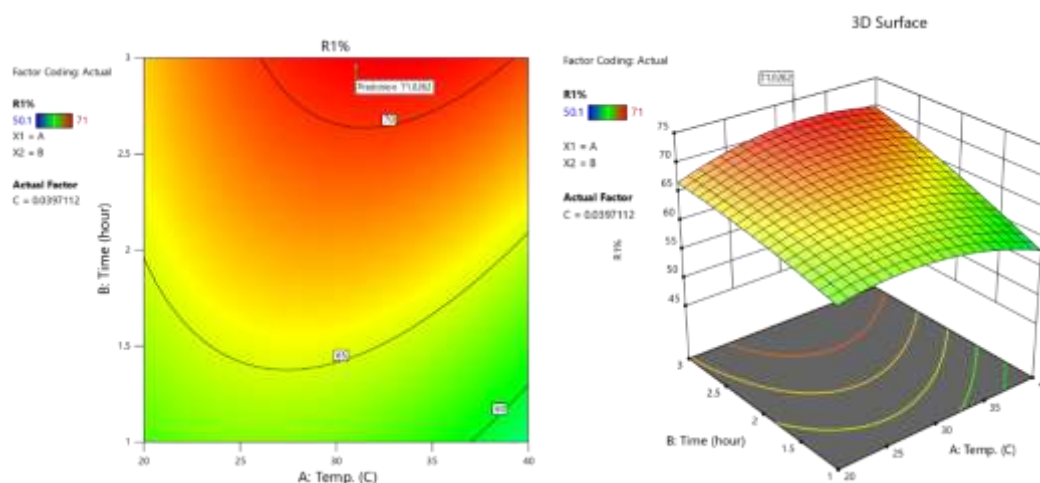


Figure 5. 3D and 2D plots of effect of temperature and time on R1%.

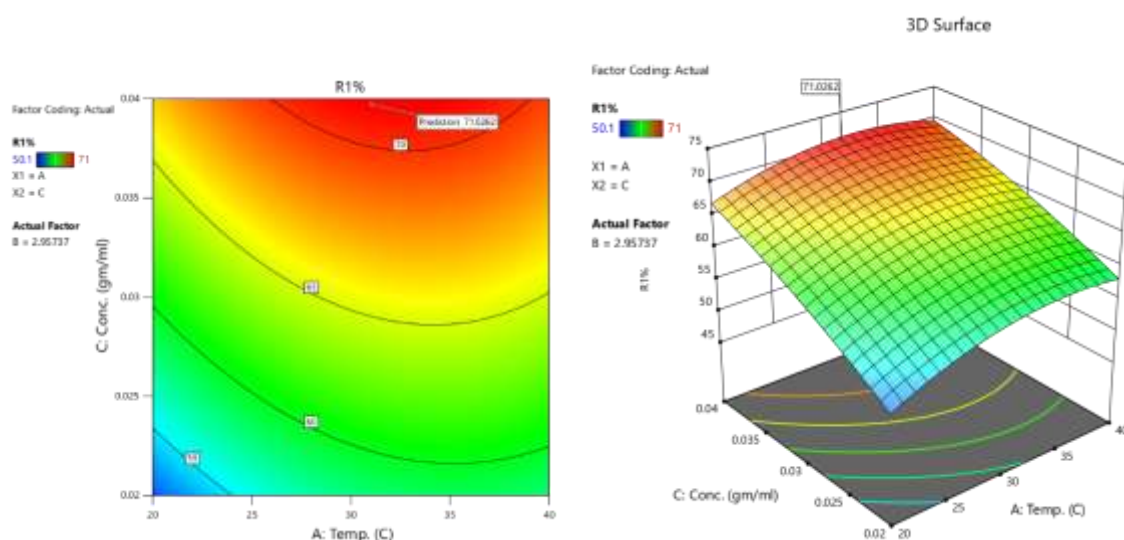


Figure 6. 3D and 2D plots of effect of time and conc. on R1%.

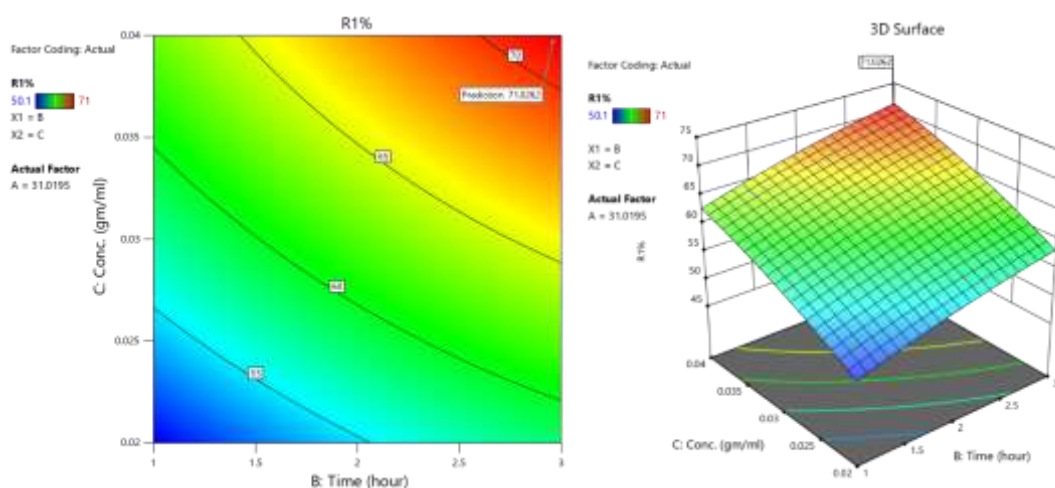


Figure 7. 3D and 2D plots of effect of Temperature and conc. on R1%.

Table 5. Process parameters that gave the optimum removal efficiency.

Parameters	Temperature(C)	Time(hr)	Con.of AC (mg/ml)	% Sulfur Removal
Optimum value	31	2.9573	0.03971	71%

5.5. Fitting of kinetic models

In this study, the kinetics of the sulfur compounds from heavy naphtha onto the prepared adsorbent were determined under the best conditions. The adsorption kinetics were evaluated using the pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models because of their simplicity and widespread use in understanding the adsorption process. The PFO model, suggested by Lagergren, is typically associated with physisorption, where the rate of adsorption depends on the availability of the adsorption sites^[30]. However, the PSO model assumes that chemisorption is the rate-controlling step, which involves the sharing or exchange of electrons between adsorbent and sulfur compounds, thus providing a detailed description of the adsorption process^[12].

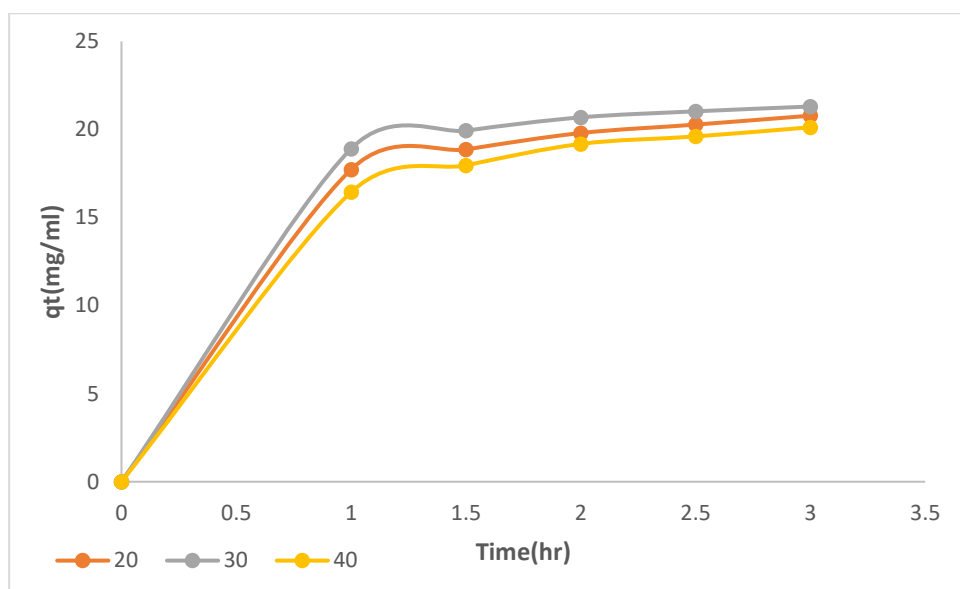


Figure 8. Rate of adsorption of sulfur on DPAC.

As shown in the **Figure 8**, the adsorption capacity (q_t) rapidly grew within the first 1.5 hours and then reached equilibrium. The equilibrium adsorption capacity dramatically reduced with the rise in temperature, in which the maximum sulfur uptake occurred at 30 °C. This suggests that the adsorption of sulfur compounds on the activated carbon is an exothermic reaction. Our results are in line with those reported on adsorptive desulfurization of petroleum fractions, which indicate that increasing the temperature results in a higher desorption rate, which in turn lowers the adsorption capacity^[5,6].

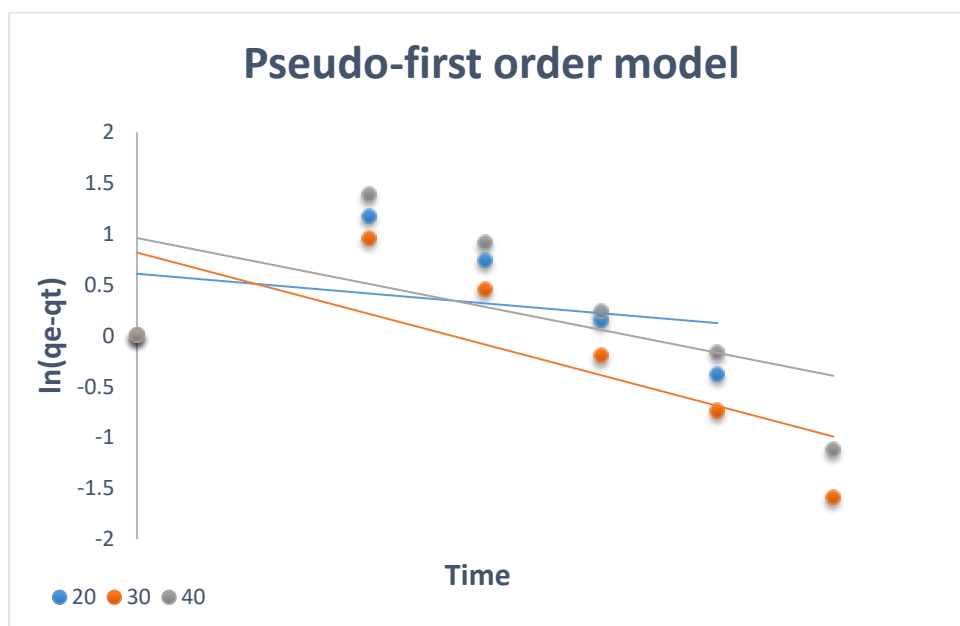


Figure 9. First order kinetic model for the adsorption of sulfur on DPAC at different temperature.

From the linear plots of $\ln(q_e - q_t)$ against time in **Figure 9**. The results showed that the rate constant (k_1) was highest at 30 °C (0.6029 hr^{-1}), followed by 40 °C (0.4514 hr^{-1}) and 20 °C (0.1941 hr^{-1}). But the low values of the correlation coefficient ($R^2 = 0.0917\text{--}0.5263$) suggest that the pseudo-first-order model is not a good fit for the kinetics of the removal of sulfur. This implies that the adsorption process may be controlled by other mechanisms, such as chemisorption or intra-particle diffusion, which are better represented by other kinetic models^[5,6].

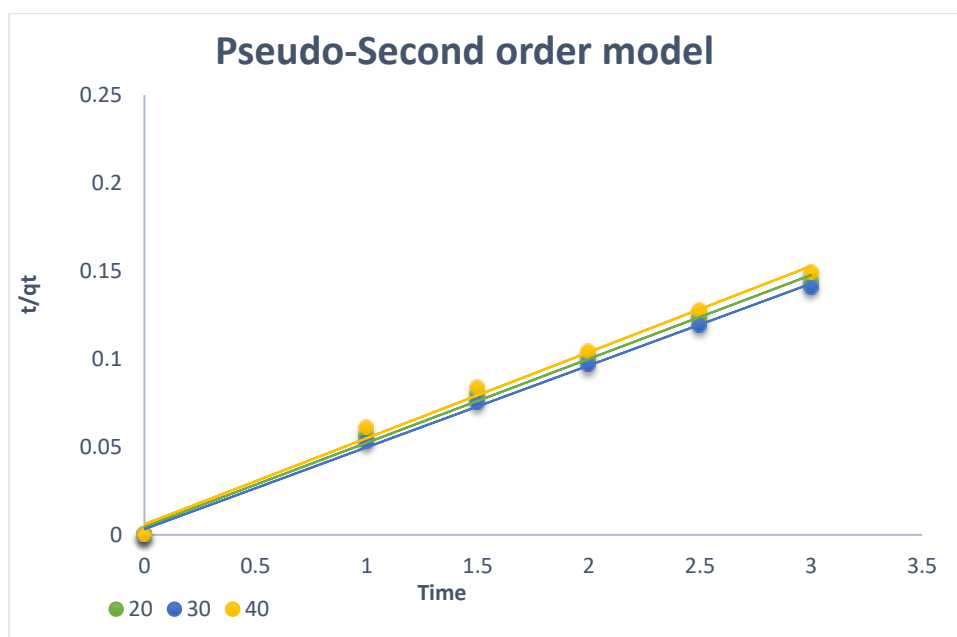


Figure 10. Second order kinetic model for the adsorption of sulfur on DPAC at different temperature.

The pseudo-second-order model was also applied to the adsorption kinetics, with t/q_t plotted against time. As displayed in the **Figure 10**, this model showed a very good fit to the experimental data for all the temperatures with correlation coefficients (R^2) above 0.992. The R^2 value (0.9976) was the highest at 30°C as show in **Table 6**, indicating that the sulfur adsorption from heavy naphtha onto activated carbon is a pseudo-second-order process. This high correlation indicates that the rate-limiting step is chemisorption, which means the binding forces are valence forces through sharing or exchanging electrons between the adsorbent and the adsorbate. In addition, the calculated value of the equilibrium capacity (q_e) using the reciprocal of the slope was found to be highest at 30°C, thereby confirming that 30°C is the most suitable temperature for desulfurization^[5,6].

Table 6. The values of R^2 and K for pseudo-second-order model.

Temp. °C	The pseudo-second-order model	
	R^2	K_2
20	0.9953	0.4843
30	0.9976	0.6552
40	0.9927	0.3985

5.6. Fitting of isotherm models

The equilibrium isotherm data of the sulfur content in the naphtha and the adsorption on the activated carbon were described by the Langmuir and Freundlich models. The Langmuir model is based on monolayer adsorption on a surface with a finite number of homogeneous sites, whereas the Freundlich model is based on multi-layer adsorption on a heterogeneous surface. The separation factor (RL) and the Freundlich constant ($1/n$) were determined to assess the feasibility of the adsorption process, which suggests that the activated carbon has a good affinity for sulfur compounds under the experimental conditions^[4,9].

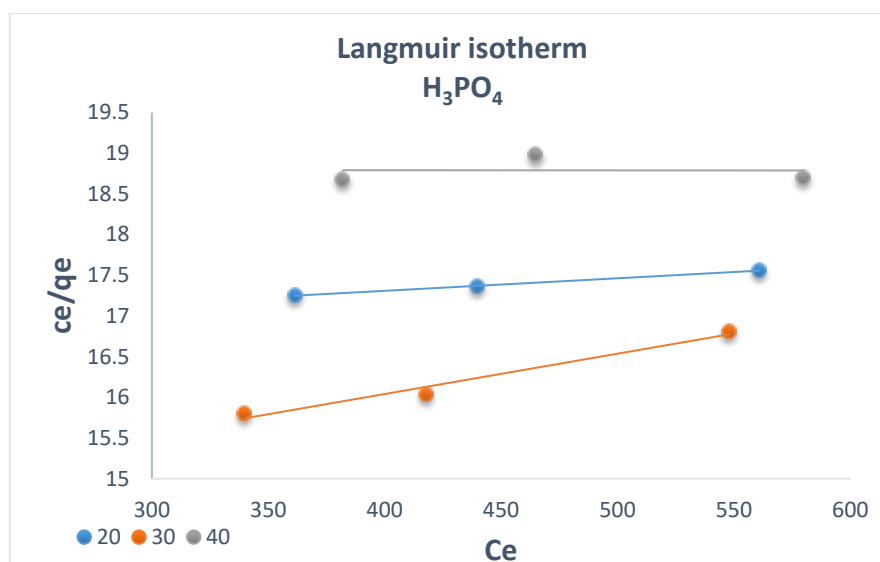


Figure 11. Langmuir adsorption isotherm model for sulfur adsorbed on the DPAC (at temperatures (20,30,40) °C).

The application of the Langmuir model to the desulfurization of heavy naphtha at various temperatures (20, 30 and 40 °C) is shown in **Figure 11**. The results demonstrated that at 20 °C, the model showed the highest correlation coefficient ($R^2 = 0.9998$), which means that the adsorption process is based on monolayer adsorption, where the surface is assumed to be energetically homogeneous. The maximum adsorption capacity (q) was calculated from the inverse slope and it was found that it decreased with increasing temperature and was highest at 20 °C. At 40 °C, the correlation coefficient ($R^2 = 0.0001$) was significantly lower, showing that the Langmuir model is inappropriate for describing the process at higher temperatures, and that the mechanism may change to a more complex system where surface homogeneity is not required.

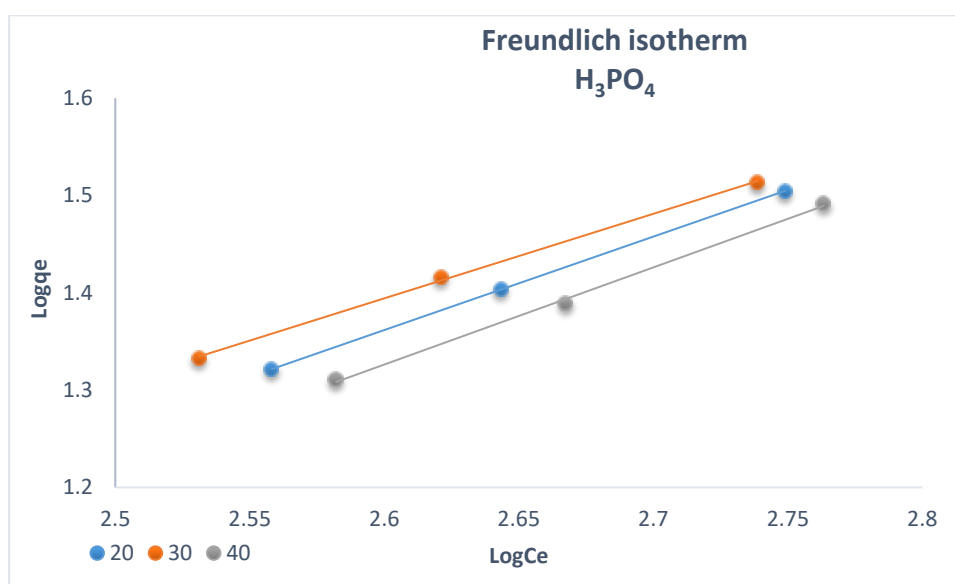


Figure 12. Freundlich adsorption isotherm model for sulfur adsorbed on the DPAC (at temperatures (20,30,40) °C).

The **Figure 12** describes the Freundlich linear model of adsorption, where the results indicate a good agreement between the model and experimental data of all the temperatures studied with the correlation coefficient (R^2) close to one (0.9983 to 1.0). This indicates the "heterogeneity" of the surface of the activated carbon prepared with phosphoric acid and multilayer adsorption. The values of the adsorption intensity coefficient (n) have been calculated from the inverse slope ($1/n$) values and were found to be in the range (1.002-1.151) as shown in **Table 7** which are all greater than one, suggesting that the adsorption of sulfur

compounds on activated carbon is favourable under the experimental conditions. The proximity of the value of $1/n$ to one also suggests a uniform distribution of the energy of the active sites on the surface of the adsorbent.

Table 7. The values of R^2 , n and K_f for Freundlich adsorption isotherm model.

Temp. °C	Freundlich adsorption isotherm model		
	R^2	K_f	n
20	0.9989	0.0732	1.0419
30	1	0.1369	1.1516
40	0.9983	0.05409	1.0021

6. Conclusion

Activated carbon (DPAC) impregnated with CuCl_2 as an adsorbent for desulfurization of heavy naphtha and proved successful in the process. The response surface methodology (RSM) approach was used effectively to determine the optimal operating conditions, leading to 71% maximum sulfur removal efficiency under mild operating conditions. The kinetic study validated the pseudo-second-order model for sulfur adsorption, suggesting that chemisorption was the dominant adsorption mechanism. The isotherms indicated beneficial sulfur sorption with Freundlich model appropriately describing the multilayer sorption mode as a function of temperature.

This study underscores the potential of agricultural biomass waste, such as date pits, as a valuable source of adsorbents for petroleum refining, providing a cost-effective and eco-friendly alternative to traditional desulfurization processes. This process not only aids in the production of cleaner fuels but also facilitates waste utilization and resource sustainability in biomass-rich areas. Future research could explore adsorbent regeneration, scalability, and commercialization to enhance this technology.

Conflict of interest

The author declares no conflict of interest.

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